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**PHASE TRANSFORMATIONS
IN TITANIUM ALUMINIDE
BASED ALLOYS
CONTAINING SILICON**

BY

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For Essay

*To believe everything,
and to disbelieve everything
are two equally convenient philosophies
that both dispense with the necessity of thought.*

H. Poincaré

Abstract.

Mechanical tests on a series of alloys based on $\text{Ti}_3\text{Al} + \text{Nb}$ carried out by D.R.A. Pyestock, Hants. U.K., have identified silicon as an alloying addition which can further enhance the mechanical properties of these alloys. The work presented here has concentrated on alloys which were found by D.R.A. to be the most promising in terms of mechanical properties, thus the range of alloy compositions covered by the 14 alloys is within alloying addition levels as follows;

Ti (at. %)	Al (at. %)	Nb (at. %)	Si (at. %)
balance	20 - 23	11 - 15	0 - 3

These alloys were heat treated over a wide range of temperatures between 380 and 1270°C, and for varying periods of time within the range from 0.1 to 1000 hrs. This provided information as to both the equilibrium microstructures, and the transformations which occur to produce them. The lattice parameters of the crystal structures were confirmed using X-ray diffraction techniques.

The majority of the examinations were carried out on alloys solution treated at 1270°C, water quenched and then aged and water quenched again. The alloys have been examined mainly by microscopy (light, TEM and SEM), both visually and analytically to determine the microstructure and the phase boundaries which occur in the system. To determine more accurately the temperature at which the phase boundaries occur within individual alloys, D.S.C. (Differential Scanning Calorimetry) has also been used.

At 1270°C, the microstructure was found to be single phase β_0 , the transus which separates this from the $\alpha_2 + \beta_0$ region was found to be within the range 1102 to 1140°C. Below this, a third phase, O, was identified, and confirmed as being orthorhombic. It has been found over a temperature range from 800 to 1050 °C. Increasing either the silicon or niobium level in the alloys was found to promote this phase. This phase was found in two markedly different compositional forms, but was identified as being a single phase.

Contents

Contents	4
List of Figures	7
List of Tables	10
1. Introduction	12
2. Literature Review.	14
2.1. Aerospace Alloys.	14
2.2. Types Of Titanium Alloys.....	14
2.2.1 Alpha Alloys.	15
2.2.2 Beta Alloys.	16
2.2.3 Alpha/Beta Alloys.....	16
2.3. Intermetallic Alloys.	18
2.4. Overview of Phase Diagrams.	19
2.4.1 Published Binary Phase Diagrams.	19
2.4.2. Ternary Isothermal Sections.	24
2.4.2.1 The Niobium - Aluminium - Silicon System.....	24
2.4.2.2. The Titanium - Aluminium - Silicon System.	27
2.5. The Titanium - Aluminium - Niobium Based Alloys System.	27
2.5.1. Phases Diagrams and Identified Structures.	27
2.5.2. Site Occupancy in Ti_3Al B2 and O.	39
2.5.3. 'Super Alpha2'.....	43
2.5.4. Quaternary Ti-Al-Nb-Si Alloys.	44
2.6. Effect of Oxygen on Phase Diagrams.	46
2.7. Mechanical Properties of Ternary Ti-Al-Nb Alloys.	46
3. Experimental.....	51
3.1. Alloy Manufacture.....	51
3.1.1. Forged Alloys.....	51

3.1.2. Cast Alloys.....	51
3.2. Heat Treatment.....	53
3.2.1. Solution Treatment.....	53
3.2.2. Ageing Treatments.....	54
3.3. Sample Preparation and Examination.....	59
3.3.1. Sample Polishing.....	59
3.3.1.1. Mechanical Polishing Using Alumina.....	59
3.3.1.2. Electropolishing.....	59
3.3.1.3. Mechanical Polishing Using Diamond.....	60
3.3.2. Sample Surface Examination.....	60
3.3.4. Transmission Electron Microscopy.....	61
3.3.5. X-Ray Diffraction.....	62
3.3.6. Calorimetric Analysis.....	62
3.4. Accuracy of EDS Analysis.....	63
3.4.1 Chemical Analysis Carried out in SEM.....	63
3.4.2 Chemical Analysis Carried out in TEM.....	63
4. Solution Treatment and Low Temperature Ageing.....	65
4.1. As Cast Microstructure.....	65
4.2. Solution Treated Microstructure.....	66
4.2.1. Solution Treated Alloys Containing 0.9 at.% Silicon.....	69
4.2.2. Solution Treated Alloys Containing More Than 0.9 at.% Silicon	75
4.3. Alloys Aged at Low Temperatures.....	80
4.4. Effect of Ageing Treatment on Alloy Hardness.....	83
5. Ageing Treatments.....	87
5.1. Introduction.....	87
5.2. 1050 and 1100°C Aged Microstructures	87
5.2.1. Base Alloys.....	87
5.2.2. Effect of Silicon Level in Ti-20-11-X Alloys	97

5.2.3. Alloys based on Ti-23-X-Y with Higher Silicon Levels.	105
5.3. 900°C Aged Microstructure.....	106
5.3.1. Alloys with a Nominal Silicon Content Below 0.9 at. %	106
5.3.2. Alloys Containing More Than 0.9 at. % Silicon	111
5.4. 800°C Aged Microstructure.....	113
5.4.1. Low Silicon Content Alloys.	113
5.4.2. Alloys Containing More Than 0.9 at. % Silicon	122
5.5. 650°C Aged Microstructure.....	122
5.6 Temperature Dependence of Terminal Hardness.....	127
5.7. Summary of Phases Present in Aged Alloys.....	133
5.8. Air Cooled Conditions	136
5.8.1. β Solution Treated and Aged Alloys	136
5.8.1.1. Microstructure of Base Alloy.....	136
5.8.1.2. Microstructure of Higher Silicon Content Alloys.....	136
5.8.2. $\alpha_2 + \beta$ Solution Treated and Aged Alloys	143
5.9. Summary.....	146
6. Phase Transformations and Crystal Structures.....	147
6.1. Introduction.....	147
6.2. Constant Silicon Content Sections.....	148
6.3. The Effect of Silicon on The Quaternary Phase diagram.	164
6.4. Crystal Structures Found In Alloys.	167
6.5. Summary.....	178
7. Conclusions.	179
8. Suggestions For Further Work.....	183
Appendix	185
References.....	188
Acknowledgements.	196

List of Figures

2.Literature Review.

2.1.	Schematic of hexagonal α crystal structure.	20
2.2.	Titanium - aluminium binary phase diagram.	20
2.3	Titanium - aluminium binary phase diagram.	22
2.4.	Titanium - aluminium binary phase diagram.	22
2.5.	Titanium - niobium binary phase diagram.	23
2.6.	Aluminium - niobium binary phase diagram.	23
2.7.	Aluminium - silicon binary phase diagram.	23
2.8.	Titanium - silicon binary phase diagram.	25
2.9.	Niobium - silicon binary phase diagram.	25
2.10.	Nb - Al - Si ternary section at 1300°C.	26
2.11.	Nb - Al - Si ternary section at 1500°C.	26
2.12.	Ti - Al - Si ternary section at 1000°C.	28
2.13.	Ti - Al - Si ternary section at 800°C.	28
2.14.	Ti - Al - Si ternary section at 1100°C.	29
2.15.	Ti - Al - Si ternary section at 1200°C.	29
2.16.	Vertical section of $Ti_3Al + Nb$.	31
2.17.	Vertical sections of $Ti_3Al + Nb$.	31
2.18.	Ti - Al - Nb ternary section at 600°C.	31
2.19.	Ti - Al - Nb ternary section at 900°C.	32
2.20.	Ti - Al - Nb ternary section at 1200°C.	32
2.21a.	Ti - Al - Nb ternary section at 1200°C.	33
2.21b.	Liquidus projection of Ti - Al - Nb ternary system.	33
2.22.	Ti - Al - Nb ternary section at 1200°C.	35
2.23.	Ti - Al - Nb ternary section at 900°C.	35
2.24.	Ti - Al - Nb ternary section at 1050°C.	36
2.25.	Ti - Al - Nb ternary section at 1200°C.	36
2.26.	Diagram of similar planes in α_2 , β and O.	42
2.27.	Continuous cooling curve for Ti-25Al-15Nb.	42
2.28.	Isothermal transformation curve for 'Super α_2 '.	45
2.29.	Effect of silicon on mechanical properties of Ti-20Al-11Nb.	45
2.30.	Yield stress against temperature in Ti-24Al-11Nb.	48

Experimental Method.

3.1.	Cross section of vertical tube furnace.	55
3.2.	Detail of release mechanism in furnace.	55
3.3.	Schematic of heating in horizontal furnace.	57
3.4.	Heating curve for samples in horizontal furnace.	58

Casting, Solution Treatment and Low Temperature Ageing.

4.1.	Cast microstructures in Ti-23Al-(11-15)Nb-(1.5-3)Si.	67
4.2.	Solution treated and quenched Ti-20Al-(11-15)Nb-0.9Si.	71
4.3.	β to β_0 transformation boundary.	73
4.4.	Solution treated and quenched Ti-23Al-15Nb-0.9Si.	76
4.5.	Solution treated Ti-23Al-11Nb-3Si.	78
4.6.	Site types in B2 structure.	81
4.7.	D.S.C. curve showing low temperature peak.	82
4.8.	Ti-20-15-0.9 S.T., w.q. and aged 380°C/1000mins.	84
4.9.	Ageing curves for alloys aged at 380°C.	86

Ageing Treatments.

5.1.	Ti-(20,23)Al-(11,15)Nb-0.9Si S.T., aged 1050°C/168hrs.	88
5.2.	Representation of distribution of silicon in eutectic and peritectic systems.	91
5.3.	Ti-20Al-15Nb-0.9Si S.T., aged 1100°C/168hrs.	92
5.4.	Ageing curves for alloys aged at 1050°C.	95
5.5.	Ti-20Al-11Nb-(0.5-1.2)Si S.T., aged 1050°C/168hrs.	100
5.6.	Ti-20Al-11Nb-(0.5-1.2)Si S.T., aged 1050°C/168hrs.	102
5.7.	Representation of changes in phase composition when moving from a two to a three phase field.	104
5.8.	Ti-23Al-(11-15)Nb-(1.5-3)Si S.T., aged 1050°C/168hrs.	107
5.9.	Ti-23Al-(13-15)Nb-0.9Si S.T., aged 900°C/168hrs.	109
5.10.	Ageing curves for alloys aged at 900°C.	112
5.11.	Ti-23Al-(11-15)Nb-(1.5-3)Si S.T., aged 900°C/168hrs.	114
5.12.	Ti-20Al-11Nb-0.9Si S.T., aged 800°C/1hr	117
5.13.	Ti-20Al-11Nb-0.9Si S.T., aged 800°C/1000hrs.	119
5.14.	Ageing curves for alloys aged at 800°C.	120
5.15.	Ti-23Al-(11-15)Nb-(1.5-3)Si S.T., aged 800°C/168hrs.	123
5.16.	Ti-20Al-11Nb-0.9Si S.T., aged 650°C/1-1000hrs.	125
5.17.	Ageing curves for alloys aged at 650°C.	128
5.18.	Temperature dependence of hardness in Ti-20-11-0.9.	129
5.19.	Temperature dependence of hardness in Ti-20-15-0.9.	130
5.20.	Temperature dependence of hardness in Ti-23-11-0.9.	131
5.21.	Temperature dependence of hardness in Ti-20-15-0.9.	132
5.22.	Ti-20Al-11Nb-(0-1.5)Si, S.T. 1150°C/1hrs, a.c., 625°C/2hrs, a.c.	138
5.23.	D.S.C. curve showing O phase precipitation.	141
5.24.	Ti-20Al-11Nb-(0-1.5)Si.	144

Phase Transformations and Crystal Structures

6.1.	Ternary section of Ti-Al-Nb at 1270°C, 0.9 at.% Si.	149
6.2.	Ternary section of Ti-Al-Nb at 1050°C, 0.9 at.% Si	150
6.3.	Ternary section of Ti-Al-Nb at 900°C, 0.9 at.% Si.	151
6.4.	Heating curve for short term aged alloys.	155
6.5.	Binary section of Ti-20-11-X.	156
6.6.	Binary section of Ti-23-11-X.	157
6.7.	Binary section of Ti-23-15-X	158
6.8.	Binary section of Ti-20-X-0.9.	159
6.9.	Binary section of Ti-23-X-0.9.	160
6.10.	Binary section of Ti-23-X-1.5.	161
6.11.	Binary section of Ti-X-11-0.9.	162
6.12.	Binary section of Ti-X-15-0.9.	163
6.13.	Schematic Diagram Showing 'Two Types' of O Phase	166
6.14a.	Effect of Silicon on β_0 lattice parameters.	172
6.14b.	Effect of Nb level on O lattice parameters.	174
6.15.	Temperature dependence of orthorhombicity.	176

Appendix

D.S.C. curve with transformations identified.	187
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List of Tables

Literature Review

2.1. Structural Classes of Some Commercial Titanium-Base Alloys	17
2.2. Reported values of lattice parameters for Orthorhombic phase.	38
2.3. Site Occupancy in 'O' Phase as Determined by Neutron Diffraction	41
2.4. Approximate Elemental Composition in 'Super Alpha2'.	43

Experimental

3.1. Forging Applied to Alloys.	51
3.2. List Of Cast Alloys.	52
3.3. Purity of Alloy Components.	53

Casting, Solution Treatment and Low Temperature Ageing

4.1. Summary of Heat Treatments for 'As Quenched' Alloy Condition.	69
4.2. Hardness of Solution Treated and Water Quenched Alloys (Hv) .	74
4.3. Comparisons of Site Occupancies in Close Packed Planes in β_o and O phases.	80

Ageing Treatments

5.1. Chemical Compositions of Phase in Alloys Aged at 1050°C as Identified by Bulk EDS Analysis.	96
5.2. X-ray Diffraction Data for 1270°C S.T, 1050°C Aged Alloys	98
5.3. Chemical Compositions of Phases in Ti-23-15-0.9 Aged at 900°C Ascertained By Thin Foil EDS.	106
5.4. Phase Chemistry in Ti-20-11-0.9 Aged at 800°C/1000 hrs.	116
5.5. Phase Chemistry in Ti-20-11-0.9 Aged at 650°C/1000 hrs.	127
5.6. Phases Present at 1100°C.	133
5.7. Phases Present at 1050°C	134
5.8. Phases Present at 900°C	134
5.9. Phases Present at 800°C	135
5.10. Phases Present at 650°C	136
5.11. Lattice Parameters (in pm)	139
5.12. Composition Of Alloys in 1150°C Solution Treated. 625°C Aged Condition (from thin foil EDS)	142

Phase Transformations and Crystal Structures.

6.1. Transformation Temperatures For Alloys During Heating.	153
6.2. Lattice Parameters (in pm) for Alloys Solution Treated at 1270°C. (excluding silicides)	167
6.3. Lattice Parameters (in pm) for Alloys Solution Treated at 1270°C, the Aged at 1050°C. (excluding silicides)	168
6.4. Lattice Parameters (in pm) for Alloys Solution Treated at 1270°C, then Aged at 900°C. (excluding silicides)	169
6.5. Lattice Parameters (in pm) for Alloys Solution Treated at 1270°C, then Aged at 800°C. (excluding silicides)	170
6.6. X-ray Diffraction Peaks for Sample α_2 Crystal.	171
6.7. X-ray Diffraction Peaks for Sample β Crystal.	173
6.8. X-ray Diffraction Peaks For Typical O Crystal	177

Chapter 1.

Introduction.

Ever since the development of aero engines began, the development of alloys for engine usage has been a drive towards a reduction in the weight of the engine, which has been coupled with the aim of producing materials which will withstand higher operating temperatures and harsher mechanical conditions. As the operating temperature of an engine increases, so the thermodynamic efficiency of thrust production is also increased. The aim of this has been to produce a higher power to weight ratio from the power unit, thus allowing either greater power, or reduced size. The structural stainless (chrome) steels used in the first aero engines rapidly gave way to alloys based on nickel. However, nickel has a major disadvantage for aerospace usage in that it has a high density ($8.90 \times 10^3 \text{ kg m}^{-3}$). Even in the latest generation of Ni - Al based alloys the density has only been reduced to around $8.3 \times 10^3 \text{ kg m}^{-3}$ [Lip84].

An initial examination of the properties inherent in both titanium and nickel seems to indicate that in the long term, titanium is a more promising base for alloying to produce high temperature super alloys. The density of titanium ($4.54 \times 10^3 \text{ kg m}^{-3}$) is almost half that of nickel, while the melting point is similar. In the long term it is envisaged that titanium may entirely replace nickel as the basis for some high temperature operations. As yet, titanium based alloys have only replaced nickel alloys at intermediate temperatures up to around 600°C . This is due to loss of oxidation and creep resistance above this temperature. This is particularly important in titanium, as oxygen has a marked effect on both the microstructure and the ductility of titanium alloys. Thus, to improve the creep and oxidation properties, alloy development has moved towards intermetallic alloys based on Ti_3Al and TiAl in the same way that nickel alloy development has concentrated on the Ni_3Al and NiAl phases.

The Ti_3Al phase (usually referred to as α_2) is an ordered variation on the low temperature hexagonal phase. Unfortunately, due to this, Ti_3Al , like many other intermetallic compounds is inherently brittle at low temperatures. Much work has been carried out to find alloying additions which will improve this ductility, either by increasing the ductility of the phase, or by producing alloys which at operating temperatures (e.g. $6\text{-}700^\circ\text{C}$) also contain the more ductile β

phase. Over the last few years it has become clear that of the β -stabilising elements conventionally used in titanium alloys (i.e. vanadium, molybdenum etc.) niobium additions can produce some of the most significant improvements in low temperature ductility properties. Niobium also has added advantages in that its addition promotes the formation of an ordered β phase. β is a b.c.c. structure, and thus when fully ordered becomes simple cubic. The ordering has beneficial effects on the high temperature creep resistance of the β phase, and thus of the alloy as a whole.

Mechanical tests on a series of alloys based on $\text{Ti}_3\text{Al} + \text{Nb}$ carried out by D.R.A. Pyestock, Hants. U.K., has identified silicon as an alloying addition which can further enhance the mechanical properties of these alloys. The aim of this work is to identify the reasons behind this improvement in properties, and to increase the understanding of the phase diagram, the transformations which occur within the system, and particularly the effect that silicon has on the microstructure of the alloys.

Chapter 2.

Literature Review.

2.1. Aerospace Alloys.

Since the development of aero engines began, there has been a desire to reduce the weight of the engine and thus produce a higher power-to-weight ratio from the power unit. This has gone hand in hand with a drive towards producing alloys that will be able to operate at higher temperatures and pressures. As the operating temperature of an engine increases, so the thermodynamic efficiency of thrust production is also increased. The structural stainless (chrome) steels used in the first aero engines rapidly gave way to alloys based on nickel. However, nickel has a major disadvantage for aerospace usage in that it has a high density ($8.90 \times 10^3 \text{ kg m}^{-3}$). Even in the latest generation of Ni - Al based alloys the density has only been reduced to around $8.3 \times 10^3 \text{ kg.m}^{-3}$ [Lip84]. Initial comparison of titanium and nickel seems to indicate that, in the long term, titanium is a more promising base for alloying to produce high temperature super alloys. The density of titanium ($4.54 \times 10^3 \text{ kg.m}^{-3}$) is almost half that of nickel, while the melting point is similar. In the long term it is envisaged that titanium may entirely replace nickel as the basis for some high temperature operations. As yet, titanium alloys have only replaced nickel alloys at intermediate temperatures up to around 600°C due to loss of oxidation and creep resistance above this temperature.

2.2. Types Of Titanium Alloys.

As titanium is an allotropic metal, i.e. it exists in different crystal structures at different temperatures in the solid state, its alloys can be grouped into three major types, depending on which crystallographic form they are based. Specifically, pure titanium, at temperatures below 882°C [McQ51] exists as a close packed hexagonal structure of non-ideal axial ratio referred to as αTi , and above that it is in the form of a body centred cubic crystal structure known as βTi . Alloying additions to Ti normally affect the temperature at which the allotropic change occurs. These are divided up into four main types, as described below.

Alpha Stabilisers - These raise the allotropic transus temperature in an alloy, and have greater solubility in the α phase than the β phase. Aluminium is a good example of this type of alloying element. Polmear [Pol81] reports that the addition of α stabilising elements is limited by the formation of an ordered phase based on Ti_3Al when the aluminium content exceeds 9wt.% aluminium equivalence, as calculated below;

$$Al + \frac{1}{3}Sn + \frac{1}{6}Zr + 10(O + C + 2N) \quad (1)$$

Beta Stabilisers:- These lower the allotropic temperature, this may reduce it as low as room temperature. These include transition elements such as niobium [Han51], vanadium [McQ51a] and molybdenum [Flo74]. This group include β isomorphous;

$$\beta \rightarrow \alpha + \beta \quad (2)$$

and β monotectoid

$$\beta_1 \rightarrow \alpha + \beta_2 \quad (3)$$

forming elements.

Neutral Elements:- For example tin and zirconium have little effect on the allotropic temperature at low concentrations .

Beta Eutectoid Formers:- These elements, for instance copper and silicon, produce a eutectoid reaction when added to titanium:-

$$\beta \rightarrow \alpha + \text{compound} \quad (4)$$

Depending upon the concentrations and mixtures of these elements three main types of titanium alloys can be produced:-

2.2.1 Alpha Alloys.

This group consists of unalloyed Ti, and alloys which include α stabilising elements such as Al and O (and Ga, which is not used in current commercial alloys) [Col84], which under the operating conditions for which they are designed, consist of

an entirely α derived hexagonal structure (see Figure 2.1). Alloys of this type which have been produced include commercial grades of titanium (alloyed with O) and alloys such as Ti-5Al-2.5Sn.

2.2.2 Beta Alloys.

Transition metal alloying additions in Ti act as stabilisers for the b.c.c. based β phase. Thus in general, β alloys contain relatively large amounts of alloying additions from Transition Metal Groups V and VI, specifically V, Nb (Group V) and Mo (Group VI) [Han51, McQ51a, Flo74]. β stabilisation of this type in binary and multi component alloys has been studied elsewhere in detail, for example by Ageev, [Age70]. The strength of the stabilisation obtained, for instance the Ti-Nb system (see later), means that even at room temperature some β based alloys (not commercial ones) are microstructurally single phase β at equilibrium. These alloys tend to be prone to ductile - brittle transitions (d.b.t.) at temperatures close to room temperature [Gor73], and thus, are generally, are not suitable for low temperature applications. Other β alloys fall in the equilibrium $\alpha + \beta$ field at room temperature although β phase may be fully retained in metastable form, and are susceptible to age or precipitation hardening reactions via α phase formation. This group includes the highest strength Ti alloys. All β alloys are limited in their service temperature range by the low creep resistance of the matrix β phase. By convention, β alloys are divided from $\alpha + \beta$ ones by their retention of β phase in either stable or metastable form on quenching (from the β phase field) to room temperature. Thus near β alloys are generally considered along with β alloys, even though from a phase diagram view they should be considered as $\alpha + \beta$ alloys.

2.2.3 Alpha/Beta Alloys

These alloys, under equilibrium conditions are two phase $\alpha + \beta$ at room temperature. Even when solution treated in the β phase field the β is insufficiently stable to be retained on quenching and transforms, at least partially, to α' martensite. Heat treatment at elevated temperatures in the $\alpha + \beta$ field results in solute partitioning and enrichment of the β in the β stabilising species. If the enrichment is sufficient, β may be retained on subsequent quenching or even on cooling at slower rates. In Ti-6Al-4V, the stability of the β depends on the equilibration temperature. If

low (700°C), the β is so highly stabilised that it remains β on air cooling. If a higher equilibration temperature is used (900°C), then the β transforms to $\alpha + \beta$ on air cooling.

A list of some examples of each of the three major alloy types is shown below in table 2.1. α plus β alloys can also be divided up into 3 main types;

normal (or alpha/beta), which are a relatively balanced ratio of α to β phases.

near α , which consist predominantly of α phase based

near β which are predominantly β phase based (see section 2.2.2)

Alloy	Classification
Ti-5Al-2.5Sn	alpha
Ti-5.5Al-3.5Sn-3Zr-0.3Mo-1Nb-0.3Si	near alpha
Ti-5.5Al-4.5Sn-4Zr-0.5Mo-0.7Nb-0.4Si	near alpha
Ti-8Al-1V-1Mo	alpha + beta
Ti-6Al-2Sn-4Zr-2Mo	alpha + beta
Ti-6Al-4V	alpha + beta
Ti-6Al-6V-2Sn	alpha + beta
Ti-3Al-2.5V	alpha + beta
Ti-6Al-2Sn-4Zr-6Mo	alpha + beta
Ti-5Al-2Sn-2Zr-4Cr-4Mo	alpha + beta
Ti-3Al-10V-2Fe	near beta
Ti-13V-11Cr-3Al	beta
Ti-15V-3Al-3Sn-3Cr	beta
Ti-8V-3Al-6Cr-4Mo-4Zr	beta
Ti-8V-3Al-8Mo-2Fe	beta
Ti-4.5Sn-11.5Mo-6Zr	beta

Table 2.1. Structural Classes of Some Commercial Titanium-Base Alloys [Col84]

2.3. Intermetallic Alloys.

Some experimental and commercial alloys which include a significant percentage of an intermetallic compound (i.e. a compound of two or more metals, such as Ni_3Al) exhibit greatly reduced ductility at room temperature. This characteristic is a great disadvantage in the engineering application of these alloys. Many of them have extremely good mechanical properties (i.e. strength and creep resistance) and oxidation resistance, as well as greatly improved ductility at elevated temperatures. For instance Ni_3Al has a high elastic modulus, reasonable high temperature creep strength and a high oxidation resistance [Fli60,Ait67].

There are a number of reasons for the lack of ductility in intermetallics, including the limited number of easily available slip systems. Other characteristics which have been shown to [Bak88] reduce the ductility of these alloys include;

restricted cross-slip,

difficulty of transmitting slip across grain boundaries,

low grain boundary strength.

These present a problem in that the source of these inhibiting factors is often also the source of the beneficial high temperature properties.

There are four broad categories of metallurgical techniques for improving the less advantageous of these alloys' properties. These come under the general headings of micro-alloying, macro-alloying, microstructural control through processing, and fibre strengthening or toughening. These have been reviewed in detail by Baker [Bak88] and will not be discussed comprehensively here.

Briefly, micro-alloying involves the addition of very small amounts of another element or compound, for example to modify the structure or characteristics of the alloy. When approximately 500ppm boron is added to Ni_3Al it segregates to the grain boundaries and changes the fracture mode from intergranular to a mixture of intergranular and transgranular failure [Liu83]. Micro alloying has also been employed to purge an undesirable element from solution, e.g. yttrium, when added to titanium reduces oxygen level in solution. Low oxygen content is very important for Ti_3Al production as ductility of titanium-based alloys is greatly affected by oxygen

content.

Macro-alloying is generally defined as the addition of greater than approximately 1 at.% of an element or compound to modify the crystal structure, e.g. from hexagonal to orthorhombic, changing the grain size, or increasing the number of operational slip systems by distorting the crystal by for instance changing the c/a ratio in a hexagonal lattice. Macro alloying is also used to produce a secondary phase in the alloy.

Microstructural control is commonly used, for example, in the control the heating cycle to refine the grain structure or to precipitate stable or metastable phases. As an alternative to grain refinement, turbine blades in many modern jet engines are produced from single crystals, thus removing any ductility problems caused by low grain boundary strength and the source of grain boundary sliding which contributes to high temperature creep. Microstructural control can also include the use of deformation and recrystallisation.

2.4. Overview of Phase Diagrams.

A large number ^{of} binary phase diagrams and ternary isothermal section diagrams have been published over the years, in systems that are of use in development of titanium alloys.

2.4.1 Published Binary Phase Diagrams.

There have been a large number of papers published which have dealt with the titanium - aluminium phase diagram. This complex system which includes a series of intermetallic compounds ranging in composition from Al_3Ti to the compound which is the basis of the current work. Ti_3Al , has been summarised to produce the widely known phase diagram published by Murray [Mur87], which is reproduced in Figure 2.2. The details of this system have, as yet not been ascertained to a degree at which there is total agreement as to the reactions occurring. Since the publication of the binary diagram by Murray, more recent work by McCullough et al [McC88], has shown that the α phase, instead of existing below a peritectoid reaction at approximately 1558K (1285°C), is an equilibrium phase up to the liquidus, at

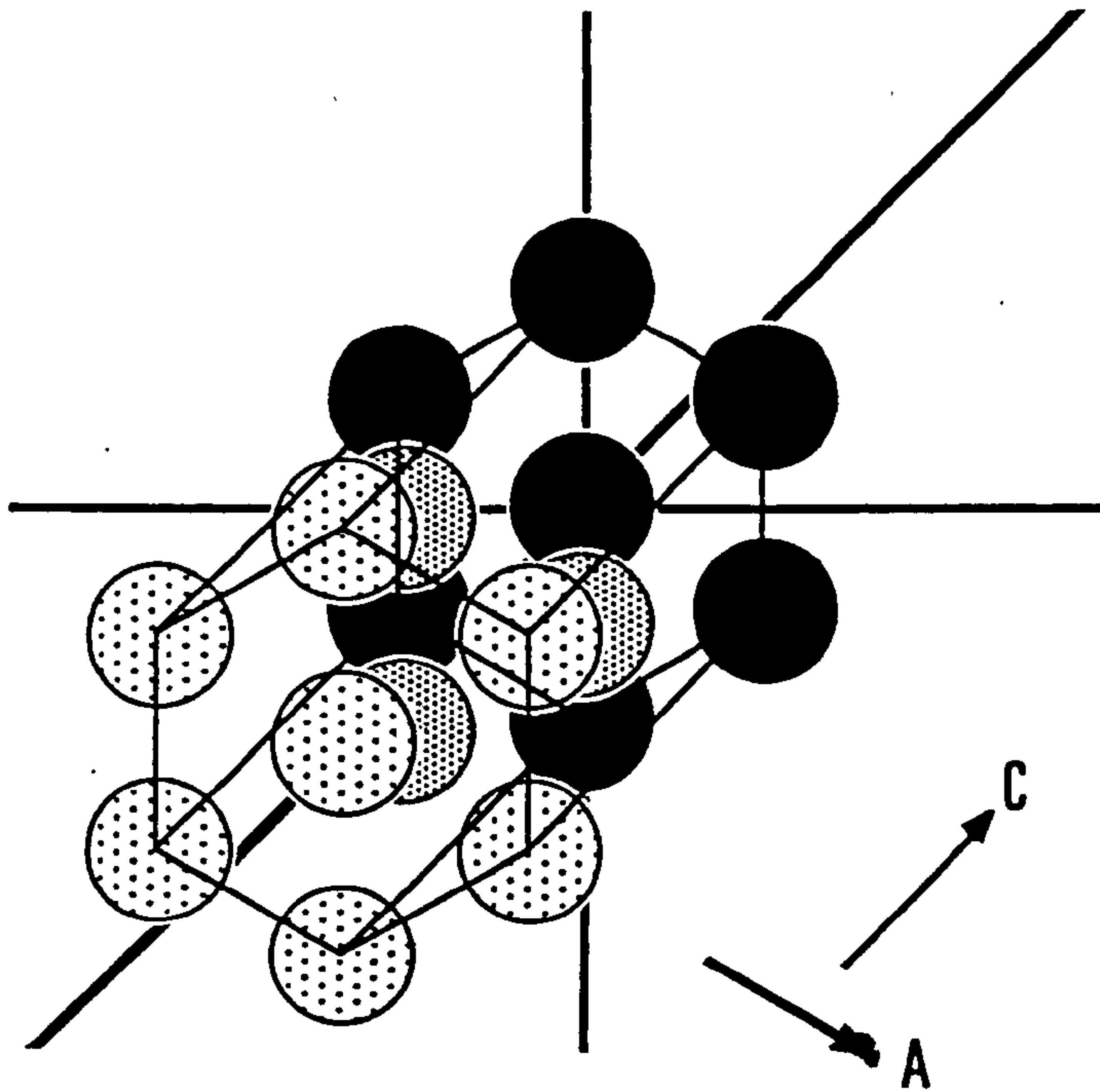


Figure 2.1. Illustration of Hexagonal α Crystal Structure.

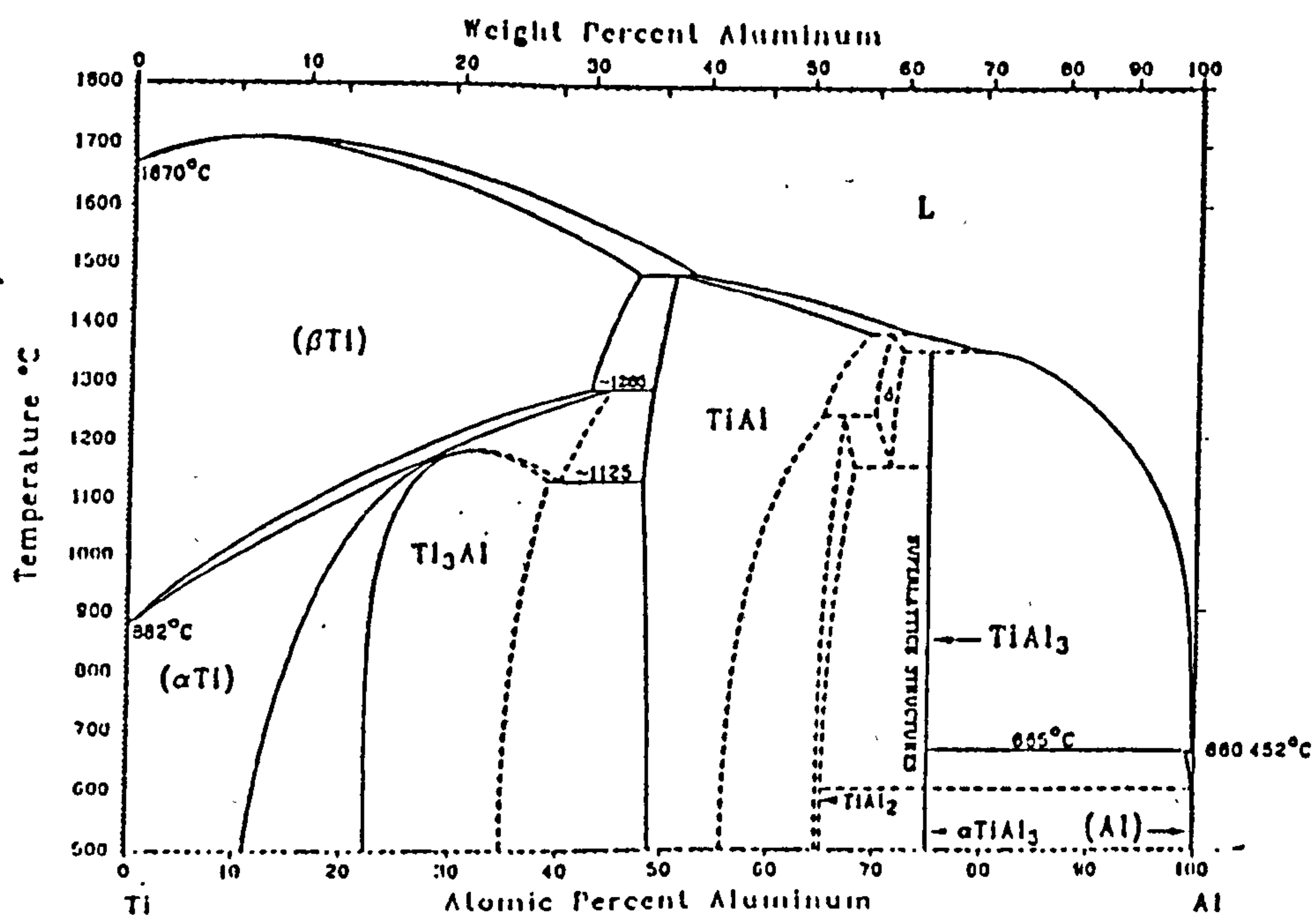
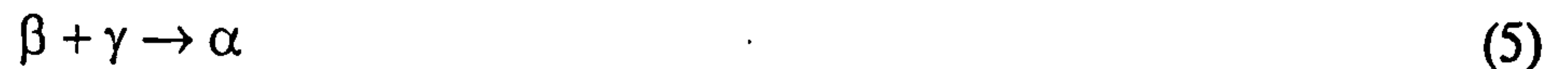


Figure 2.2. Titanium - Aluminium Binary Phase Diagram (Murray).

approximately 1750K. This paper suggests that the peritectoid reaction ;



which according to Murray [Mur87] had not had its temperature experimentally measured, does not actually occur in the system. The proposed modifications to the Ti-Al phase diagram published in this paper are shown in Figure 2.3.

That the α field extends as high as the solidus has been verified by Mishurda et al [Mis89], who, using a combination of theoretical modelling and experimental results, have produced a modification to the extent of the α phase field. This suggests that the α phase exists in two entirely separate regions of the phase diagram, being completely separated by the ordered species Ti_3Al . This appears to be thermodynamically unlikely, and does not correspond to data produced by other authors. This paper uniquely suggests that the $\alpha + \beta$ two phase region does not extend without a break across the entire region from pure Ti to the solidus. The proposed modifications to the phase diagram are shown in Figure.2.4 .

The assessed phase diagram for the niobium - titanium system [Mur81] shown in Figure 2.5., in contrast to that of the Ti-Al system is extremely simple. As niobium is a strong β stabiliser, the β transus is rapidly lowered to 500°C or below with 20at.% addition of niobium. The system consists of a solid solution of niobium and β titanium across the entire compositional range beyond 20at.%, at room temperature.

There have been four major examinations of the aluminium - niobium binary system by Nedomov, Baron, Lundin and Richards [Ned61, Bar61, Lun66, Ric64]. Elliot [Ell81] summarised the results produced by the work of these authors (in total, during those studies, more than 200 different alloy compositions were examined). The combination of these four works has produced the phase diagram which is shown in Figure 2.6. There is broad agreement between these studies as to the phases which exist in this binary system. These being a series of intermetallics with compositions centred around the stoichiometric compositions of Al_3Nb , AlNb_2 and AlNb_3 . Both of the high Nb phases have a solubility range of around 10at.% with parallel, vertical phase boundaries. It is generally agreed that Al_3Nb compound is a compound with a very narrow compositional range, probably a line compound. Richards [Rich64] also suggests that two further high temperature phases, AlNb_5 and Al_2Nb_5 are also present in the system, which as yet has not been confirmed.

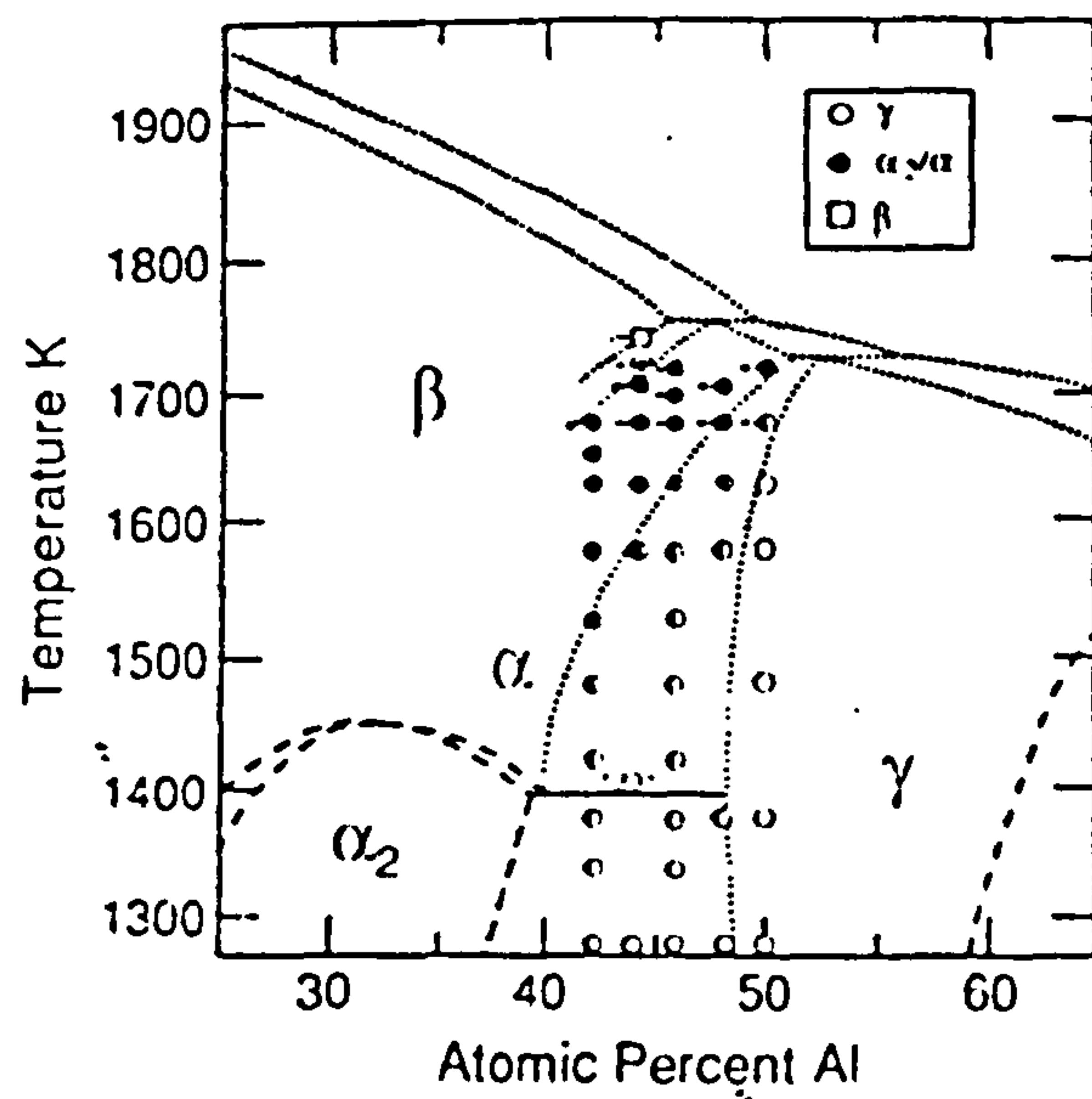


Figure 2.3. Titanium - aluminium binary phase diagram. [McCullough]

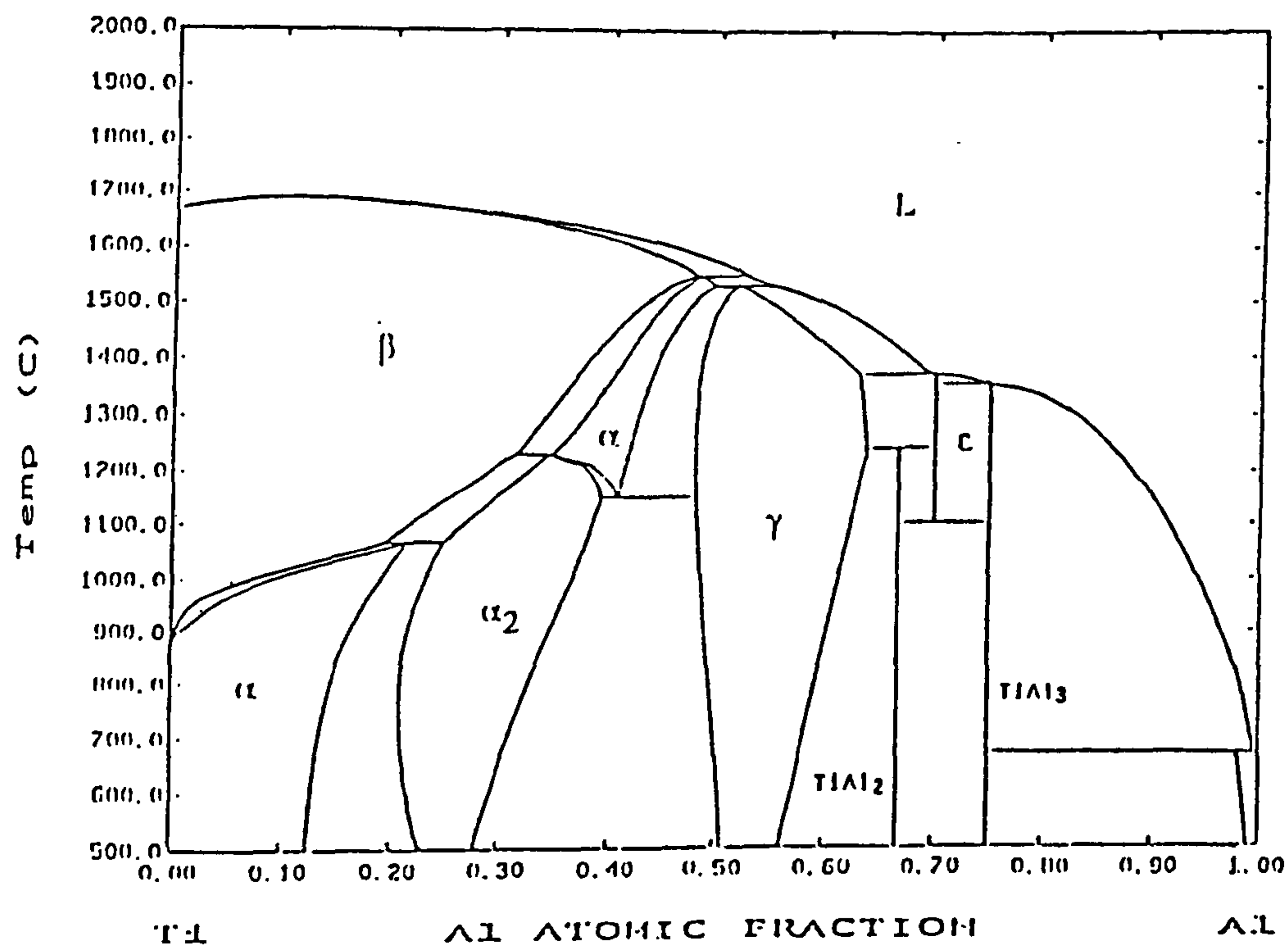


Figure 2.4. Titanium - aluminium binary phase diagram. [Mishurda]

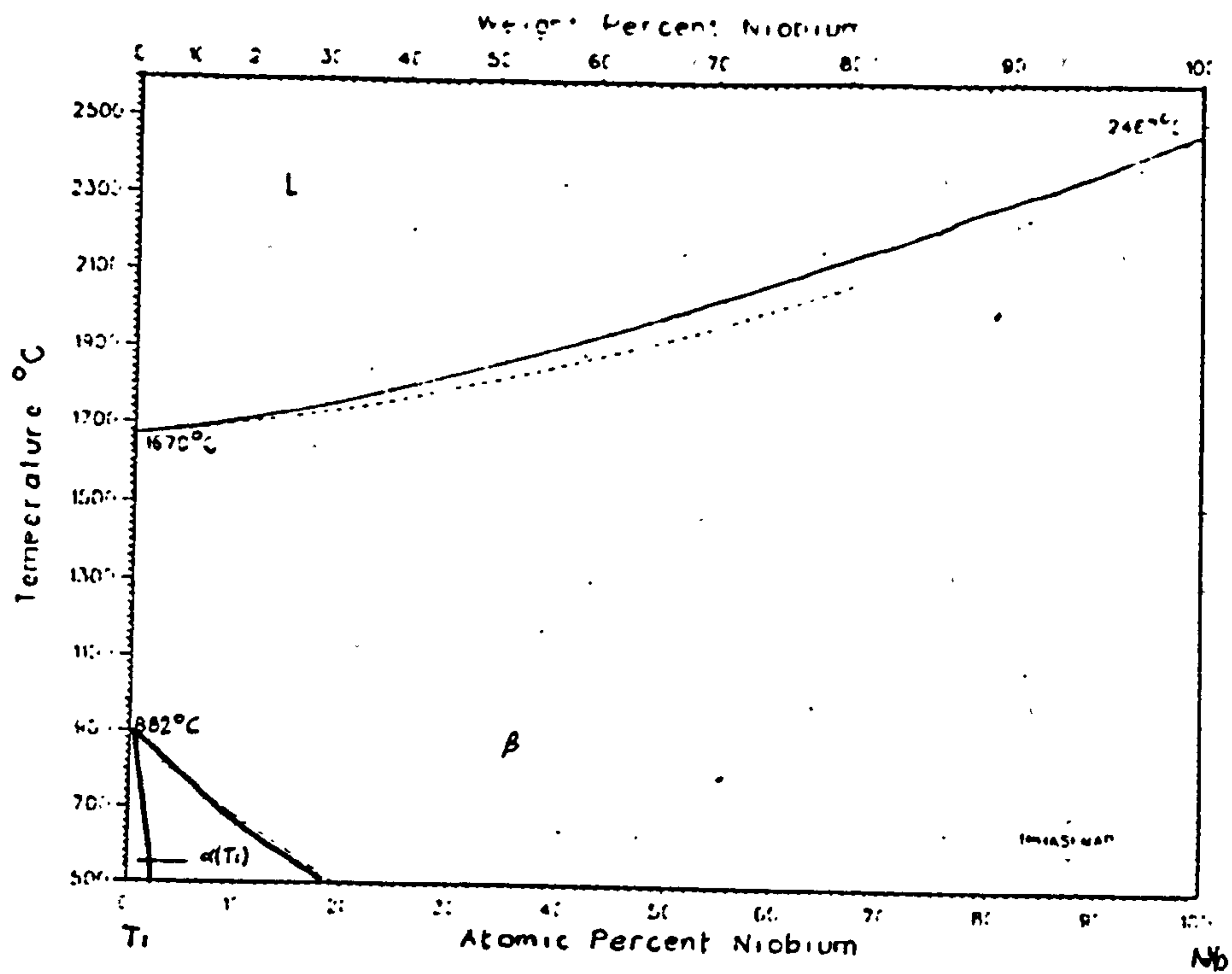


Figure 2.5. Titanium - niobium binary phase diagram. [Murray]

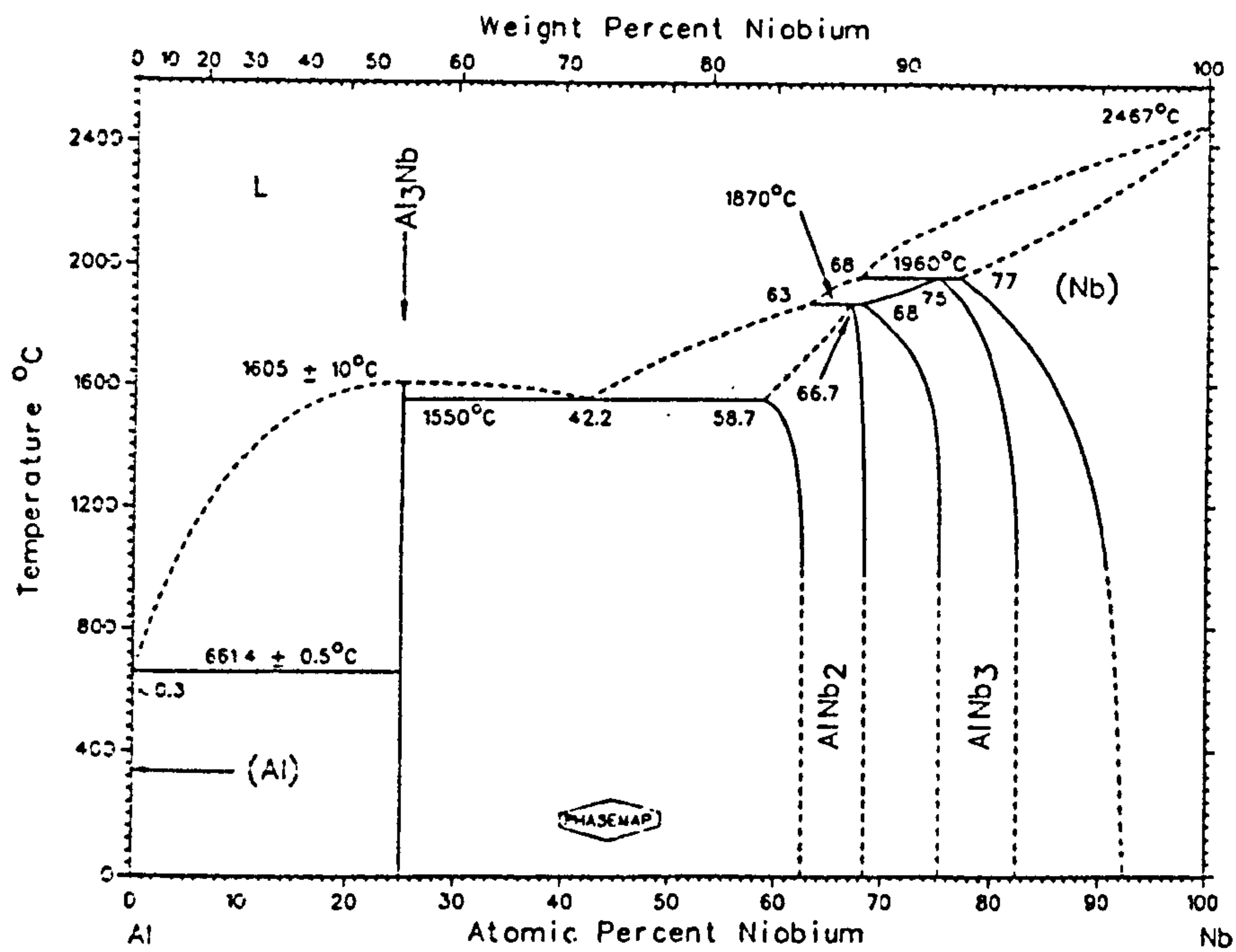


Figure 2.6. Aluminium - niobium binary phase diagram. [Elliot]

The addition of silicon to any of the three previously mentioned elements (i.e. Ti, Al and Nb) in each case, in the assessed phase diagram produces a eutectic at low silicon addition levels. The aluminium - silicon system, the work on which has been summarised by Murray [Mur84], is shown in Figure 2.7. This shows a simple eutectic system, with a eutectic point at approximately 12.2 at.% silicon (12.6wt.% Si).

The titanium - silicon system (Figure 2.8), as reviewed by Murray [Mur87a] includes a series of five intermetallic compounds. Silicon is soluble in β titanium up to approximately 6at.%. The addition of silicon reduces the β transus slightly to around 865°C. However the solubility is much lower in α titanium, and is limited to about 1at.%. When the Si in Ti solubility level is exceeded a silicide of the composition Ti_5Si_3 is generally formed, although at low temperatures the equilibrium phase is Ti_3Si . This forms only slowly upon heat treatment.

The niobium - silicon phase diagram, as summarised by Knapton [Kna54], (see Figure 2.9.) involves the formation of two intermetallic compounds, namely Nb_5Si_3 and NbSi_2 , both of which are identified as congruently melting line compounds. This phase diagram is based on the work of Wallbaum [Wal47], with a range of modifications from various authors, but retaining the same basic shape and structure.

2.4.2. Ternary Isothermal Sections.

2.4.2.1 The Niobium - Aluminium - Silicon System.

The ternary system consisting of the three components Nb, Al and Si has not been studied in great detail to date, however two isothermal sections have been developed [Al73] which are reproduced here (Figures. 2.10,2.11) at temperatures of 1300 and 1500°C. In the region which was studied in this work, and a second paper [Mol73], which both examined the system at niobium levels of up to 25at.%, the system is partially liquid.

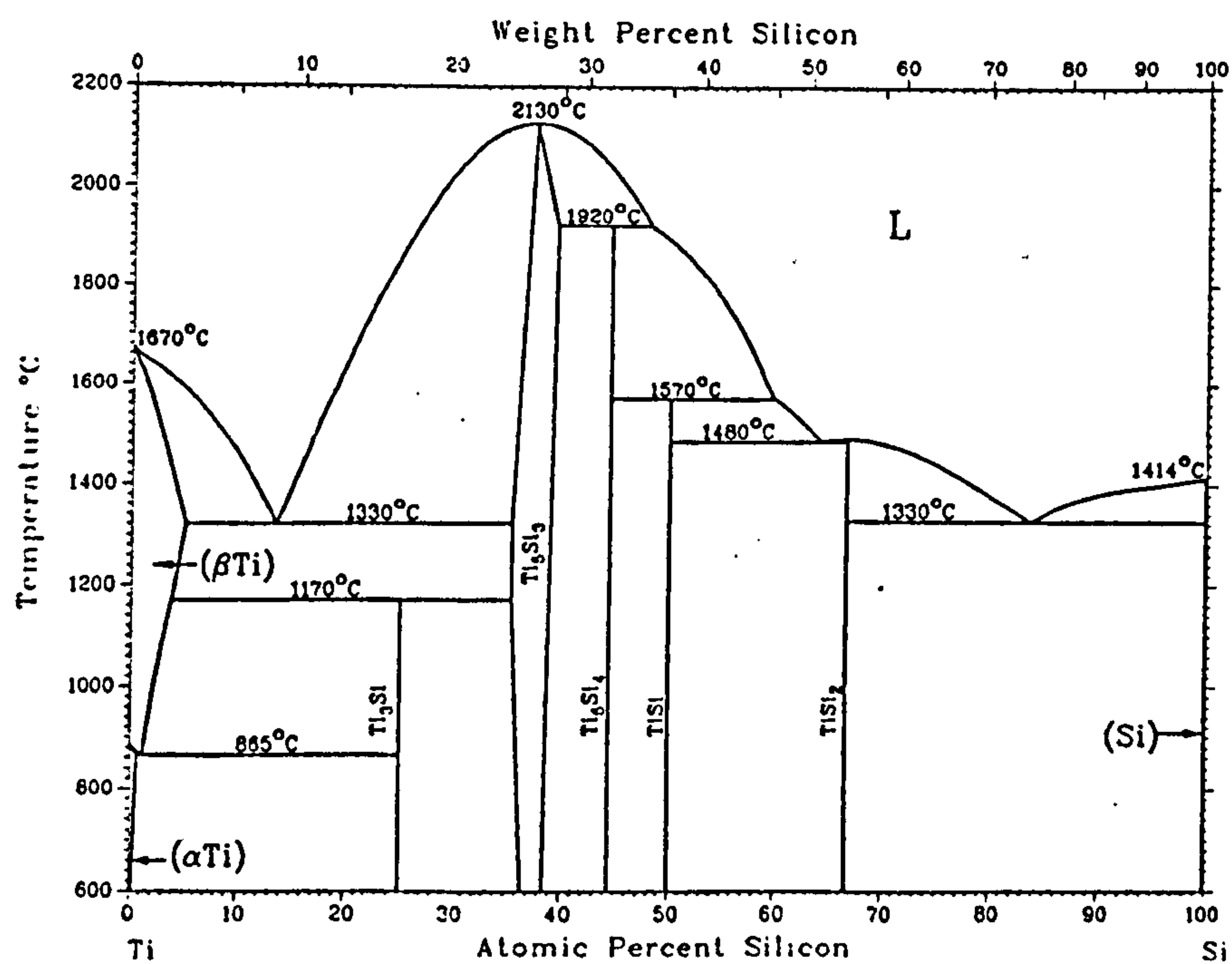
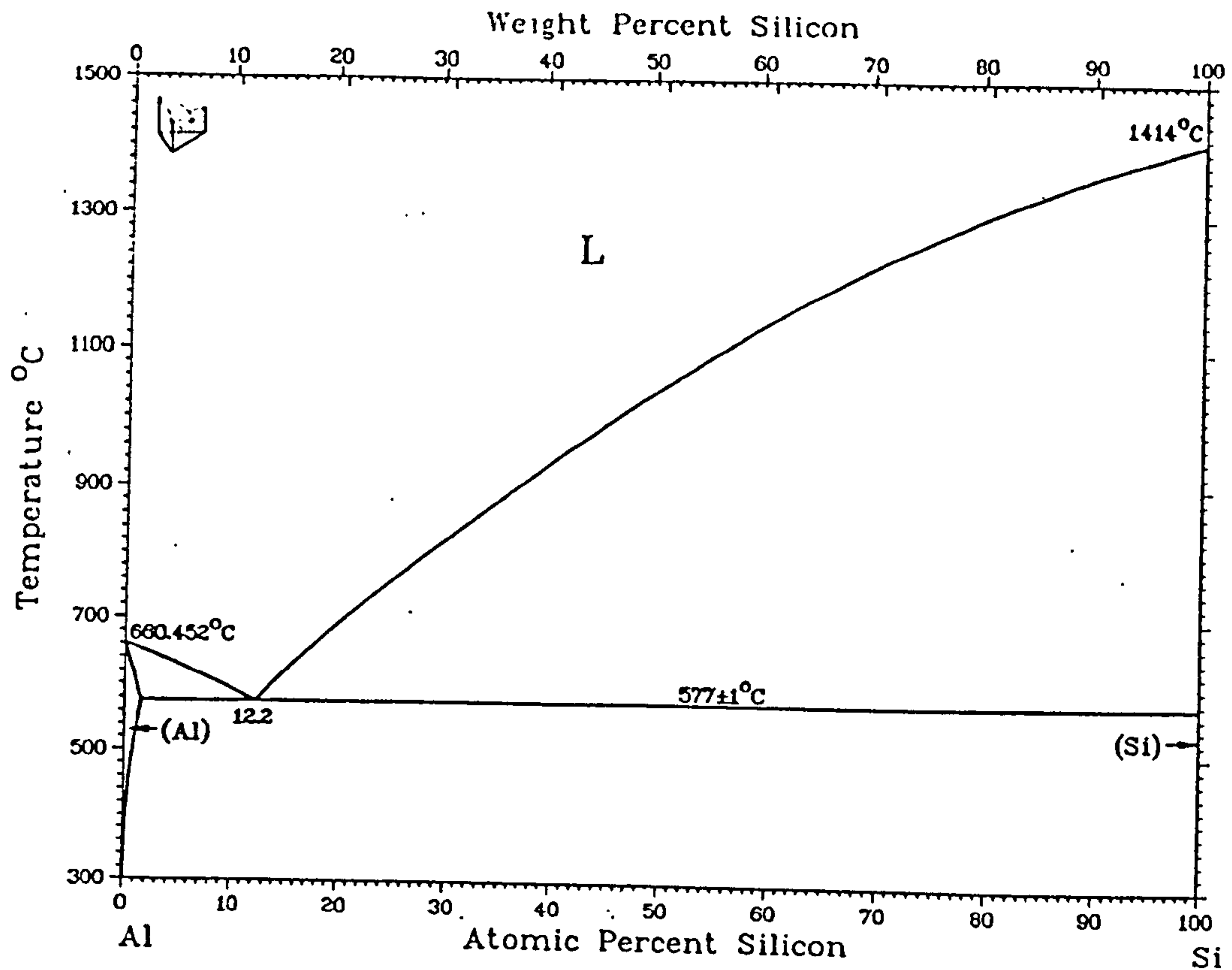


Figure 2.7. Aluminium - silicon binary phase diagram. [Murray]

Figure 2.8. Titanium - silicon binary phase diagram. [Murray]

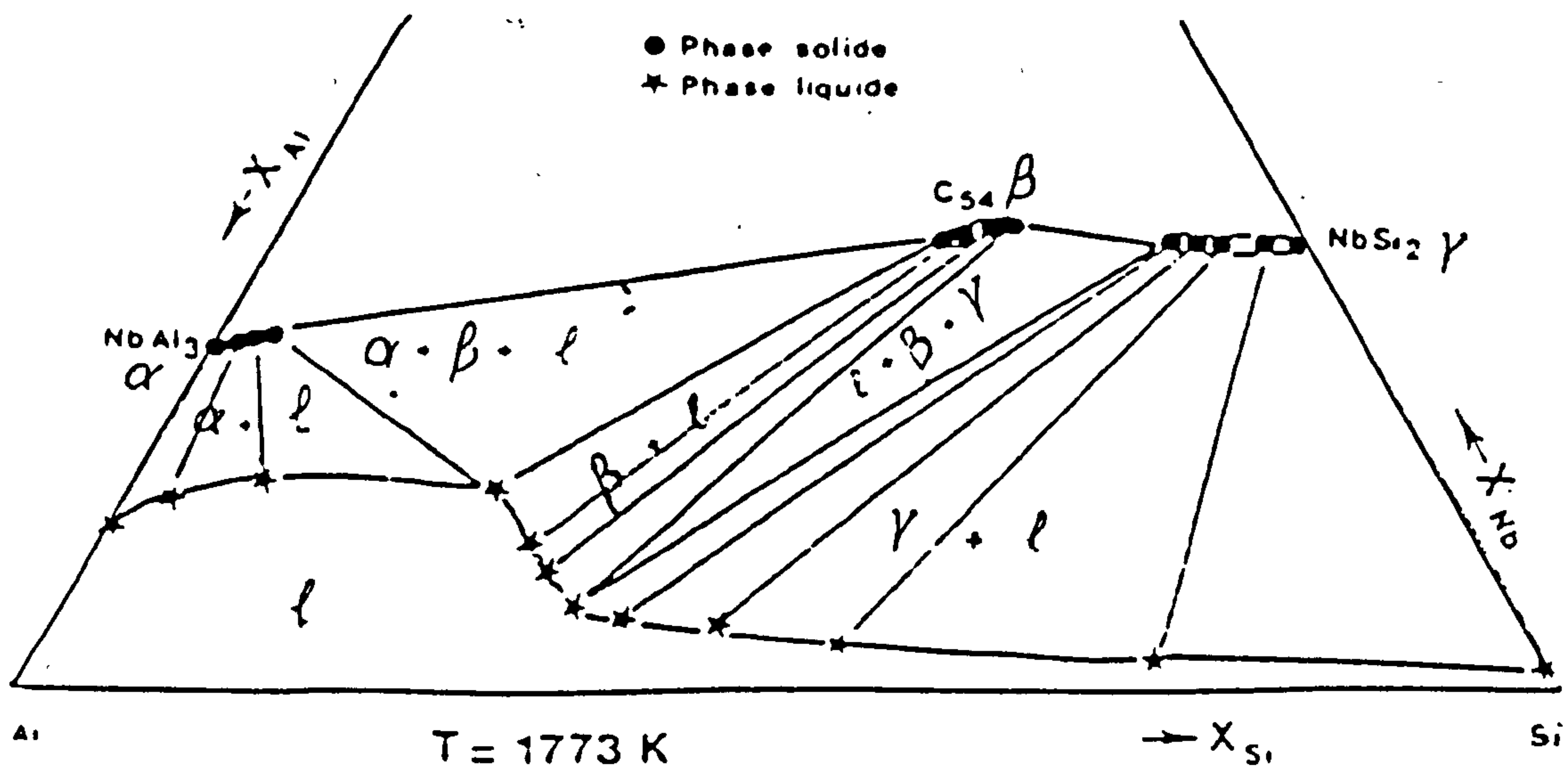
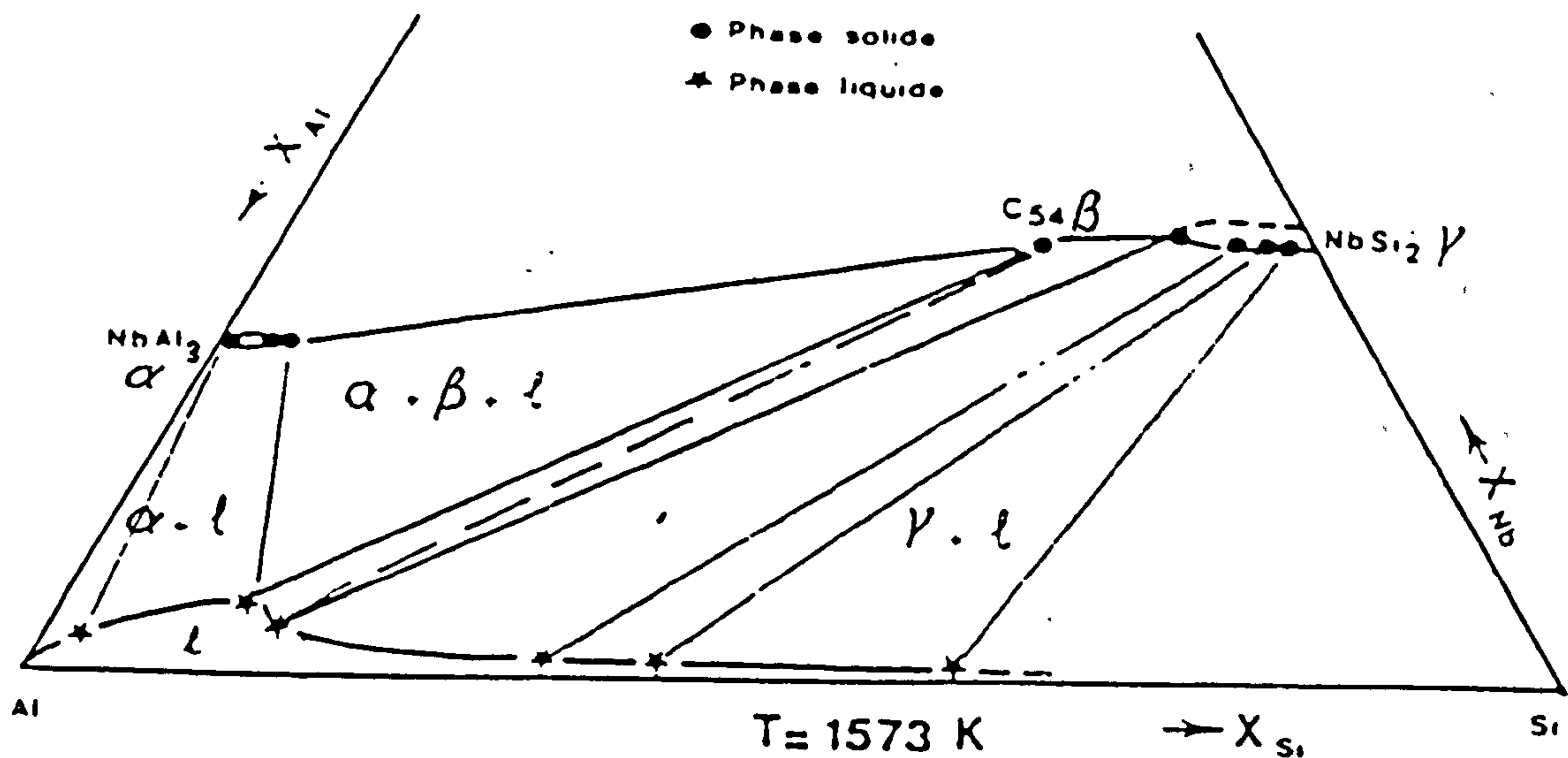
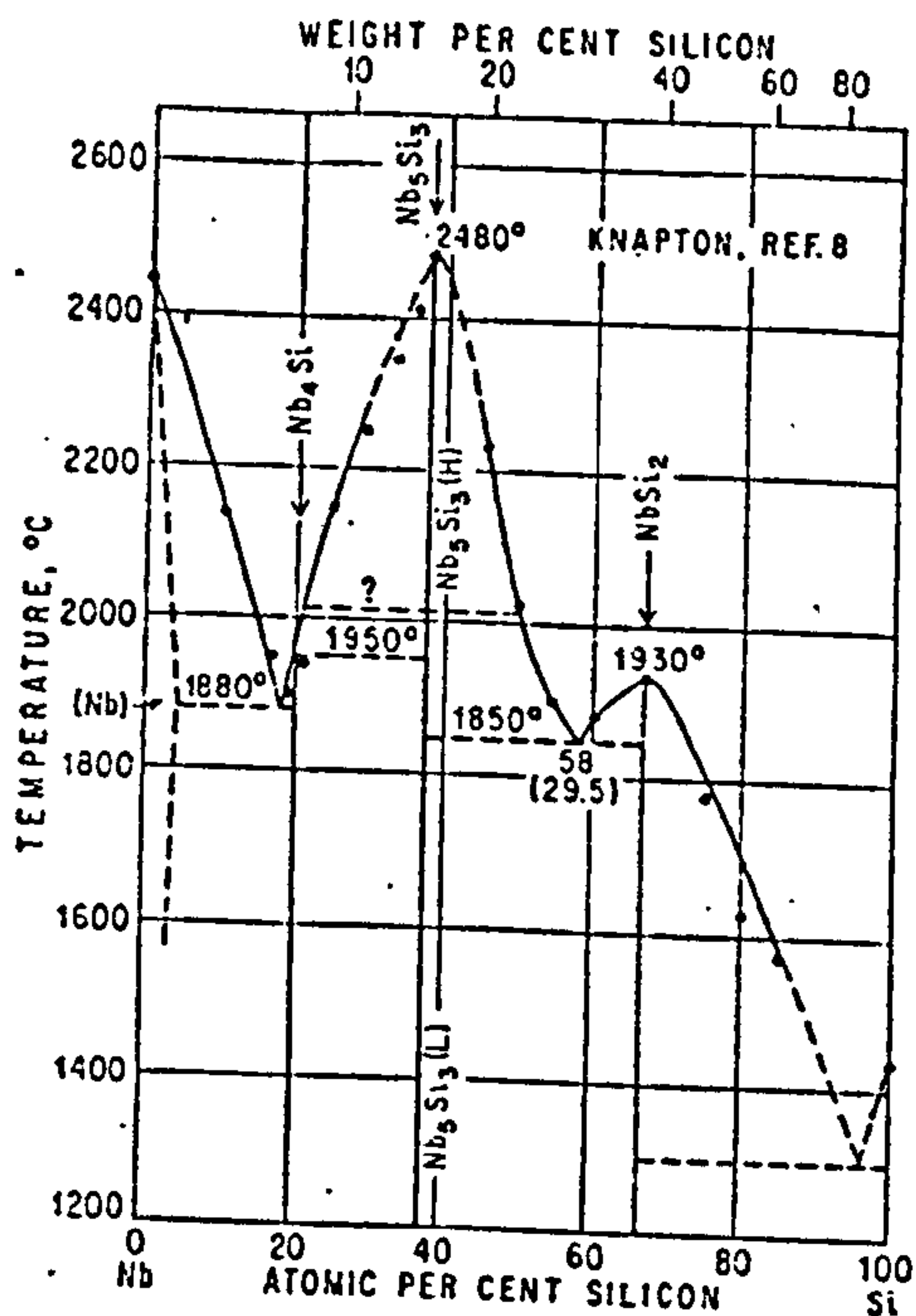


Figure 2.9. Niobium - Silicon binary section [Knapton]
Figure 2.10. Nb - Al - Si ternary section at 1300°C [Alibert]
Figure 2.11. Nb - Al - Si ternary section at 1500°C [Alibert]

2.4.2.2. The Titanium - Aluminium - Silicon System.

Crossley [Cros58], produced a series of partial isothermal sections for the titanium-rich corner of the Ti-Al-Si system through a range of temperatures from 600°C up to 1000°C. In the binary Ti-Si system, the phase diagram at low silicon levels forms a eutectoid between β Ti and Ti_5Si_3 . With the addition of aluminium this eutectoid is modified such as to produce a peritectoid. An example of which (the partial isothermal section at 1000°C) is reproduced in Figure 2.12. These sections show that the addition of the silicon to a Ti-Al alloy produces a relatively simple system. At low silicon additions, the silicon is held in solution in either α or β -based titanium.

At higher concentrations, a second phase, Ti_5Si_3 , occurs in the system. At high temperatures, e.g. 1000°C, the silicon additions appear to reduce the β transus temperature, as the extent of the $\alpha + \beta$ phase field is reduced by approximately 1at.% Al. A more recent study in the titanium rich corner of the system by Khataee [Kha89], has produced isothermal sections in the compositional range of 70 - 100% Ti plus Al and Si at 800, 1100 and 1200°C (see Figures 2.13-15) showing equilibration between silicide and aluminide phases. These diagrams also indicate the presence of a peritectoid reaction. This series of diagrams indicate that the percentage of silicon in solution in the aluminide is independent of temperature. In the β phase region, the solubility of silicon increases with increasing temperature.

2.5. The Titanium - Aluminium - Niobium-Based Alloys System.

2.5.1. Phases Diagrams and Identified Structures.

In a series of isothermal sections published in 1962 [Pop62], Popov and Rabezova investigated the niobium rich corner of the phase diagram at 20, 1200 and 1400°C. The 20°C isothermal section was constructed from examinations of samples slowly cooled from 1200°C, and the higher temperature sections were deduced from quenched samples. This work, using X-ray analysis and light microscopy, identified a range of solid solutions based mainly on binary intermetallic compounds identified in the Nb - Al system by Baron and Savitskii [Bar61]. This work identified 6 phases in the system, which were solid solutions based on the following compounds; α Ti, β Ti,

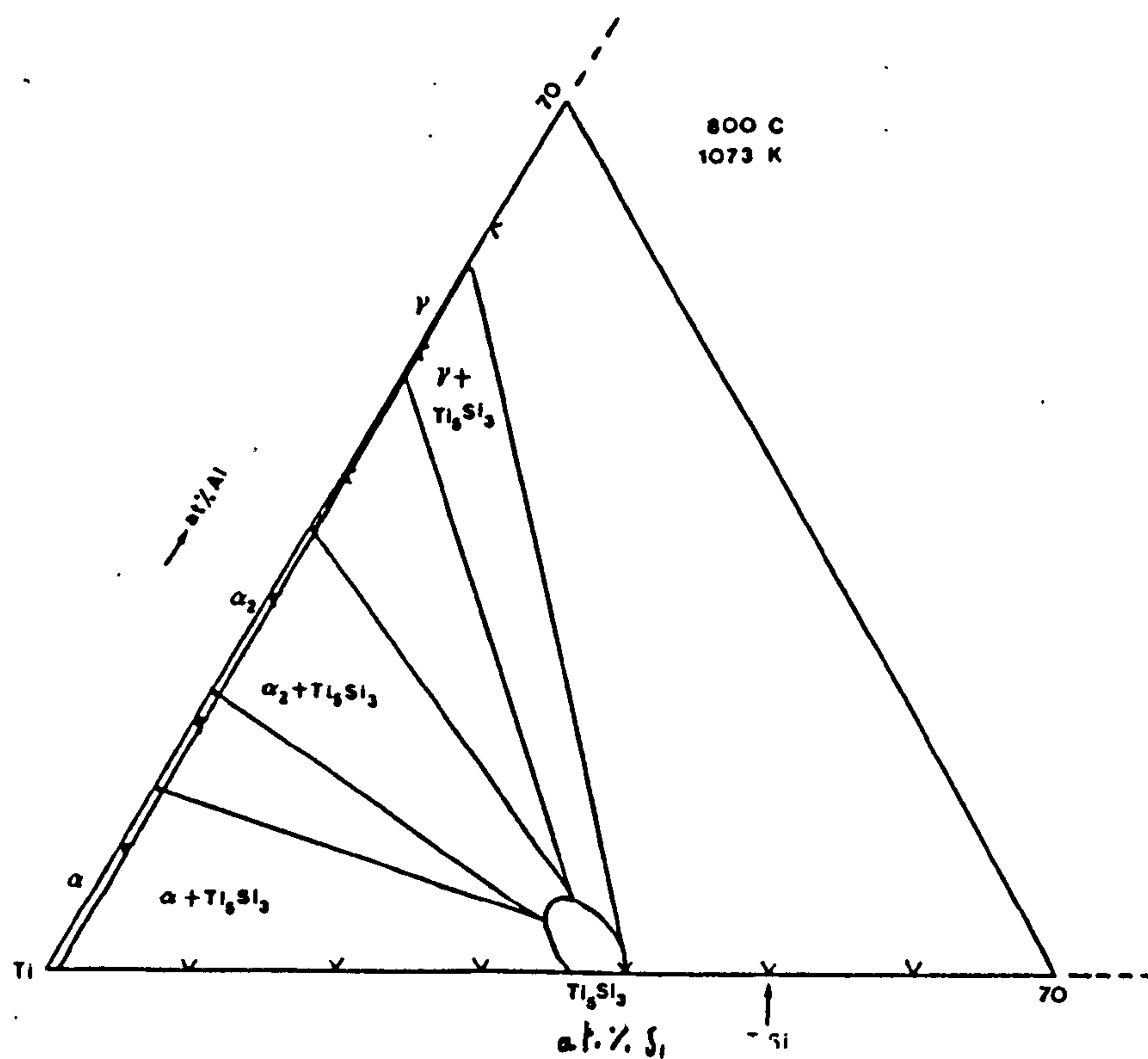
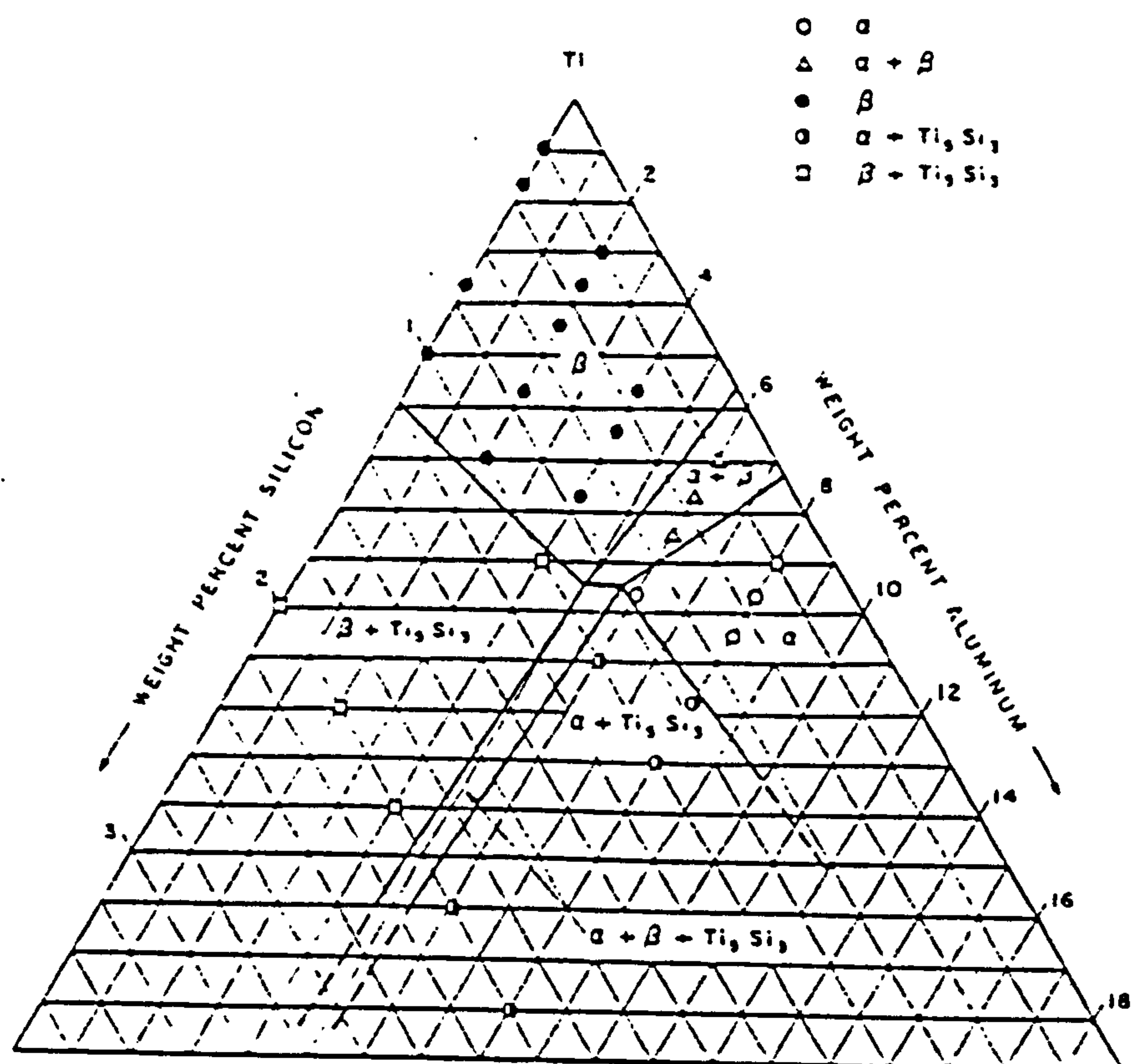


Figure 2.12. Ti - Al - Si ternary section at 1000°C [Crossley]

Figure 2.13. Nb - Al - Si ternary section at 800°C [Khataee]

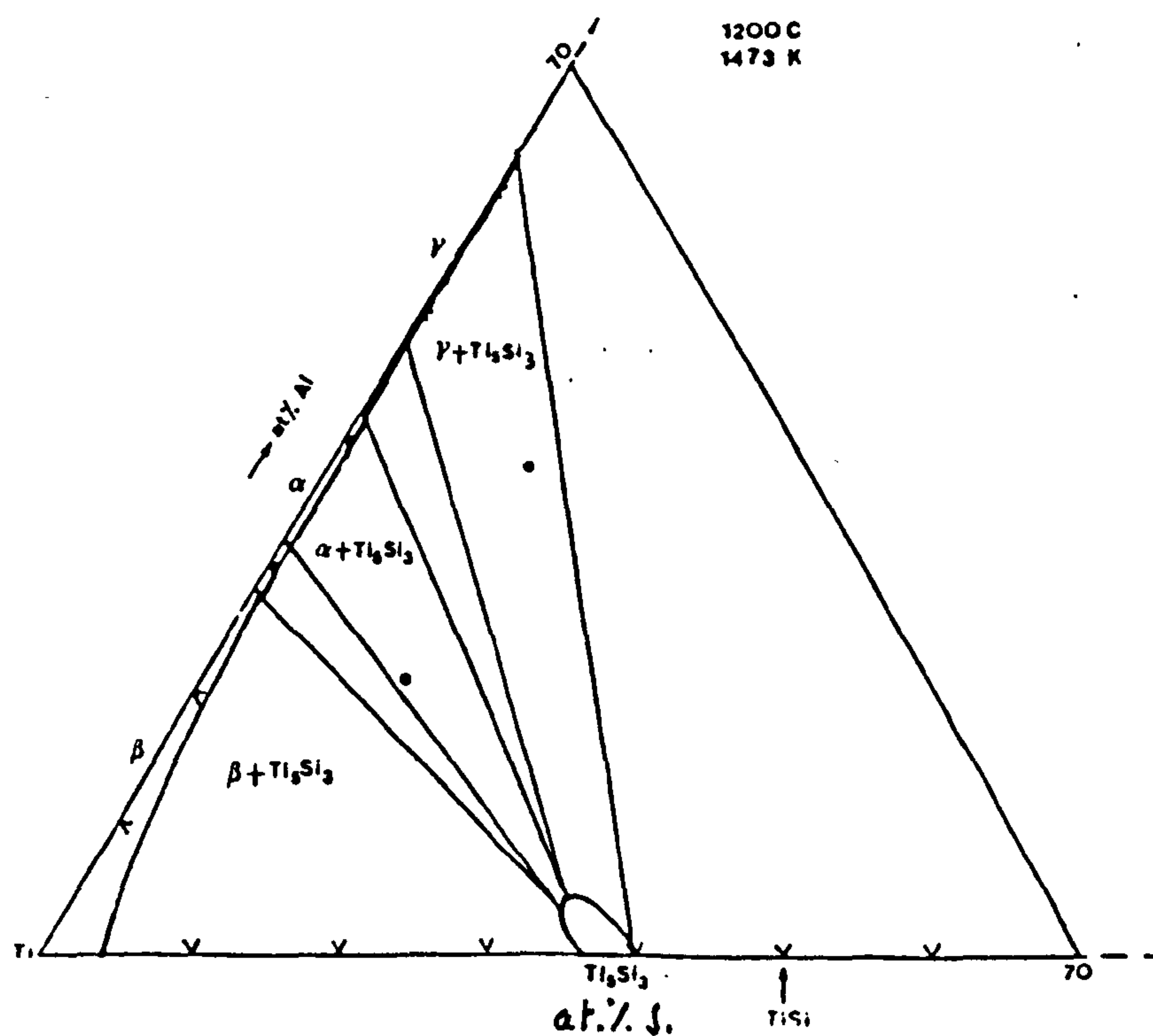
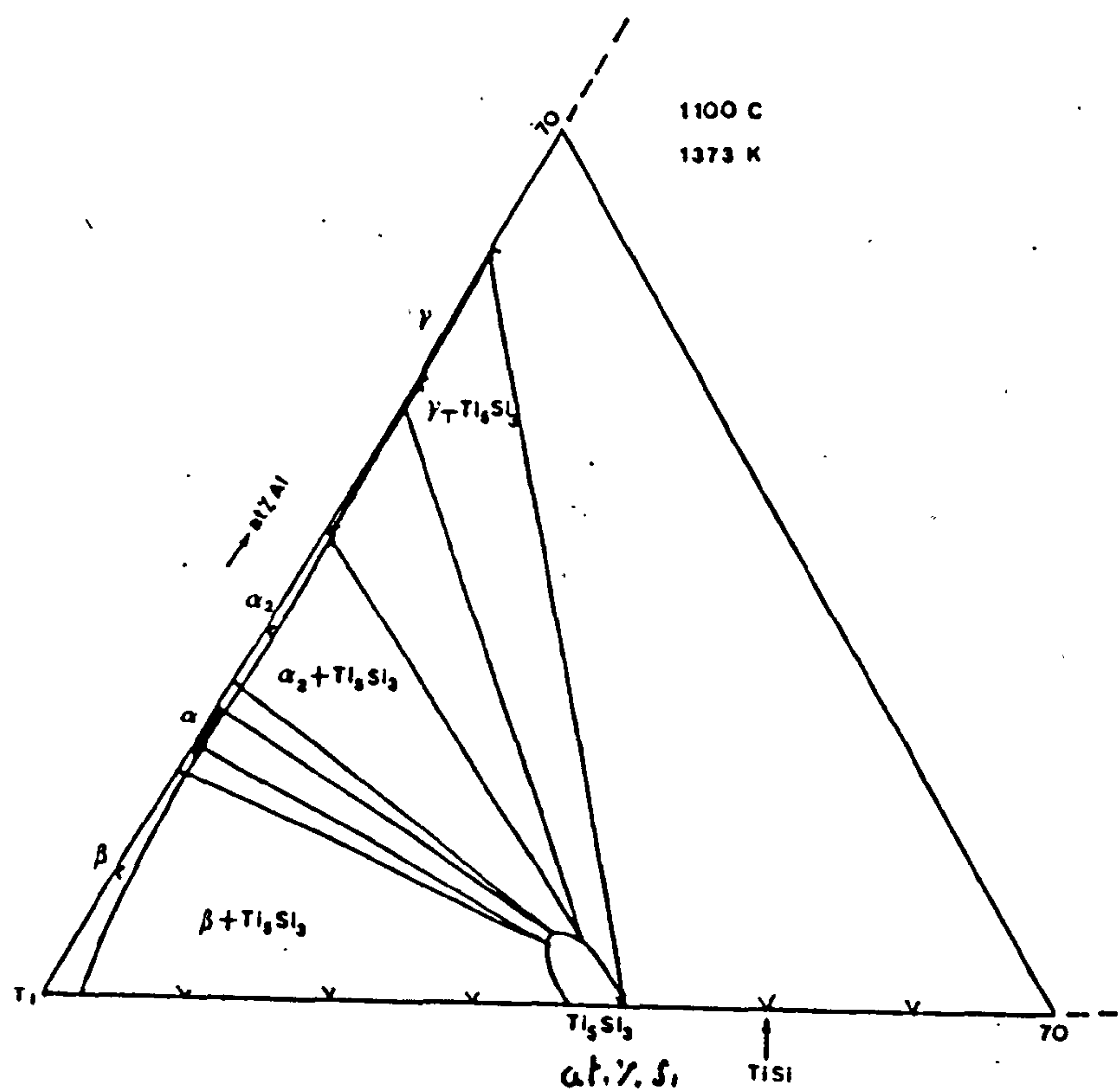


Figure 2.14. Nb - Al - Si ternary section at 1100°C [Khataee]

Figure 2.15. Nb - Al - Si ternary section at 1200°C [Khataee]

Nb_3Al , Nb_2Al , TiNbAl_3 and NbAl_3 . The notable absence of α_2 is probably due to the authors basing the Ti-Al side of the diagram on the binary diagram produced by Ogden et al [Ogd51] instead of the then more recent work of Sagel [Sag56], in which the α_2 phase was first reported.

More recent work [Nar70, Zak84, Kal89, Kha89, etc.] on the system, from a range of sources, has concentrated on alloy chemistry in the titanium rich corner of the phase diagram. Nartova [Nar70] conducted an extensive examination into alloys along a vertical section of the ternary section through a line between Ti_3Al and Nb within a temperature range from 600-1200°C. This was produced using thermal analysis to determine the phase transformation temperatures, and X-ray data to identify the phases present over the temperature range separated by two transformation temperatures. Annealing of the samples was carried out for long periods of time (up to 600 hours for a 600°C equilibration). No indication was given as to any gaseous impurity pick-up during the annealing process, which appears to have been carried out in air. The vertical section developed by Nartova is reproduced as Figure 2.16. This examination produced a vertical section which behaves in an analogous manner to that of the binary Ti-Nb system as summarised by Elliot [Ell81] with α_2 replacing α , and indicates that the β stabilising effect of the niobium inhibits the production of a single phase α_2 field at between 5 and 6 wt.% Nb when the $\alpha_2 + \beta$ field is extended to higher Nb content at 600°C.

In a series of three polythermal sections in the system with up to 60 at.% Nb and varying ratios of Ti:Al produced by Troiskii [Tro83], and shown here in Figure 2.17, the effect of niobium on the equilibrium between β , and a phase designated γ_1 (NbTiAl_3) formed by a eutectic reaction is shown. The γ_1 phase is identified as tetragonal with lattice parameters of $a=841\text{pm}$ and $c=454\text{pm}$. Alloys on the same compositional line (between β and NbTiAl_3) have also been examined by Zakharov et al [Zak84], who combined these with a range of alloys with lower Nb contents to produce a set of isothermal sections at 600, 900 and 1200°C (Figures 2.18-20) along with a liquidus projection.

The most recent isothermal sections produced in this system [Kal89, Jew89, Kha90] both concentrate on sections at 1200°C (1473K). The diagram produced by Kaltenbach (Figure 2.21) involved the examination of alloys that were previously solution treated at 1400°C. It is important to note that after heat treatment (between 22 and 168hrs), the samples were gas cooled in a flowing Ar stream. This *relatively* slow cooling rate may have affected the final microstructure due to the possibility of

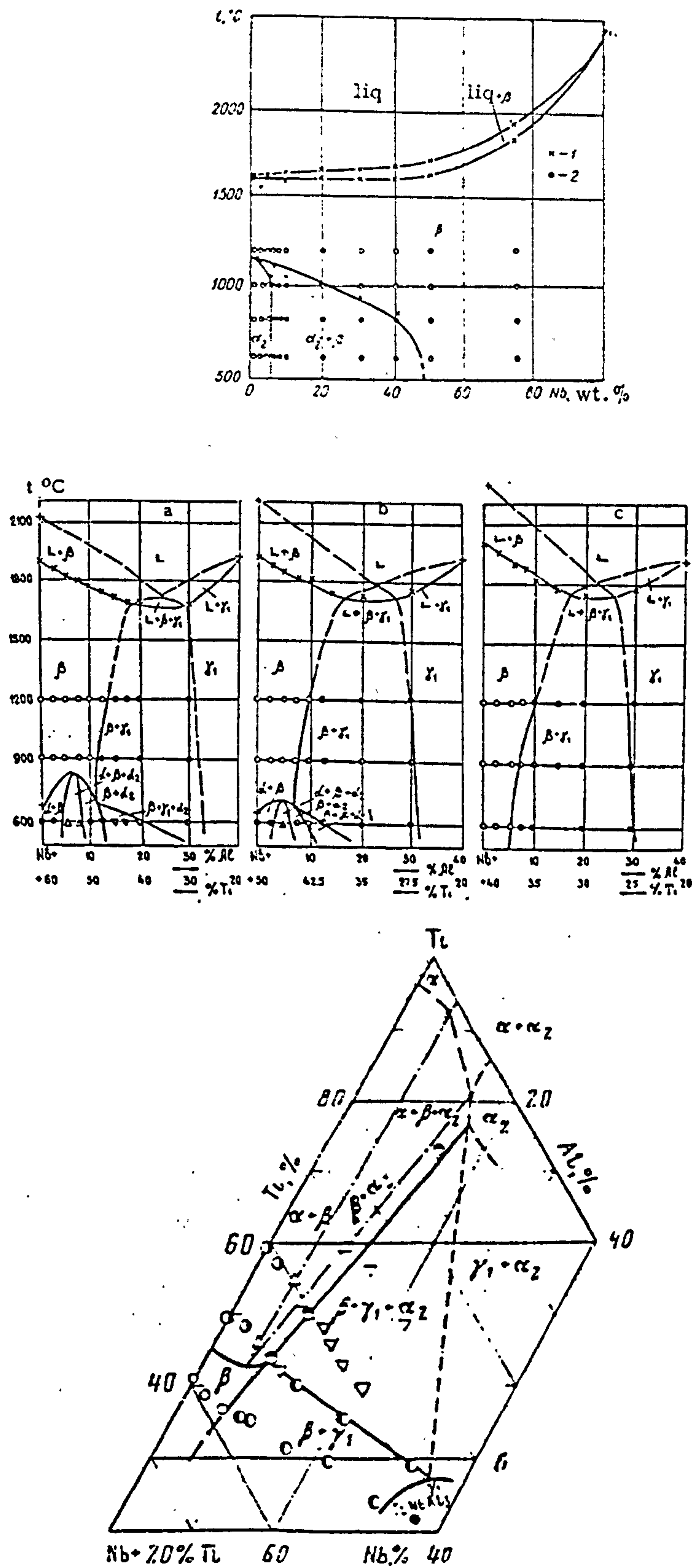


Figure 2.16. Vertical section of $\text{Ti}_3\text{Al} + \text{Nb}$. [Nartova]

Figure 2.17. Vertical section of $\text{Ti}_3\text{Al} + \text{Nb}$. [Troitskii]

Figure 2.18. Ti - Al - Nb ternary section at 600°C [Zhakharov]

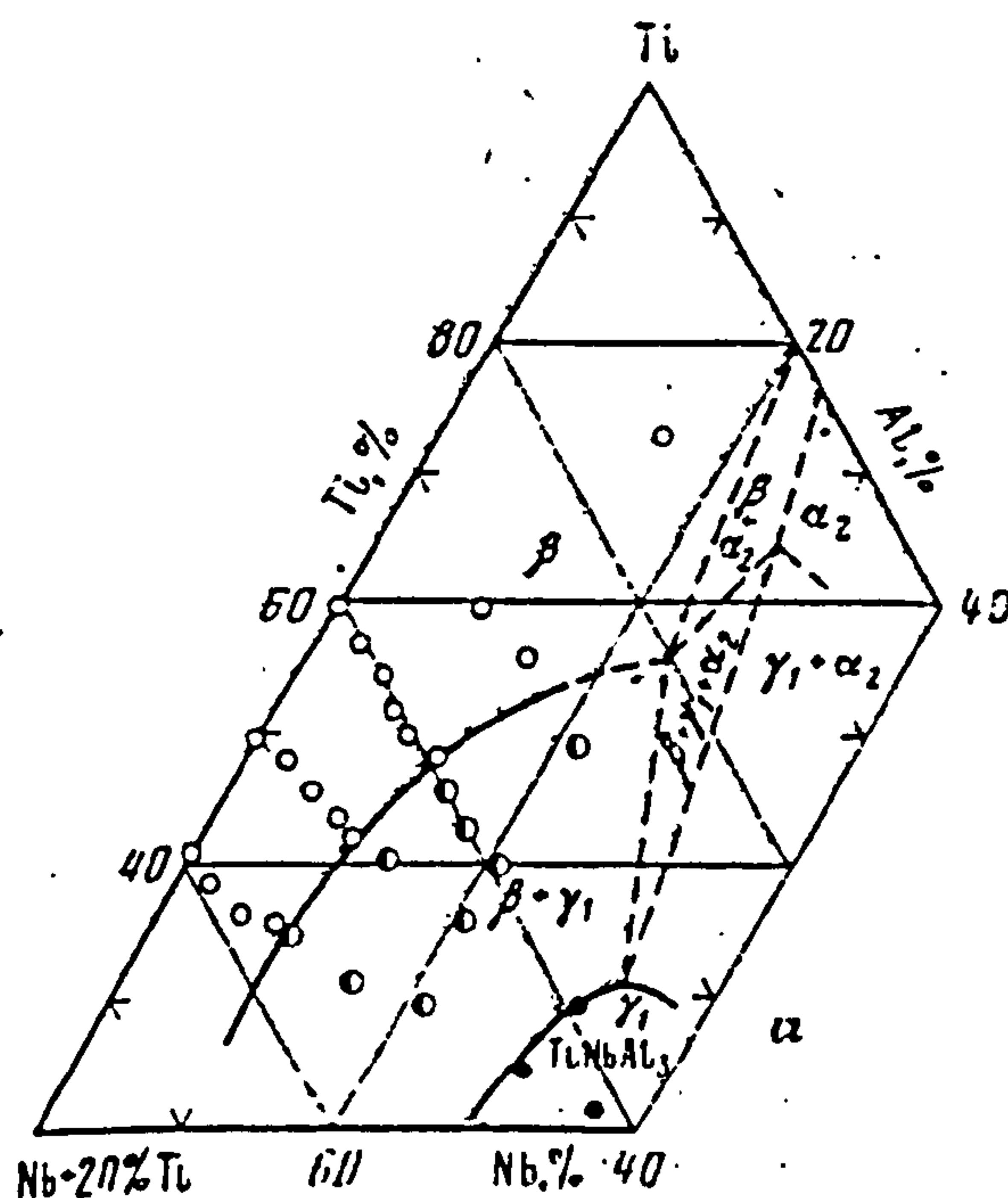
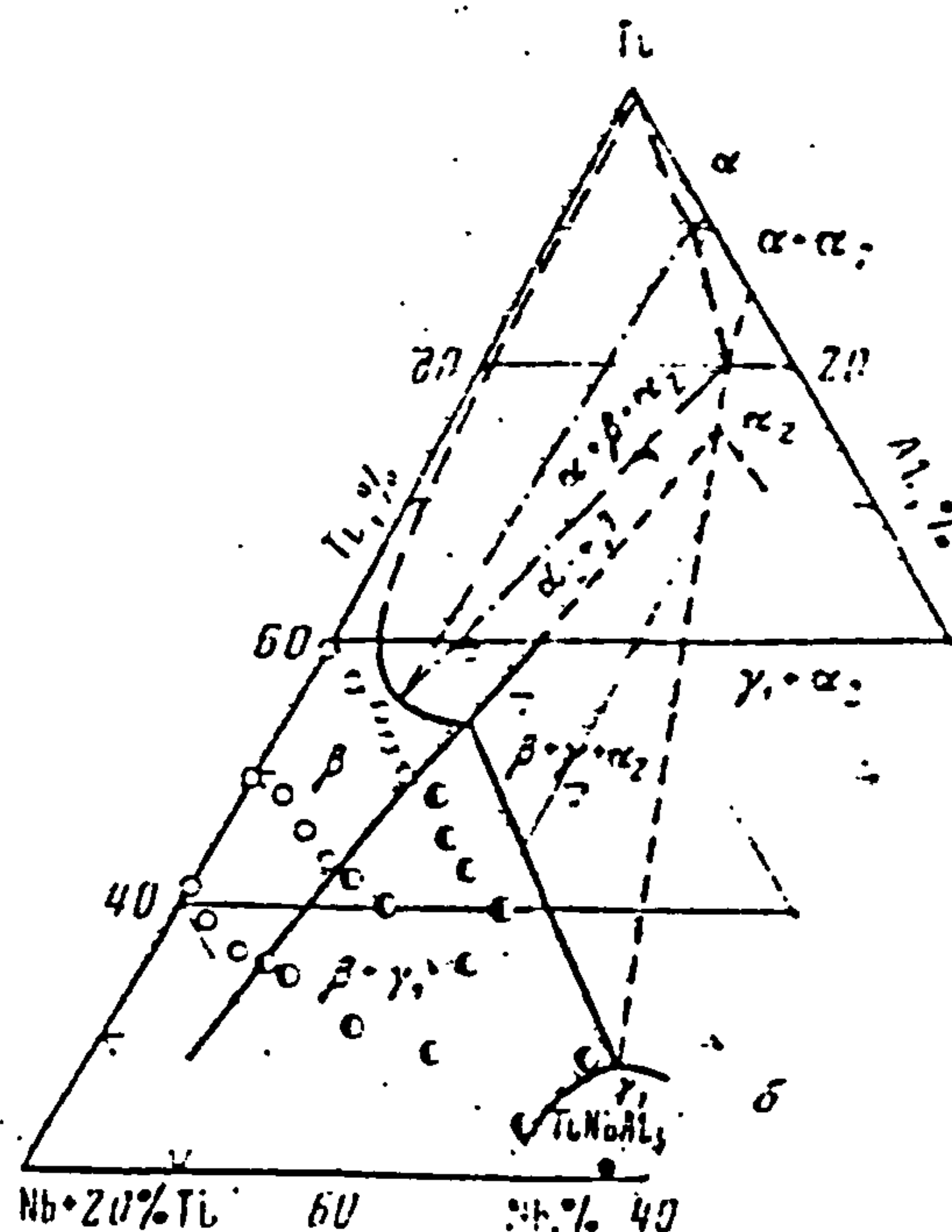


Figure 2.19. Ti - Al - Nb ternary section at 900°C [Zhakharov]

Figure 2.20. Ti - Al - Nb ternary section at 1200°C [Zhakharov]

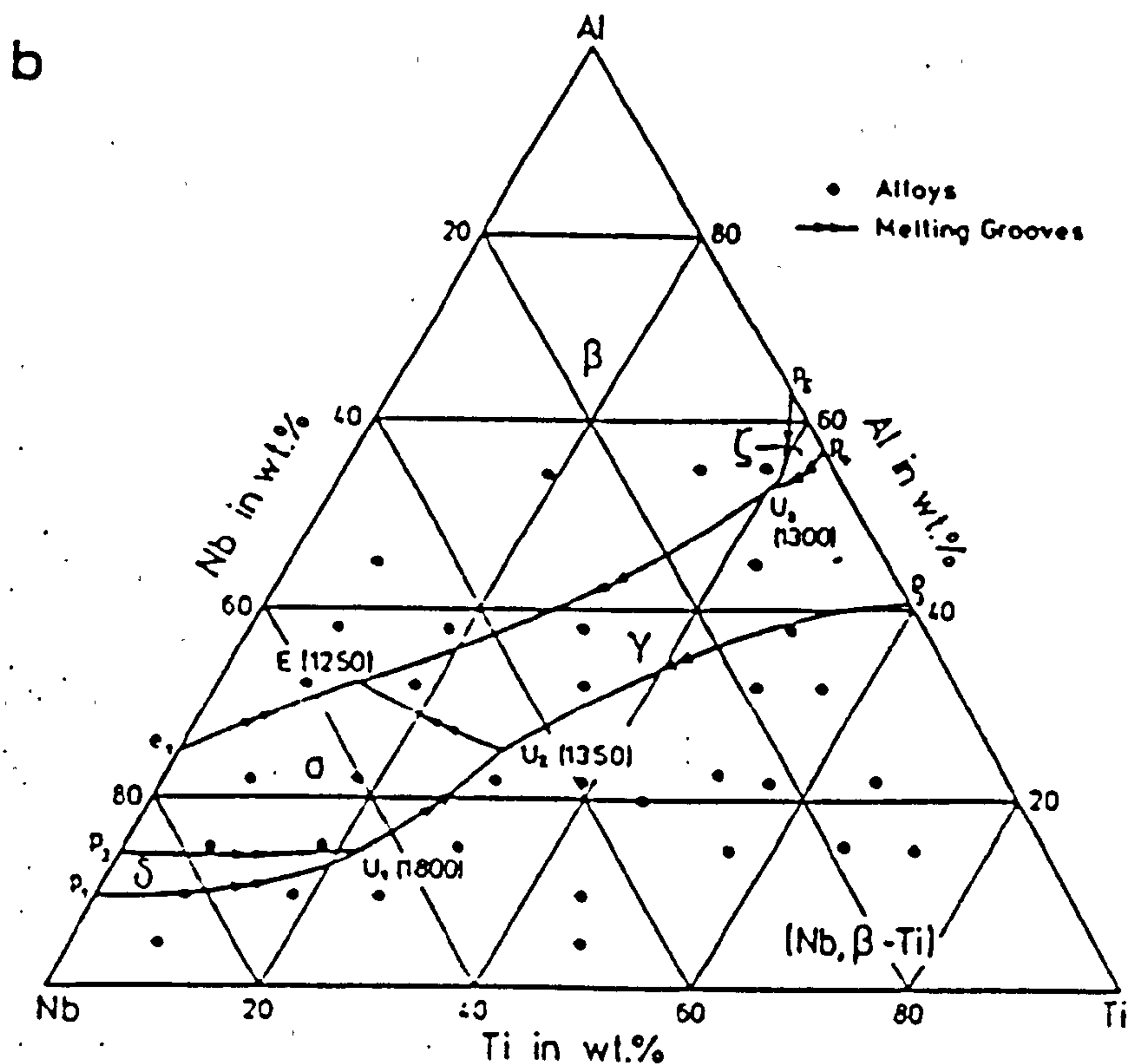
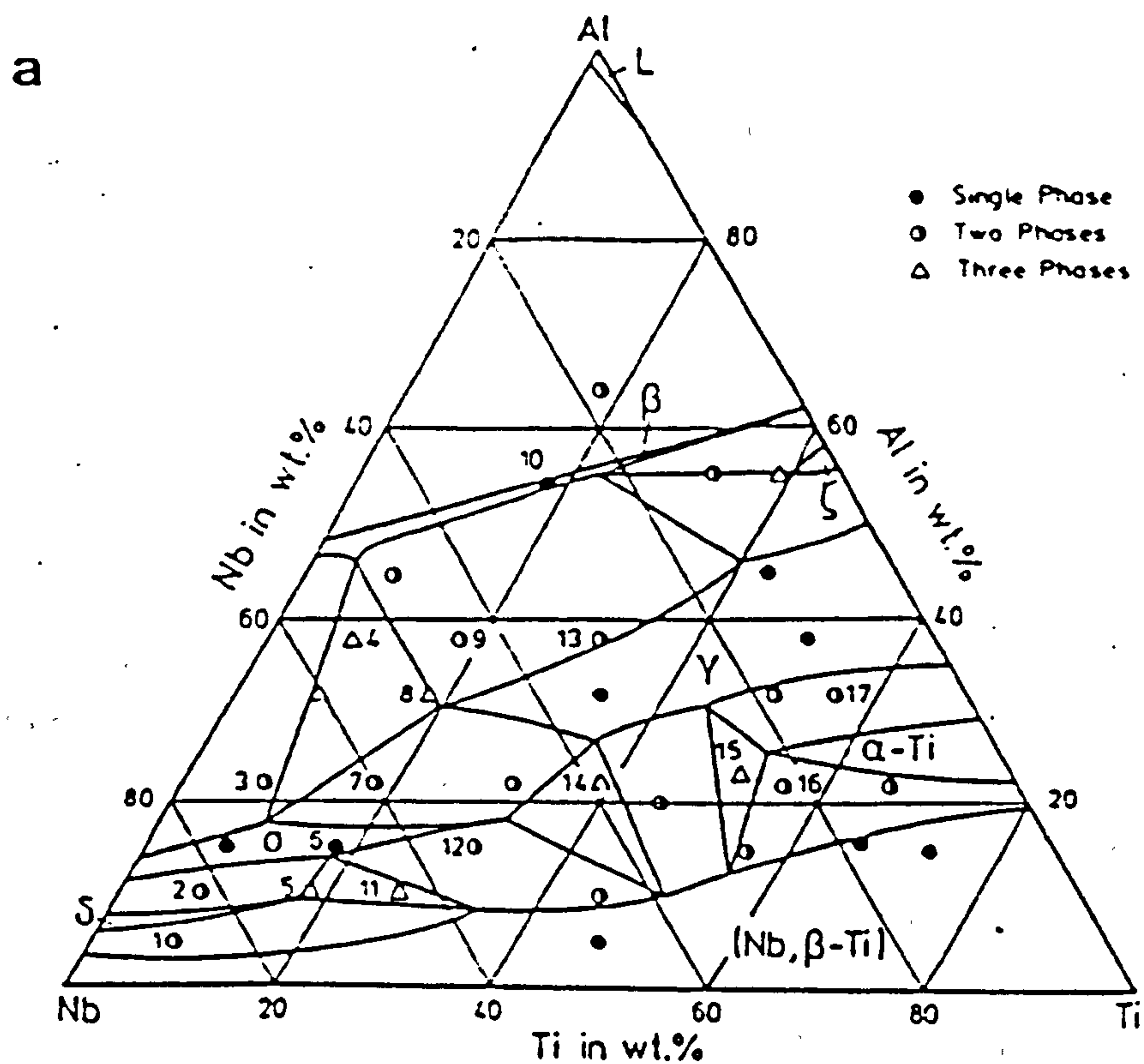


Figure 2.21a. Ti - Al - Nb ternary section at 1200°C [Kaltenbach]

Figure 2.21b. Liquidus projection of Ti - Al - Nb ternary system [Kaltenbach]

fine scale precipitation and other transformational behaviour during the cooling process. This work is based on a range of 57 different compositions, though most of these were only examined metallographically. This work identifies a high temperature α phase region, though the room temperature X-ray analysis used for phase identification identified an α_2 phase rather than α , but was judged to be present due to an ordering reaction which occurred on quenching. This phase was also identified by Jewett et al [Jew89] in another examination of the same isothermal section (Figure 2.22). This also identified two previously unreported phases which were designated as T_1 and T_2 . These were reported as having compositions of Ti -18Nb -34Al and Ti -11Nb -44Al (values in atomic %) respectively, as identified by EPMA (Electron Probe Micro Analysis). These phases, unreported anywhere else should be judged in the light of the ageing treatment which was carried out on them. Each sample was heat treated in flowing argon for between 192 and 384 hrs at 1200°C. Even with conventional high purity argon (< 3 ppm O₂), the amount of oxygen coming into contact with the alloy will be significant after such long ageing times. Thus it is possible that these phases may be part of the Ti-Al-Nb-O quaternary system, and not of the Ti-Al-Nb ternary system.

The titanium rich corner of the Ti - Al - Nb phase diagram has similarly been examined at 1200°C, and also at 1050 and 900°C by Khataee [Kha90]. The alloys examined were aged for between 24 and 96 hrs, depending on the temperature. Analysis was carried out using light, scanning electron and transmission electron microscopy. Samples were also examined using X-ray diffraction and EDS techniques. This work has produced three partial isothermal sections, at 900, 1050 and 1200°C in the compositional range from 0 - 70at.% Al and Nb. These are shown in Figures 2.23-25 respectively. At 1200°C, the isothermal section produced by this work is in agreement with Kaltenbach as to the extent, and shape of the phase boundaries in the isothermal section. At the lower temperatures examined, the isothermal sections show that the ordered Ti₃Al region expands towards the niobium rich corner of the system as the temperature is reduced. At 900°C this region reaches out to nearly 30at.%Nb. This differs markedly from the niobium solubility in Ti₃Al reported by Nartova [Nar70], as discussed previously, to extend only as far as 5-6wt.%Nb at temperatures below 800°C.

As well as the conventional α_2 and β phases which are found in the binary titanium - aluminium system, a number of other phases have also been identified. The first of these, reported by Strychor et al. [Str88], is an ω type (a metastable hexagonal phase which is a possible precursor structure for the formation of α or α_2 from β)

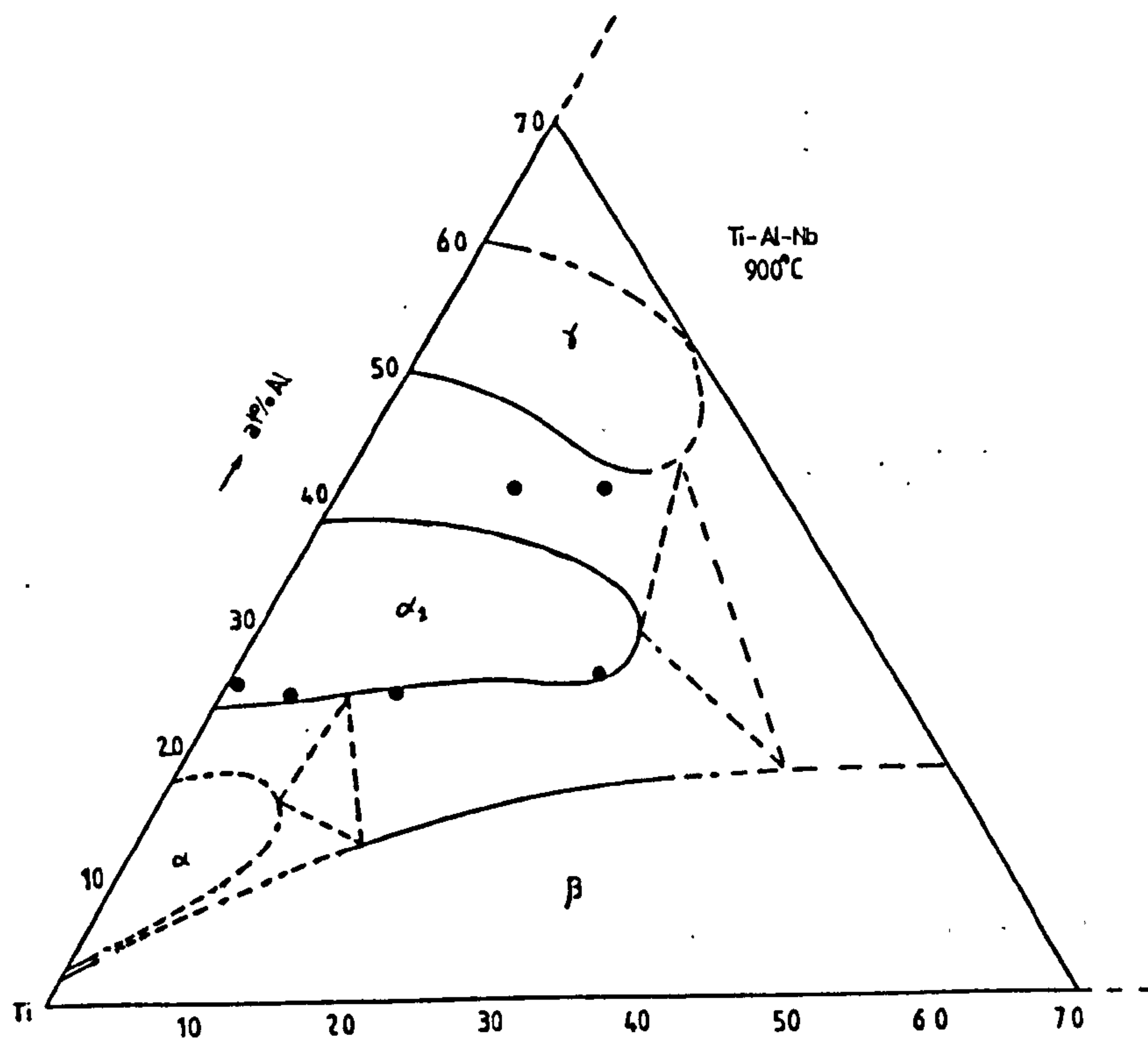
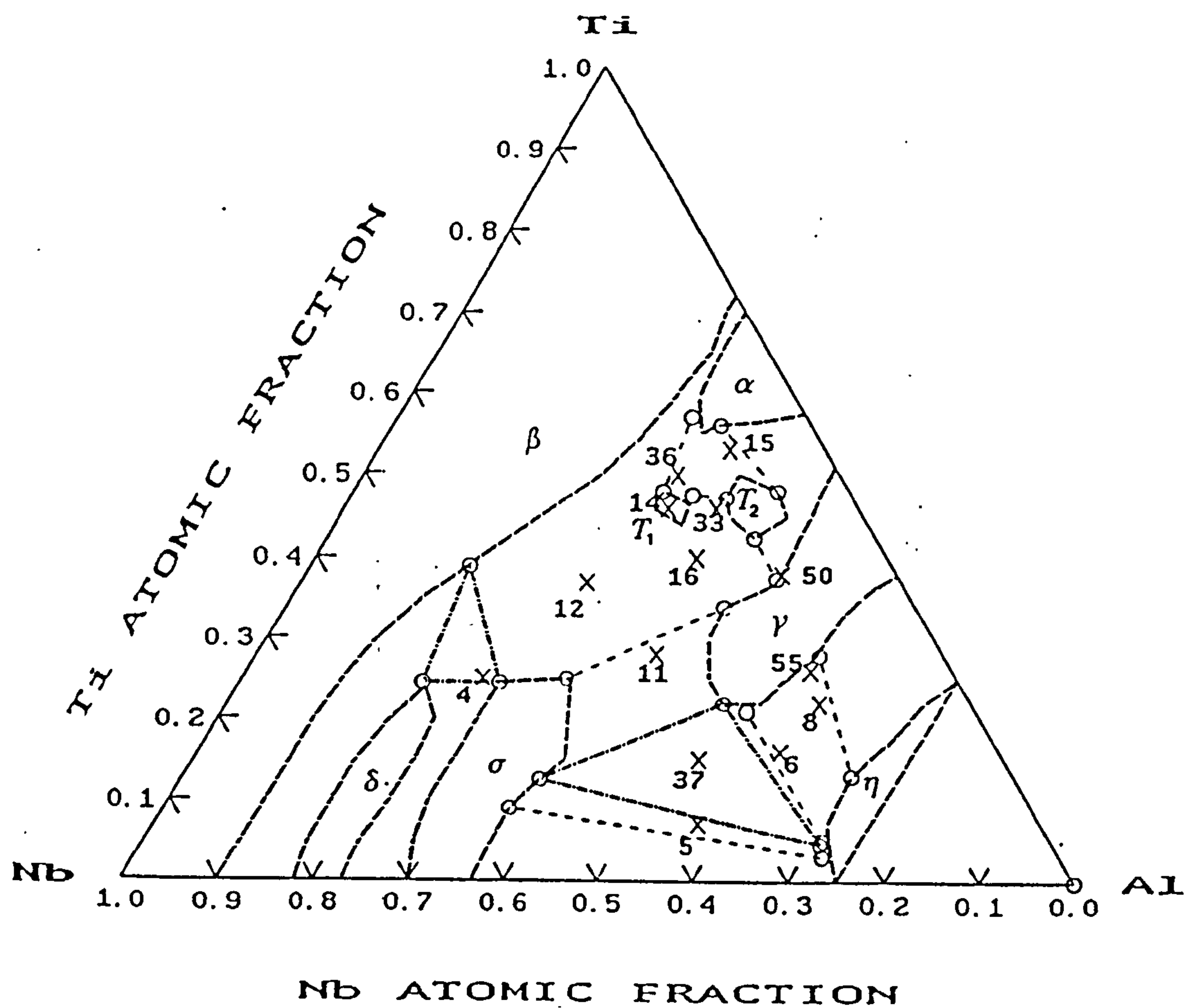


Figure 2.22. Ti - Al - Nb ternary section at 1200°C [Jewett]

Figure 2.23. Ti - Al - Nb ternary section at 900°C [Khataee]

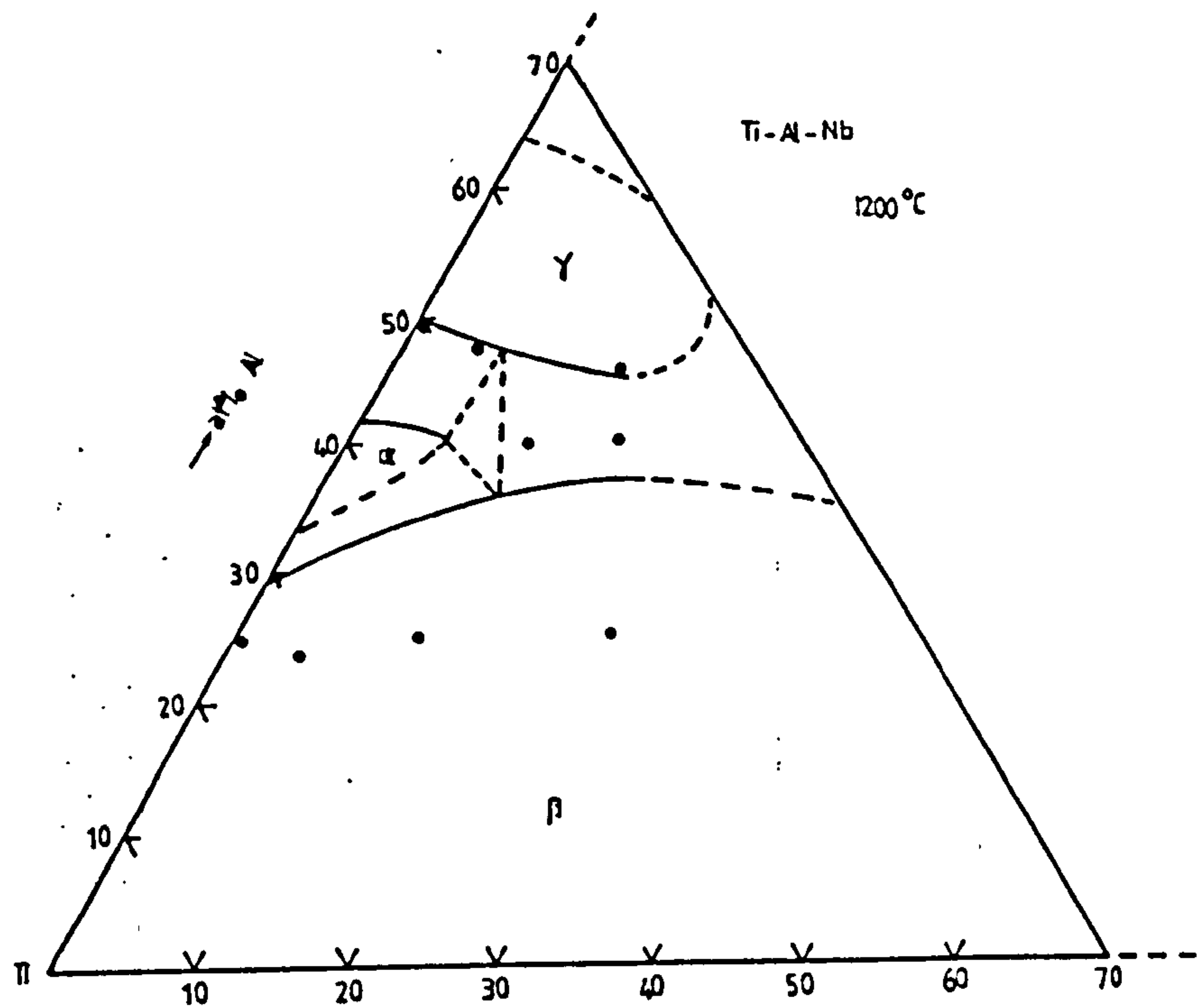
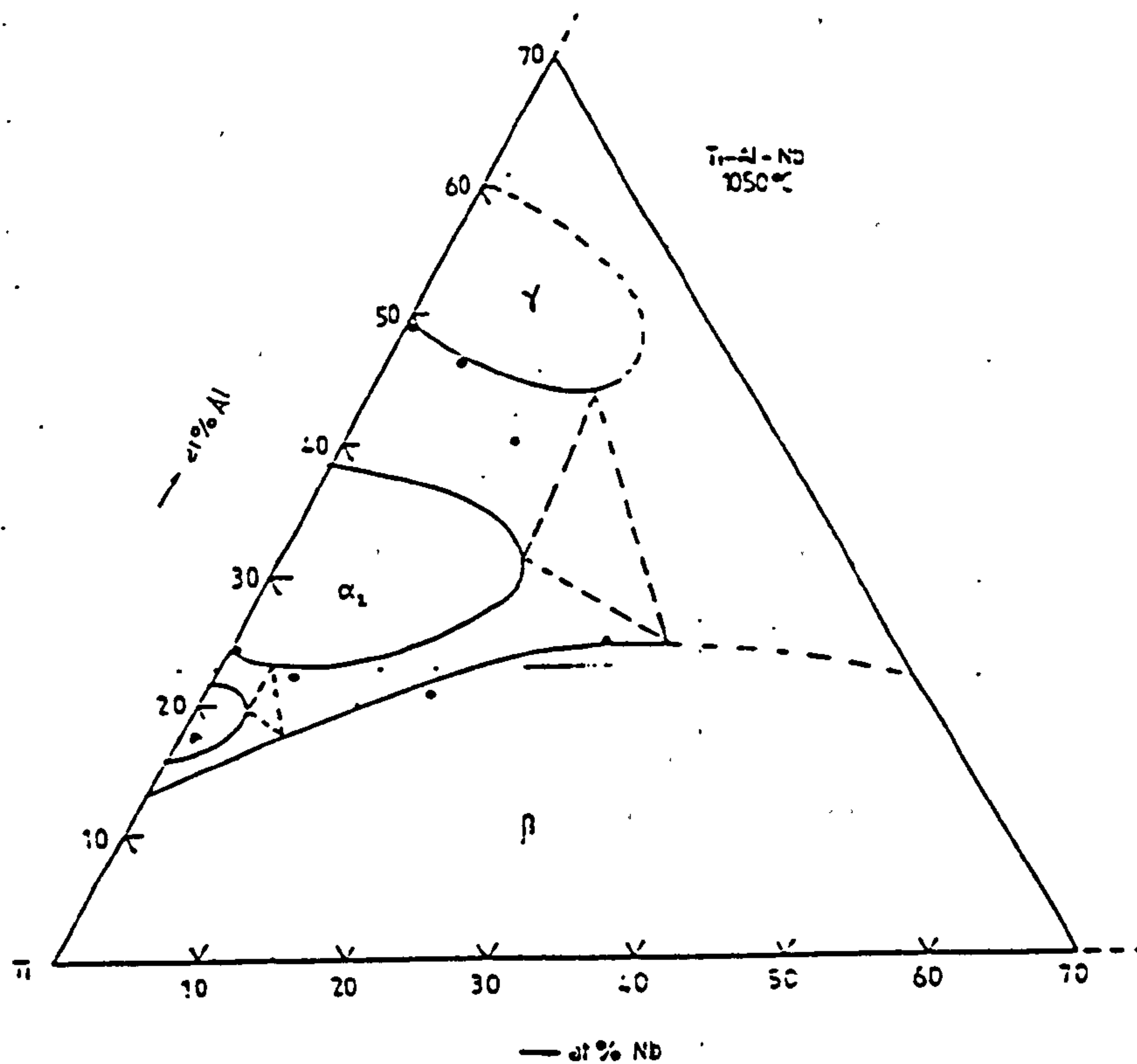


Figure 2.24. Ti - Al - Nb ternary section at 1050°C [Khataee]

Figure 2.25. Ti - Al - Nb ternary section at 1200°C [Khataee]

structure. ω phase is produced, which is produced by quenching from the β phase.

The ω phase is found in two main forms in a wide range of titanium and zirconium based alloys, athermal ω which is a product of rapid quenching from the β phase in which bulk thermal transformations to α_2 are prevented, and thermal ω which is the product of low temperature ageing in metastable β alloys. Early X-ray studies identified the structure as being hexagonal [Sil58] or trigonal [Bag59]. The morphology of the particles has been investigated by Blackburn and Williams [Bla68,Bla70] who showed that in Ti-transition metal binary alloys, the morphology is determined by the Ti : addition atomic volume ratios, and thus the lattice misfit. When this is low ($< \sim 0.5\%$) the precipitates are ellipsoidal [Bla68,Hic69] and otherwise they are cubic. It has been well established by a wide range of authors [for example Sil58, Bag58] that the orientation relationship between β and ω is as follows;

$$(0001)_{\omega} // (111)_{\beta}; [2\bar{1}\bar{1}0]_{\omega} // [1\bar{1}0]_{\beta} \quad (6)$$

streaked ω was found by Strychor [Str88] in β solution treated Ti-Al-Nb alloys which were subsequently aged at between 400 and 500°C. On low temperature ageing, these streaks condense into spots corresponding to an ordered hexagonal ω phase in which $\langle 0001 \rangle_{\omega} // \langle 111 \rangle_{\beta}$, which is a characteristic which is also reported in a variety of ω type phases in titanium and zirconium alloys [Flo72]. In alloys with a higher aluminium content (Ti-37.5Al-12.5Nb against Ti-27.8Al-11.7Nb), Bendersky [Ben90] has identified similar ω type particles precipitated from the B2 (i.e. ordered β) phase field which have a trigonal structure. The particular alloy chosen was used to maximise the ordering present in the B2 phase while preventing the formation of TiAl. The resultant microstructure was almost completely ω on quenching, indicating that raising the Al content in these alloys has a marked effect on the quenching transformations, as Strychor found only a small amount of ω phase present on quenching, which increased dramatically on ageing.

In alloys containing less than 5at.% Nb, the alloy transforms martensitically to the hexagonal α' phase. Martensites are metastable structures which can form via a military transformation on rapid quenching from the β phase down to a temperature at which the β is highly metastable. This will only occur if the cooling is fast enough for the inhibition of diffusion-controlled transformations. In titanium-based alloys there are two types of martensite, designated α' and α'' . α' is a hexagonal structure and α'' is orthorhombic. Most martensitic transformations produce the hexagonal α' structure, but when the β stabiliser content is increased, and the martensite start temperature,

M_s , (i.e. the temperature at which martensite will start to form during quenching) is low, then the orthorhombic form will be produced [Mur80]. It is the high solute content that causes the distortion, and this tends to be associated with low M_s . Thus it is likely that the low M_s does not cause the distortion of the martensite, but is just another effect of the high solute content. Above 5at.% Nb, the M_s (Martensite start) temperature drops rapidly to below room temperature, and significant streaking is visible in diffraction patterns.

The most significant recent developments in the production of an accurate ternary phase diagram was the identification of a ternary orthorhombic phase at low temperatures [Ban88a] and of an ordered derivative of the solid solution based on β Ti [Ben88].

An orthorhombic phase was first reported by Banerjee in an alloy with the composition of Ti-25Al-12.5Nb (atomic %), though more recent work has identified it over a wide range of compositions with niobium contents of 11at.% and above [Kes89, Ban91, Moz90, Mur90]. Varying the composition and heat treatment temperature in this phase gives a wide range in reported lattice parameters (table 2.2).

Reference	a (pm)	b (pm)	c (pm)	Composition (at. %)
Moz90	60.893	95.694	46.666	Ti-25Al-25Nb
Mur90	59.6	98.6	46.7	Ti-24Al-15Nb
Ben91	60.5	96.1	46.5	Ti-25Al-25Nb
Kes89	59.0	98.5	46.5	Ti-25Al-12Nb
Kes89	60.8	96.2	46.6	Ti-25Al-20Nb
Kes89	61.2	95.6	46.6	Ti-25Al-25Nb
Kes89	61.5	95.3	46.6	Ti-25Al-30Nb

Table 2.2. Reported values of lattice parameters for Orthorhombic phase.

It was shown by Banerjee [Ban88] that the orthorhombic structure has a crystal structure which is intermediate between that of α_2 and β . The closest packed planes in each structure are parallel in the orientation relationship obtained between the planes:-

$$(110)_\beta // (001)_O // (0001)_{\alpha_2} \quad (7)$$

This similarity between the planes in (7) above is shown in Figure 2.26. The structure of the O phase was identified as one of *Cmcm* symmetry containing 16 atoms per unit cell (oC16 in Pearson notation) which is isomorphous with the NaHg structure type. The O phase was shown to form either directly from ordered β (this structure, with a simple cubic lattice is generally referred to as either B2 or β_0) or by precipitation from α_2 . i.e.;



and



The orientation relationship between these two phases in the decomposition reaction was identified as being;

$$(110)_O // (10\bar{1}0)_{\alpha_2} ; [001]_O // [0001]_{\alpha_2} \quad (10)$$

The determination of the equilibria was carried out using samples which had been solution treated and then furnace cooled. Thus the possibility of the structures failing to reach equilibrium during furnace cooling should not be ignored in the consideration of this data.

In an examination of a series of alloys on the compositional line between Ti_3Al and Ti_2AlNb , Kestner-Weykamp et al [Kes89] also report that the formation of the O phase is via the decomposition reaction shown below (11), in alloys which at equilibrium contain α_2 at 800°C. However, in higher Nb content alloys (> 20 at.% Nb), the transformation is reported to occur directly from B2 to O.



2.5.2. Site Occupancy in Ti_3Al B2 and O.

In Ti_3Al (and also $TiAl$), the addition of niobium, at least in small quantities up to 5at.%, results in the direct substitution of niobium onto titanium lattice sites

[Kon85]. However, in the β structure it mainly substitutes on the aluminium sites. It should be noted that the B2 phase region does not extend to any of the two component edges of the diagram, and thus would not have been reported until ternary examinations had been carried out. The ordering to the B2 crystallographic structure has been examined by Banerjee [Ban87], who concluded, with the use of ALCHEMI (Atom Location by CHanneling Enhanced Microanalysis), that in a Ti - 25Al - 10Nb (at. %), the distribution is probably as below;

<i>A Sites</i>	Ti - 96	Nb - 4	
<i>B Sites</i>	Ti - 28	Nb - 24	Al - 48,

where the 'A' sites are situated at the corners of the unit cell (i.e. at (0,0,0)), and the 'B' site is the one at the centre of the unit cell (i.e. at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$). Agreement with this was reached by a more recent study of spot intensities in SADPs by Kestner-Weykamp et al [Kes89]. Using ALCHEMI, Qian et al. [Qia91], produced an atom location which differs significantly from this result, in that no titanium is reported on the nominally aluminium sites. Their calculations produce a crystal formula as below;

<i>A Sites</i>	Ti -86	Nb-14	
<i>B Sites</i>	Al-82	Nb-18,	

where the site locations are as above.

The marked difference between the two separate investigations can be explained by an examination of the base assumptions used for both examinations. Banerjee et al assumed that each lattice point was inhabited by a combination of all three atom species, and so calculated the locations using ratios of each atom type to the other two. When using an alloy of a composition of Ti-24Al-11Nb, Qian et al assumed that the structure was based on a perfectly stoichiometric TiAl structure, i.e. one with an Al to Ti ratio of 1:1, and then only examined the Ti:Nb and Al:Nb ratios. This accounts for the fact that Qian does not report any titanium atoms on the Al sites, in contrast to Banerjee.

To date, there has been one detailed examination of the site occupancy in the orthorhombic structure, which was undertaken using neutron diffraction by Mozer et

al. [Moz90]. The crystal structure was also determined in detail in this examination, as being highly ordered (table 2.3). From the complete order on aluminium sites, and partial disorder on the Ti and Nb sites, Mozer suggests that the solubility range along the pseudo-binary TiAl - NbAl should be low, and that along the Ti_3Al - TiNb line to be markedly higher. The limited amount of work carried out on this ternary system is not great enough to confirm or deny this suggestion. It has been suggested by Muraleedharan [Mur92] that the O phase examined by Mozer et al differs from that examined by Banerjee et al [Ban87] in that separate Ti and Nb sites were found by Mozer, whereas Banerjee found the two species coexisted on the same sites. This could explain the inconsistencies in the proposed phase diagrams [Mur92], which indicate that the β_o phase has a higher Nb content than the O, whereas Mozer et al [Moz90] indicated a nominal composition of Ti_2AlNb for both β_o and O.

Atom	Wychoff Positions			Relative Occupancy
	x	y	z	
Ti(8g)	0.23	-0.096	0.25	0.823
Nb(8g)	0.23	-0.096	0.25	0.177
Al(4cl)	0.00	0.163	0.25	0.500
Nb(4c2)	0.00	-0.634	0.25	0.323
Ti(4c2)	0.00	0.364	0.25	0.177

Table 2.3. Site Occupancy in 'O' Phase
as Determined by Neutron Diffraction [Moz90].

To date there has not been a large amount of attention paid to detailed examination of the effect of cooling rate on the transformations occurring, and their effect on the resultant microstructure. Weykamp et al [Wey90] suggest that the B2 phase which other workers [Str88, Ban87, Ban88] have suggested to be an equilibrium phase, is a metastable phase caused by rapid quenching from the β phase field. It is not clear why this has been suggested, as the appearance of B2 phase in the most rapidly quenched microstructure could also be produced by a stable B2 alloy being quenched, with its microstructure retained down to ambient temperature. No APBs were reported which would indicate a $\beta \rightarrow \text{B2}$ ordering reaction during cooling. Weykamp et al [Wey90] describe the B2 phase region microstructure as being a 'tweed type like that reported elsewhere' by Strychor [Str88], who reported the B2 phase as being an equilibrium phase. The cct (continuous cooling transformation) diagram generated has been reproduced here as Figure.2.27. Slightly slower cooling was observed to

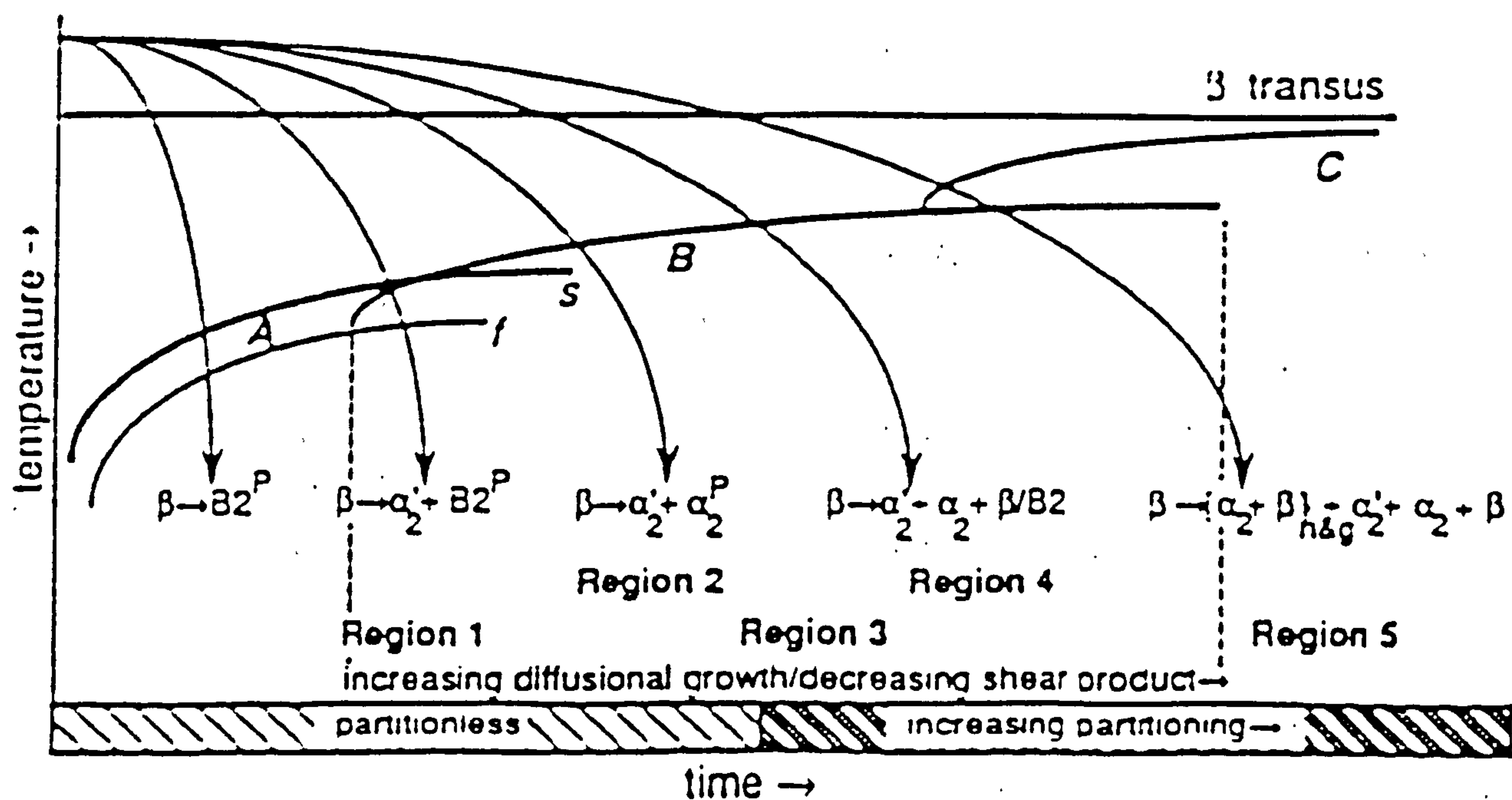
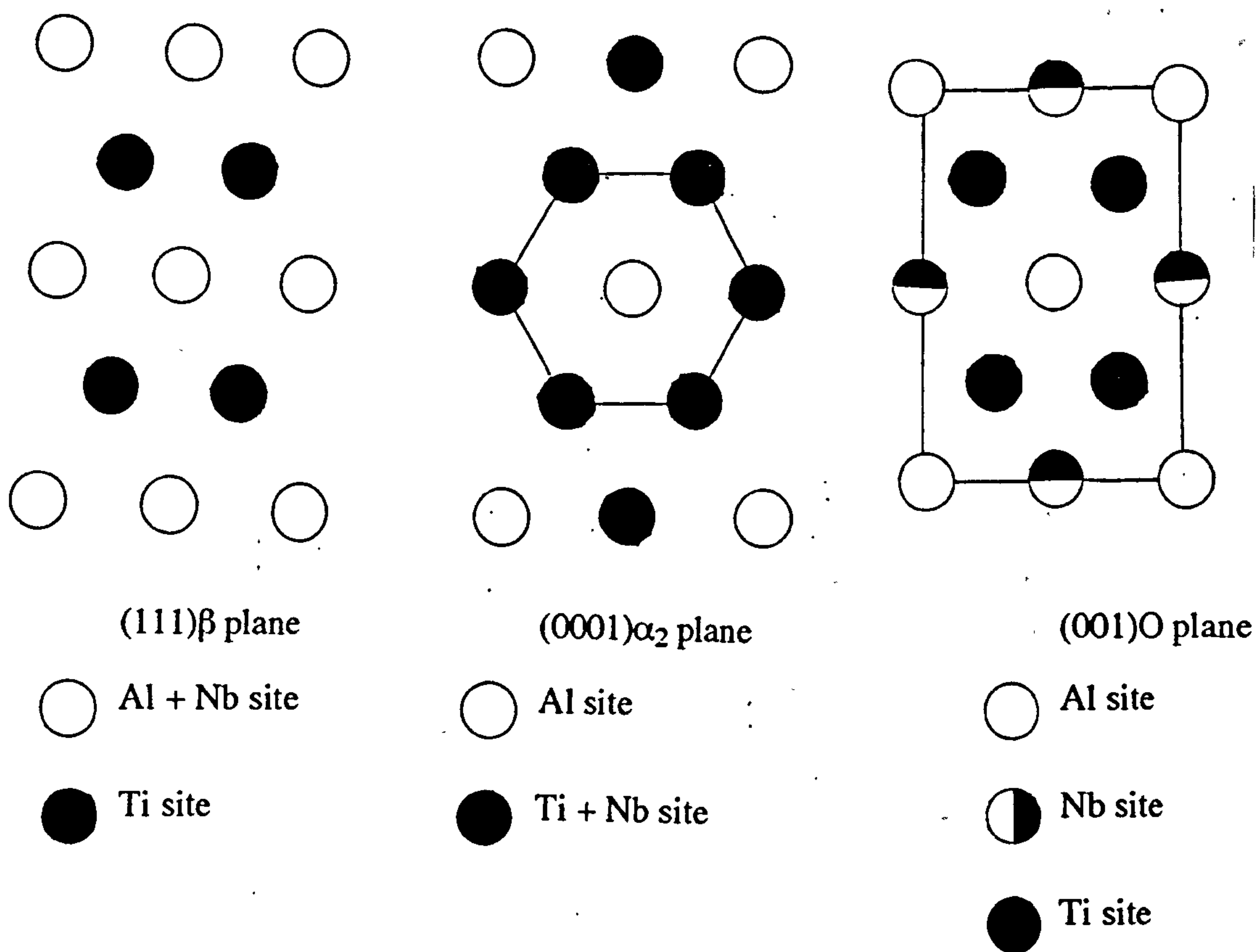
Figure 2.26. Diagram of similar planes in α_2 , β and O.

Figure 2.27. Continuous cooling curve for Ti-25Al-15Nb. [Weykamp]

produce a martensitic phase as well as β . No explanation for this, ^{is given} but it is possible that X-ray peaks identified as being produced by a martensitic transformation were mis-identified, and that the peaks were actually produced by the O phase.

2.5.3. 'Super Alpha2'.

The recently produced second generation (i.e. with alloying additions to the basic ternary alloys) commercial alloy 'Super α_2 ', is based on the system of Ti₃Al-Nb, but has been modified to produce a lower density alloy. Some of the niobium in the previous generation of alloys has been substituted by vanadium and molybdenum. This produces an alloy of the approximate composition shown below in table 2.4.

Element	at. %
Ti	60
Al	26
Nb	10
V	3
Mo	1

Table 2.4. Approximate Elemental Composition in 'Super Alpha2'.

An examination of the transformations occurring isothermally [Pet90] in this alloy was carried out using dilatometry to identify the start and end of the transformations. Each sample was solution treated to produce β (at a temperature which is within the β phase field at 1200°C for 2 hours, and then quenched to the desired temperature. Examination of the microstructures allowed identification of the phases present at known times and temperatures to be undertaken. From this an isothermal transformation curve was produced (Figure 2.28.). At high temperatures only α_2 was produced, however as the temperature was reduced, the previously reported [Ban88] orthorhombic phase was detected. Below about 600°C, thermal ω was also detected.

The precipitation sequences for these phases were not investigated. In an investigation of a similar alloy (Ti -25Al -10Nb -3V -1Mo), by Ward [War90], the stability of the microstructure with time, has been examined. The structure was examined in two heat treated conditions. In both of the conditions, the alloy had

undergone annealing at 1085°C for 1hr. In the first examination the sample then underwent an eight hour furnace age followed by quenching. It was found that a recrystallisation reaction had occurred. In the second ageing condition (salt bath aged for 1 hour at the same temperature) the recrystallisation was not detected. Unlike Ti - 25Al -5Nb with a similar initial fine α_2 structure, this microstructure was said not to be due to tempering of martensite produced in the quench down to the ageing temperature (as martensite tempering did not occur in the salt bath aged specimen). This occurrence of recrystallisation is of great importance as it precludes the use of this alloy in situations which require maximum strength (generally produced by refining of the grain structure). An examination by Baeslack [Bae90] into the effect of cooling rates on the structure of a super α_2 type alloy (Ti-26Al-10Nb-3V-1Mo) as compared to a similar Ti₃Al -Nb alloy (Ti-26Al-11Nb), concluded in that the super α_2 alloy the CCT curve was lowered and extended to longer times which suggests that the $\beta \rightarrow \alpha_2 + \beta$ phase transformation temperature was lowered by the alloying additions. However, as this alloy has a higher β stabiliser content than Ti-26Al-11Nb, then this is to be expected, and does not give any indication as to the actual effect of the vanadium and molybdenum on the alloy microstructural properties. As niobium occupation of atom sites is different in α_2 and B2 [Ban87], then it is possible that this behaviour is duplicated by molybdenum and vanadium atoms. However it is unwise to assume that this is true without further examination.

Work has been undertaken [Kha90a] to examine the effect of substitution of vanadium and molybdenum into quaternary alloys based on the Ti-Al-Nb-Si system. This has so far been unable to provide an accurate basis for assessing the effect of the elements, due partially to the increased β phase production caused by these strong β stabilising elements. These elements also appear to have a stronger β grain refining effect on the alloy than that of niobium, as a much finer microstructure is produced than in similar quaternary alloys.

2.5.4. Quaternary Ti-Al-Nb-Si Alloys.

The addition of silicon [Ker90] has been shown to improve the ductility of titanium aluminides significantly, particularly for silicon contents of greater than 0.5 at.%. For example 0.9at.% Silicon increases the ductility of Ti-20Al-11Nb aged at 625°C from less than 1% up to 2%. (see Figure 2.29.), It also increases rupture life, though not to such a great degree. This study also shows that for a given niobium content, increasing the aluminium content improves rupture life and reduces tensile

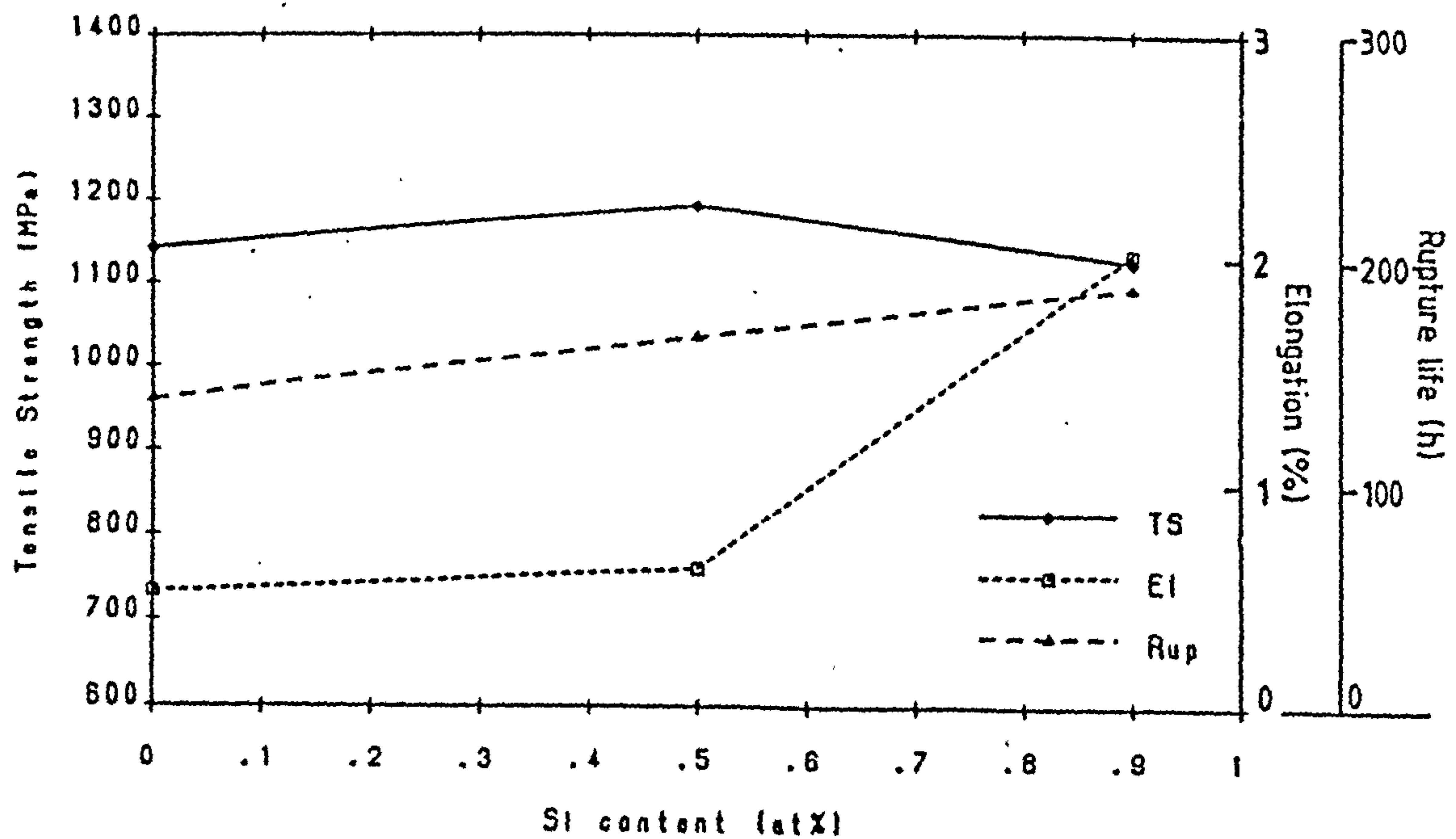
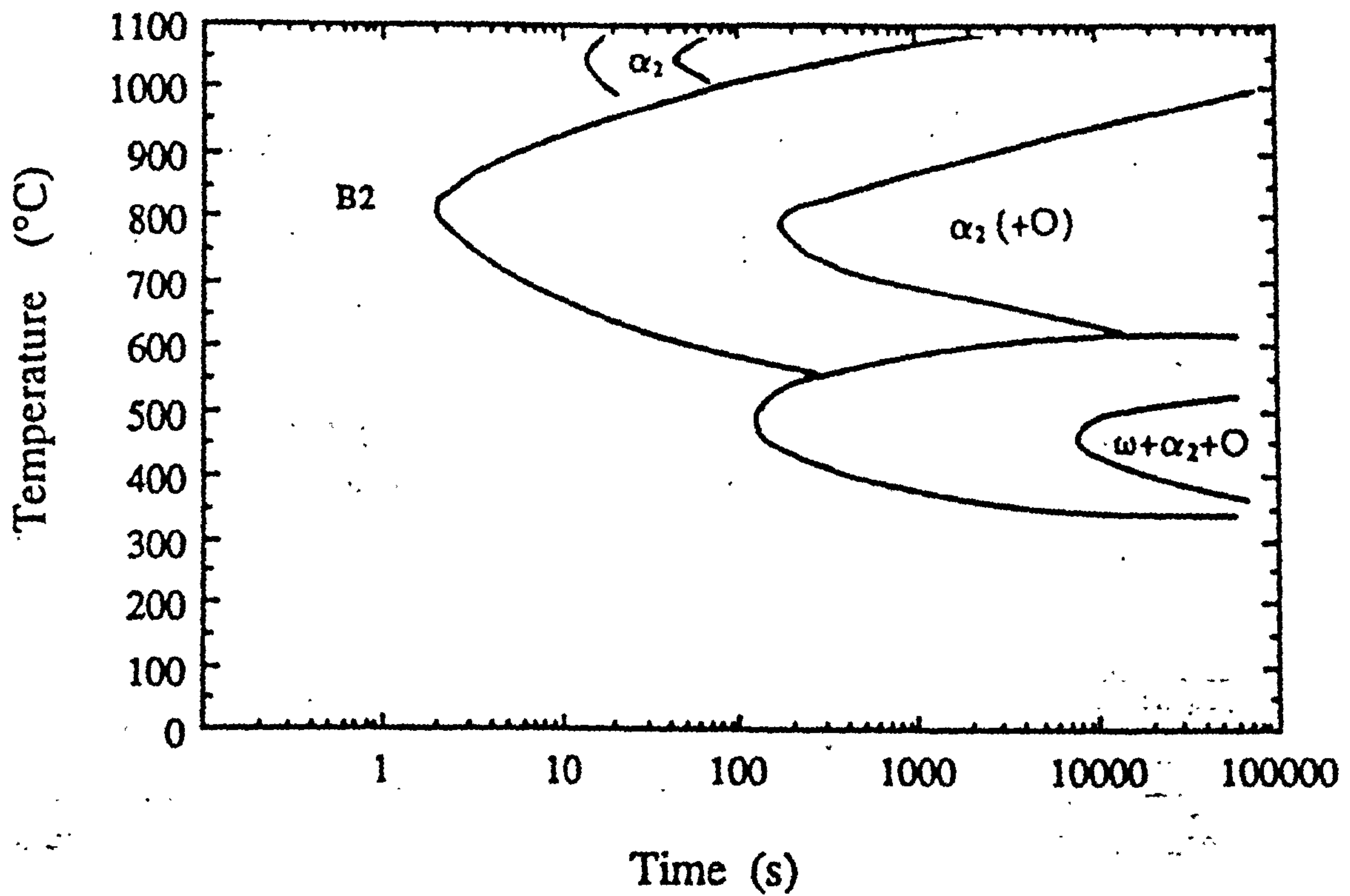


Figure 2.28. Isothermal transformation curve for 'Super α_2 '. [Peters]

Figure 2.29. Effect of silicon on mechanical properties of Ti-20Al-11Nb. [Kerry]

strength. This is to be expected as creep is controlled by the α_2 phase, and strength by the β phase. So increasing the amount of aluminium in the system increases the α_2 content of an aged alloy.

Alloys containing a much higher silicon level (6.5at.%) have been examined [Che91] with the aim of producing alloys containing a Ti_3Si_3 based structure as well as the more usual α_2 , β and O phases. This examination suggests that the silicon partitions to the β phase, as opposed to the α_2 or O phases, as this is where most silicide precipitation occurs on ageing. The orthorhombic phase is reported at up to 900°C in the composition Ti-23.5Al-10Nb-6.5Si (at.%) after short (4 hr) ageing times.

2.6. Effect of Oxygen on Phase Diagrams.

Oxygen has a marked effect on the $\beta/\alpha_2+\beta$ transus temperature. The strong α stabilising effect which it has on aluminide alloys has been examined by Szaruga [Sza92], who found that not only is the transus raised strongly by the addition of oxygen (it has a stabilising effect approximately 10 times greater than Al [Pol84] at this level), but that the order/disorder reaction in the β phase is also affected by it. The oxygen is reported to raise the transus by 17.2°C/100ppm oxygen at levels of <1000 ppm, and at a much lower rate of 3.5°C/100 ppm at higher oxygen levels. At the composition of the intersection of these two linear regimes, the order/disorder reaction occurs. This reaction is suggested to be responsible for the abrupt change in the rate of change in the β transus with increasing O content. The absolute values ascertained in this work however do not take any account of the effect of the variation in the aluminium (1.7at.%) and niobium (1at.%) content between the alloys studied, therefore the values obtained should be treated with caution.

2.7. Mechanical Properties of Ternary Ti-Al-Nb Alloys.

Alloys based on the Ti - Al - Nb system within the range of 23-27at.%Al, 10-16at.%Nb [Bla80] have produced mechanical properties which are superior in room temperature ductility to those produced in unmodified Ti_3Al alloys. This work showed that adding niobium to Ti_3Al produced an increase in room temperature bend elongation from <1% to ~4.5% at 15at.% Nb addition levels. However, it was also

reported that the creep strength-to-density ratio (very important for aerospace applications) dropped consistently due to the density of the niobium additions. As detailed figures were not provided, it is not clear as to whether the entire change in the ratio is due to this. Thus, it should be noted that the effect of increasing β content would also adversely affect the creep strength-to-density ratio. Increasing both the aluminium and niobium levels in the compositional range mentioned above, dramatically increases the creep life of the system. Though this is not discussed, the β phase may have been present as B2, which would improve creep life relative to that in the disordered structure, by reducing solute diffusivity. In a study of the creep behaviour of 'super α_2 ' [Cho90] Cho et al. identified a range of microstructural effects on the creep resistance of the material. Firstly, β solution treatment improved the creep resistance relative to that exhibited by $\alpha_2 + \beta$ solution treated samples. This however, does not hold entirely true at low temperatures (650°C), as the creep resistance is only greater at low strain rates. As the strain rate is increased, so the $\alpha_2 + \beta$ solution treated material shows a relative improvement which was not explained. Cho also noted that, as expected, increasing the cooling rate from the solution treatment temperature refined the final microstructure and thus improved the tensile strength and ductility of the material.

In an examination of the deformation properties of Ti-24Al -11Nb (one of the first generation of commercial aluminide alloys), Gittis [Git89] compared the deformation characteristics of Ti -24Al -11Nb (two phase $\alpha_2 + \beta$) with that of two alloys, each of the same composition as the phases in the single phase α_2 (Ti -25Al -9Nb) or β (Ti-11Al -23Nb) phases in the Ti -24Al -11Nb alloys, to try to analyse how the phases contribute to the deformation characteristics of the two phase alloy. The temperature dependence of the absolute value of the yield stress in the two phase alloy closely follows that of the α_2 alloy. From this, it was decided that the strength is controlled by α_2 strength. It should be noted that the yield stress of the β_0 increased dramatically at temperatures above 400°C (see Figure 2.30). The β_0 alloy when aged at 760°C for 1 hour had a considerably higher yield strength, indicating that an ageing reaction occurs in this alloy. It was suggested by Gittis that this ageing occurs at a temperature between 650°C (the highest temperature at which tests were carried out) and 760°C. However, from the data provided it seems more likely that ageing occurs rapidly between 400 and 650°C, and produces the increase in strength reported in the 650°C aged alloy by a reaction occurring during the deformation test. In a separate examination of the same commercial alloy [Luk90], it was reported that, over the temperature range 25 - 500°C, the rate of strain hardening is independent of temperature. Though the rate of strain hardening is constant over the entire

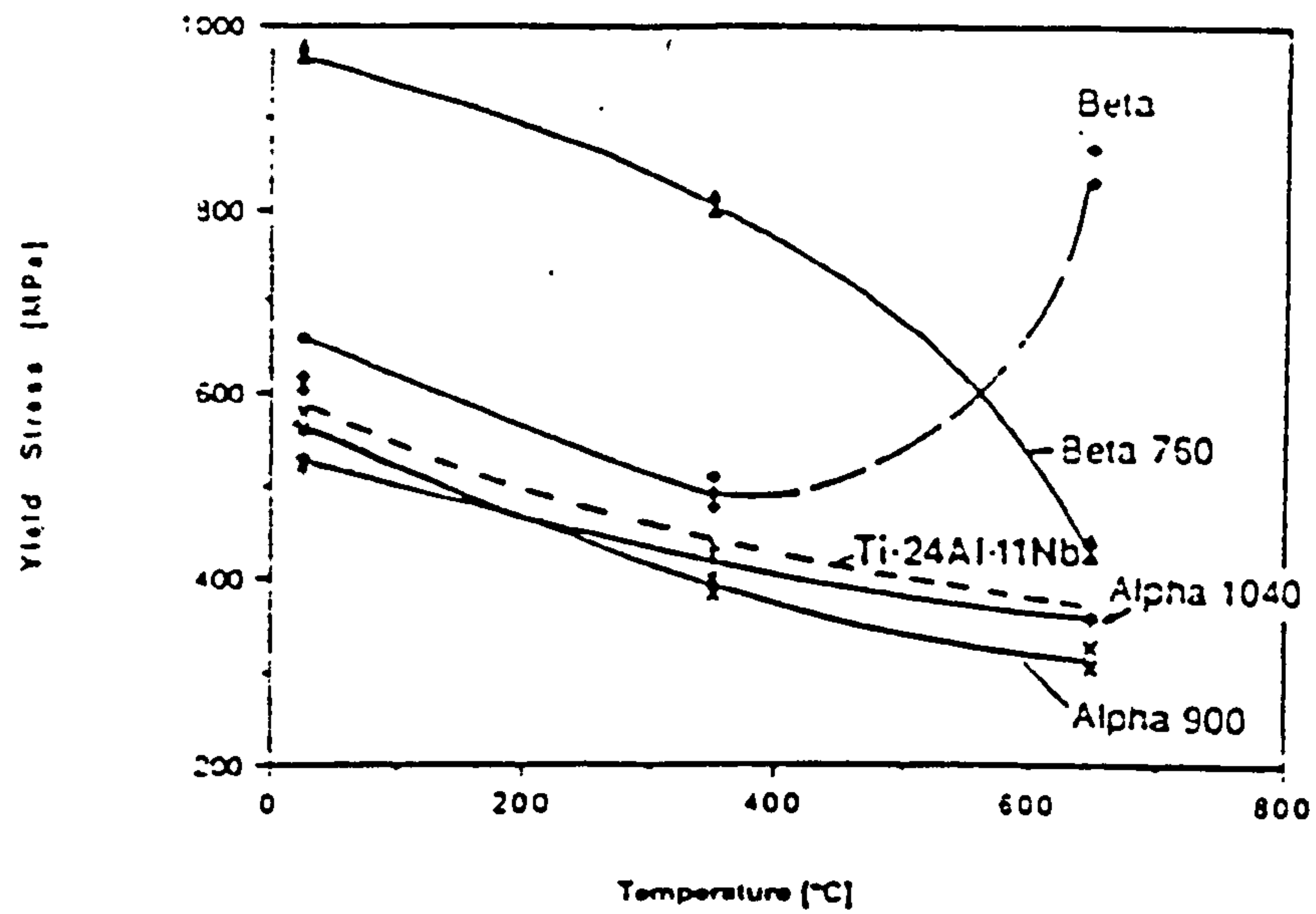


Figure 2.30. Yield stress against temperature in Ti-24Al-11Nb. [Gittis]

temperature range, the flow stresses decrease as temperature rises within the range of 25-500°C. The reasons for this behaviour are not clear, as the strain hardening rate is related to the plastic flow. It was also noted that the rate of strain hardening was considerably greater than for traditional titanium alloys. For example, room temperature stress - strain data show that the work hardening exponent, $n = 0.065$ for a Ti-5Al-2.5Sn alloy [Cha83], where

$$n = \frac{d \ln (\text{stress})}{d \ln (\text{strain})} \quad (12)$$

but $n = 0.20$ for the Ti-24Al-11Nb alloy examined. The ductility of the alloy is reported to be ~1% at room temperature and rises to ~8% at 300°C. However at higher temperatures it is suggested that apparent (i.e. not flow-controlled) ductility is increased by the following mechanism; microcracks, which are produced in the alloy do not grow, (but due to environmental oxygen are blunted) instead produce large crack opening diameters without failing. The enhanced resistance to crack growth is suggested to be due to $\alpha + \beta$ slip and/or thermally activated slip within the β phase. Gogia [Gog90] has also examined the structural properties of this alloy, concentrating on the effect of ageing treatments on the room temperature ductility. In the β heat treated state, the cooling rate dramatically affects the mechanical properties. In examining the alloy when quenched using cooling rates from 1 to 10°C/sec, the elongation varies from approximately zero at 1°C/sec up to a maximum of 2% with a cooling rate of 4°C/sec. Similarly by use of an intermediate $\alpha + \beta$ ageing treatment, the ductility is increased by raising the ageing temperature. Whether or not this is due to the microstructural changes caused by the raised temperature, or simply the increased amount of β phase reported to be present is not addressed.

Rowe et al. [Row92], have recently found that the addition of significantly larger amounts of Nb to the alloy (e.g. Ti-24.7Al-30Nb at.%), which transforms the microstructure from $\alpha_2 + \beta$ to 'high Nb' $O + \beta$ produces significant benefits in mechanical strength and ductility, with a yield strength to density ratio for Ti-22Al-27Nb being approximately 4x greater than for Ti-24-11 within a temperature range from room temperature up to 650°C. Ductility of this alloy is approximately 5% at room temperature, and increases to nearly 20% at 800°C. Fracture toughness is also markedly greater at 28MPa.m^{1/2} as compared with 14MPa.m^{1/2} for super α_2 . This type of alloy appears to show a large amount of promise, and is likely to be studied in more detail in the future. The O phase in these alloys is of the type whose structure

was characterised by Mozer [Moz90]. If two separate O types do exist [Mur92], then the mechanical properties of each will need to be assessed, so as to determine which is of most use, particularly as the density of each appears to be significantly different due to the large change in the Nb content of the two materials.

The possibility of producing superplastic deformation of $\text{Ti}_3\text{Al} + \text{Nb}$ alloys has been examined [Dut90], and some very promising findings have been obtained. Sample components were hot rolled in the $\alpha_2 + \beta$ phase field, to produce a fine grained two phase structure. Deforming the sample at an initial strain rate of $3.3 \times 10^{-4} \text{ sec}^{-1}$ produced a total elongation of up to 520%. Interestingly, the maximum elongation was not produced by alloys containing a 50:50 ratio of α_2 to β grains, the highest deformation being produced by an alloy containing 75% α_2 grains. As this is a preliminary study, the reasons for this, and the mechanisms behind the deformation have not as yet been identified. In $\alpha + \beta$ alloys, the superplastic flow is controlled by the β phase, α is only required to inhibit grain growth.

A series of papers [Bae88, Bae89, Bae89a and Cie90] have been produced on the effect of cooling rates during welding, on the microstructure of the weld and HAZ (Heat Affected Zone). It is suggested [Bae88] that the addition of niobium to aluminides improves the ductility by slowing ordering kinetics, reducing slip length and increasing non-basal slip in the α_2 phase. It is also proposed that the β phase can be stabilised down to room temperature in small proportions. β stability is sufficient to allow the development of α_2/β microstructures which are morphologically similar to α/β ones in conventional Ti alloys. Ageing of the α_2/β microstructure [Bae89a] at 600°C produces a heterogeneously precipitated semi-continuous network of extremely fine α_2 grains on β grain boundaries. This did not affect the room temperature ductility of the alloy adversely. Using Nd:YAG (Neodymium: Yttrium Aluminium Garnet) laser welding on a Ti-24at.%Al-11at.%Nb alloy appears to be feasible [Bae89] as the bend ductility of the weld can be raised to that of the unwelded material by use of a post weld heat treatment at around 850°C .

Chapter 3

Experimental.

3.1. Alloy Manufacture.

The alloys were produced by one of two different processing routes prior to the heat treatments carried out for this work.

3.1.1. Forged Alloys.

These alloys, on which the majority of the work is based, were arc-melted to produce 200g ingots by a commercial producer. Sections of these alloys were then hot forged in air by Royal Aerospace Establishment as detailed below in table 3.1.

Alloy Number	Nominal Composition (at. %)	Received Condition (Forging Temp. Unspecified)
1	Ti-20Al-11Nb-0.9Si	Forged to 51.9% reduction at 10^{-3} sec^{-1}
2	Ti-20Al-15Nb-0.9Si	Forged to 53.6% reduction at 10^{-3} sec^{-1}
3	Ti-23Al-11Nb-0.9Si	Forged to 40.3% reduction at 10^{-3} sec^{-1}
4	Ti-23Al-15Nb-0.9Si	Forged to 45.7% reduction at 10^{-3} sec^{-1}

Table 3.1. Forging Applied to Alloys.

3.1.2. Cast Alloys.

The remainder of the alloys (table 3.2.) were produced by melting in a Materials Research Corp. V-4 arc furnace with a water cooled copper hearth using a non-consumable tungsten electrode. The ingots produced had a mass of approximately

25g. These were formed from high purity components (see table 3.3.) in the desired ratio. The alloy components were cleaned in acetone and methanol and then weighed to an accuracy of $\pm 0.0005\text{g}$. The surface of the arc melter hearth was ground with 1200 grade SiC paper to remove contamination from previous usage. Then the whole melter was freshly cleaned for each melting process using acetone and methanol, and then dried. Due to the wide variation in the melting points of the components, particularly aluminium and niobium (see table 3.3.), they were not directly melted together, so that loss of aluminium from evaporation could be minimised. Instead, the melting process was carried out in stages, with the niobium being melted so that it flowed over the silicon and formed an alloy with a lower melting point. Then the titanium was melted into this mixture and finally the aluminium. The current required to perform these operations varied from 190A for the melting of niobium, down to 100A for the final alloy remelting.

Alloy Number	at. % Al	at. % Nb	at. % Si
5	20	11	-
6	20	11	0.5
7	20	11	1.2
8	20	11	1.5
9	23	11	1.5
10	23	11	3
11	23	15	1.5
12	23	6	0.9
13	23	6	1.5
14	25	12.5	-
15	25	25	-
16	23	13	0.9

Table 3.2. List Of Cast Alloys.

Component	Purity %	Form	Melting Point (K)
Ti	99.5	sponge	1948
Al	99.997	block	932
Nb	99.9+	rod	2741
Si	99.9999	chips	1680

Table 3.3. Purity of Alloy Components.

To reduce oxygen and nitrogen contamination as much as possible, the arc melter was flushed with high purity argon (specified as 99.998%) and then pumped down to below 150Nm^{-2} , and then back-filled with argon to produce an atmospheric pressure of 25KNm^{-2} , the process was then repeated a minimum of three times before melting. Further oxygen and nitrogen extraction was carried out by gettering the system by melting a piece of titanium in the furnace between each operation. To monitor oxygen take-up, the hardness of the titanium was measured before and after the arc-melting operation. If the titanium hardness rose above about 115Hv , then the alloy was discarded.

The final alloy was re-melted a minimum of three times, and then transferred to a cylindrical hearth in the arc melter for final casting into cigar-shaped rods of roughly 10mm diameter.

3.2. Heat Treatment.

3.2.1. Solution Treatment.

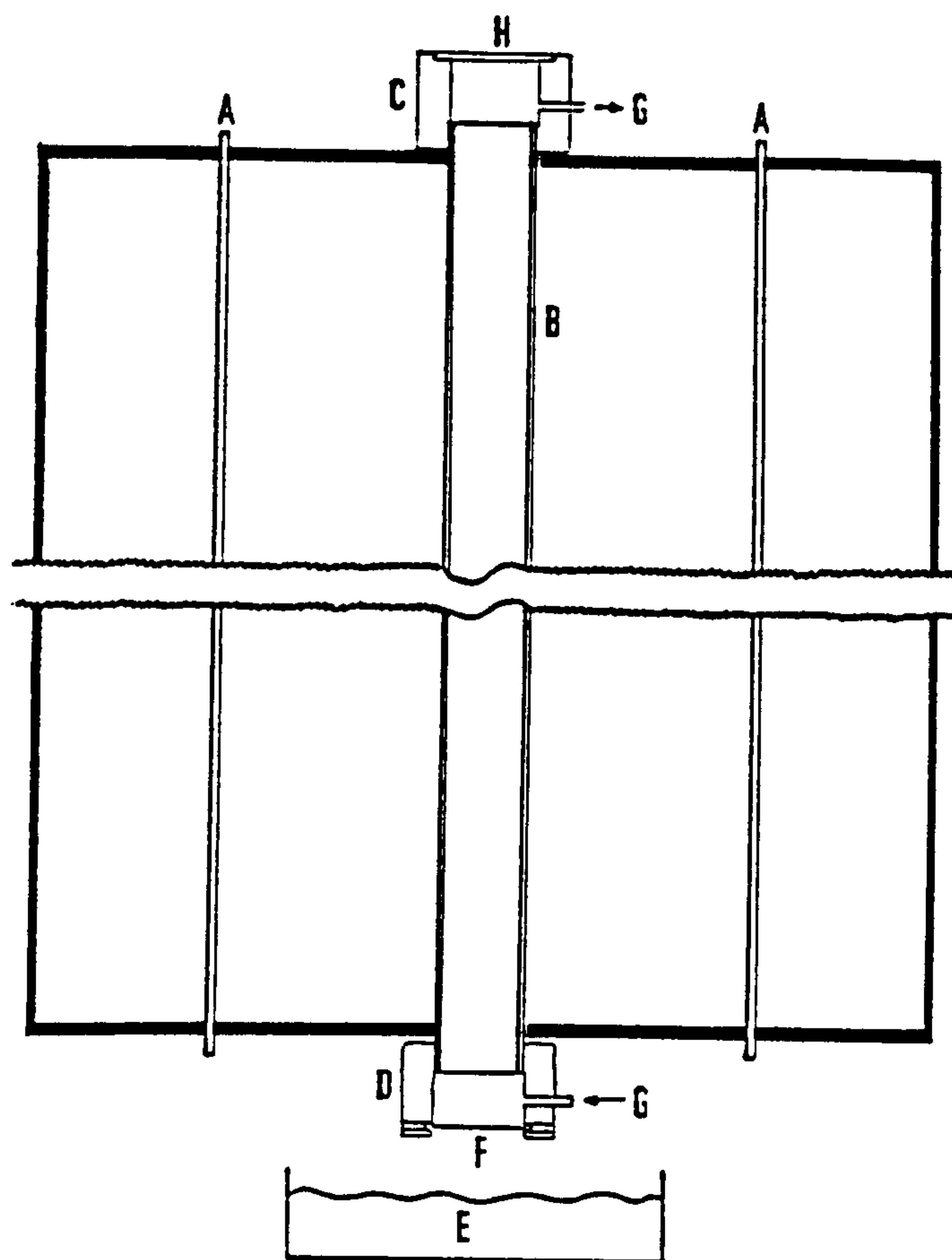
Forged samples for solution treatment (at 1270°C), were prepared by initial grinding with silicon carbide paper (using 120, 240, 400, 800 and 1200 grades in sequence) on a water lubricated grinding wheel to remove any thick surface oxides, and to reduce oxygen contamination in the matrix i.e. to remove any alpha case which had built up. Samples were then cut into sections of approximately $40*10*10\text{mm}$ in size using a water and oil based lubricant cooled silicon carbide slitting wheel. These

samples, after cleaning with acetone and methanol, were then wrapped in molybdenum foil and then sealed in silica tubes which were vacuum pumped and then back-filled so that they contained an approximately 2.5kNm^{-2} high purity argon atmosphere. Sealing the samples in silica tubes was necessary to reduce to a minimum the amount of oxygen reaching the sample. The molybdenum foil wrapping was used, as at the temperatures at which the heat treatment was carried out, titanium reacts strongly with the silica glass when in physical contact with it. This would cause both a modification of the chemical make-up of the alloys, and a weakening of the silica tube. A pressure of approximately 2.5kNm^{-2} was chosen as this corresponds to an atmospheric pressure of roughly 120kNm^{-2} at the operating temperature of 1270°C , and thereby produces a slight pressure differential which allows for a gradual diffusion of gas outwards, and reduces oxygen flow into the tube. A higher pressure would have caused deformation of the silica tube due to it being used at a temperature which is close to its softening point (1350°C) [Smi89].

The actual solution treatments were carried out in an argon atmosphere in a vertical tube furnace specifically designed for the purpose (see figure 3.1.). The ampoules were suspended on nicral wire from the lid of the furnace. When the solution treatment was completed, then the wire was detached from the furnace, by means of a mechanism which allows the furnace to remain sealed (figure 3.2.) up to the moment of release. This caused the ampoule to fall through the aluminium foil seal at the bottom of the furnace into a water quenchant held at ambient temperature. The force with which the ampoule strikes the quenchant container, coupled with the thermal shock produced in the glass normally causes it to shatter. This in turn releases the samples, which are then cooled rapidly by their contact with the water. The cooling rate was estimated to be approximately 400K sec^{-1} .

3.2.2. Ageing Treatments.

All of the samples which were to be aged were first solution treated, as detailed above in section 3.2.1. Then each of these was cut into small slices of approximate dimensions of $10*10*5\text{mm}$ using a water cooled silicon carbide slitting wheel. These were subsequently cleaned by grinding their surfaces with 1200 grade SiC paper on a water lubricated grinding wheel. This was carried out to remove both the oxide which formed during the quenching process, and also any heat affected layer which may have formed at the cutting surface.



- a) Heating elements
- b) Alumina tube
- c) Water-cooled jacket (top)
- d) Water-cooled jacket (bottom)
- e) Quenching medium
- f) Aluminium foil seal
- g) Argon inlet/outlet
- h) Release mechanism

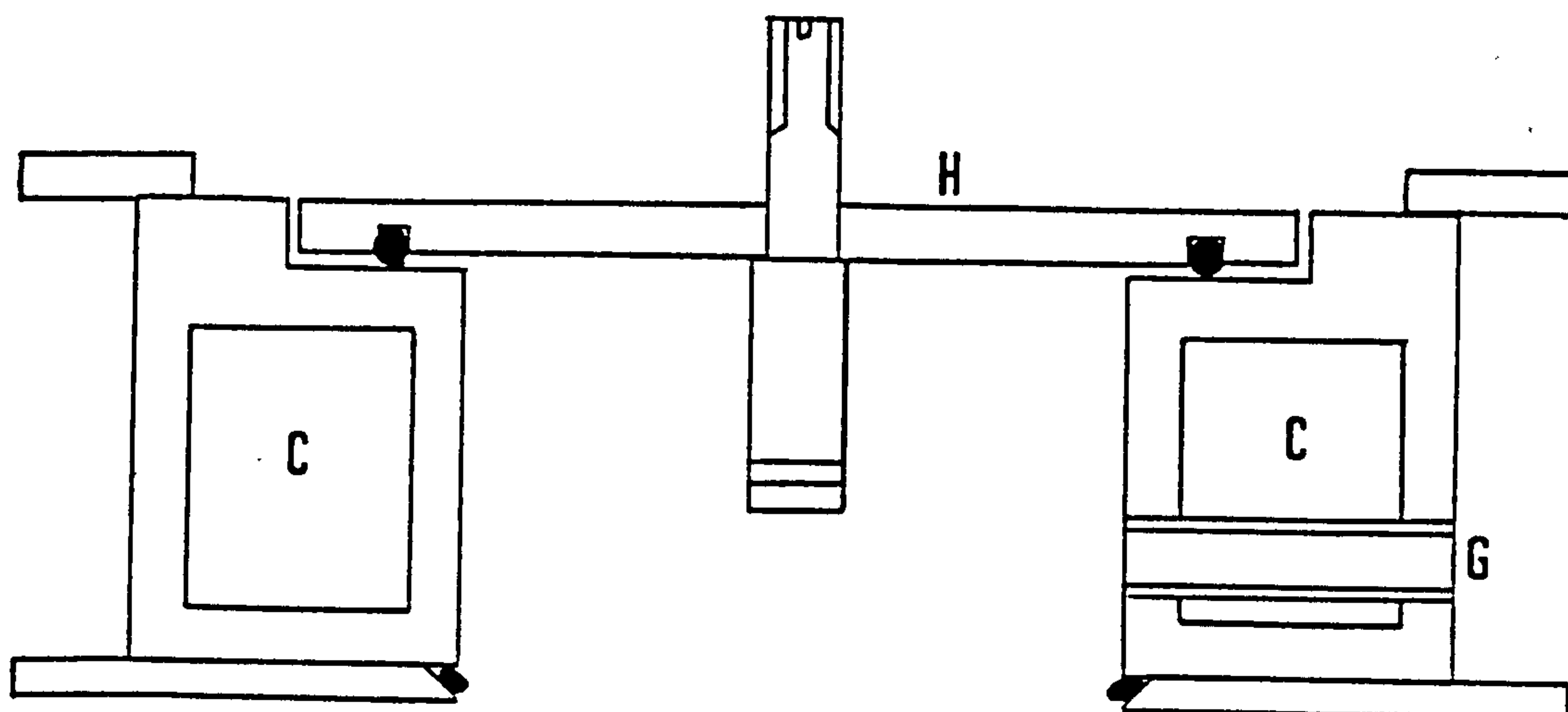


Figure 3.1. Schematic Diagram of Vertical Tube Furnace.

Figure 3.2. Detail of Quick Release Mechanism in Tube Furnace

Samples which were used for ageing for periods of time of 1hr or greater were then wrapped in molybdenum foil and sealed in 3kNm^{-2} Ar atmosphered silica tubes. For samples of the four major alloys (1-4), where it was desired to have heat treatment conditions which were as close to each other as possible, a specimen of each alloy was sealed up in the same silica tube, which allowed for identical lengths of ageing time and quenching conditions. In the furnaces used for these heat treatments, the hot zone in which the temperature varied by less than 1°C (as measured using a Pt/Pt13%Rh R-type thermocouple), the hot zone was at least 50mm long, which allowed each sample in the silica tube to be comfortably within the region. All of these samples were quenched into water at ambient temperature after the heat treatments.

The process by which samples were heat treated for short periods of time differed from that described above. As the technique above encloses the samples, and separates them from the furnace walls, heating by conduction is not possible. This has the effect that the heating rate which is achieved in the samples is relatively low. For samples aged for long periods of time, this is not a problem, as even if a sample takes 5 minutes to reach its' ageing temperature, then this has little percentage effect on the ageing time. This, however, does not apply if the sample is only to be aged for a period of as little as 6 minutes. Thus for short ageing times, the heat treatments were carried out in air. The samples were placed on pre-heated stainless steel blocks in a horizontal tube furnace (see figure 3.3.), to increase the rapidity of the heating process through conduction. The samples were each attached to a K-type thermocouple, which was used to measure the temperature rise in the sample, and also as a means of moving the sample into and out of the furnace. This heating technique produced enhanced heating rates of up to 40K/sec . Oxygen contamination of the samples was not considered to be a problem over such short periods of time as diffusion into the bulk sample was considered to be minimal. The oxide which formed on the sample surface was removed by mechanical grinding. An example heating curve is shown in figure 3.4.

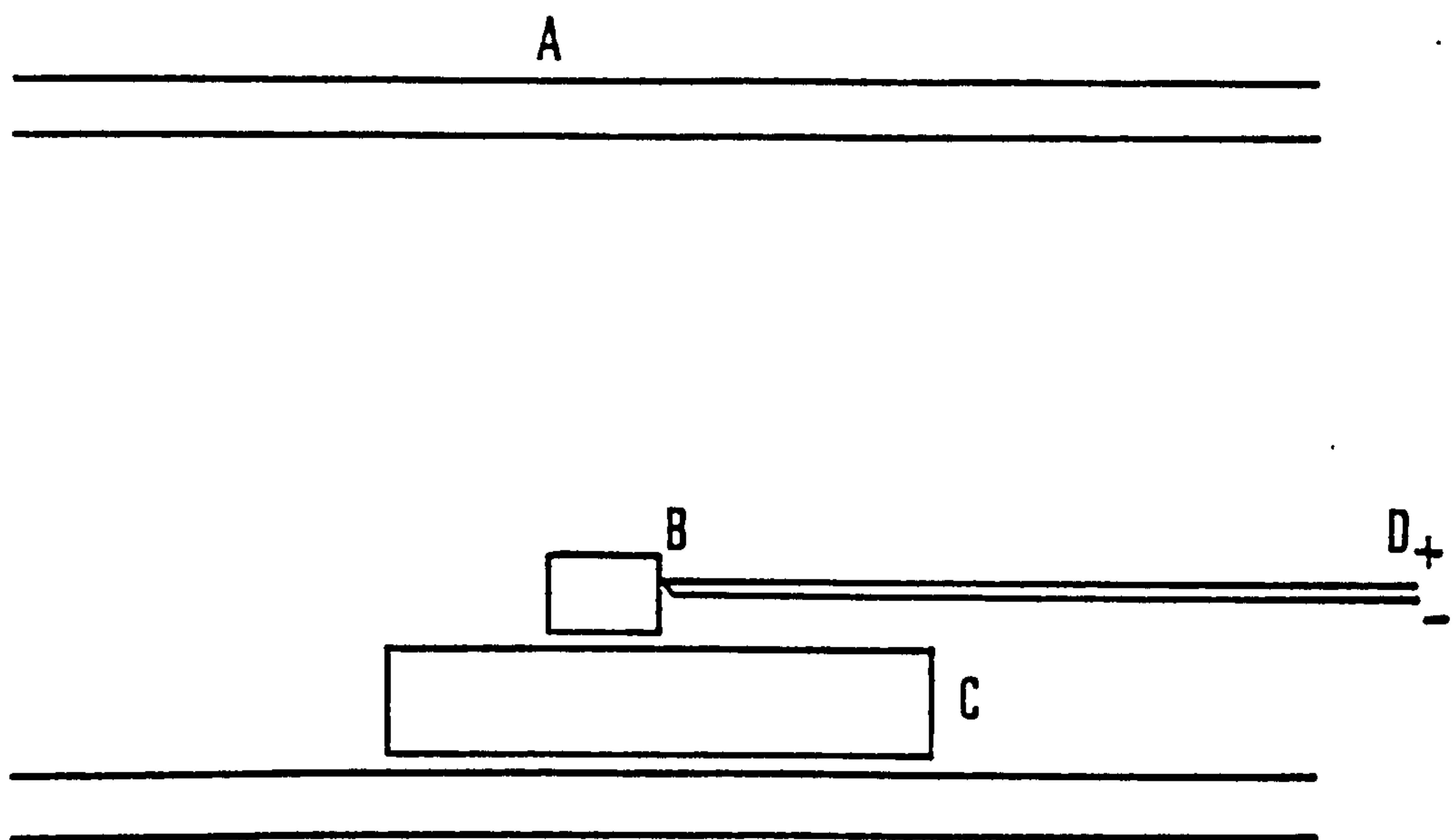
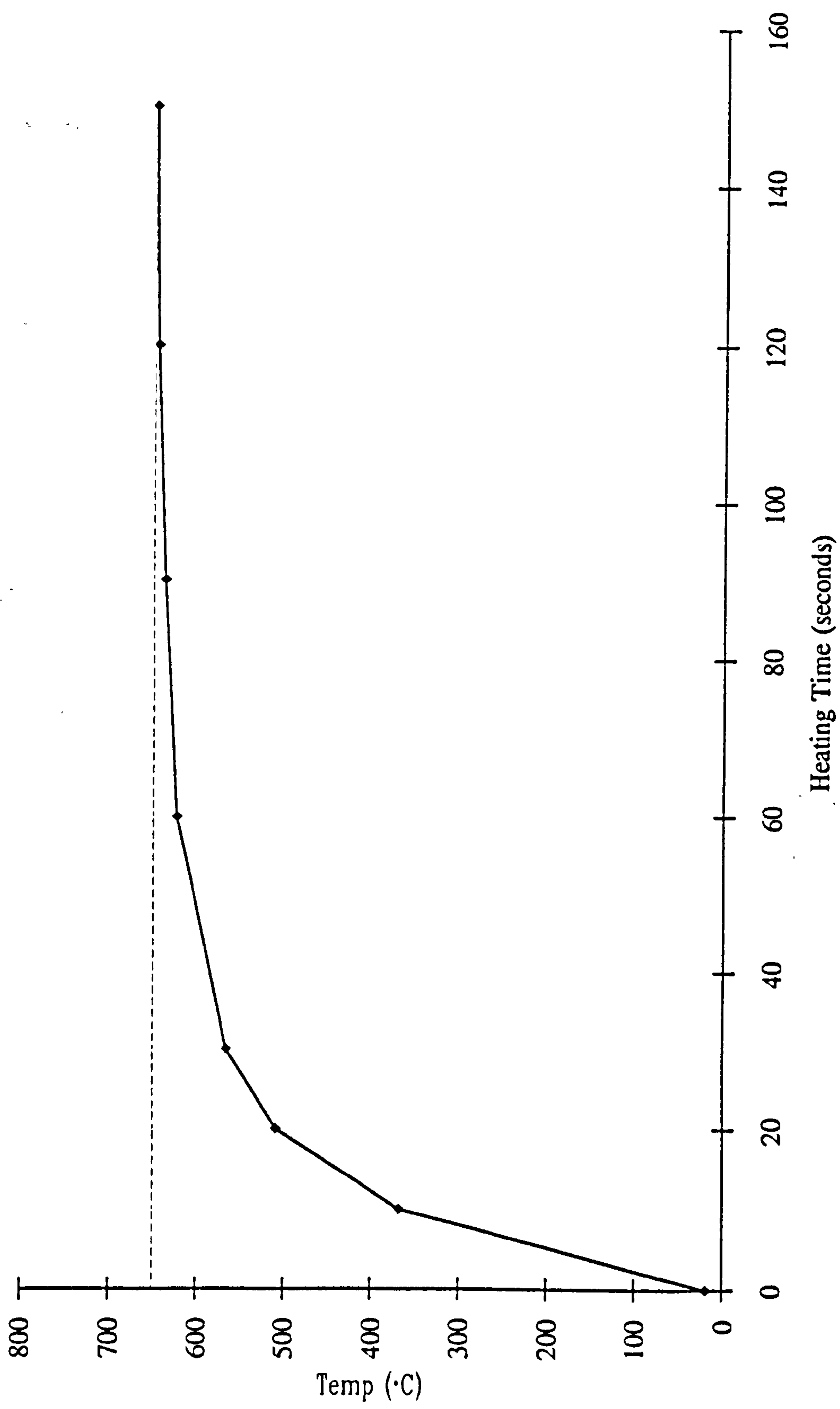


Figure 3.3. Schematic diagram showing heating arrangement for short ageing treatments

- a) Furnace wall
- b) Sample
- c) Pre-heated stainless steel block
- d) Thermocouple

Figure 3.4. Heating Rates For Sample Aged At 650°C On Pre-Heated Block



3.3. Sample Preparation and Examination.

3.3.1. Sample Polishing.

All samples were mechanically ground using water lubricated silicon carbide grinding paper starting with coarse paper of between 120 and 400 grade, depending on the sample roughness. The samples were then ground using sequentially finer paper from 120 to 1200 grade via 240, 400 and 800 grade grinding paper.

A variety of polishing techniques were initially tested, so as to ascertain the most effective method.

3.3.1.1. Mechanical Polishing Using Alumina.

After grinding, samples were conventionally polished using an alumina - in - water suspension [Kha88] using alumina with average particle sizes of 5, 1, 0.3 and 0.05 μm respectively. This technique provided a fine polished surface on softer samples but resulted in a large number of embedded alumina particles being left in the surface. These were not removable using an ultrasonic cleaning bath. When this polishing technique was used on samples of hardness greater than approximately 350Hv, it was found that the polishing effect was greatly reduced.

3.3.1.2. Electropolishing.

Samples previously polished using alumina down to 1 μm alumina particle size, were then subjected to an electropolishing technique. These samples were electropolished in 10% H_2SO_4 in water with an applied potential of between 18 and 25V. The operation was carried out at a temperature within the range of -25 to -35°C. This method was discarded because the polishing caused preferential dissolution of silicide particles to the point that only surface holes remained. Particles of alumina were also retained in the surface. Another problem, reported by Muraleedharan [Mur91] is that electropolishing induces transformations in the surface structure due to

hydride precipitation. This prohibited the use of electropolished samples for X-ray diffraction examination.

3.3.1.3. Mechanical Polishing Using Diamond.

Using this technique, the samples were polished using diamond particles of average size of 6, 1 and 0.25 μm in sequence. This was found to be the most effective technique, as the diamond did not embed itself in the sample surface, and was abrasive enough to polish the harder alloys with little difficulty. Overall, diamond polishing was found to be the most effective method for sample polishing, and thus was used for polishing all but the first few samples.

3.3.2. Sample Surface Examination.

Initial examination of the alloys was carried out using light microscopy on samples etched in Kroll's Reagent (3%HF, 10% HNO_3 in water). Use of this technique was soon discarded as the fineness of the microstructure was such that most features were unresolvable. SEM examination also was carried out on samples etched in Kroll's Reagent. This reagent gave varying levels of surface dissolution depending on the phase present, which gives strong contrast in the microscope. It was found that the etch was deepest in niobium-lean α_2 -based grains and lower in β and titanium silicide (Ti_5Si_3) grains. The SEM metallography was carried out using JEOL JSM35CF, T200 and T220A microscopes. The T220A, which had the best SE (Secondary Electron) detector, was used for the majority of the metallography. When back scattered imaging was desired, the T200, fitted with a KE back-scattered detector, was used. The JSM35 which was fitted with a Link 890 EDX (Energy Dispersive X-ray) system running ZAF4 software was used for quantitative analysis. Previously, Khataee [Kha87], had found that in a similar alloy system (Ti-Al-Ru), prior etching of titanium aluminides tended to distort the analysis of aluminium, giving an error of up to 20at%, when compared to unetched material. This was not found to be the case with the particular alloys examined here. However, Maeda [Mae88], found that the ZAF corrections in the system gave consistent reduction of 10% in aluminium content in Ti-Al-V alloys, due to the position of absorption edges in the energy spectrum. Comparison of results with those found elsewhere indicated that this is also true for these alloys.

3.3.4. Transmission Electron Microscopy.

Foils for transmission examination were first ground down to a thickness of approximately 150 μ m using 1200 grade water lubricated silicon carbide paper. After grinding, they were then fixed to a polished copper block with cyanoacrylate cement, and sputter coated with carbon to enhance conductivity. They were then cut into 3mm diameter sections using a Materials Science spark erosion unit. Sample cutting took an average of 5 minutes per sample. Each foil was then removed from the block by dissolving the cement in acetone overnight. The surfaces were then ground to remove the carbon coating. Sample thinning was initially carried out using a variety of methods and solutions including ion thinning of dimpled samples and jet thinning in a small range of solutions including 10% perchloric acid and 30% butanol in methanol and 5-10% H_2SO_4 in methanol. Ion thinning in a Gatan Ion Thinner was ineffective due to the materials resistance to ion beam attack. Foil penetration took in excess of 50hrs. This has also been found by Kestner-Weykamp [Kes89]. The method which produced the most effective thinning was using a Struers Tenupol twin jet thinner with the automatic penetration detector removed. Experimentation has shown that relatively slow thinning produces the most consistent thin area in the foil. Thus, a lower than normal acid content electrolyte (7 vol.% H_2SO_4 in methanol) was found to be most effective. However, contamination of the electrolyte quickly degraded its properties. Under typical operating conditions (-30°C, 18V, 120mA), the degradation was sufficient that only the first foil to be produced was usable, and the solution then had to be discarded. It was also found that a greater thin area was obtained if the detection of the penetration of the electrolyte through the sample was carried out by eye, rather than using the photo-detector system conventionally used with the Tenupol system. Hydride precipitation in the foils produced in this way was not found to be a problem provided the electrolyte was kept below approximately -25°C. Above this temperature, the amount hydride formation was markedly increased.

Examination of the thin foils was carried out in a range of instruments. A 100kV Philips EM301 machine was used for initial examinations. Later work was carried out using either a 120kV JEOL 120CX or a 200kV JEOL 2000FX, both of which were fitted with STEM (scanning transmission electron microscopy) facilities and a LINK EDX detector. The EDX system on the 2000FX also used had a windowless light element detector fitted. Any analysis of the thin foils was undertaken on the 200kV instrument, which had elemental standards specifically recalibrated for this work. Experimentation showed that the compositions analysed with this system were not greatly affected by foil thickness.

3.3.5. X-Ray Diffraction.

X-ray diffraction was carried out on a Philips PW1710 diffraction unit using CuK_α radiation at 40kV and a current of 40mA. Diffraction was carried out on samples ground flat using 1200 grade SiC paper. Similar alloys are reported to undergo some phase transformations which are detectable using X-ray diffraction when electropolished or etched [Mur91], so this was avoided. Calibration of the diffractometer was carried out using a polycrystalline silicon standard, with the angle being modified with reference to a silicon $\langle 111 \rangle$ peak (d spacing 313.53pm). This was repeated until a consistent and accurate peak position was identified. Each sample was first examined over an angular range of 20 to 140° 2θ at 1°/mm. Lattice parameter measurements were taken over smaller angular ranges at a trace spacing of 4°/mm. The accuracy of the diffraction peaks was estimated to be $\pm 0.005^\circ$ for the narrow trace, and $\pm 0.001^\circ$ for the wider trace.

3.3.6. Calorimetric Analysis.

A Stanton - Redcroft (now P.L. Thermal Sciences) D.S.C.1500 Differential Scanning Calorimeter (D.S.C.), was used to identify phase transformation temperatures. This was operated at temperatures up to 1300°C under a dynamically pumped H.P. argon atmosphere. Data from this was logged using an Epson PCAX2, IBM PC/AT compatible microcomputer running Version 4.1 to 4.3 of P.L. Thermal Sciences' data logging and interpretation software. Samples of between 20 and 90mg were used in matched platinum crucibles, and heated together with either a platinum or alumina standard. Heating and cooling was carried out at a rate of between 3 and 50 °C per minute. The temperature and temperature differential was measured at 1.5sec intervals throughout the experimental runs.

3.4. Accuracy of EDS Analysis.

3.4.1 Chemical Analysis Carried out in SEM.

The analysis undertaken on the SEM is inherently limited by the EDS technique. The limitation is caused by the excitation volume of the x-rays which are analysed. The volume of the sample which is required to produce the x-rays for analysis is typically $3\mu\text{m}$, which indicates that for reliable analysis a particle size of at least $5\mu\text{m}$ diameter would be desirable. As this technique relies on the characteristic energy of x-rays from each element being different, then any overlap of peaks can cause inaccuracies in the analysed data. As the characteristic X-ray energies of the Al K_{α} , Si K_{α} and Nb L_{α} lines are relatively close together, some inaccuracies in the relative values of the compositions may be expected due to the overlap of the broadened peaks. The analysis is also affected by the tail off in energy produced by using a detector shielded with a beryllium window. From the results produced in the current work, and that of previous authors [Mae88], it appears that the aluminium content is underestimated by the software by approximately 10%. Thus all chemical analyses used in this work have been corrected for this. Another problem which occurs in the chemical analysis of these alloys is that the silicon content, being approximately 1at%, does not produce a large peak, and accuracy would be expected to be affected by partial masking caused by the relatively high background noise to peak ratio. Fortunately this does not appear to be the case, as Si contents in individual samples have a scatter of around 0.1at.% with an average 2σ value equivalent to about ± 0.09 at.% for each analysis.

3.4.2 Chemical Analysis Carried out in TEM.

EDS analysis of thin foils using a TEM greatly reduces one of the problems which is inherent in bulk sample analysis, namely the relatively coarse spatial resolution which is achievable, but instead presents another. As TEM foils are by nature 'thin', then the excitation volume producing the X-ray emissions is much smaller. The excitation volume can be thought of as being in the shape of a water droplet, and consequently if the sample is thin enough that significant broadening of the excitation volume does not occur within the sample, then the area from which the analysis is taken can be much smaller. However, this does lead to greater variations in

the analysed composition due to the thickness of the sample and the local composition. Increasing the thickness of the sample may reduce the number of low energy X-rays (i.e. those produced by the lighter elements such as aluminium) which escape from the sample. Spot analyses of known phases in individual samples which have been analysed in this work do not show significant variation with thickness in these alloys, indicating that the effect described above is not highly significant in the samples studied.

Chapter 4

Casting, Solution Treatment and Low Temperature Ageing

4.1. As Cast Microstructure

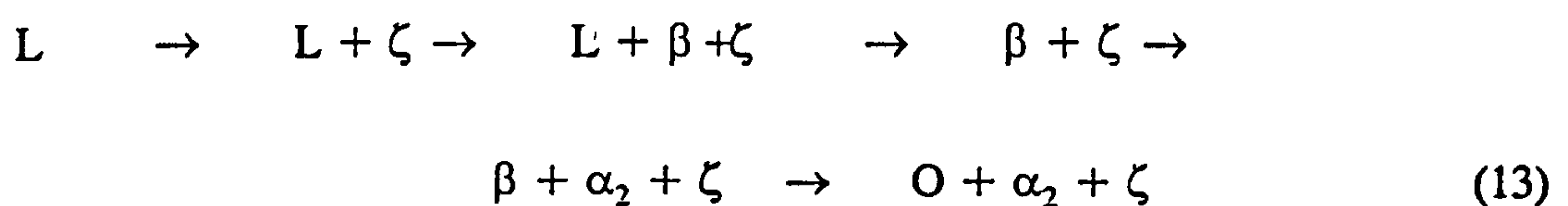
some of the alloys that were not forged commercially (i.e. not the four 'base' alloys) have been examined in the 'as cast' condition, and their microstructures are detailed below. This examination was carried out on the alloys which had a silicon content of 1.5at.% or more. The alloys with lower silicon content have all of their microstructural characteristics removed by the solution treatment, but the silicide particles which form in the higher silicon level alloys during the casting process are retained in the solution treated condition. Thus as the solution treatment process does not remove all of the microstructural features which are present in the high Si alloys, it is necessary to examine the 'as cast' microstructure to see how much effect its morphology has on the microstructures after subsequent heat treatment. As the solution treatment process removes all traces of the 'as cast' microstructure in the lower silicon-content alloys, the prior structure will not be discussed here.

In the 'as-cast' condition the microstructure of the Ti-23-11-1.5 alloy consists of a distribution of α_2 platelets in a background of O phase (see Figure 4.1a). A small number of silicide particles are also present. The phases present have been identified mainly using X-ray diffraction techniques. This is indicative that the microstructure that is found is a result of the relatively slow cooling of the alloys, that is inherent in the arc-melting procedure used to form these alloys. This must be so as the two metallic phases found do not occur at very high temperatures, and thus must be formed by diffusional transformations which occur well below the solidus during the cooling process. The amount of O phase present in the Ti-23-11-1.5 alloy is relatively small, as would be expected due to the increase in the amount of α_2 stabilising elements. A more detailed view of the microstructure can be seen in figure 4.1b.

When the composition is changed to increase the β stabilisation, as in Ti-23-15-1.5, the microstructure becomes noticeably finer in scale (Figure 4.1c), with a

greater proportion of O phase. The small number of silicide particles evident in the Ti-23-11-1.5 have disappeared (Figure 4.1d).

As compared to Ti-23-11-1.5, as would be expected, the addition of 1.5 at.% more silicon to the matrix results in a large increase in the amount of silicide phase present. Figure 4.1e shows that this silicide is formed in large amounts during the solidification process, as it is present along the matrix grain boundaries, producing a eutectic lamellar structure at the intersections of three grains (Figure 4.1f). When compared to Ti-23-11-1.5, the grains of α_2 are much larger, with apparently less O phase along the boundaries of the α_2 laths. A schematic solidification and phase transformational route for this alloy is shown below;



4.2. Solution Treated Microstructure

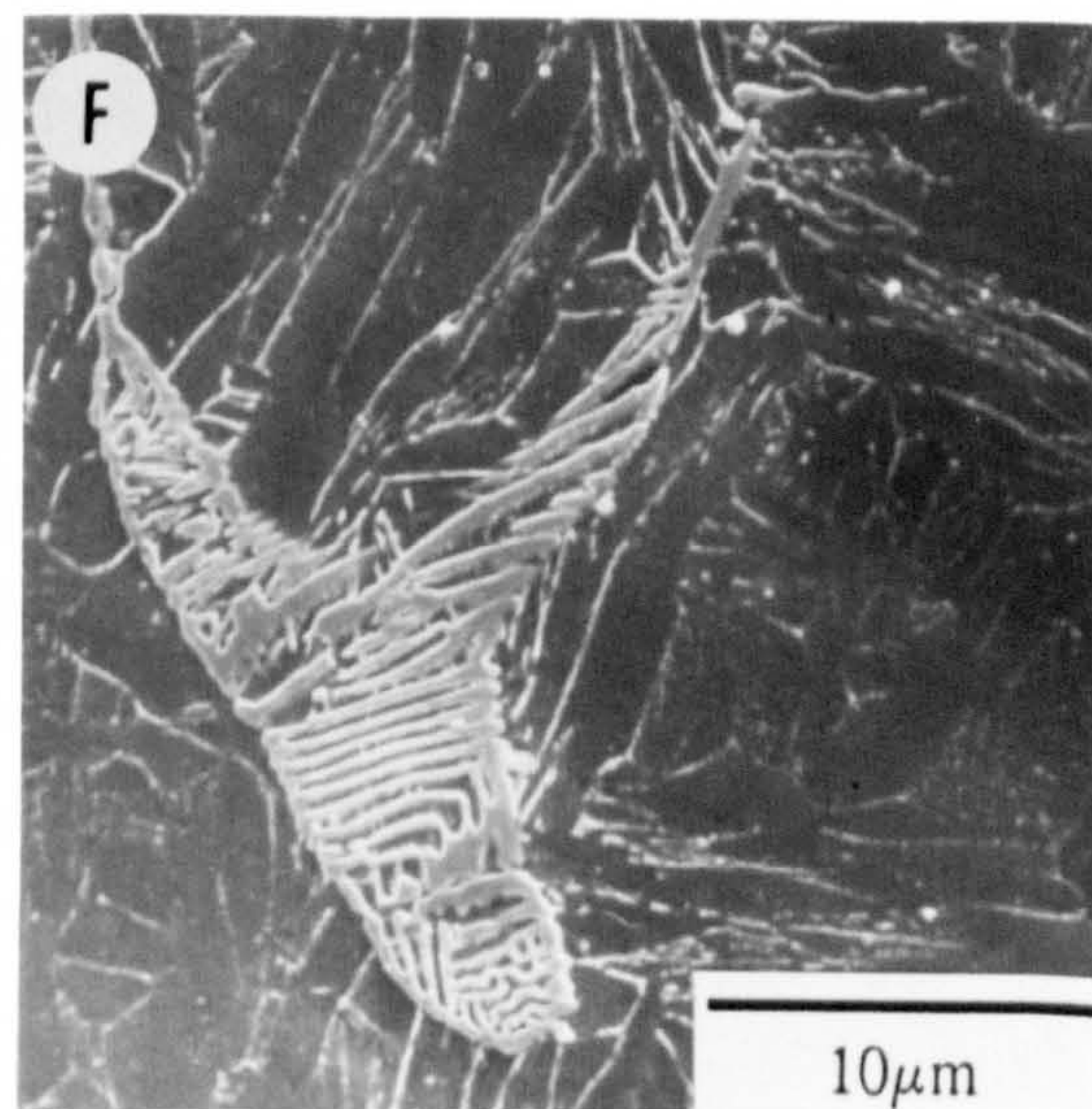
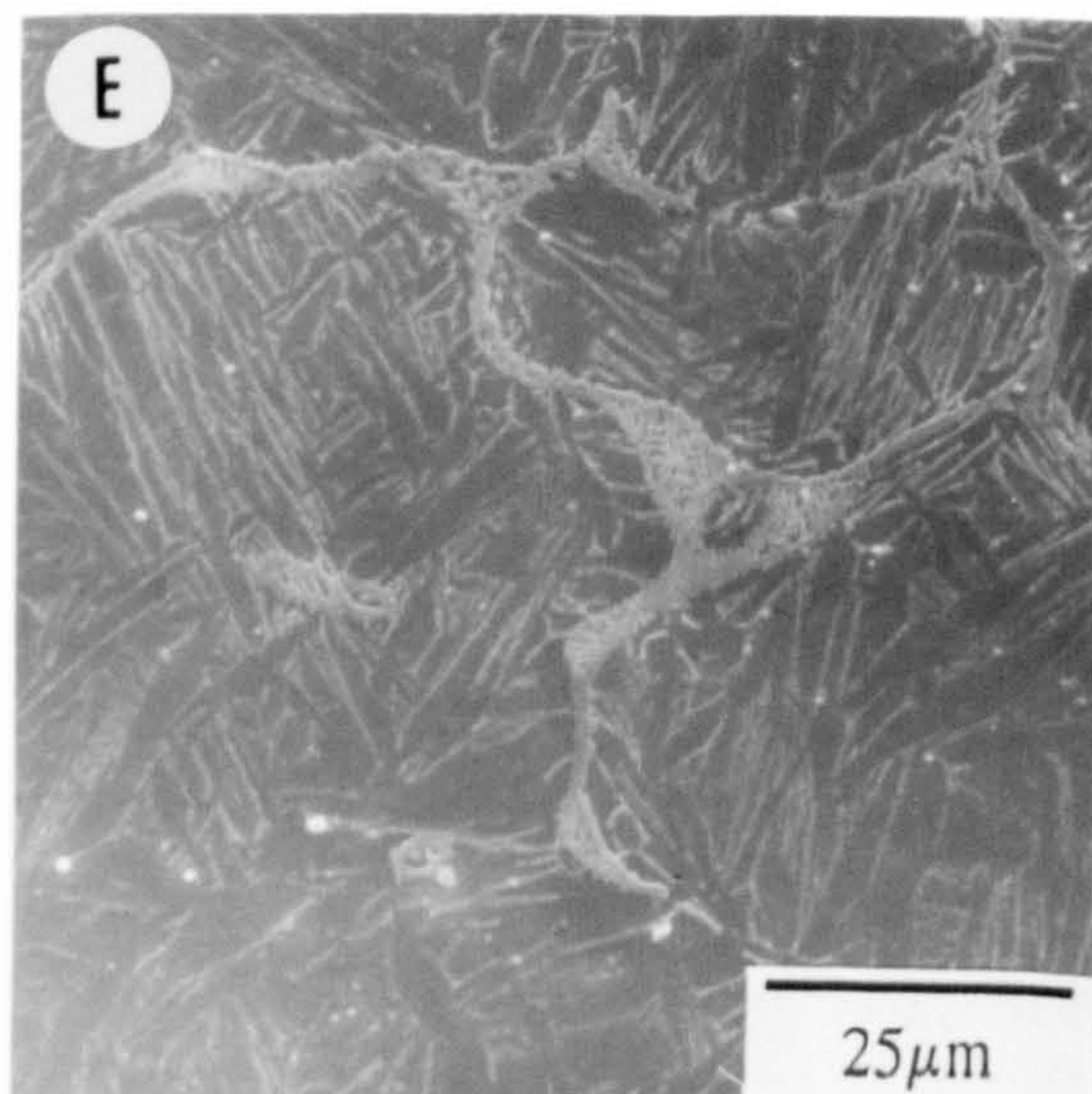
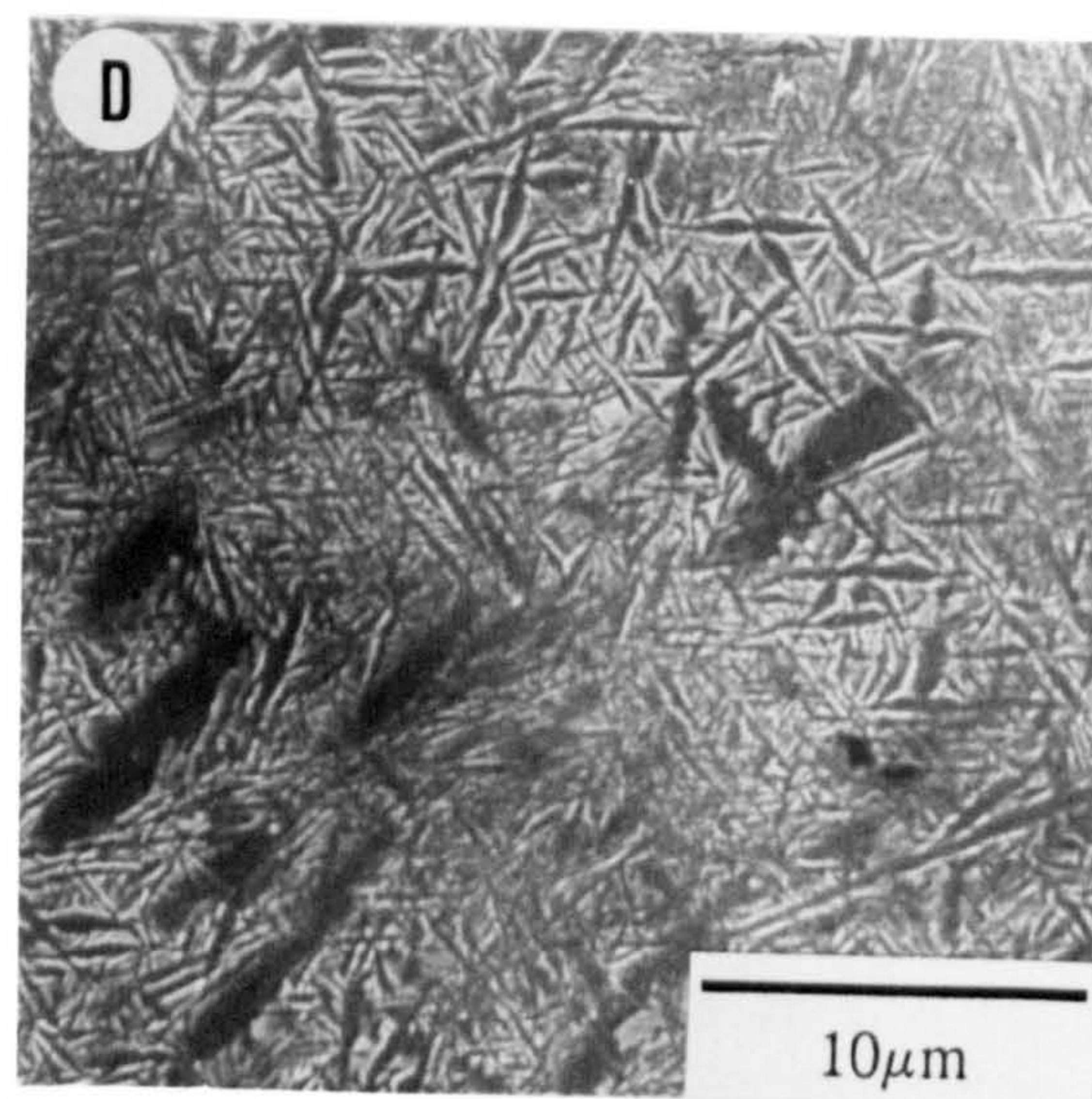
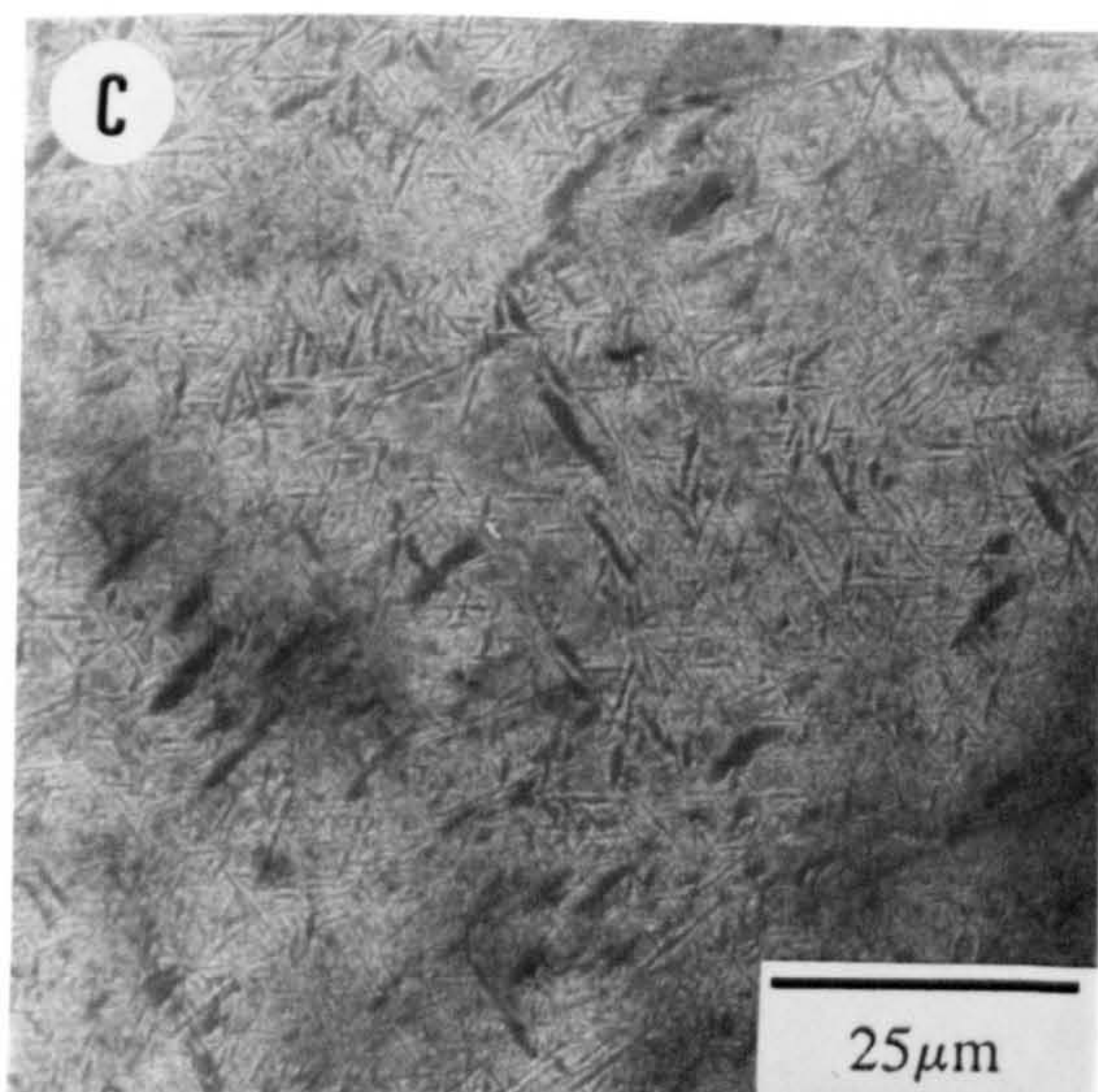
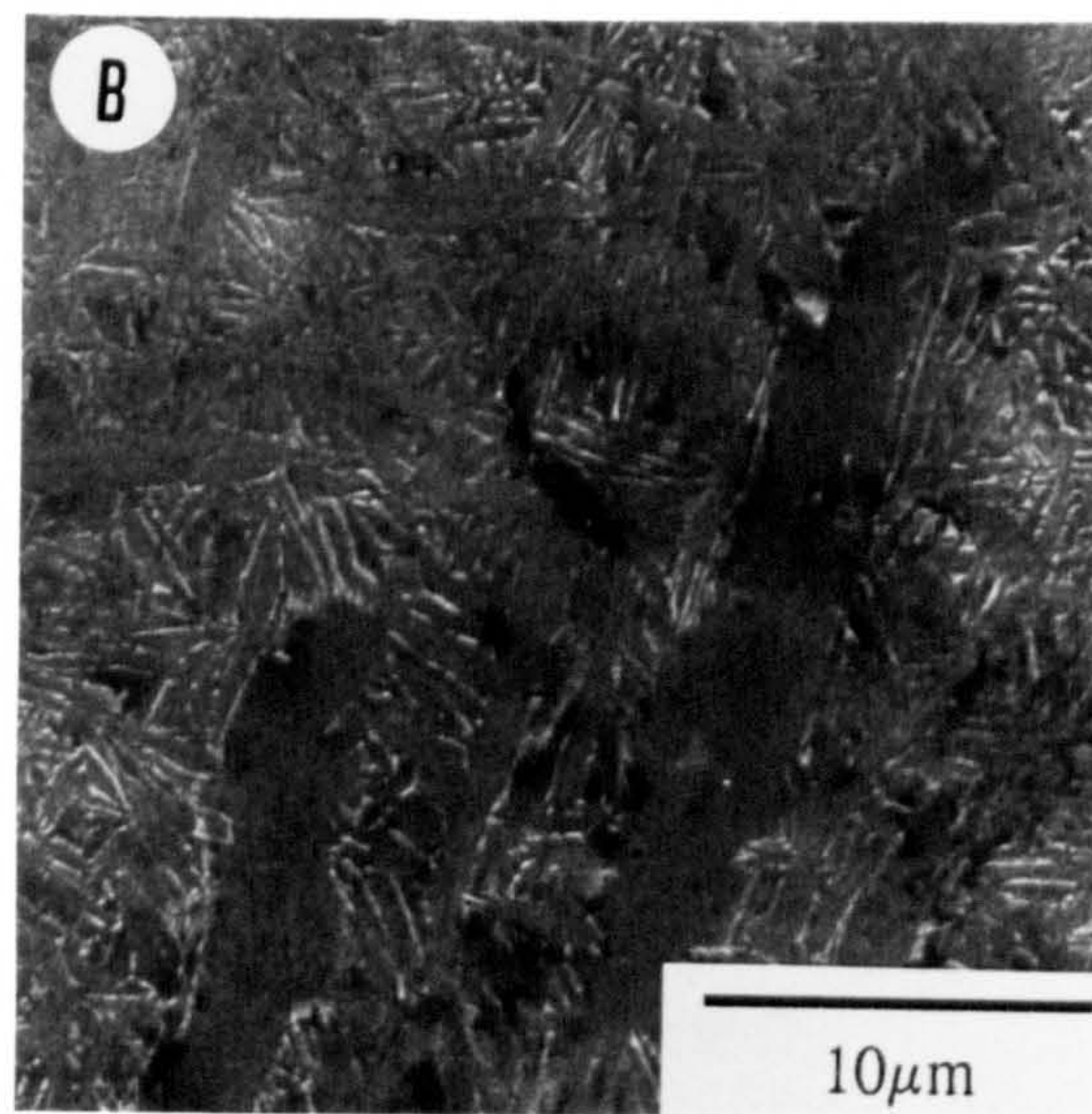
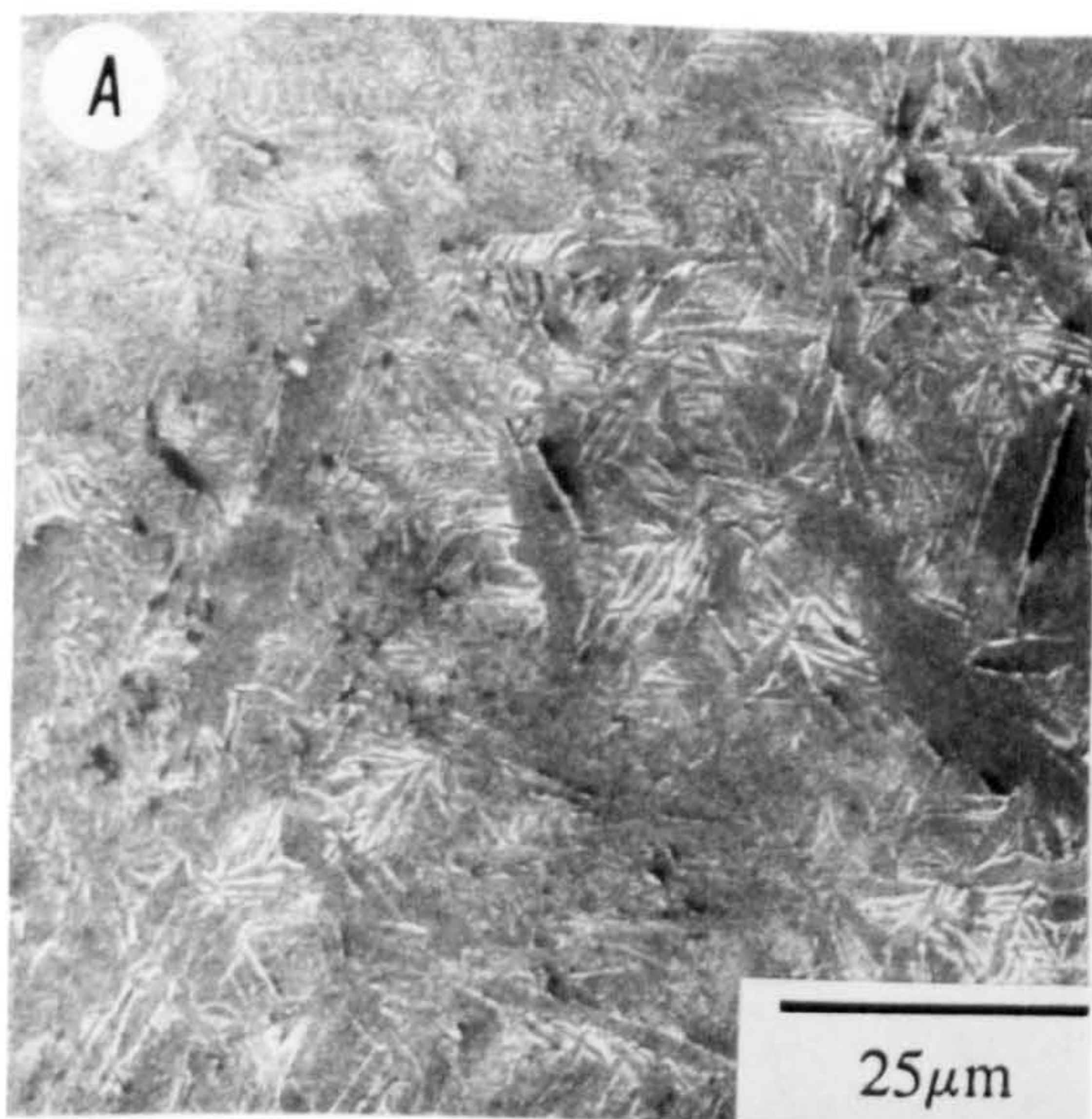
In ternary titanium - aluminium - niobium alloys based on the binary composition Ti_3Al it has been previously found that the addition of niobium increases the stability of the β_0 phase with respect to quenching [Str88]. Strychor found that the addition of 11at.% Nb to the alloy produced an increase in stability of the quenched β with respect to the $\beta \rightarrow \alpha'$ transformation, but found other transformations to occur instead. Similar examinations have been carried out on two of the quaternary alloys used in this work, as detailed in Table 4.1. below. The reason for choosing these heat treatments will be explained in section 4.3.

Figure 4.1.

Ti-23-X-Y alloys showing cast microstructure.

SEI images of all alloys mechanically polished, etched in Kroll's Reagent.

- (a) Ti-23-11-1.5. Microstructure shows α_2 (dark) platelets in a background of O. Small raised light coloured particles are titanium silicide $(\text{Ti,Nb})_5(\text{Al,Si})_3$.
- (b) Detailed view of (a).
- (c) Ti-23-15-1.5. Microstructure shows α_2 (dark) platelets in a background of O. Microstructure is finer and more even than that of Ti-23-11-1.5 (cf. (a)).
- (d) Detailed view of (c).
- (e) Ti-23-11-3. Microstructure shows α_2 (dark) platelets in a background of O. The α_2 /O grain structure is markedly coarser than in Ti-23-11-1.5. Also clearly visible is a matrix of lamellar eutectic silicide which has etched to a much smaller degree than the other phases.
- (f) Detail of the silicide eutectic structure (bright) at a matrix-grain triple point.



Alloy	Heat Treatment
Ti-20-11-0.9	1270°C/24hrs w.q. (s.t.)
Ti-23-11-0.9	1270°C/24hrs w.q. (s.t.)
Ti-23-11-1.5	1270°C/24hrs w.q. (s.t.)
Ti-23-11-3	1270°C/24hrs w.q. (s.t.)
Ti-23-15-0.9	1270°C/24hrs w.q. (s.t.)
Ti-23-15-1.5	1270°C/24hrs w.q. (s.t.)
Ti-20-15-0.9	1270°C/24hrs w.q. (s.t.)
Ti-20-15-0.9	S.T. then 380°C/600sec.
Ti-20-15-0.9	S.T. then 380°C/6ksec.
Ti-20-15-0.9	S.T. then 380°C/60ksec.

Table 4.1. Summary of Heat Treatments for 'As Quenched' Alloy Condition.

4.2.1. Solution Treated Alloys Containing 0.9 at.% Silicon

On quenching, each of the 20at.% Al, 0.9at.% Si alloys examined produced a similar microstructure, as can be seen in Figures 4.2a&d. Figure 4.2a shows the overall microstructure with no evidence of the β to α' transformation (α' is a hexagonal martensite phase which occurs in a range of titanium based alloys when cooled rapidly) that occurs in lower Nb alloys. Closer examination (Figure 4.2d&f) reveals an even distribution of tweed structure in the matrix.

Electron diffraction patterns produced from the alloys shows that, as found by Strychor and others [Str88,Pet90,Mur92], the quenched alloys show evidence of ordering in the β phase. This can be detected by the appearance of (001) type β_0 spots in the diffraction pattern. In the normal b.c.c. structure, diffraction by these planes is forbidden (the structure factor is zero). However, when the alloy orders to the B2 (CsCl) structure, then these spots can be found. There has been debate as to whether this ordering is produced by an ordering transformation during quenching. A range of authors have attributed the ordering to a quenching reaction including Strychor and Weykamp [Str88,Wey90], though more recent work has failed to find the small domains which would be expected [Ben89,Mur92,Ban89].

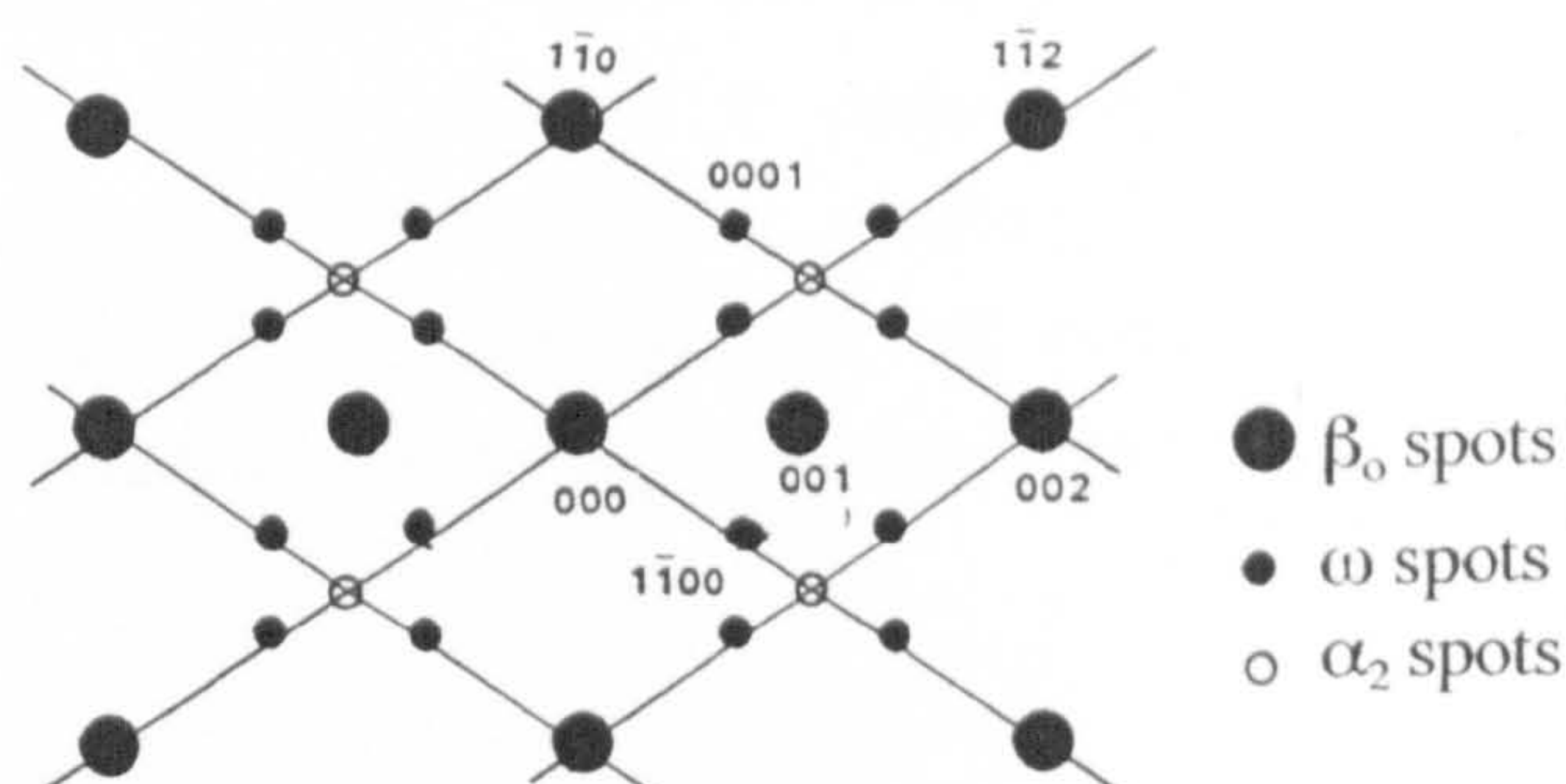
Dark field images produced using the (001) type spots in this work (Figure 4.2e) have not produced visible domains except in isolated areas on one sample (see below), and from this it is inferred that the domain size is large enough to be a product of the solution treatment, and not a 'quenched in' phenomenon, which would be expected to produce a very fine domain structure. If it is assumed that the ordering transformation is an equilibrium reaction, then as the compositions in the alloys in the two studies differ (Strychor - Ti-27.8Al-11.7Nb, current work Ti-20 $\leftrightarrow$ 23Al-11 $\leftrightarrow$ 15Nb-0.9Si), it is possible that the alloy used in the current work has a sufficiently different composition to move it from the β to the β_0 phase field at the solution treatment temperature as suggested by Bendersky [Ben90] (see Figure 4.3). If the vertical section in the Ti-Al-Nb ternary phase diagram suggested by Banerjee and Muraleedharan [Ban89,Mur92] is correct, then the alloys used by Strychor may pass through a $\beta \rightarrow \beta_0$ phase boundary during quenching (see later for more detailed discussion of phase diagrams). Alternatively, it has been suggested that the oxygen content in the alloy alters the order-disorder reaction in this system (see section 2.6), and this may explain the variation in the results produced by different authors.

Figure 4.2.

Alloy Ti-20Al-11Nb-0.9Si (at.%), solution treated at 1270°C/24 hrs, water quenched, TEM foils, electrochemically thinned in 10 vol.% H₂SO₄ in CH₃OH.

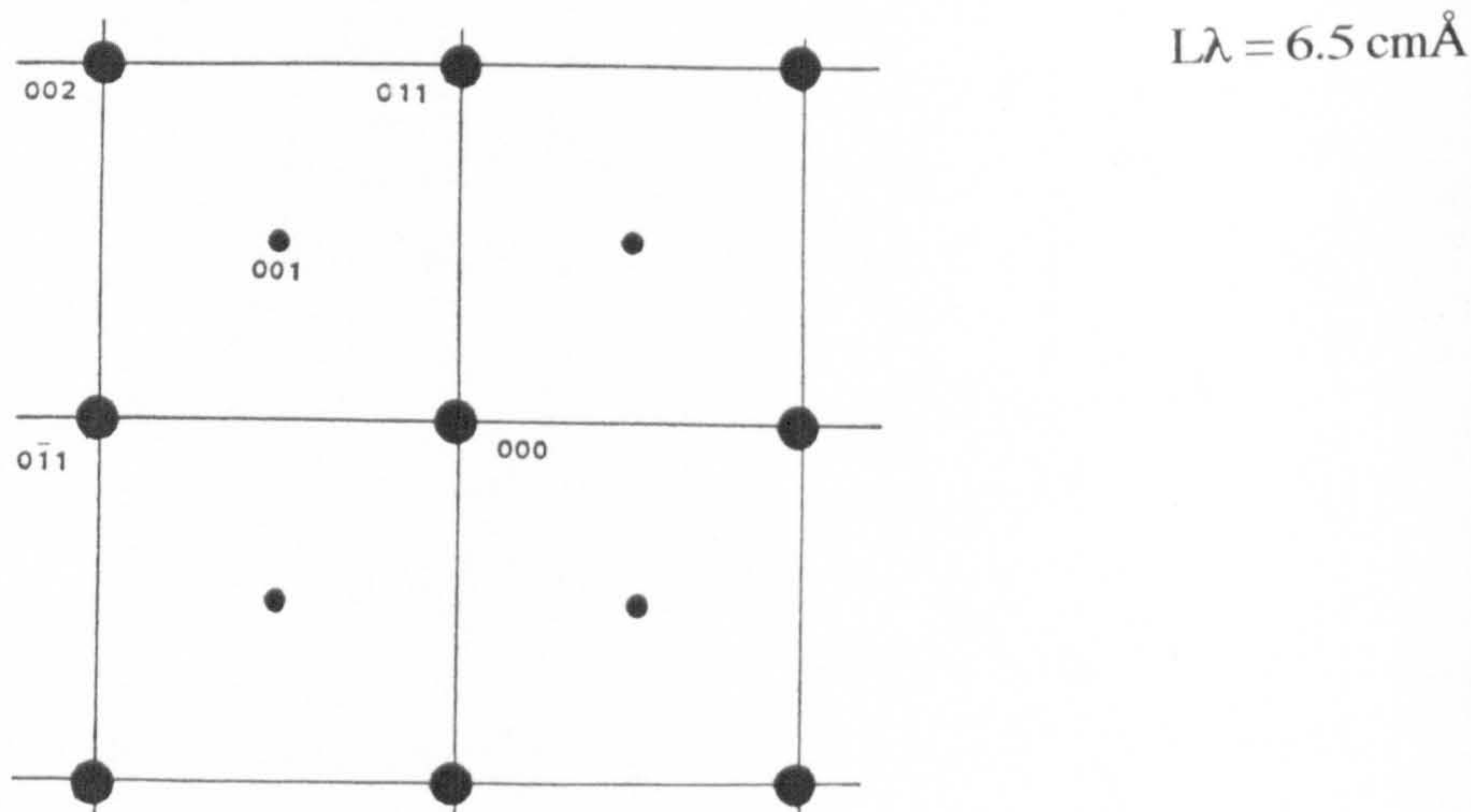
- (a) Low magnification micrograph showing single phase β in solution treated condition.
- (b) SADP on $[110]_{\beta_0}$ zone axis. This diffraction pattern shows strong $(001)_{\beta}$ diffraction spots produced by the ordering of the alloy. These are disallowed when the alloy is in a disordered state. Intense streaking is produced along the $\langle 112 \rangle$ type directions. Along these 'streaks' higher intensity areas can be observed at positions corresponding to those characteristic of an ω -type phase.

$$L\lambda = 4.0 \text{ cm}\text{\AA}$$



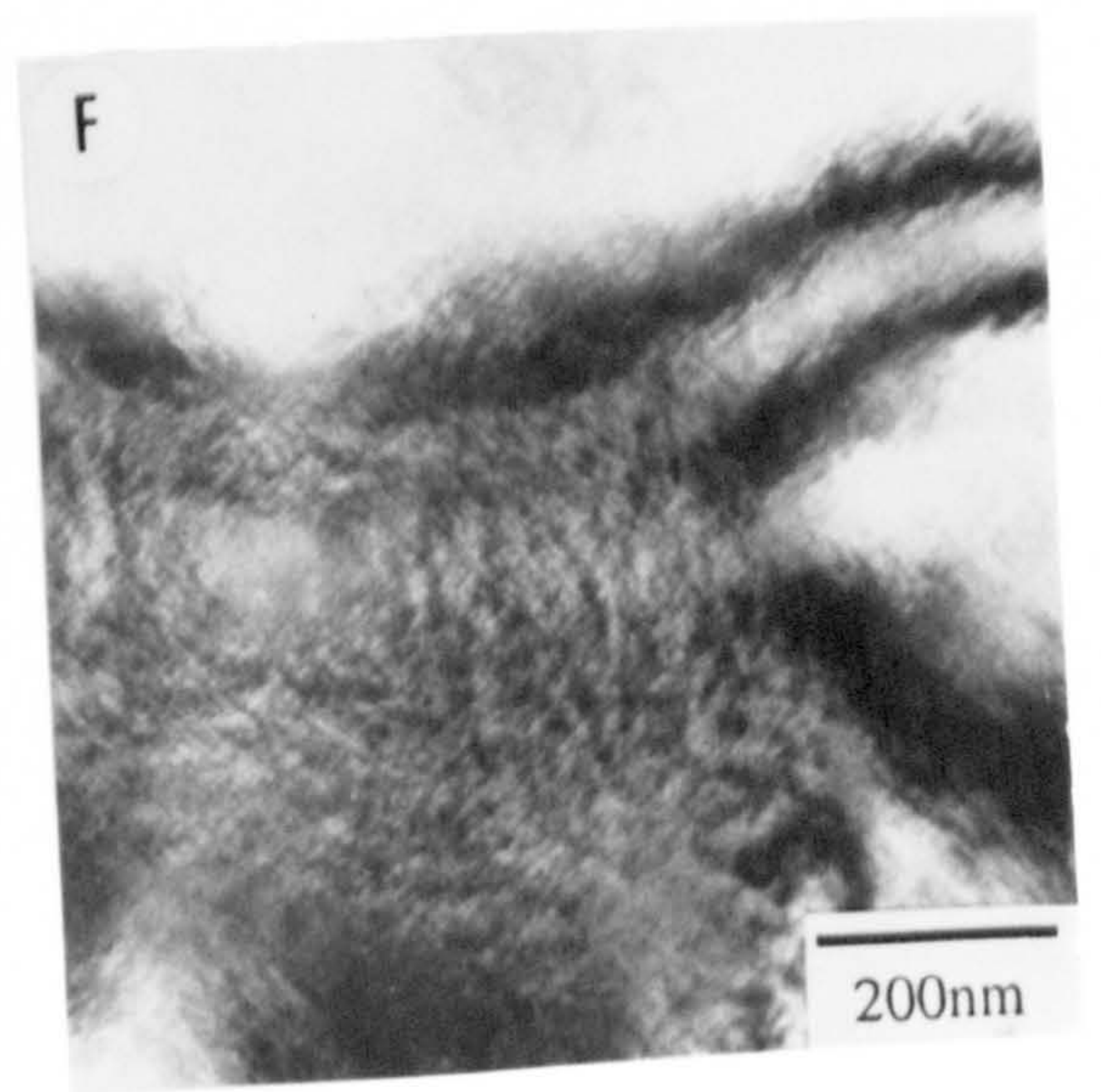
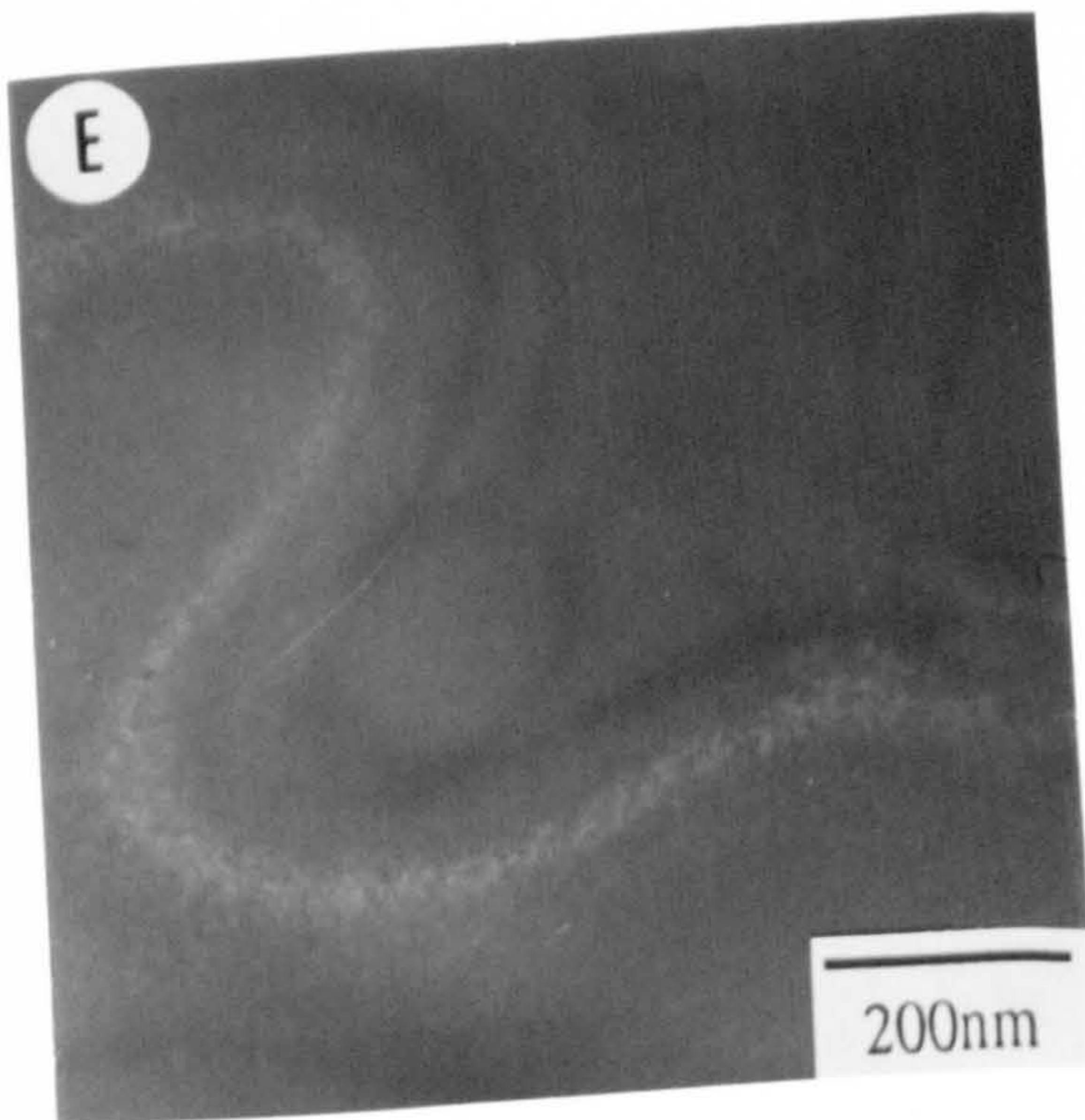
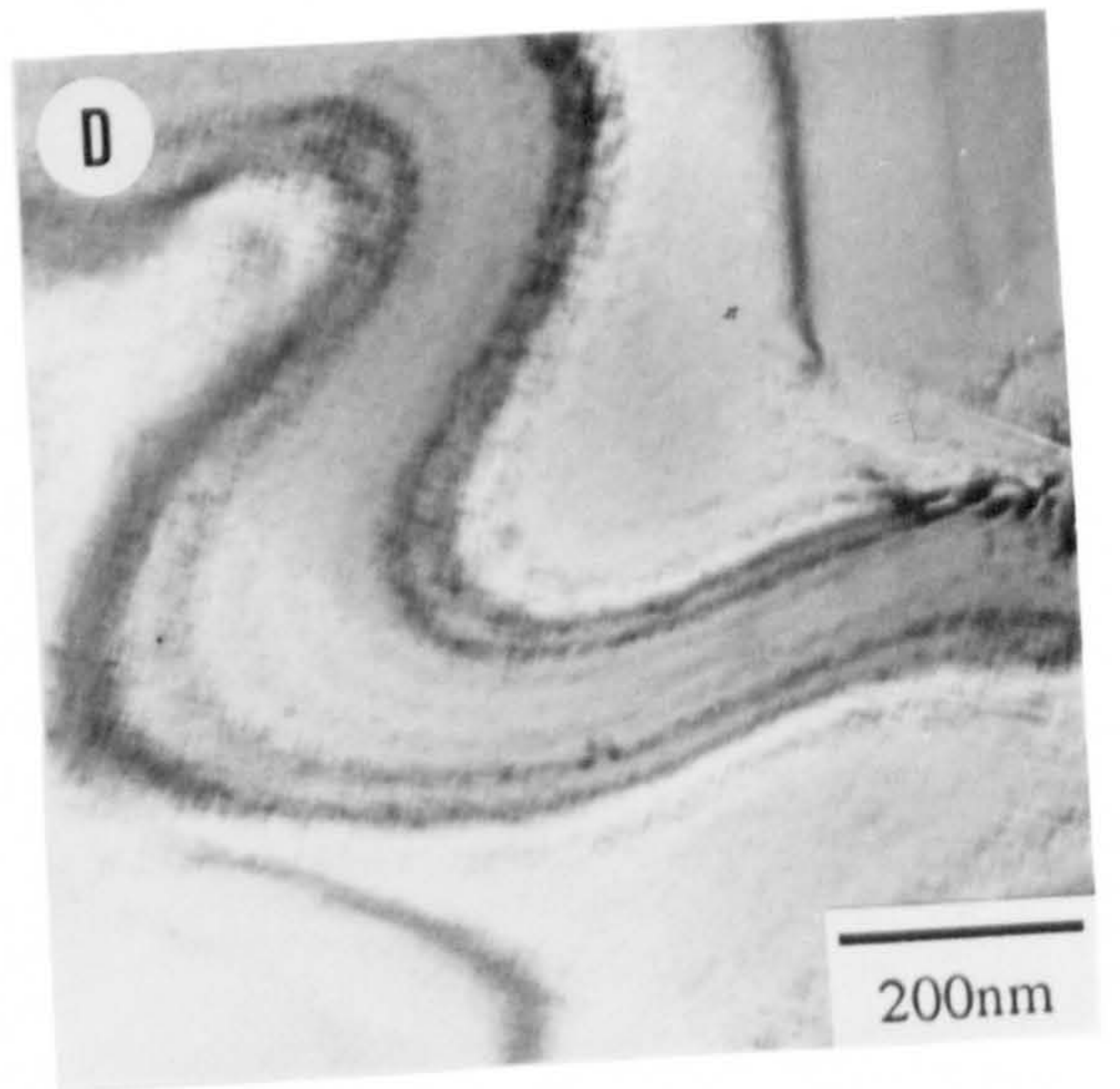
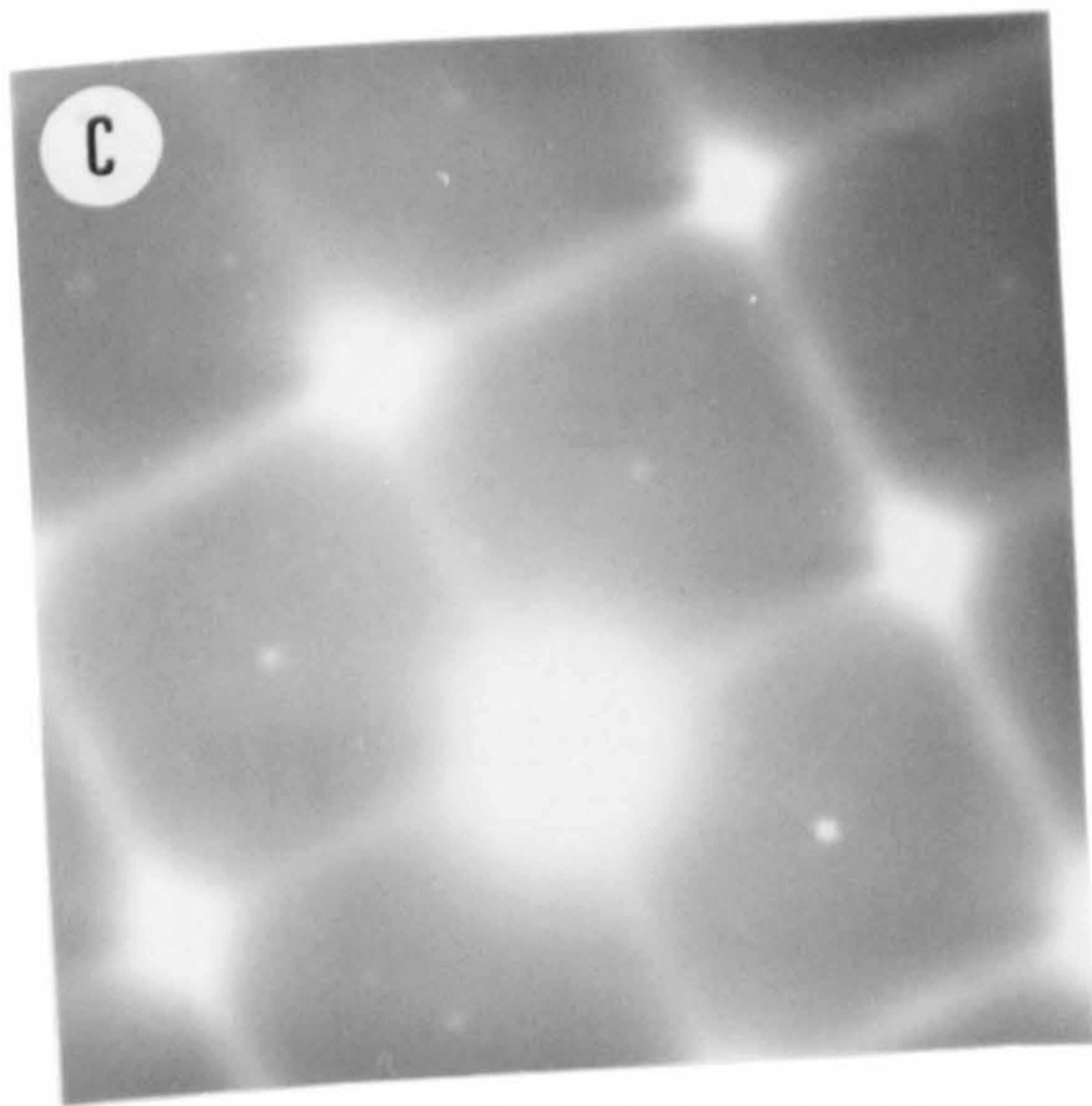
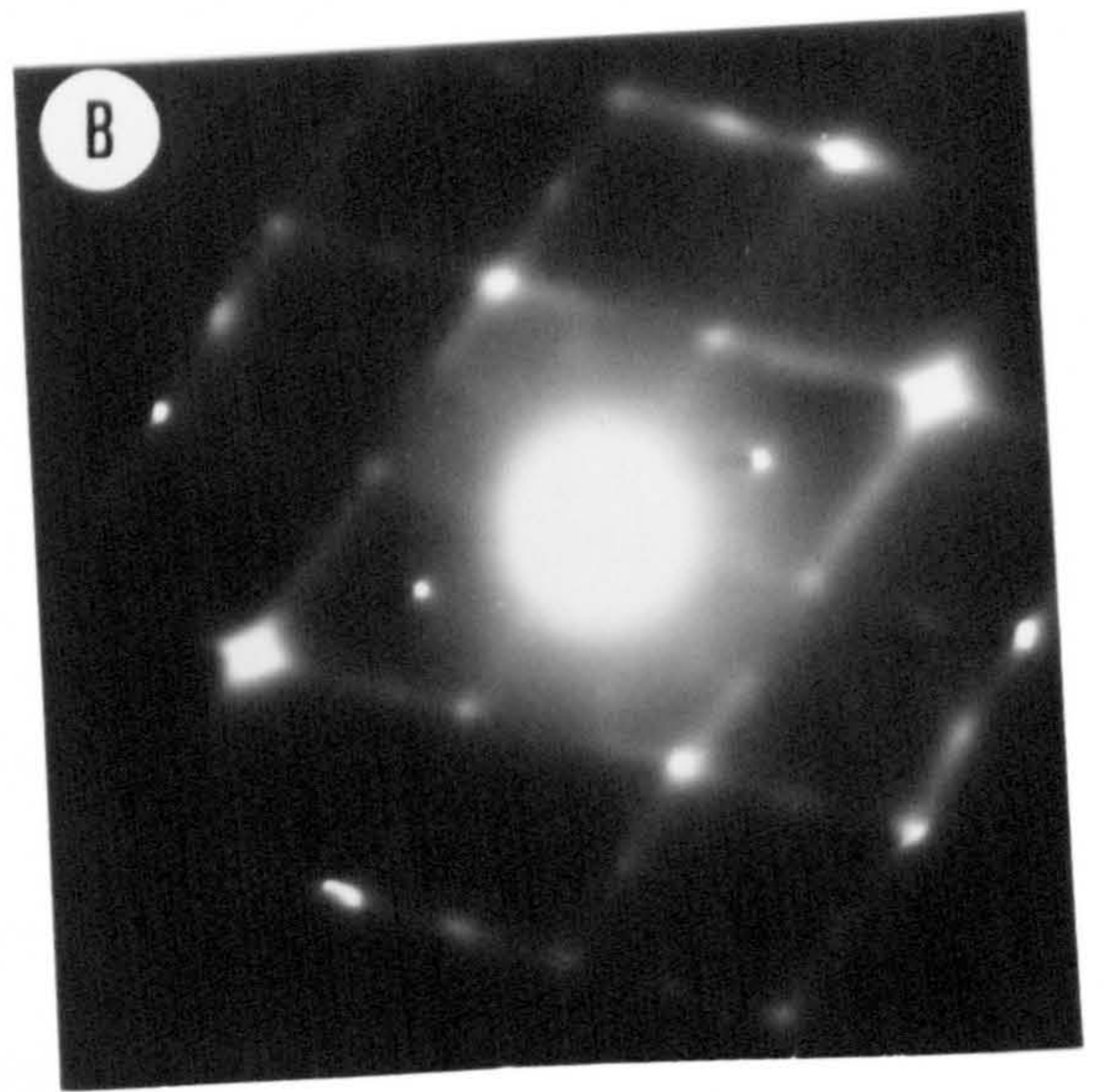
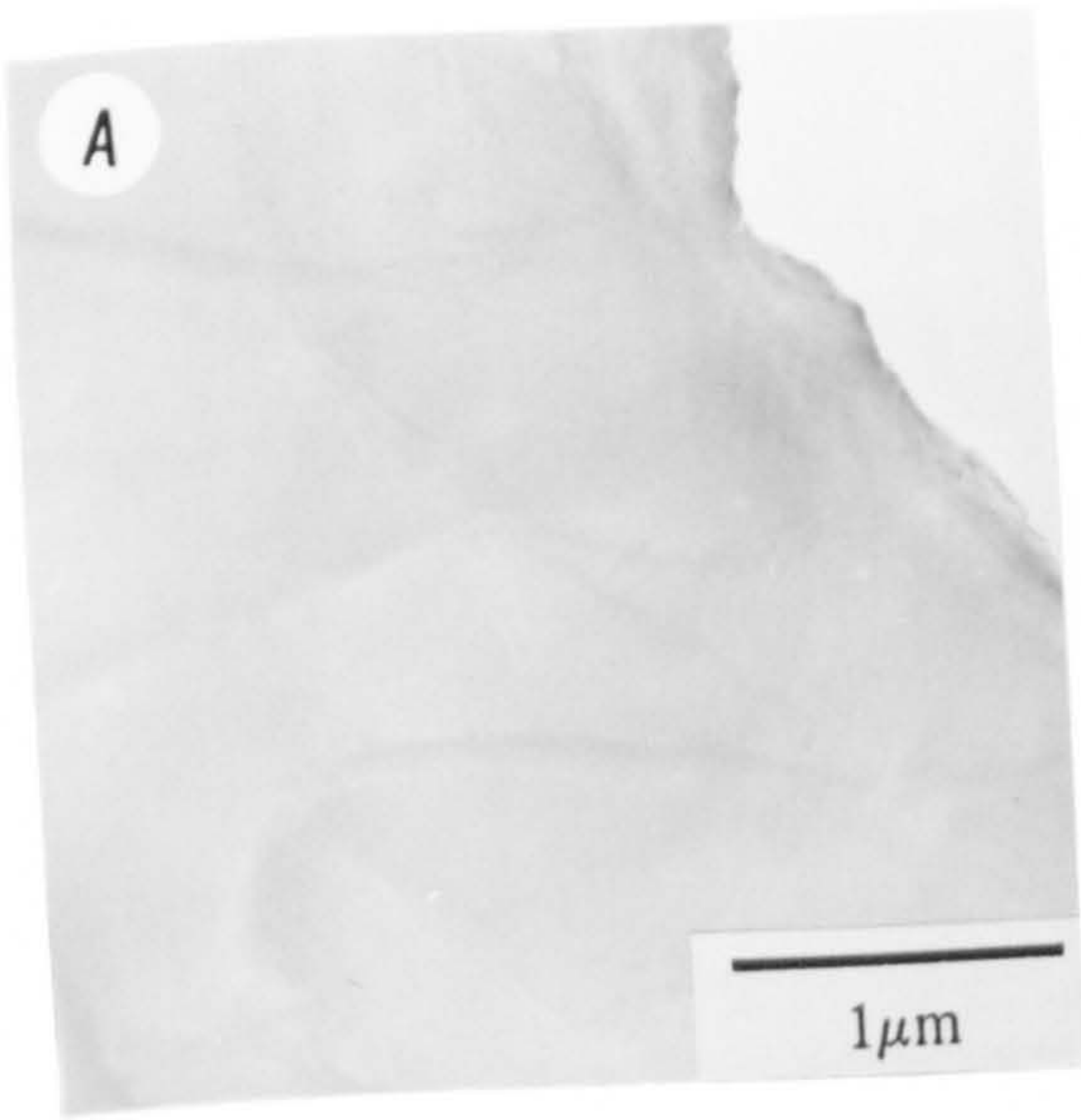
Alloy Ti-20Al-15Nb-0.9Si (at.%), solution treated at 1270°C/24 hrs, water quenched, TEM foils, electrochemically thinned in 10 vol.% H₂SO₄ in H₂O.

- (c) $[100]_{\beta}$ zone axis SADP showing intense streaking and (001) ordering spots. In this orientation ω spots are not observed.



$$L\lambda = 6.5 \text{ cm}\text{\AA}$$

- (d) Bright field micrograph, which shows tweed structure on bend contours.
- (e) Dark field micrograph produced by $(001)_{\beta}$ spots. The overall contrast shows no appearance of any domain boundaries.
- (f) Bright field micrograph showing detail of tweed structure on bend contours.



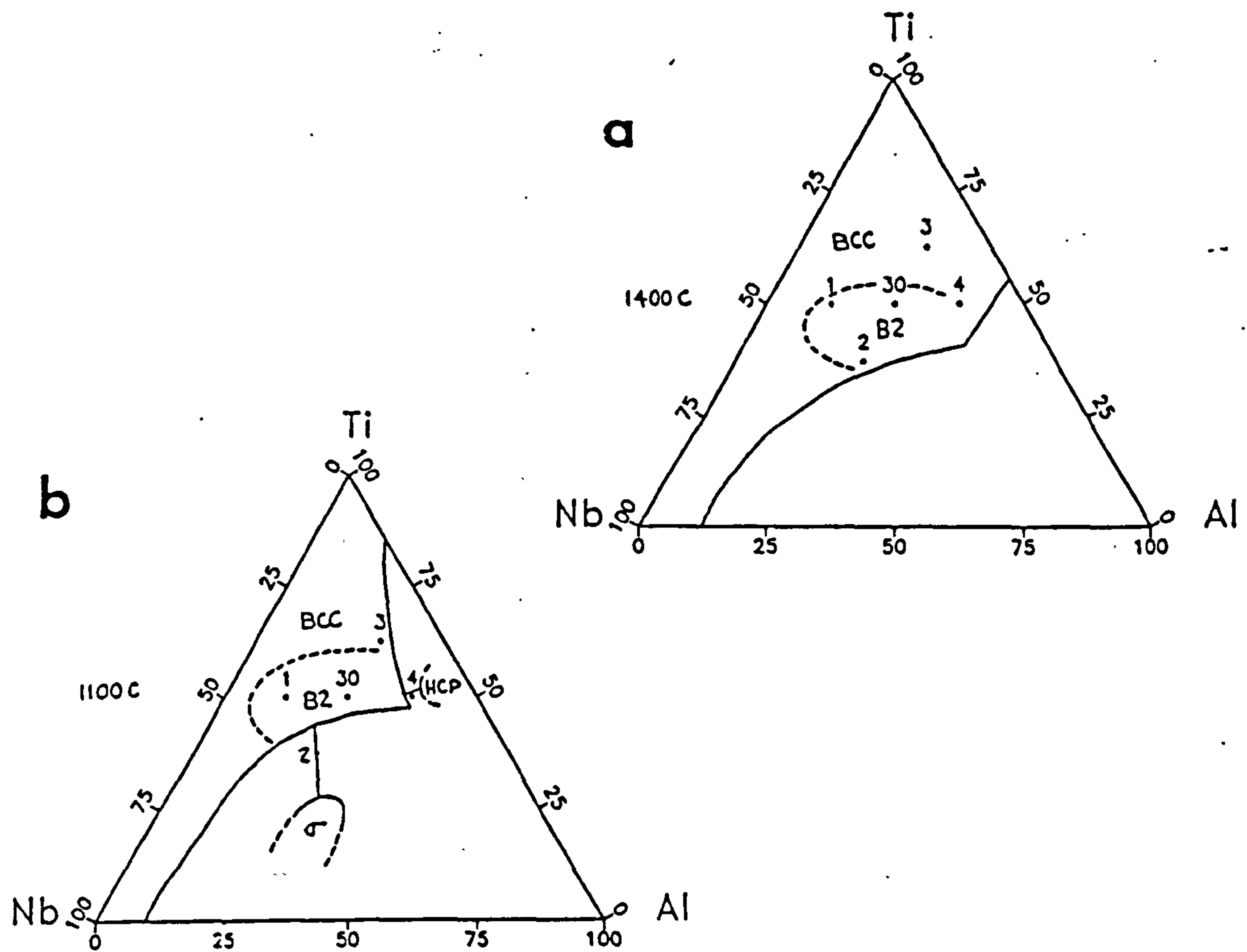


Figure 4.3. Extent of B2 (ordered β) field within the disordered phase field at
(a) 1400°C and (b) 1100°C

Examination of the diffraction patterns produced by these alloys shows strong streaking between the β spots. These streaks, in the $[110]_{\beta}$ zone axis contain intensity maxima at positions which correspond to those produced by an ω type phase. A similar phase is also reported by Strychor. However the diffraction patterns which were found in that work showed small intensity maxima which indicated that the ω found had an ordered structure. This was designated as ω_o . These ordering spots were not found in the current work. These ω precipitates can be clearly seen in Figures 4.2d&f . There is also another intensity maximum which has been found at the intersection of two of the streaks at the $\frac{1}{2}(112)$ position. The origin of these maxima is discussed in section 4.3.

When the Vickers hardness values for the four alloys are compared, it is clear that the hardness found in the 23 at. % Al alloys is significantly greater than that found in the alloys which contain a lower concentration of aluminium.

Atomic % Nb	Atomic % Al	
	20	23
11	318	426
15	288	415

Table 4.2. Hardness of Solution Treated and Water Quenched Alloys (Hv) .

Examinations of the Ti-23-15-0.9 alloy indicate that the microstructure is basically similar to that of the lower aluminium content alloys, but there are some important differences. Firstly, the mottling effect produced by the 'Tweed' structure [Srr88], is more intense (Figure 4.4a) than in the Ti-20-15-0.9 alloy (Figure 4.2d). Secondly, anti-phase domain boundaries have been found (Figure 4.4b), though it should be emphasised that they were only present in a small region of one foil, and thus should be considered as anomalous. The diffraction pattern streaks which are clear in the lower aluminium alloys are much fainter, but with the intensity maxima which were found at the half way points between the $(1\bar{1}0)_{\beta}$ and $(200)_{\beta}$ spots (Figure 4.2b) are much more clearly defined in the higher aluminium alloys (Figure 4.4d). These maxima are produced by precipitate platelets which have formed in the material. A bright field image of an area in which these 'extra' diffraction spots occurs is shown in Figure 4.4c, which shows a region of the foil that has been deformed by the precipitation of the platelets. Dark field images taken with the

unknown spot shows clearly that a plate-like precipitate is present in the alloys (Figure 4.4e). Confirmation that the extra diffraction spots are produced by these precipitates is given in Figures 4.4f-h., which show a bright field image (Figure 4.4g) of a region in the (100) plane containing precipitate platelets, and two diffraction patterns produced by regions which do (Figure 4.4h), and do not (Figure 4.4f) contain the precipitate particles. As can be seen, the extra diffraction spots are clearly visible in the precipitate-containing region. The diffraction pattern produced is characteristic of the Burgers orientation relationship for α_2 precipitates in a β matrix;

$$(110)_\beta // (0001)_{\alpha_2}; [111]_\beta // [\bar{1}\bar{1}0]_{\alpha_2} \quad (14)$$

Thus, the alloys precipitate small amounts of α_2 phase in the form of small platelets on quenching from the β_0 phase field. It is likely to be this that causes the marked increase in hardness that is noted when the 20 and 23 at.% aluminium alloys are compared.

4.2.2. Solution Treated Alloys Containing More Than 0.9 at.% Silicon

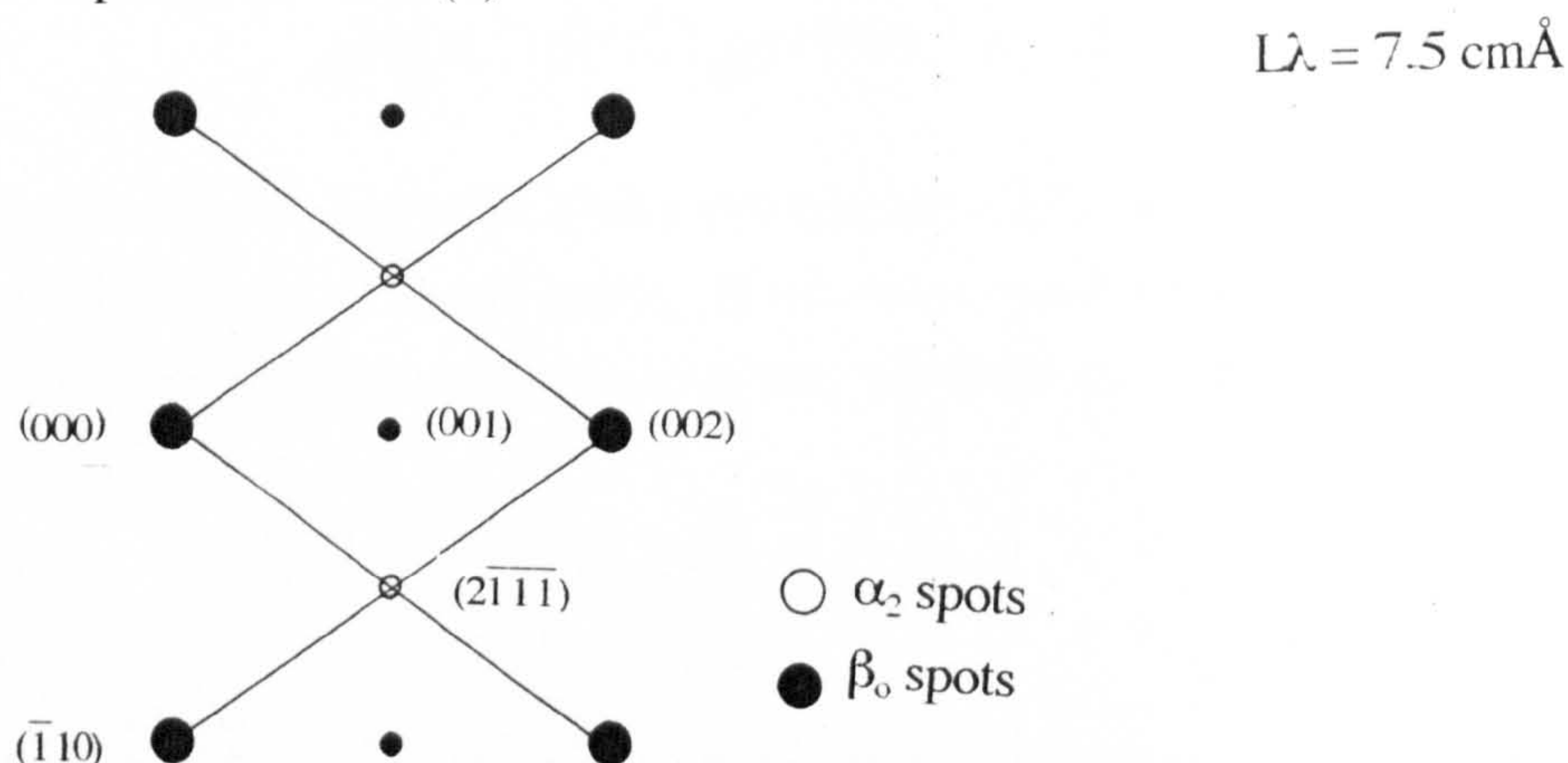
When the silicon content of the alloys is raised above 0.9 at.%, the microstructure of alloys in the solution treated and quenched condition changes markedly. The first microstructural difference is that a series of Ti_5Si_3 particles are distributed along the β_0 grain boundaries. Other silicide particles are found distributed throughout the matrix. These are much smaller than the grain boundary particles. These particles can be seen clearly in Figure 4.5a. The other, more significant change in the microstructure is the formation of a large number of martensite plates. X-ray diffraction indicates that the martensite is orthorhombic with lattice parameters of $a = 605$ pm, $b = 980$ pm and $c = 465$ pm. The backscattered electron micrograph shown in Figure 4.5b indicates that no chemical transformations occur during the quenching process. Strychor reported that the addition of more than 5 at.% Nb to Ti_3Al suppressed any martensitic formation [Str88], but the addition of silicon has been found to re-introduce martensitic formations in these alloys, even with considerably more than 5 at.% Nb in the alloy.

As the formation of the martensite phase does not involve diffusional transformations, it is clear that the orthorhombic martensite formed here is not the same phase as the orthorhombic phase reported by Banerjee [Ban87]. However, if the close packed planes in β_0 and the O phase examined by Banerjee [Ban87a] and Mozer

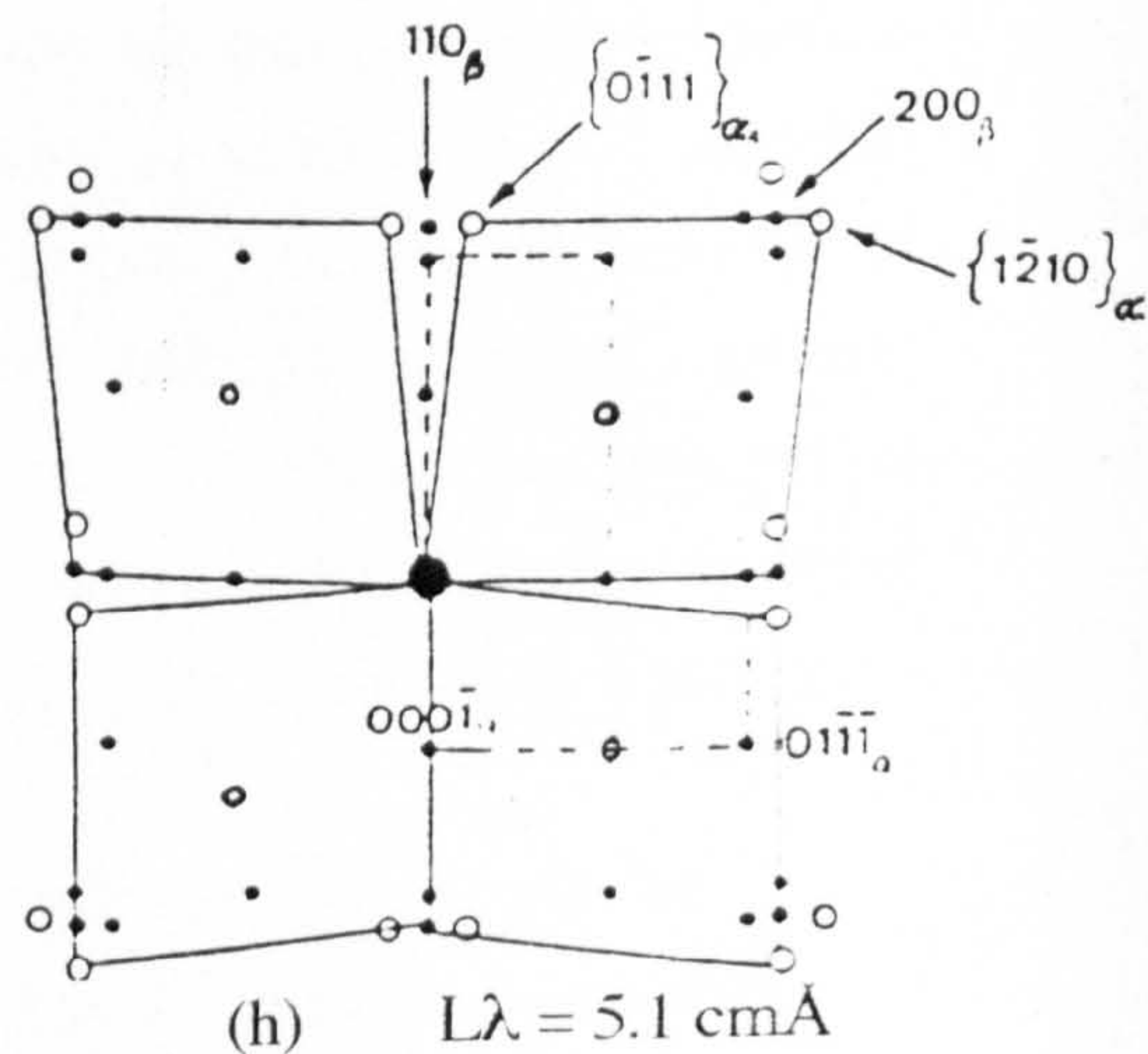
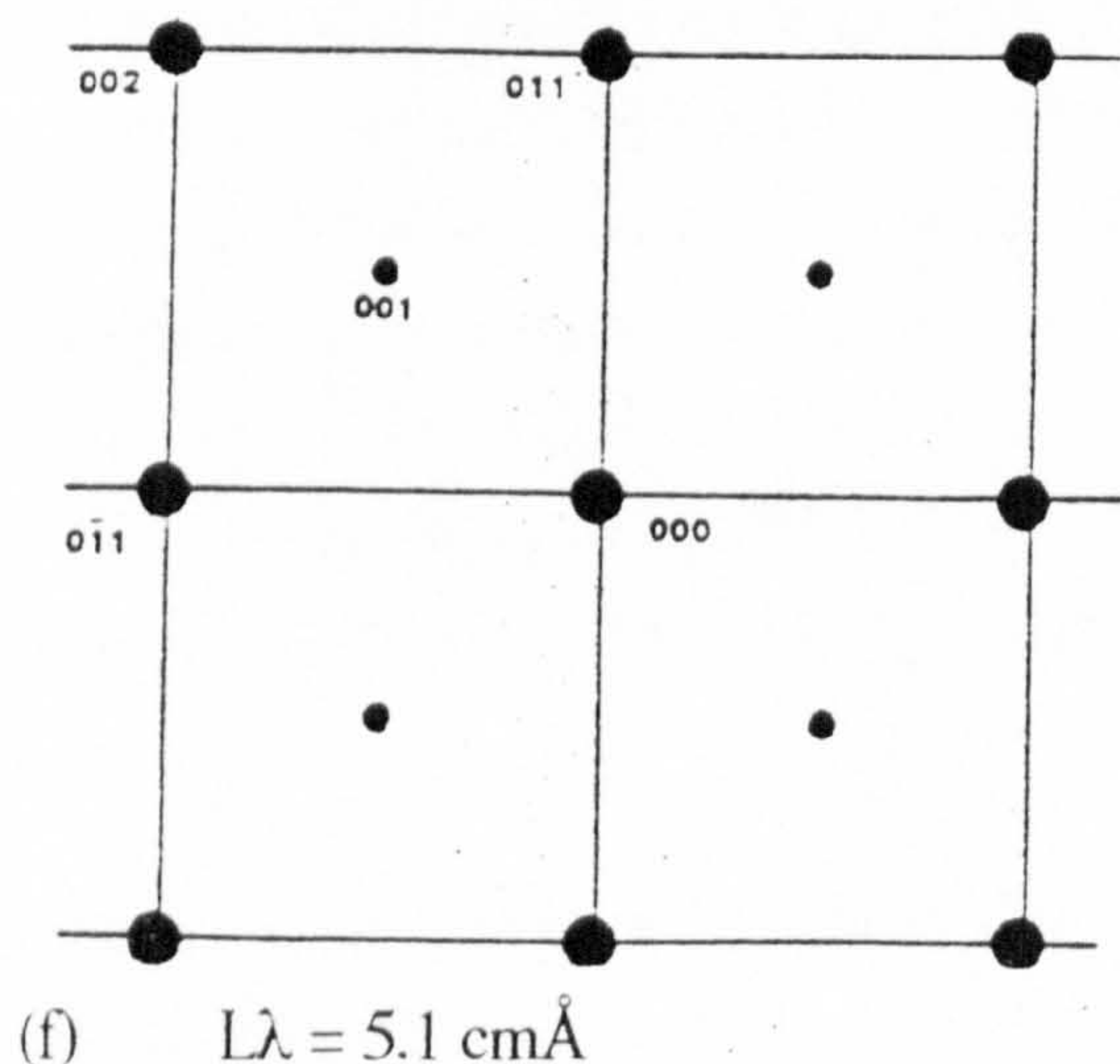
Figure 4.4.

Alloy Ti-23Al-15Nb-0.9Si (at.%), solution treated at 1270°C/24 hrs, water quenched. TEM foils electrochemically thinned in 7 vol.% H₂SO₄ in CH₃OH, then ion thinned for 2 hrs.

- (a) Mottled surface showing tweed structure within β_0 grains.
- (b) Antiphase domain boundaries produced by dark field diffraction on (100) spots. These were only found in a small region of the foil and are believed to be anomalous.
- (c) Bright field image of foil in heavily distorted area around precipitate.
- (d) [110] SADP produced from (c)



- (e) Dark field image of foil showing small needle-like precipitate using illumination from the spot marked in (d).
- (f) [100] SADP showing ordering spots.
- (g) Bright field micrograph showing precipitates on right hand side. The SADP shown in (f) is taken from the precipitate-free region on the right. The SADP in (h) is produced from the precipitate-containing area on the right.
- (h) [100] SADP showing extra spots produced by the precipitates.



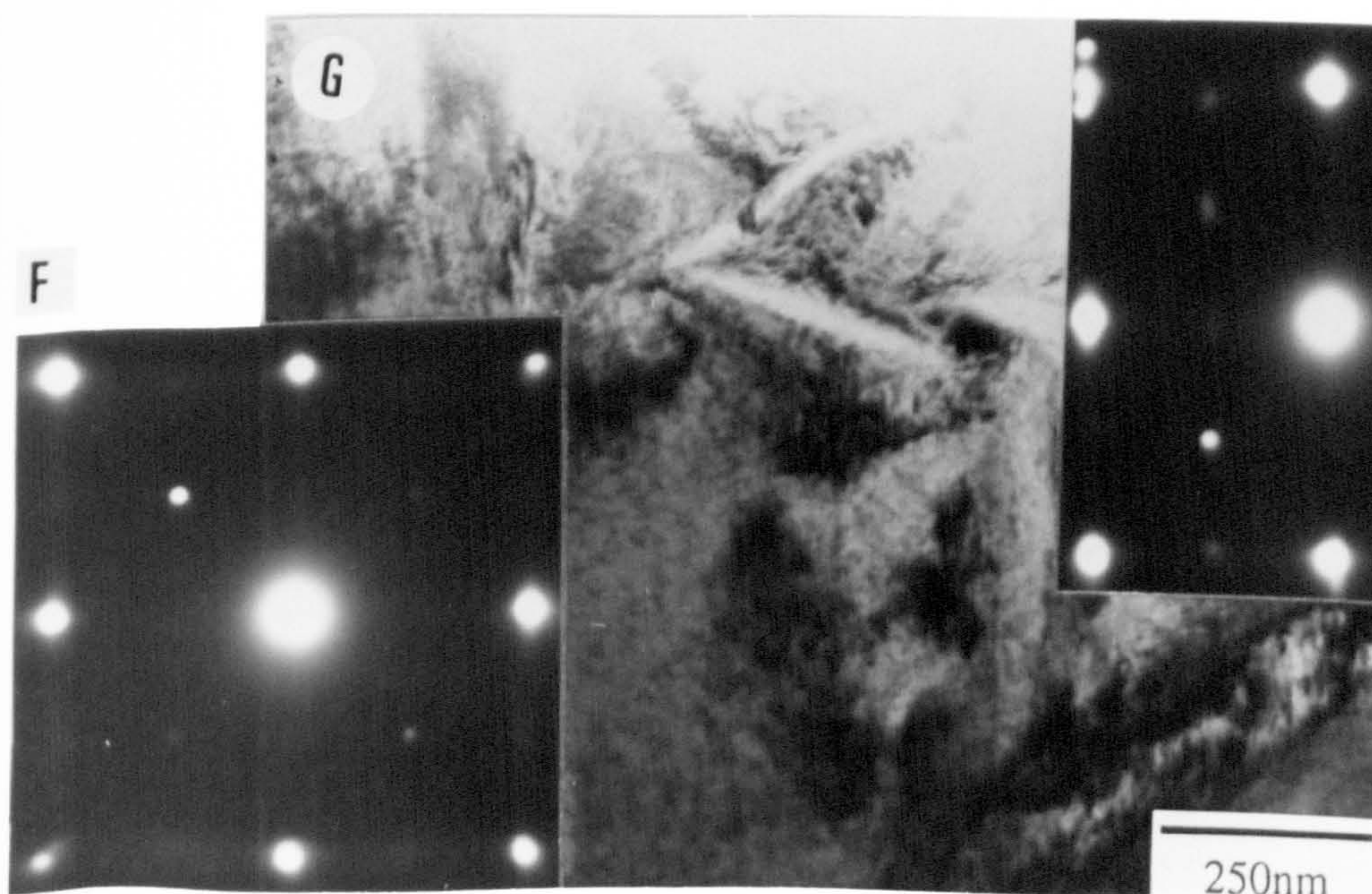
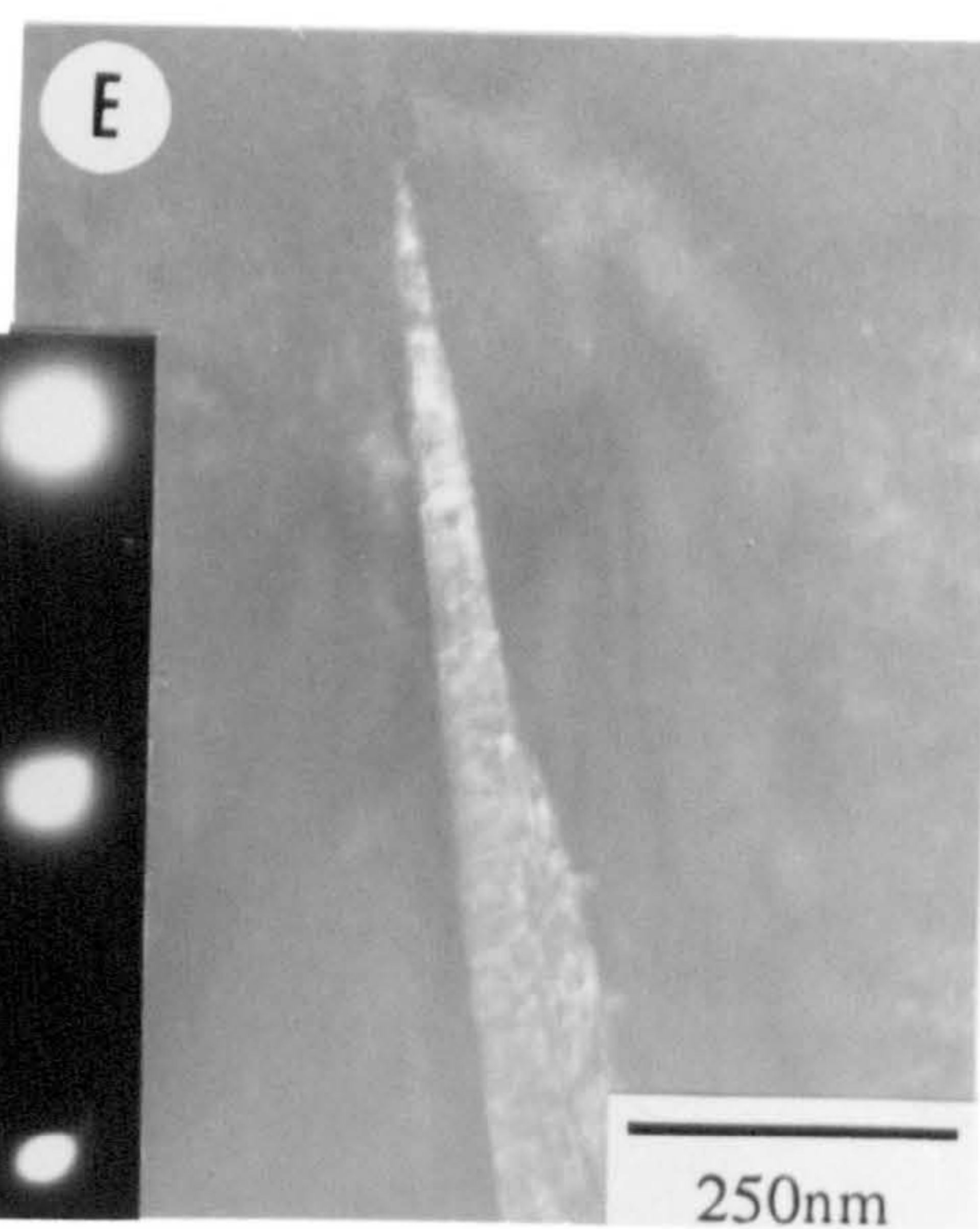
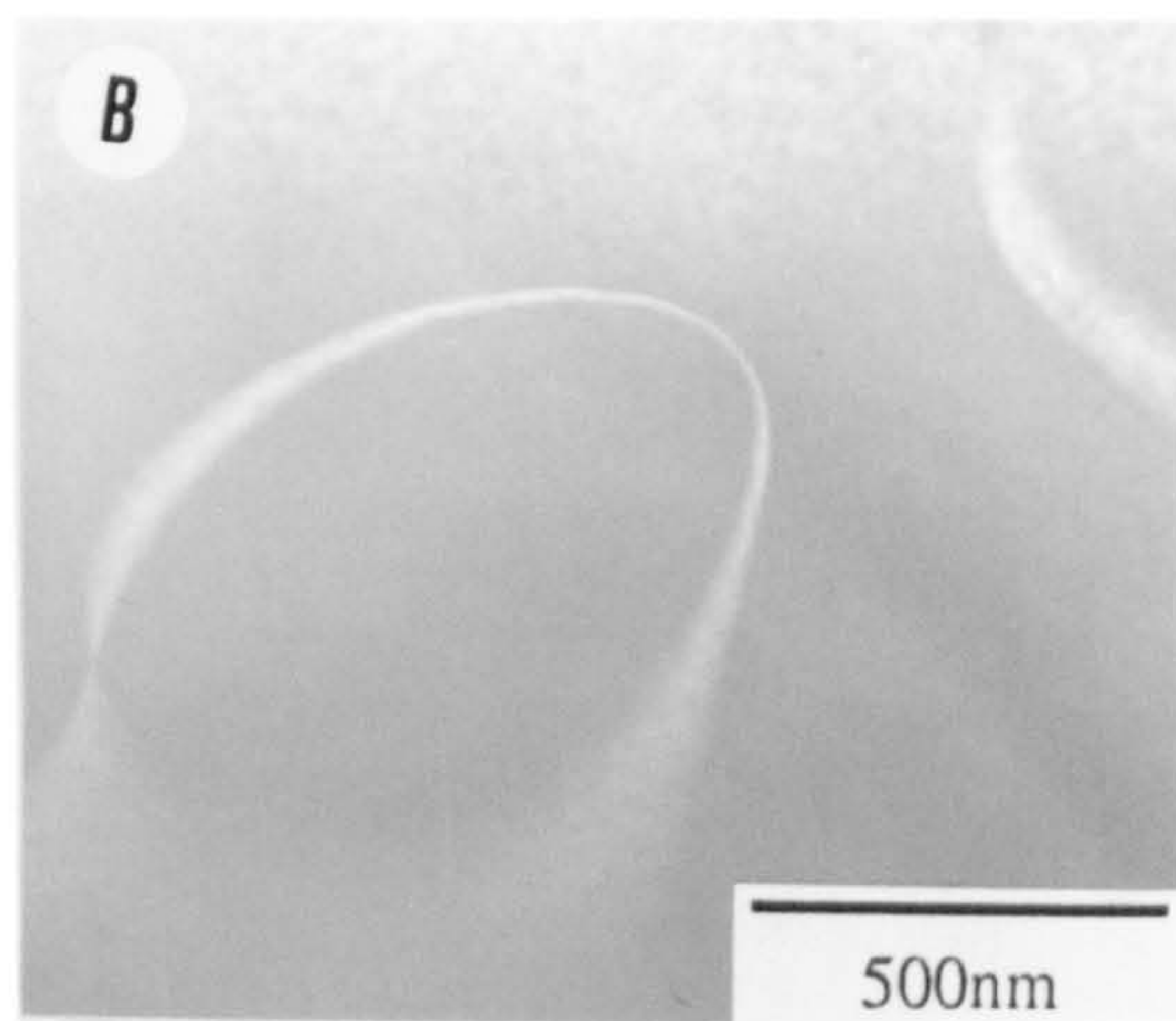
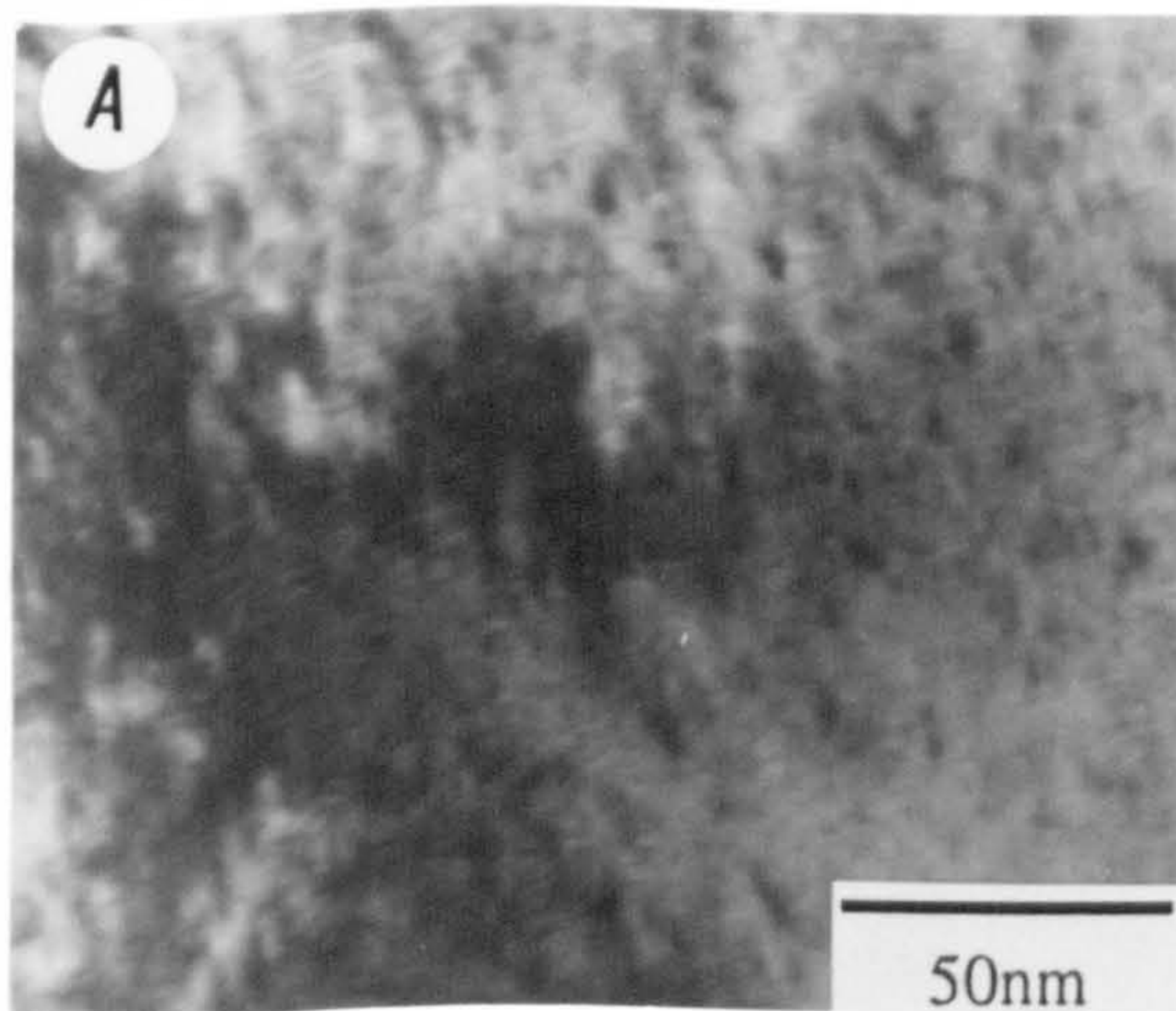
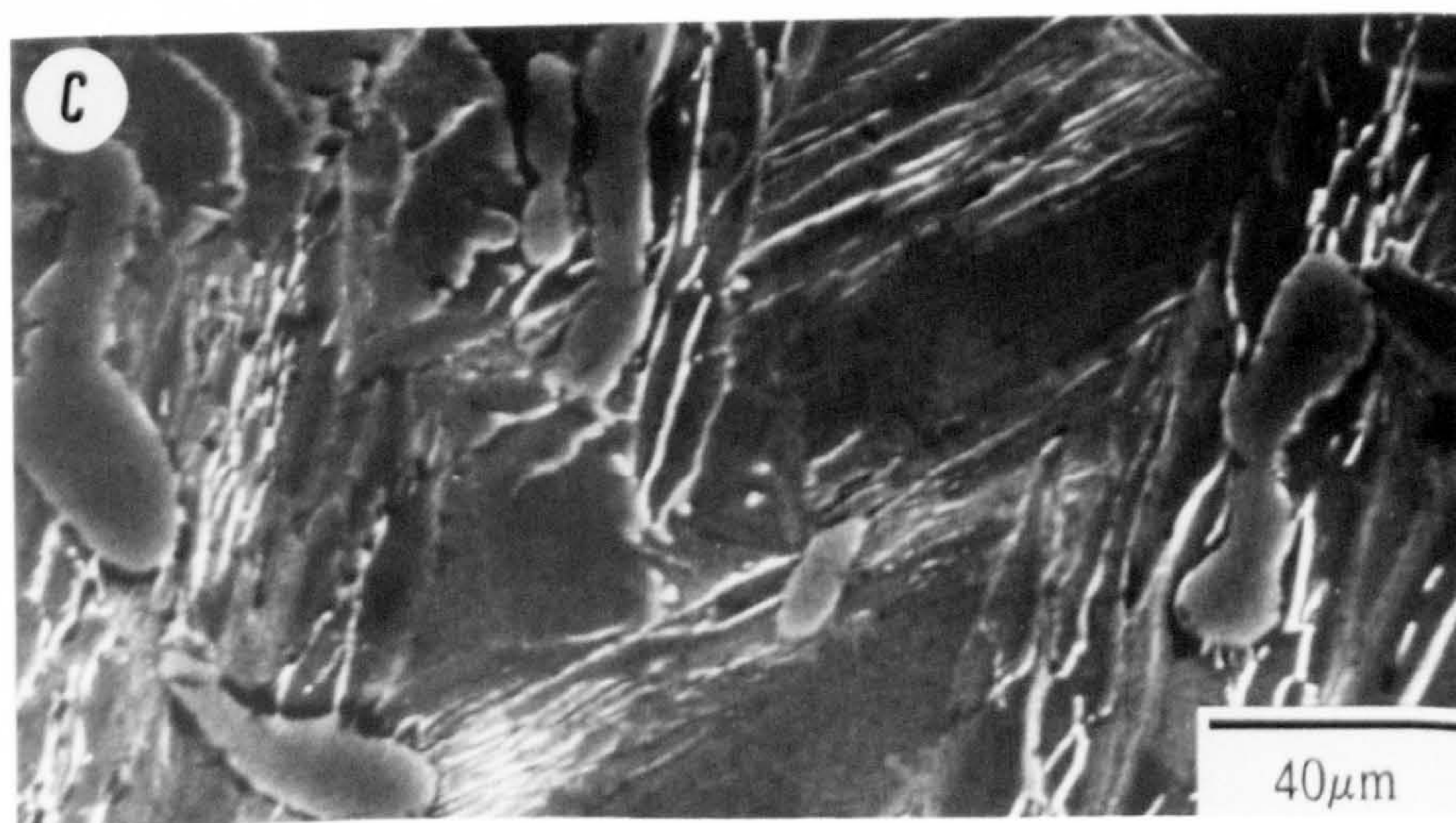
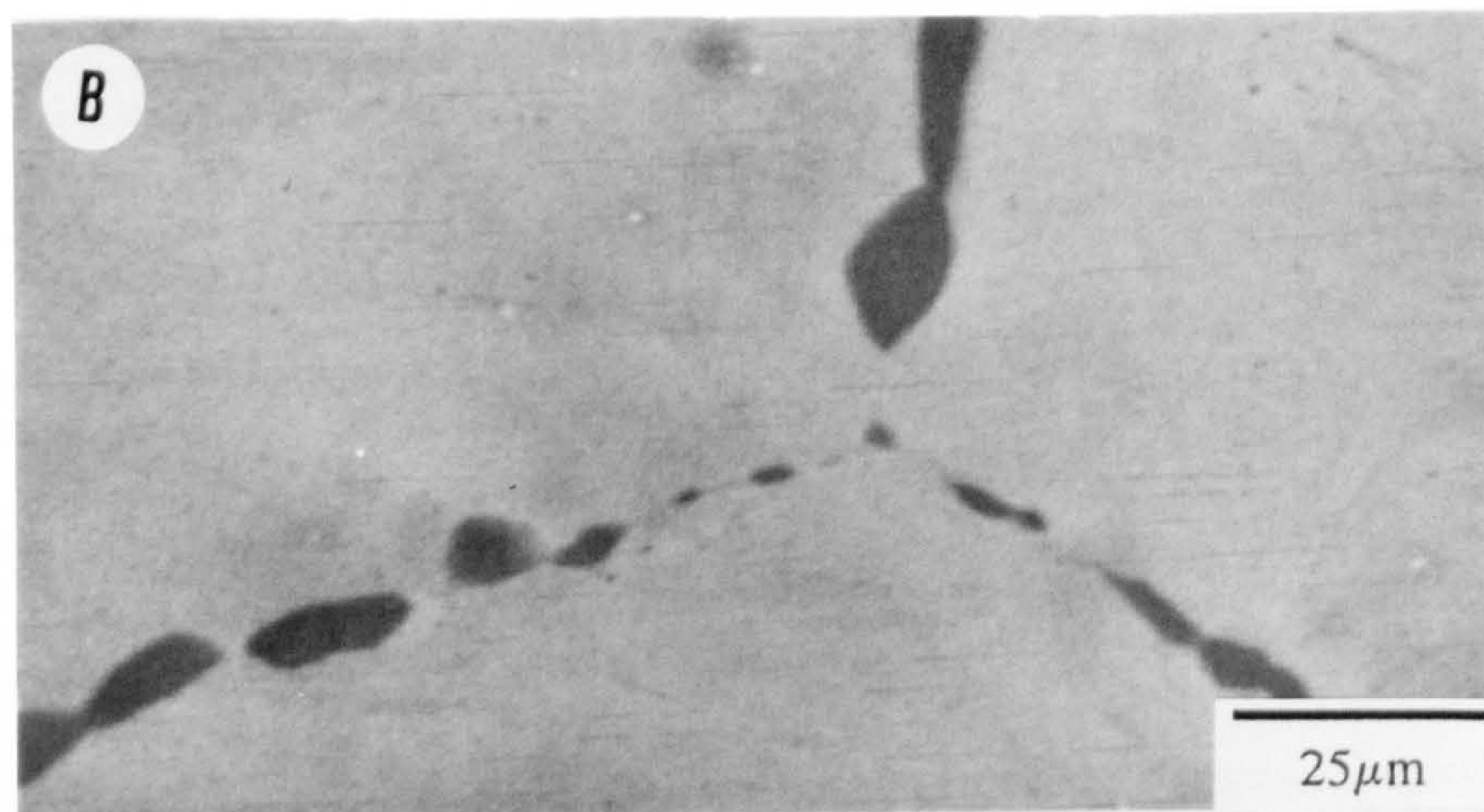


Figure 4.5.

Alloy Ti-23Al-11Nb-3Si (at.%) solution treated at 1270°C/24 hrs, water quenched.

Samples etched in 3 vol.% HF in H₂O.

- (a) SE image showing large silicide grains on β_0 grain boundaries. Smaller silicide particles are distributed throughout the matrix. Close examination shows laths of martensitic phase.
- (b) BE image showing silicide particles on the grain boundary (dark). No contrast is visible in the matrix indicating that no diffusional transformations have taken place while the lath-like structure was produced.
- (c) Detailed view of grain boundary, showing large silicide particles and colonies of martensite. Note the martensitic structure is not fully transformed, and β_0 is still found in large quantities within the alloy.



[Moz90] respectively are compared for atom sites, the similarity shown below in Table 4.3 indicates that a diffusionless transformation between β_0 and the martensitic phase is possible. A diagram of the two site types in the close packed planes is shown in Figure 4.6. The difference in site occupancies is due to the markedly different Nb contents which have been used (Ti-25-10 for β_0 and Ti-25-25 for O). The aluminium levels on the two sites are very similar. This *could* explain why the martensite is only found in small areas of the alloy, if the alloy is formed from a two phase mixture of β and β_0 at the solution treatment temperature, as suggested by Banerjee [Ban87].

Phase	Close Packed Plane	A Site			B Site			Reference
		Ti	Al	Nb	Ti	Al	Nb	
β_0	(110)	96	0	4	28	48	24	Banerjee [Ban87a]
O	(001)	82	0	18	32	50	18	Mozer [Moz90]

Table 4.3. Comparisons of Site Occupancies in Close Packed Planes in β_0 and O phases.

4.3. Alloys Aged at Low Temperatures.

Ageing of alloy II was carried out over a range of times (see Table 4.1.), to study phase changes that may occur. The temperatures to be used were identified by the use of Differential Scanning Calorimetry (D.S.C.) carried out on solution treated and quenched samples of the alloy. Examination of the results heated at 20°C/min (Figure 4.7.) show that the alloy remains essentially untransformed at temperatures up to approximately 390°C, above which, transformation occurs with a peak rate at about 420°C.

Comparison of [110] zone axis diffraction patterns produced before and after ageing (Figures 4.3a and 4.8b respectively) show that the streaking is reduced on ageing, producing discrete ω spots of a higher intensity, as well as a series of other spots. These were reported by Strychor in Ti-27.8Al-11Nb when aged at 400°C for up to 26hrs. Strychor identified these spots as being "caused by lattice displacement waves of the transverse $\{110\} \langle 1\bar{1}0 \rangle$ type". In the current work, the author has

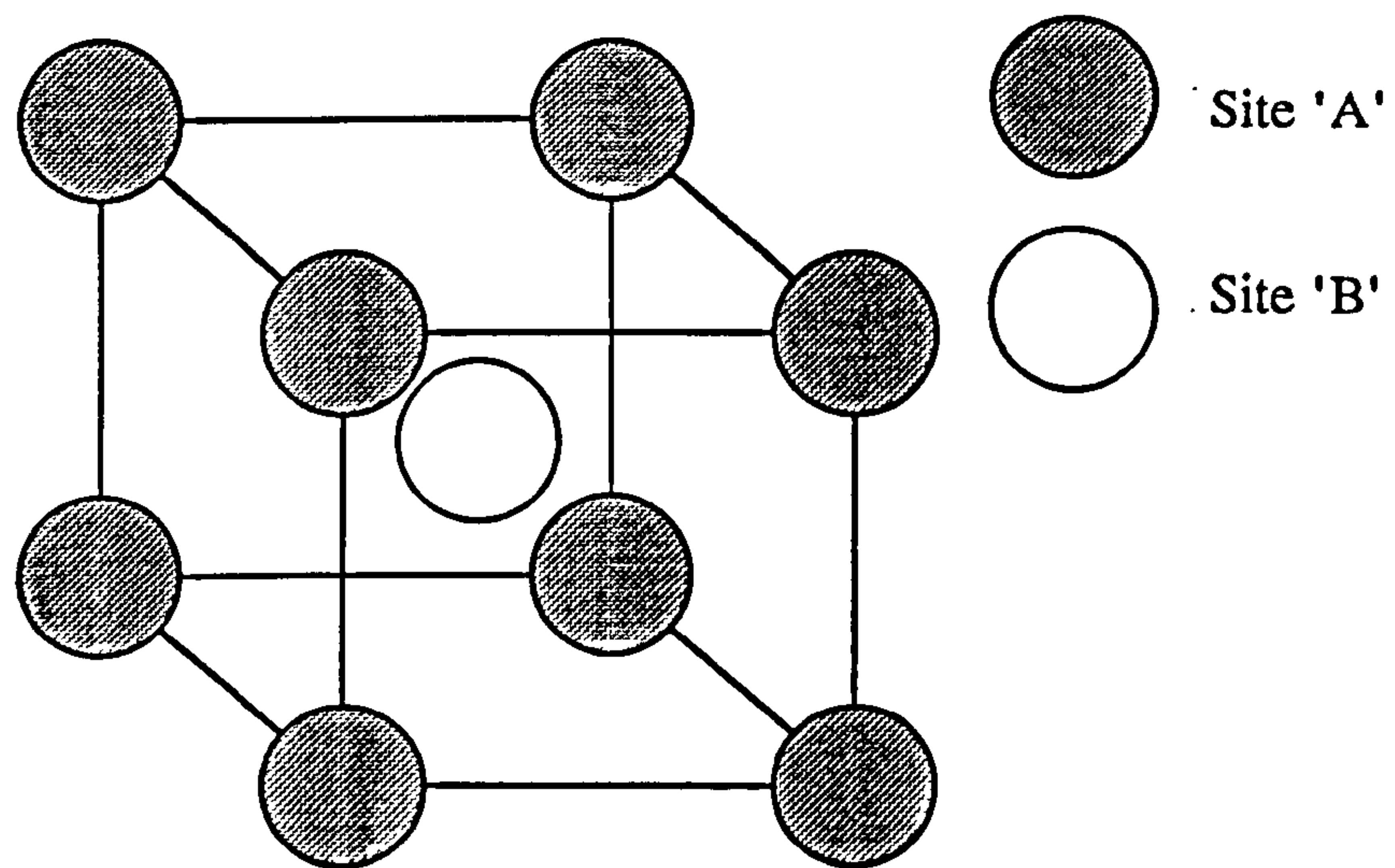
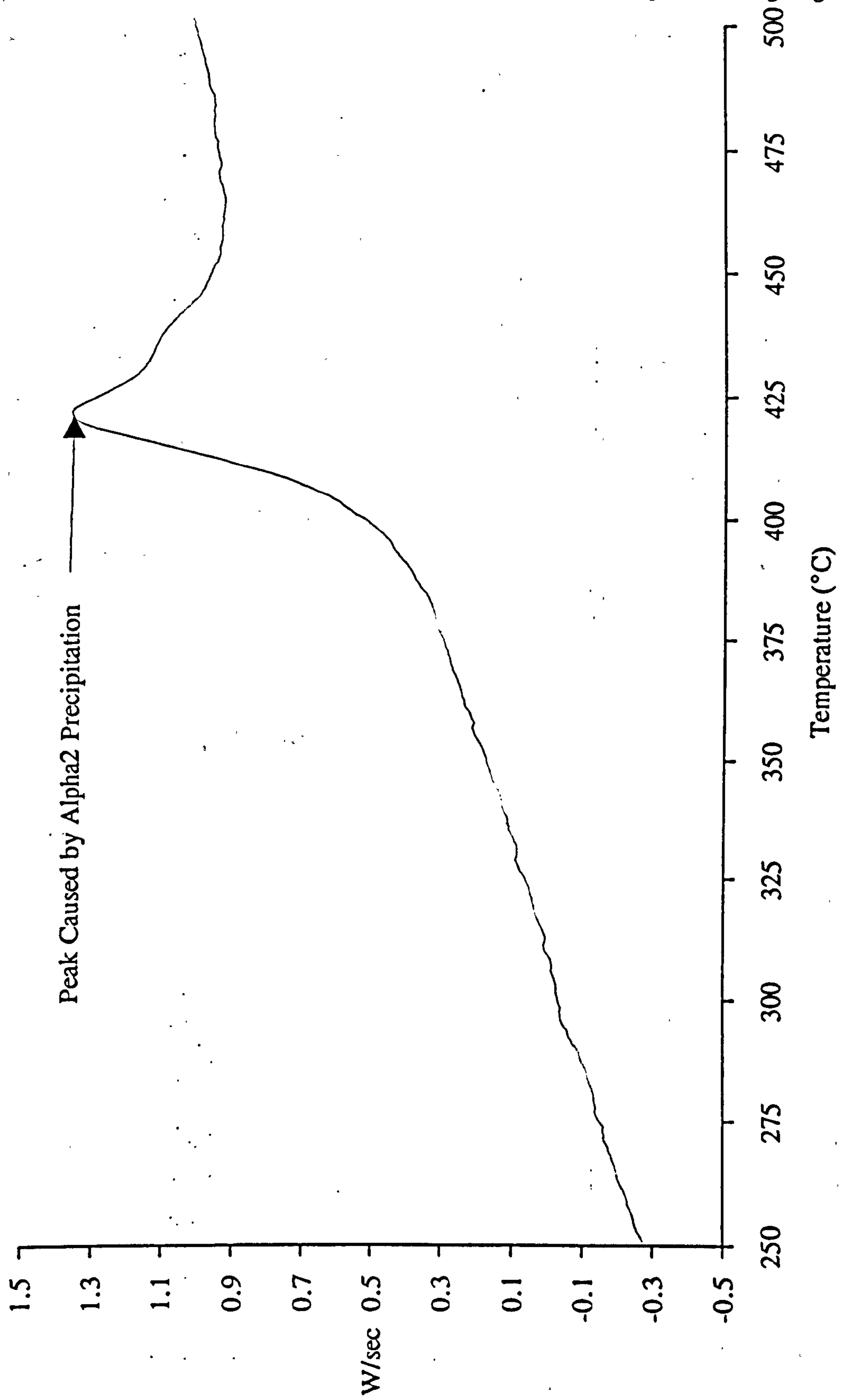


Figure 4.6. Schematic of site types identified in B2 (ordered b.c.c.).

Figure 4.7. D.S.C. Trace Showing 'Alpha2' Precipitation Peak in Metastable Material



proposed a different interpretation for the presence of these spots. As can be seen in the keys to Figures 4.8a&b, and below, these diffraction spots can be indexed as α_2 spots using the conventional Burgers Orientation Relationship;

$$(110)_\beta // (0001)_{\alpha_2}; [111]_\beta // [11\bar{2}0]_{\alpha_2}. \quad (15)$$

It is possible that in the solution treated condition, the diffuse maxima which appear at the intersection of the $\{\bar{1}12\}_\beta$ -type streaks is also produced by α_2 precipitation, though it is difficult to be certain. Assuming that this is correct, then it is probable that the α_2 was precipitated during the quenching procedure, as the spot intensity does not appear to increase on ageing. A bright field examination of this material (Figure 4.8c) shows heavy mottling in a similar way to that reported by Strychor. This mottled appearance is probably caused by the very fine structure of ω particles between the tweed-type structure. A similar precipitation effect has been reported by Peters [Pet90] in a more highly β stabilised alloy (Ti-25Al-10Nb-3V-1Mo), in which, in addition to the β_0 and ω phases, O phase is also identified.

4.4. Effect of Ageing Treatment on Alloy Hardness

The continued precipitation of ω (and possibly α_2) can be followed from ageing curves produced by these alloys at 380°C (see Figure 4.9.). The hardness of the 20 at.% Al alloys increases markedly for ageing times of up to 6ksec. after which it slows down, though it has not peaked after 60ksec. As the hardness in these alloys is likely to be produced by a precipitation hardening mechanism (as it is known that the amount of ω phase found in the alloys after ageing is markedly higher than that found in the unaged material), it can be seen that the precipitation is fairly slow at this temperature. The hardness of the 23 at.% Al alloys is almost unchanged by the ageing process, as the fine α_2 precipitates that form during the quenching process appear to produce a strong hardening effect relative to the hardness found in the lower aluminium alloys. This inhibits any increase in hardness that the ageing process may produce.

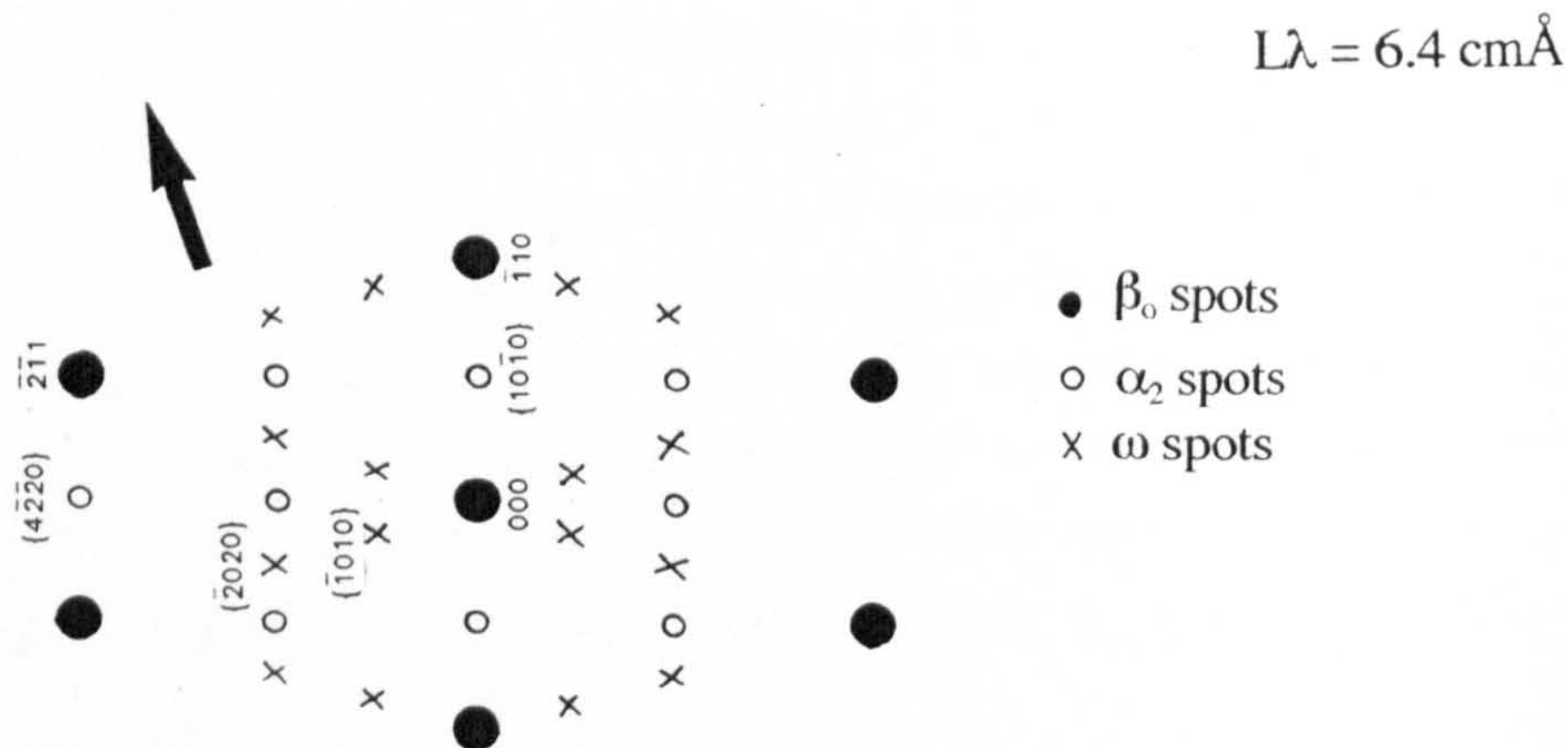
The hardness values produced are the average of a minimum of 10 indentation measurements. If the scatter of these values was high ($>\pm 2\text{Hv}$), then a further 10 measurements were taken, and the average of the 10 closest values was used.

Figure 4.8.

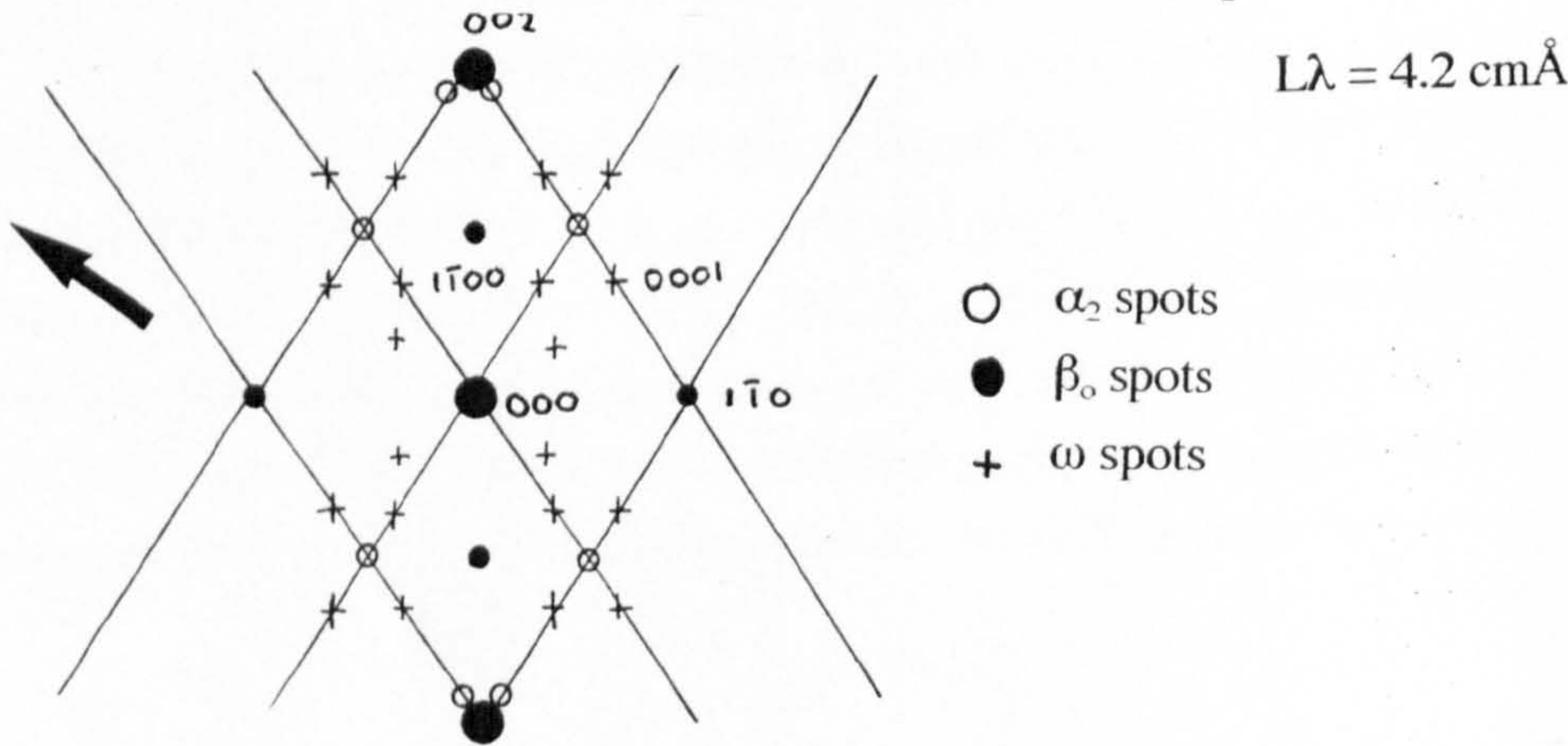
Alloy Ti-20Al-15Nb-0.9Si (at.%), solution treated at 1270°C/24 hrs, water quenched, then aged at 380°C/ 16.6 hrs, water quenched.

TEM foils, electrochemically thinned in 7 vol.% H₂SO₄ in CH₃OH.

(a) SADP showing diffraction spots from β , α_2 and ω phases diffracting along these zone axes; $[113]_{\beta} // \{01\ \bar{1}6\}_{\alpha_2} // \{2\ \bar{1}\ \bar{1}3\}_{\omega}$.



(b) This diffraction pattern shows that the streaks which are visible in the the $[110]_{\beta}$ zone axis in the solution treated and quenched condition are very marked have partly condensed, and when aged contain distinct α_2 spots as well as more intense ω spots. After this ageing treatment the β (001) ordering spots are clearly visible. Arrow indicates vertical direction on plate.



(c) Bright field image of alloys showing a mottled structure.

(d) $(1\ \bar{1}00)_{\omega}$ dark field image, showing a wide distribution of fine ω precipitates.

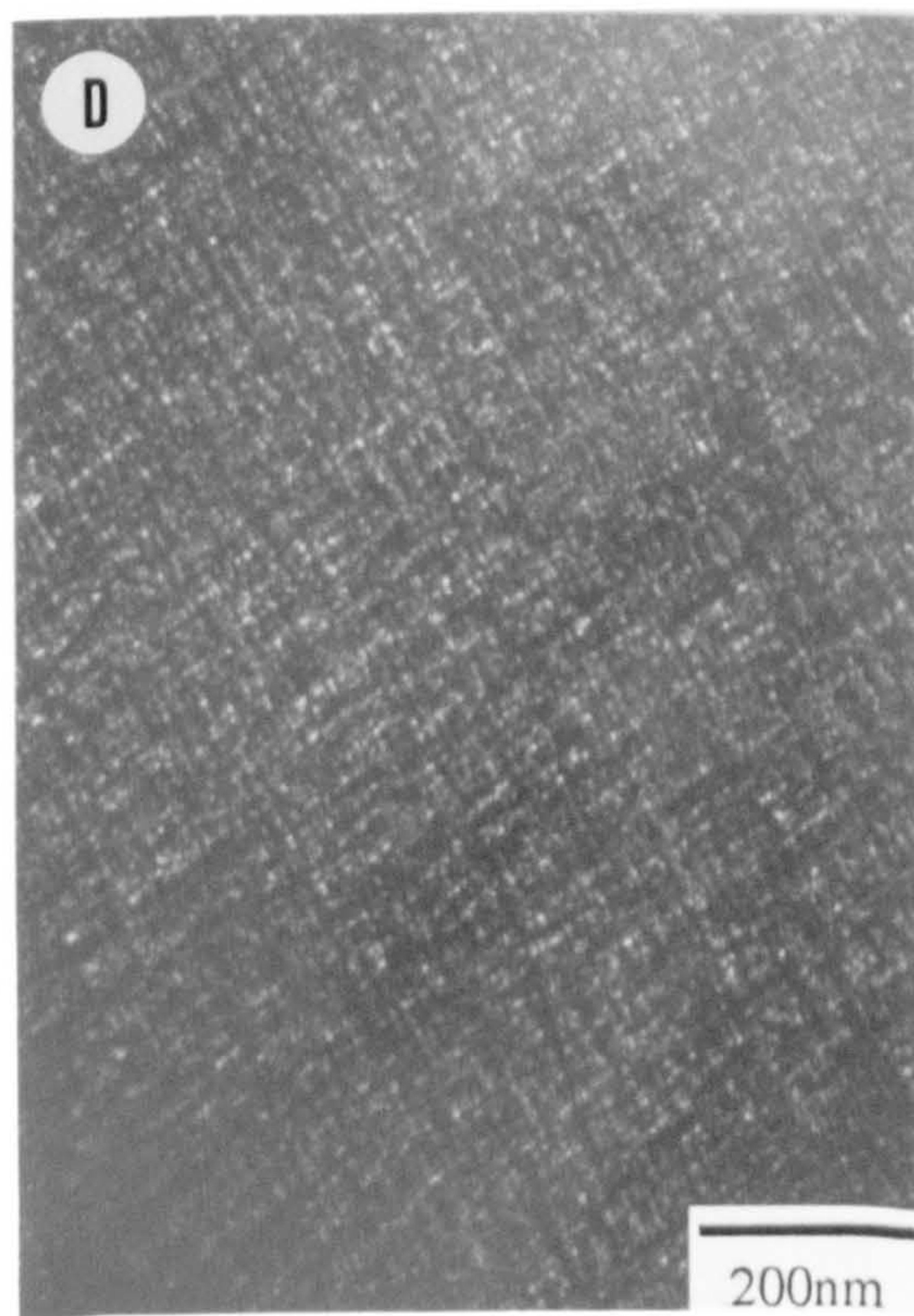
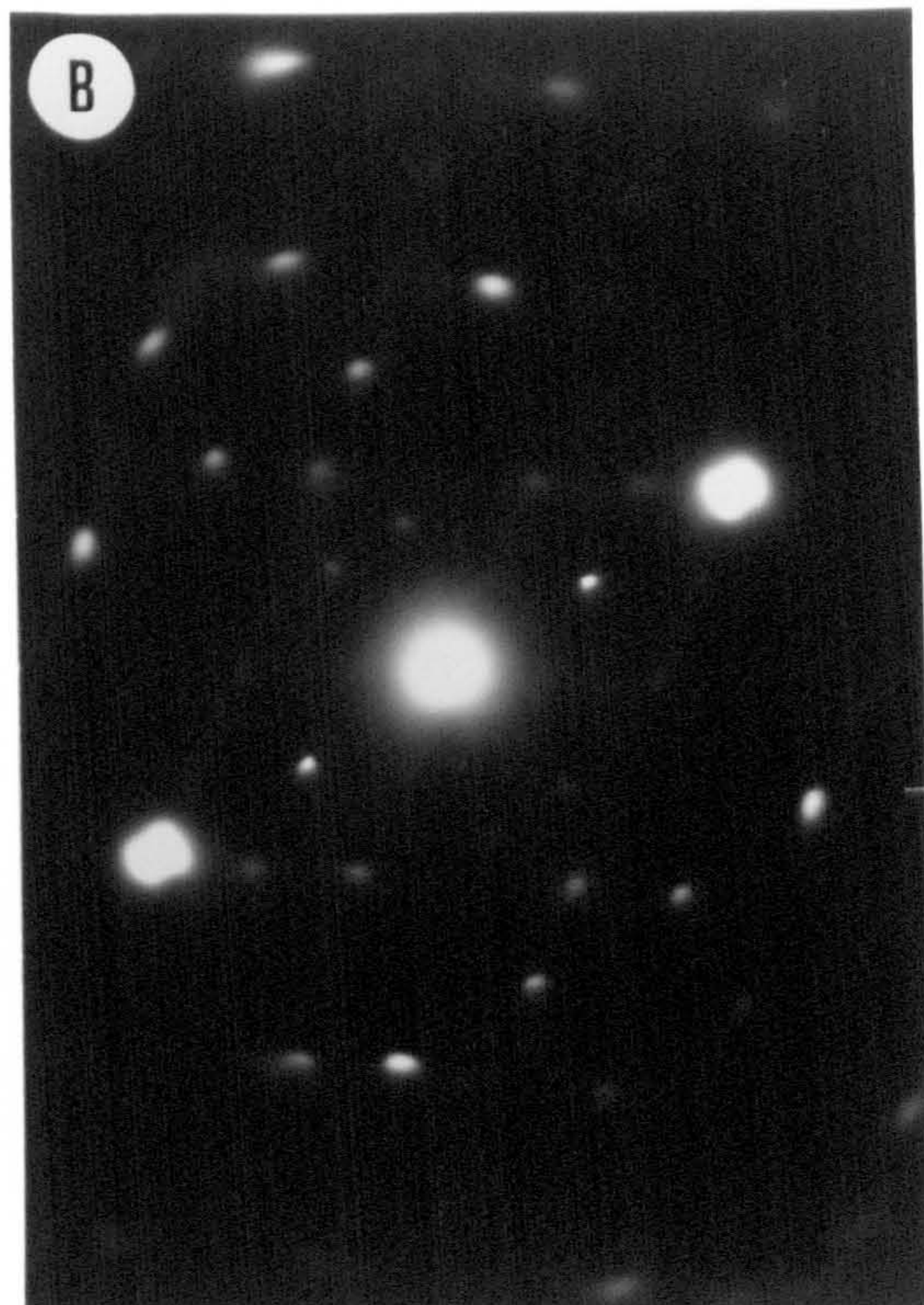
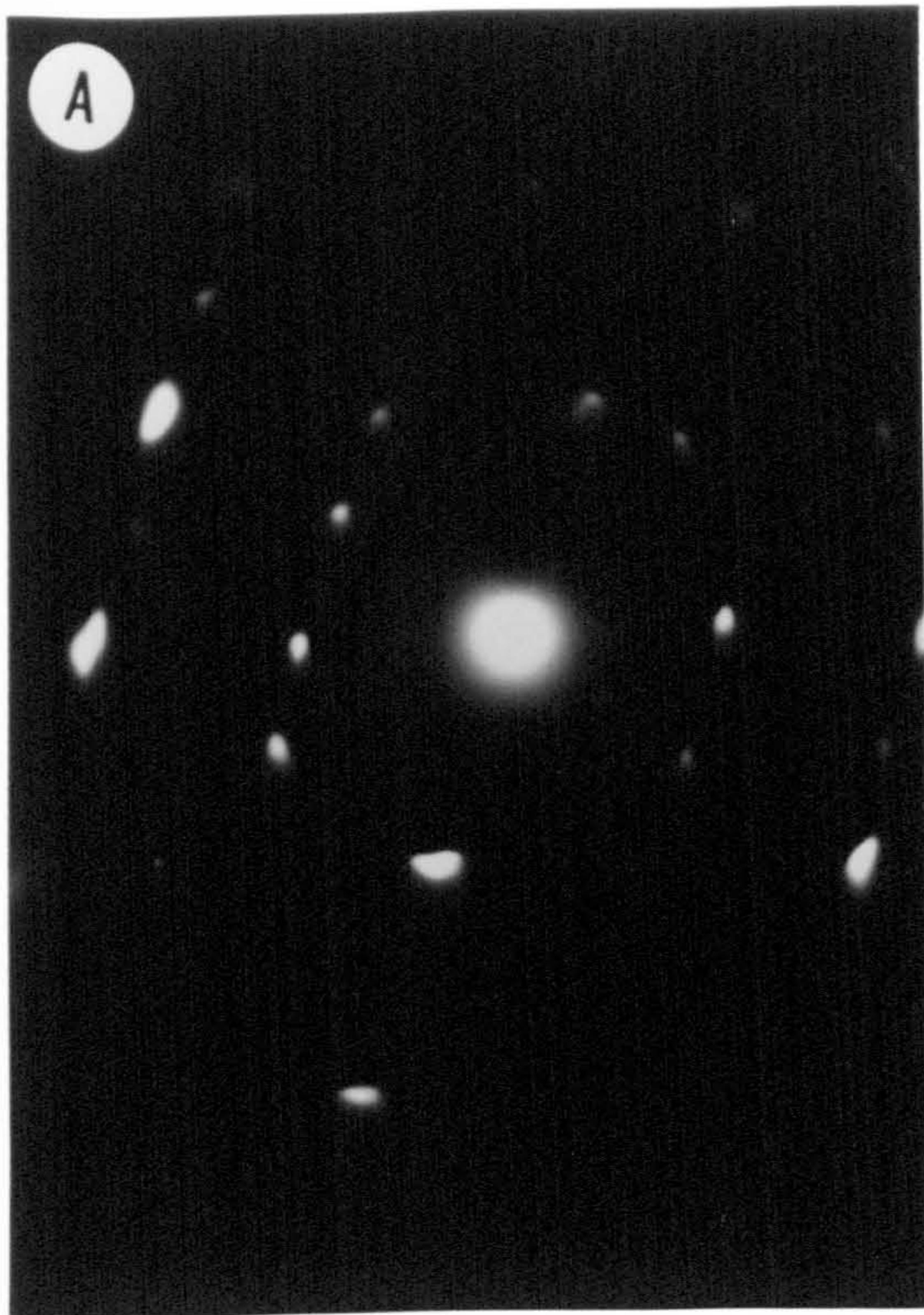
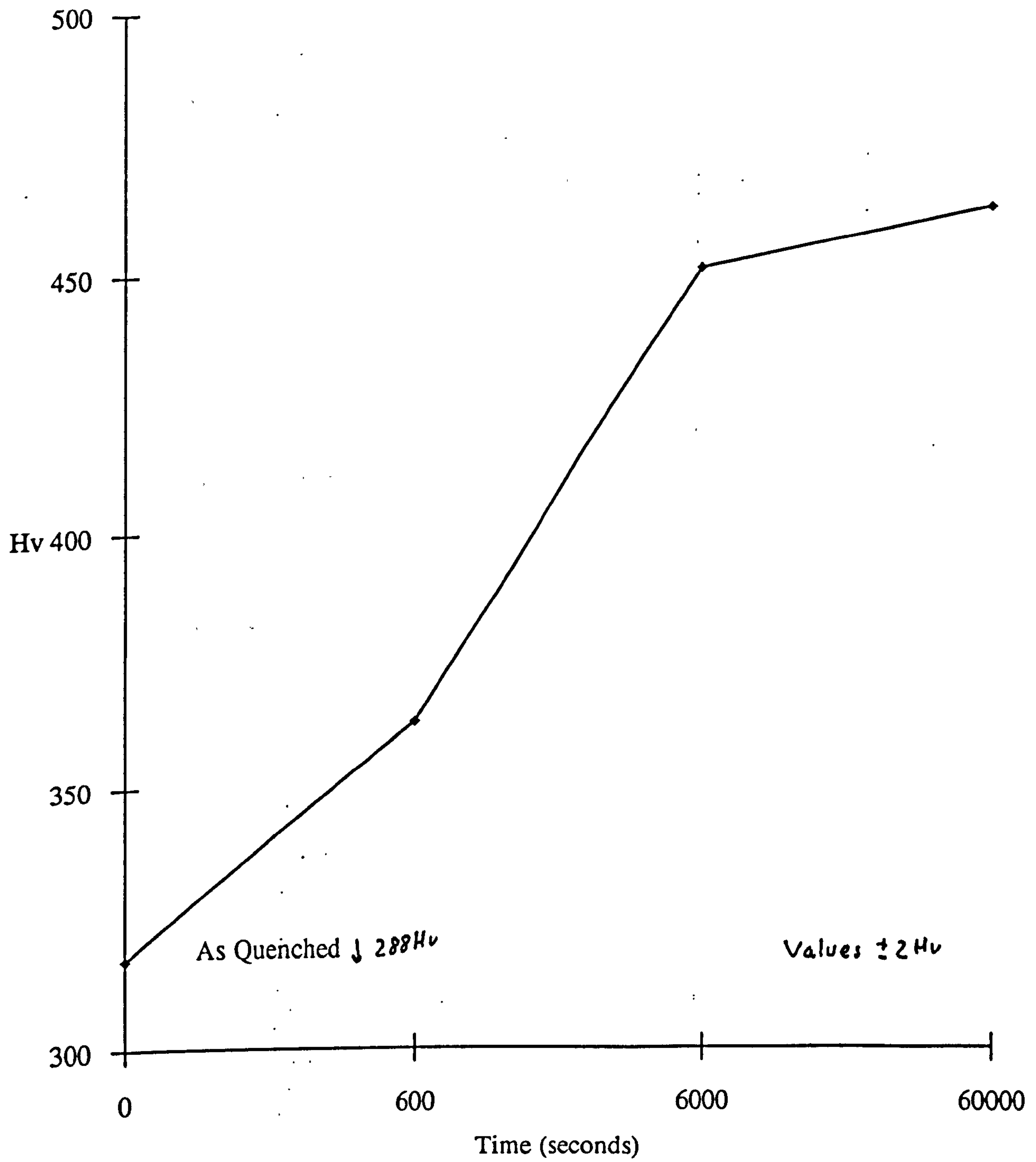


Figure 4.9. Ageing Curve For Ti-20Al-15Nb-0.9Si at 380°C



Chapter 5.

Ageing Treatments

5.1. Introduction

A range of alloys within the composition range Ti-(20-23)Al-(11-15)Nb (0-3)Si (at.%) have been examined when solution treated at 1270°C (see section 4) and then aged within a temperature range from 650 to 1100°C. A summary of the phases present in the equilibrium aged conditions (i.e. 1000hrs at 1050, 900, 800 and 650°C) is given in section 5.7.

5.2. 1050 and 1100°C Aged Microstructures

5.2.1. Base Alloys

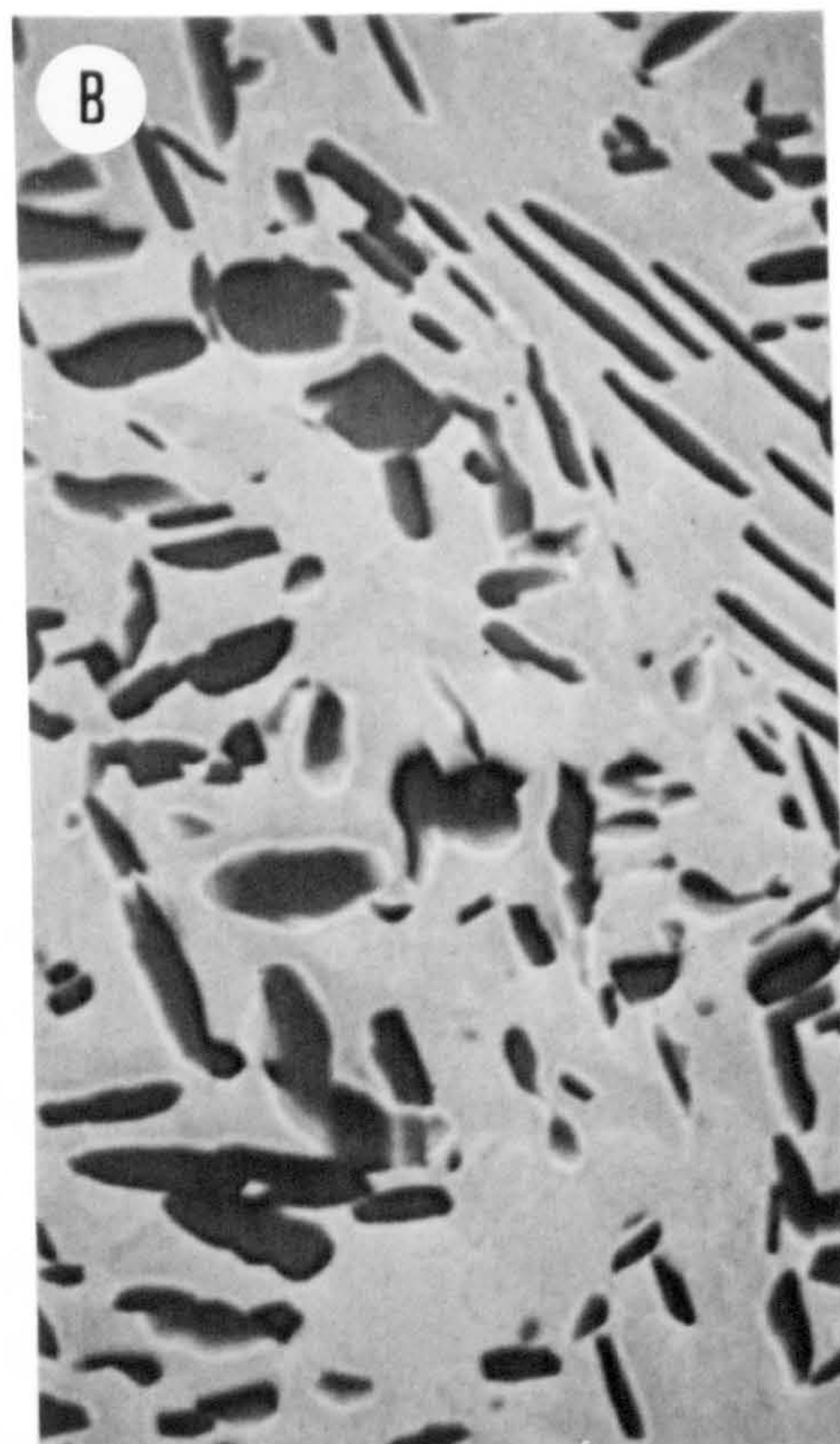
Samples of the four main alloy compositions (alloys I to IV), when solution treated at 1270°C for 24 hours, water quenched and then aged at 1050°C for 168 hrs all result in a similar microstructure (Figures 5.1a-d), which consists of a two phase structure of α_2 platelets in a β_0 matrix. The orientation of these platelets can most clearly be seen in Figure 5.1d, which shows two orthogonal orientations of α_2 platelets within the β_0 matrix. Figures 5.1a-c do not show this clearly due to the orientation of the β_0 grains with respect to the sample surface. As would be expected, the α_2 : β_0 volume fraction ^{ratio} decreases with increasing Nb content (Figures 5.1c & d) due to the known β_0 stabilising effect of Nb on a wide range of titanium based alloys [Mur83]. Conversely increasing the Al content raises the volume fraction of α_2 in the alloy (Figures 5.1a & c).

Chemical analyses of these alloys, as well as other similar alloys discussed below, are shown in Table 5.1. Of particular interest is the ratio of Ti+Nb to Al+Si in the α_2 structure. Despite being a compound, Ti_3Al in its binary form exists over a

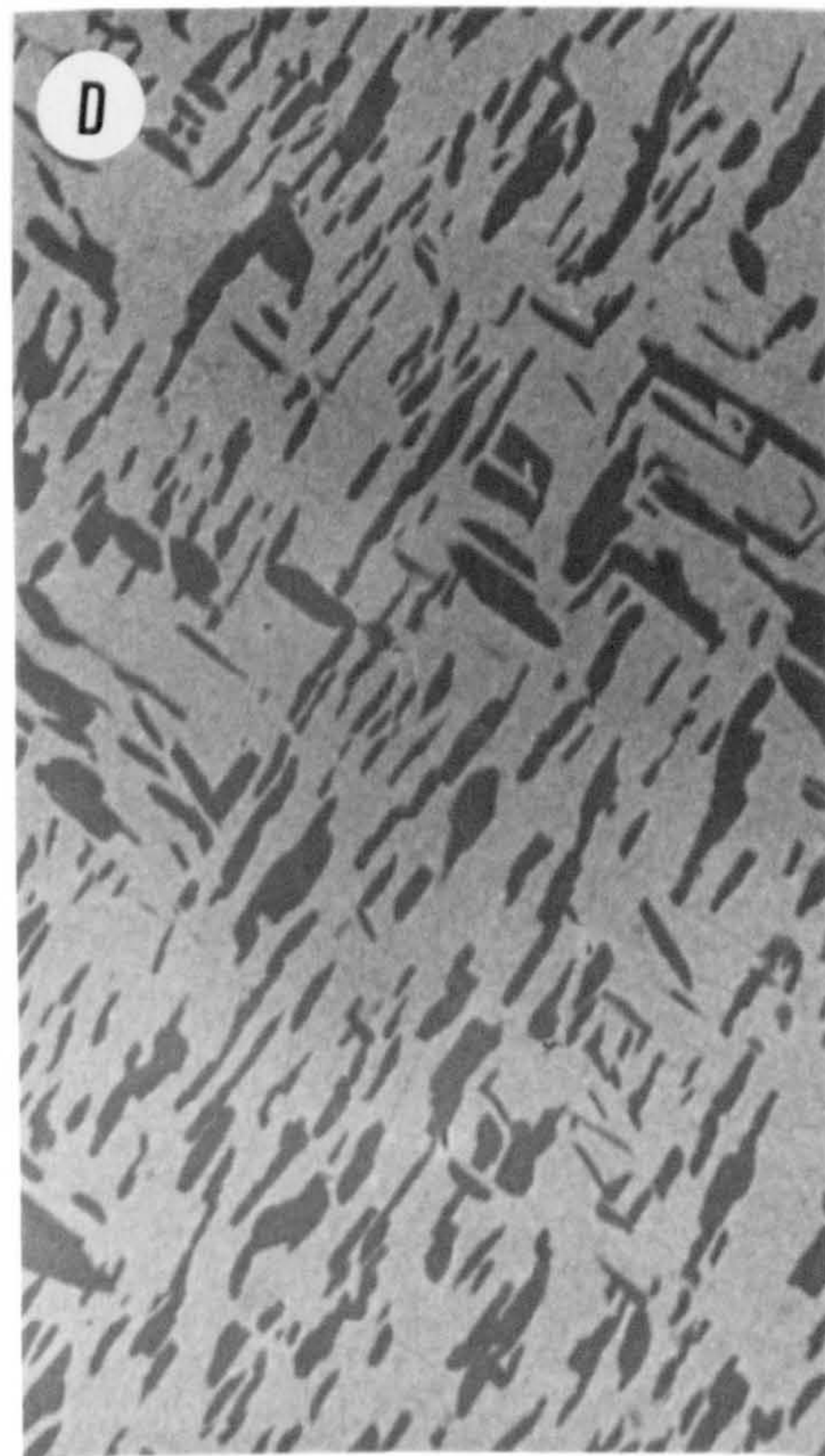
Figure 5.1.

The four micrographs illustrated here are produced by solution treatment at 1270°C for 24 hrs. water quenched, then ageing at 1050°C for 168 hrs. Each is an SEI image produced by etching the samples in Kroll's reagent. Each shows α_2 platelets (dark) within a β matrix.

- (a) Ti-20-11-0.9 (at.%)
- (b) Ti-20-15-0.9 (at.%)
- (c) Ti-23-11-0.9 (at.%)
- (d) Ti-23-15-0.9 (at.%)



25 μ m



25 μ m

range of compositions [Mur87]. In this heat treated condition, each of these alloys shows an elemental ratio that is very close to that of the stoichiometric ideal i.e. Ti_3Al . As has been reported in section 2, other authors [Ban87, Moz90, Qia91] have determined that Nb has a tendency to inhabit Ti sites. It is likely from the data produced here that Si has the same affinity for Al sites in the α_2 phase. Ti+Nb to Al+Si ratio for the silicide phase produces a deviation from stoichiometry giving a ratio of 5.1:3 in all but one case. No silicide particles with a 3:1 ratio (corresponding to the Ti_3Si phase) have been found.

As can be seen from Table 5.1., the solubility limit for silicon at 1050°C in the α_2 phase is approximately 1.5at.%, while that of the β_0 phase is markedly lower (about 0.8 at.%). At 1270°C each of the main alloys which contain 0.9 at.% silicon are single phase, indicating that the solubility of silicon in β_0 decreases with decreasing temperature. Both of these phenomena are indicative that the phase transformations exhibited by the alloys when the silicon level is modified are peritectoid in character (see Figure 5.2). In the binary Ti-Si system the silicon acts as a β eutectoid-forming element [Mur84].

As the silicon solubility in the β_0 phase is below 0.9at.% the β_0 phase, it is only the presence of the α_2 phase with its' higher solubility limit which prevents any silicide particles being precipitated. Thus by raising the ageing temperature slightly, and thus reducing the volume fraction of α_2 present, it may be possible to force the silicide particles to precipitate provided that the solubility of silicon in α_2 does not increase significantly as the ageing temperature is raised. As can be seen in Figure 5.3a, this is possible in the most heavily β stabilised alloy (Ti-20-15-0.9) when aged at 1100°C, which is just below the β transus. Figure 5.3c shows silicide particles which have precipitated in the β_0 phase. These are much larger than those which are found within α_2 particles. It cannot be ascertained with a high degree of certainty as to whether the silicide particles formed within the α_2 phase, or if the α_2 grains nucleated around the silicides. As the solubility of silicon in α_2 is higher than in β_0 it is unlikely that silicide particles would have formed in the α_2 grains, so it is most likely that the silicide particles acted as nucleating agents for the α_2 grains. The amount of α_2 and silicide phases present is small, and none of the micrographs illustrated in Figure 5.3. show representative volume fractions. The silicide phase has not been found in any of the other three main alloys.

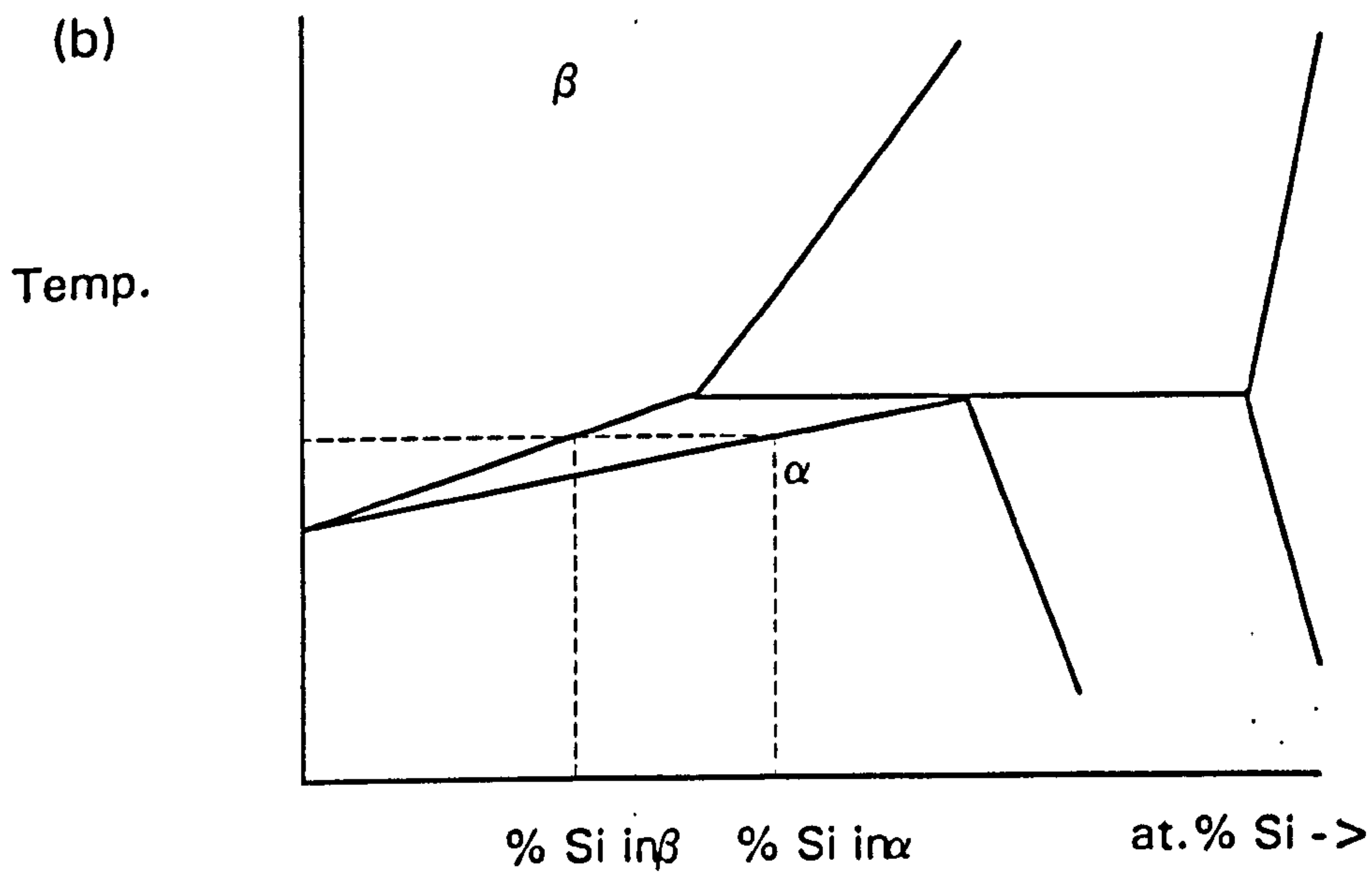
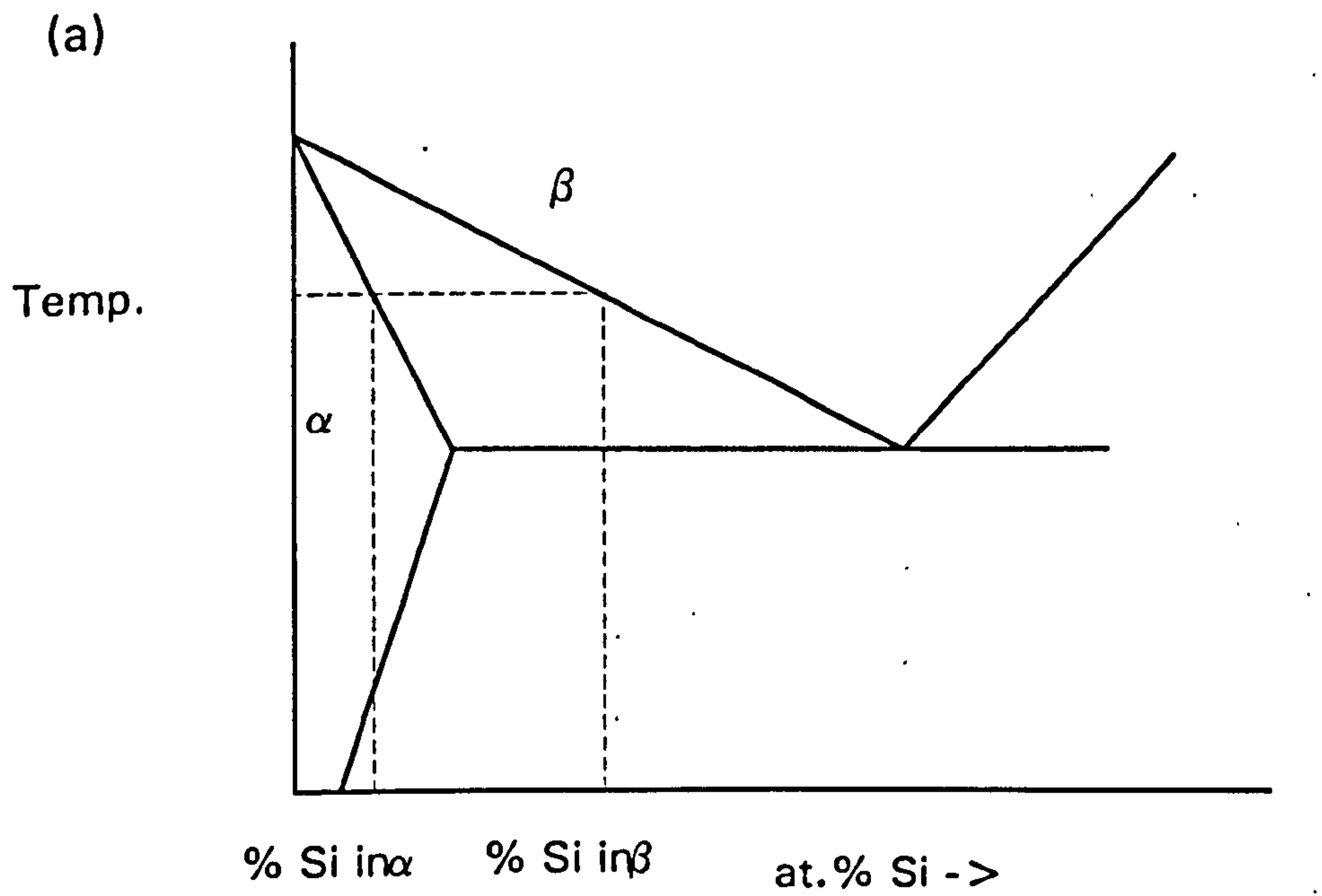


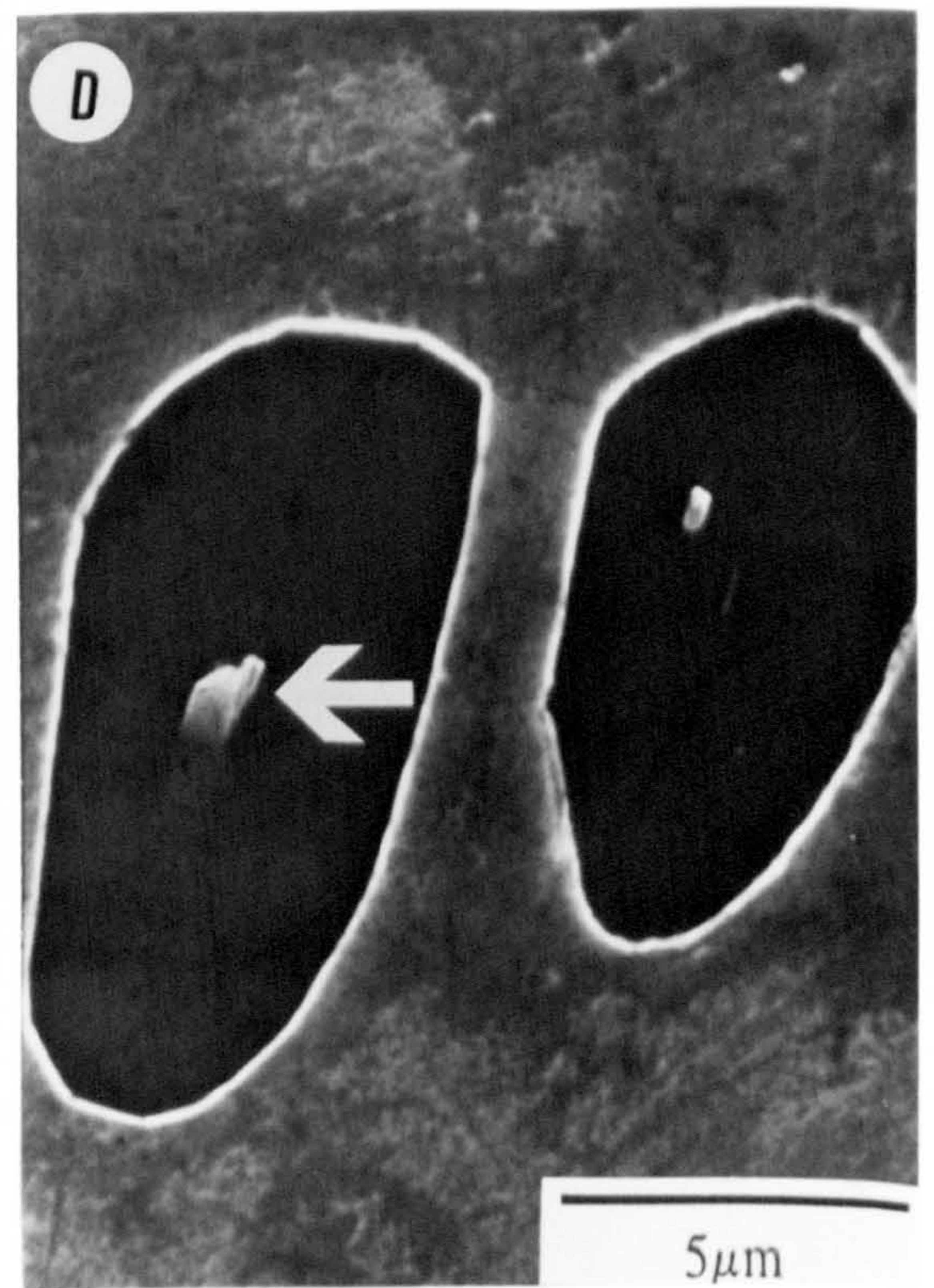
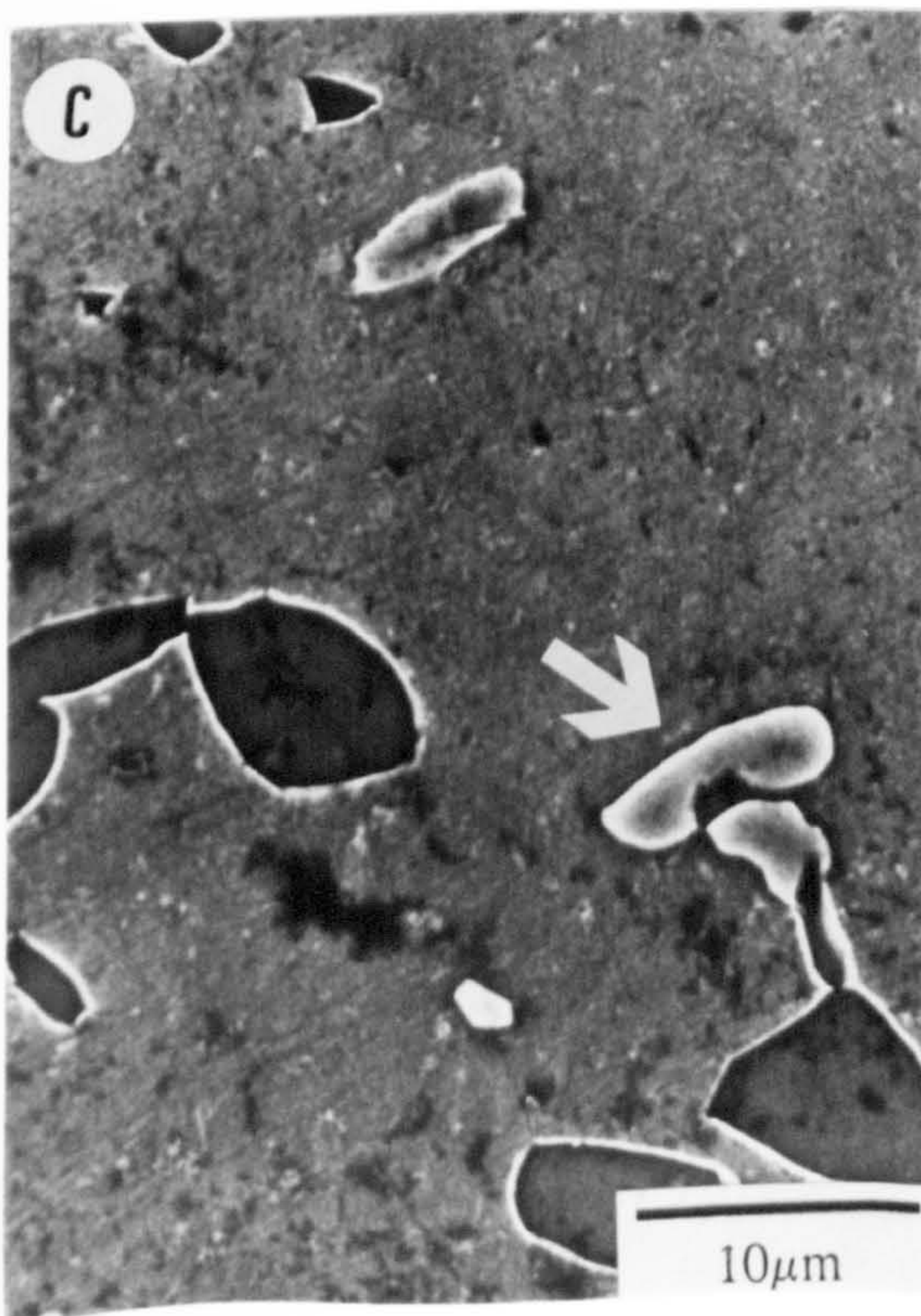
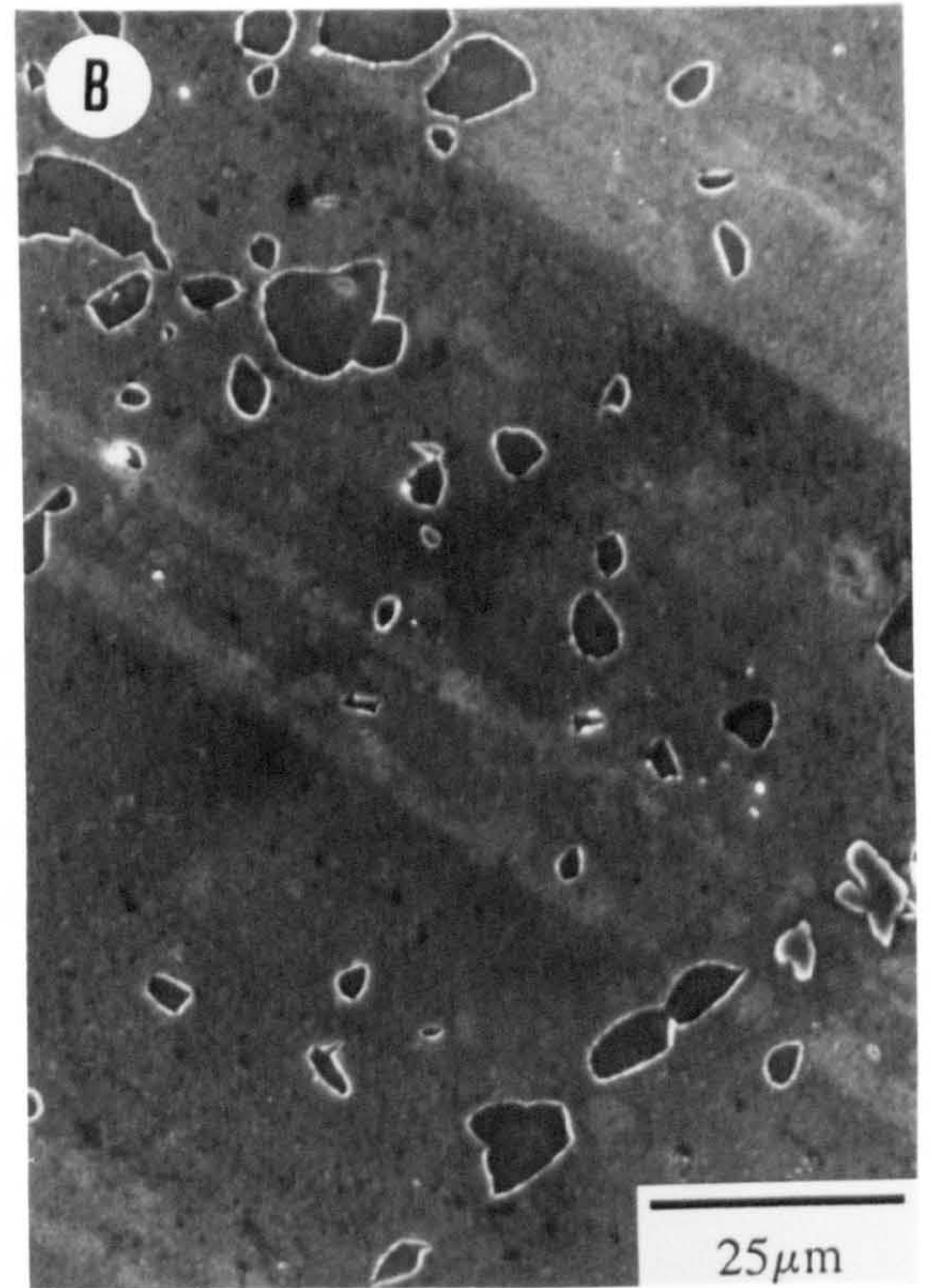
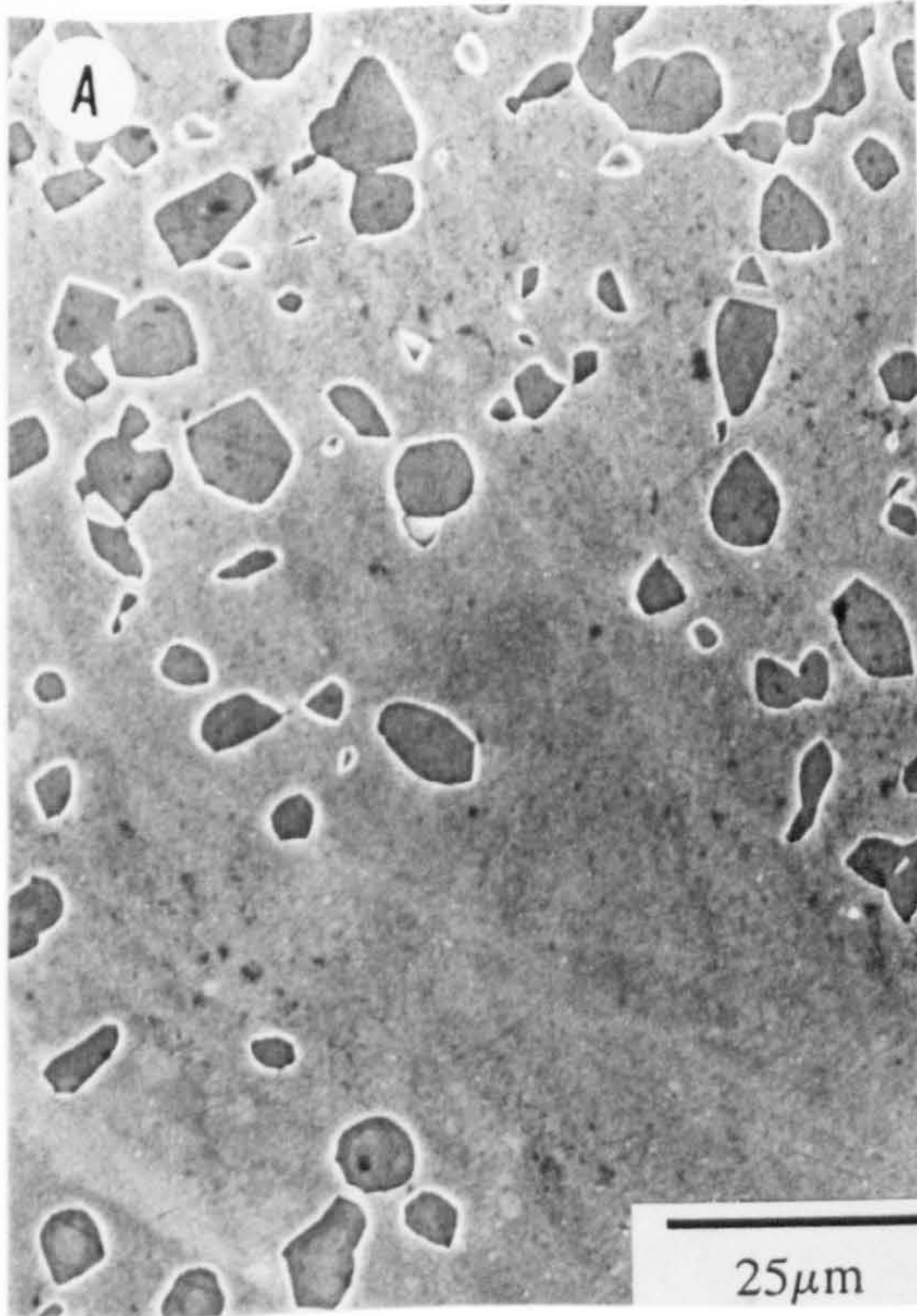
Figure 5.2. Schematic Diagram Representing the Distribution of Silicon in the Alloys in Terms of (a) Eutectoid and (b) Peritectoid Reactions.

Figure 5.3.

Alloy Ti-20-15-0.9 (at.%) Solution treated at 1100°C for 24 hrs.

SEI images of alloy etched in Kroll's reagent.

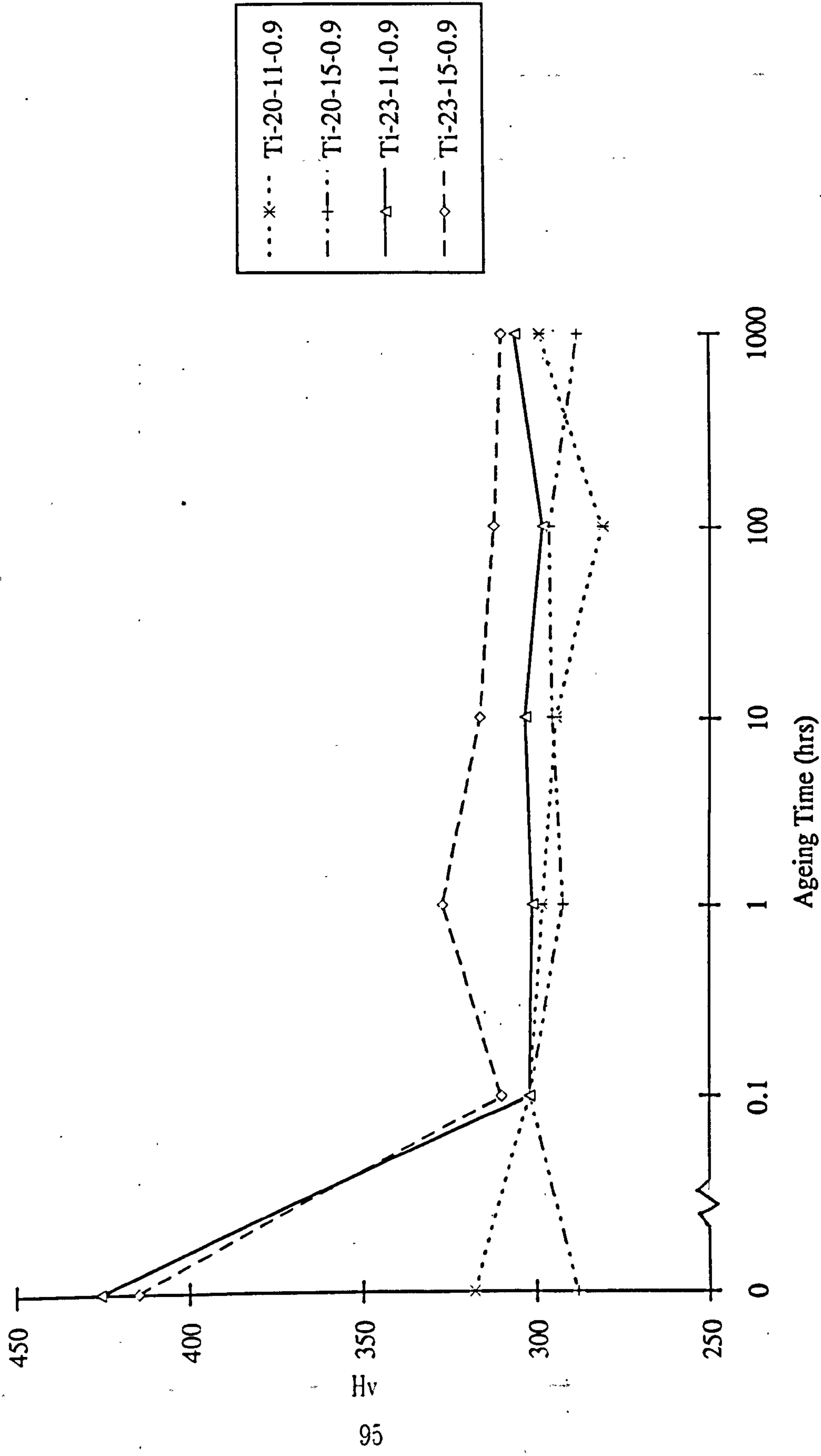
- (a) View of a series of α_2 particles within a β background. This is atypical in this alloy.
- (b) **Enlarged** View of α_2 grains. Also at the bottom right corner two silicide particles can be seen within the β matrix.
- (c) Enlarged view of silicide particles within the β matrix.
- (d) View of α_2 grains containing silicide particles. Note the much smaller size of these silicides when compared to those shown in (c).



From this evidence it is suggested that for the production of alloys containing as large an amount of silicon in the matrix as possible, where solution treatments in the β_0 phase field is desired, then it should be carried out at very high temperatures, e.g. above 1200°C. When an α_2/β_0 solution treatment is desired, a low temperature should be used to enhance the α_2 volume fraction, and thus the overall silicon level.

During the ageing (Figure 5.4), the hardness of the alloys drops markedly from that exhibited by the solution treated alloys in the Ti-23-X-0.9 alloys, and then remains approximately constant throughout a range from 0.1 to 1000 hrs. The hardness of the Ti-20-X-0.9 alloys is significantly lower than that of the higher aluminium ones when solution treated, and is not modified significantly by the ageing process.

Figure 5.4. Ageing Curve for Alloys Heat Treated at 1050°C



All hardness values are quoted to $\pm 2\text{Hv}$.

Nominal Composition	Phase	at.% Ti	at.% Al	at.% Nb	at.% Si	Ratio of Ti+Nb : Al + Si
Ti-20-11-0.9	α_2	bal.	23.6	7.1	1.1	3.0:1
	β_0	bal.	18.7	12.1	0.8	
Ti-20-15-0.9	α_2	bal.	24.0	8.9	1.1	3.0:1
	β_0	bal.	18.9	15.9	0.7	
Ti-23-6-0.9	α_2	bal.	24.1	5.4	0.8	3.0:1
	β_0	bal.	19.8	8.4	0.4	
Ti-23-11-0.9	α_2	bal.	24.2	10.4	0.9	3.0:1
	β_0	bal.	21.0	15.5	0.6	
Ti-23-13-0.9	α_2	bal.	23.5	10.7	1.1	3.0:1
	β_0	bal.	19.8	16.5	0.7	
Ti-23-15-0.9	α_2	bal.	25.2	11.2	1.0	2.9:1
	β_0	bal.	22.4	18.3	0.5	
Ti-20-11-0.5	α_2	bal.	24.2	7.4	0.5	3.0:1
	β_0	bal.	18.5	12.9	0.5	
Ti-20-11-1.2	α_2	bal.	23.4	7.4	1.5	3.0:1
	β_0	bal.	18.4	12.9	0.8	
Ti-20-11-1.5	α_2	bal.	23.4	7.4	1.5	3.0:1
	β_0	bal.	18.4	12.9	0.9	
	Ti_5Si_3	bal.	5.9	7.7	31.1	
Ti-23-6-1.5	α_2	bal.	24.1	5.4	0.8	3.0:1
	β_0	bal.	19.8	8.4	0.4	
	Ti_5Si_3	bal.	7.0	9.3	29.1	
Ti-23-11-1.5	α_2	bal.	23.8	9.2	1.1	3.0:1
	β_0	bal.	21.5	14.5	0.6	
	Ti_5Si_3	bal.	7.0	9.1	29.1	
Ti-23-15-1.5	α_2	bal.	23.6	10.8	1.4	3.0:1
	β_0	bal.	21.5	17.3	0.7	
	Ti_5Si_3	bal.	7.0	10.8	29.3	
Ti-23-11-3	α_2	bal.	23.5	9.9	1.1	3.0:1
	β_0	bal.	21.0	15.8	0.7	
	Ti_5Si_3	bal.	7.0	8.8	29.1	

Table 5.1. Chemical Compositions of Phase in Alloys Aged at 1050°C as Identified by Bulk EDS Analysis.

5.2.2. Effect of Silicon Level in Ti-20-11-X Alloys

Sections of each of the five alloys based on the Ti-20Al-11Nb-XSi (at.%) composition range in the solution treated condition described in section 4 were heat treated at 1050°C for 168 hours to allow comparison with the alloys discussed in section 5.2.1. As would be expected the microstructure produced was based on the two phase structure of $\alpha_2 + \beta_0$. Figure 5.5a shows clearly an even distribution of α_2 platelets in a matrix of β_0 . When the silicon content is raised to 1.2at.% the volume fraction of α_2 in the alloy has increased markedly (Figure 5.5b). From an approximate 'lever rule' type calculation of volume fraction, the volume fraction of α_2 in the 0.5at% Si alloy should be 34%, and that of the 1.2at.% Si alloy should only change slightly to 36%. Image analysis of the two microstructures produces an estimate of the volume fractions as being 32% and 39% respectively. This lower than expected β_0 volume fraction in the 1.2at.% Si alloy has also been reported by Es-Souni et al. [Ess92], who explained it as being caused by a rapid transformation from β_0 to α_2 during quenching. If this is considered to be correct, then the reason that it does not occur when the silicon content is lower should be identified. In the current examination, the use of BE imaging indicates that any β_0 that was transformed to α_2 would not be detected as a large diffusional change would be required, and thus the explanation of the different volume fractions given by Es-Souni is invalid. Examination of X-ray diffraction data for these alloys indicates that the expected peaks for β_0 and α_2 are to be found in both of these alloys (see Table 5.2.). However in the 1.2at.% Si alloy other peaks are produced by the formation of α_2 phase which are formed by the diffraction of X-rays from crystal planes which would normally be forbidden by the structure factor of the α_2 crystal (see Table 5.2.). This is indicative of the α_2 being formed with a different composition, such that some type of secondary ordering occurs. The possibility that this ordering is a result of β_0 transforming to α_2 on quenching, with the effect that the stoichiometric composition in the α_2 is not being retained in the 'quenched in' α_2 has not been examined in this work. These 'disallowed' reflections may alternatively be caused by secondary ordering of Ti and Nb onto separate sites in the α_2 phase.

α_2 Diffraction Peaks *	α_2 Indexing	Diffraction 'Allowed'?	β_0 Diffraction Peaks ⁺	β_0 Indexing	Ti-20-11-0.5 Peaks	Ti-20-11-1.2 Peaks
3.407	(1 $\bar{1}$ 01)	Yes	-	-	3.402	3.400
2.890	(2 $\bar{1}$ $\bar{1}$ 0)	Yes	-	-	2.885	-
2.503	(20 $\bar{2}$ 0)	Yes	-	-	2.502	2.496
2.387	(21 $\bar{1}$ 1)	No	-	-	-	2.391
2.325	(0002)	Yes	-	-	2.325	2.332
-	-	-	2.291	(110)	2.294	2.291
2.204	(2 $\bar{2}$ 01)	Yes	-	-	2.203	2.201, 2.204 [#]
1.706	(2 $\bar{2}$ 02)	Yes	-	-	1.703	1.703, 1.706 [#]

* For lattice parameters of $a=578\text{pm}$, $c=465\text{pm}$.

⁺ For lattice parameter of $a=324\text{pm}$.

[#] Peak splitting evident.

Table 5.2. X-ray Diffraction Data for 1270°C S.T, 1050°C Aged Alloys

Although silicon is a β eutectoid former in titanium based alloys, the effect of its addition in these alloys is rather different. As can be seen in Table 5.1., the solubility of silicon in the β phase is approximately 0.8-0.9 at.% at 1050°C. However, in α_2 it is markedly higher, at a level of around 1.4 at.%. The amount of silicon present in the α_2 rises as the silicon content in the alloy as a whole is increased. As silicon is believed to substitute onto aluminium sites in this stoichiometric phase in preference to the aluminium atoms, this would be expected to cause some of the aluminium to be 'rejected' from the aluminide were it to remain stoichiometric. This is confirmed by quantitative analysis of the phase chemistry. To maintain the equilibrium between the α_2 and β_0 phases, the silicon has the effect of producing a larger volume fraction of α_2 phase. Thus the silicon acts on an isothermal basis as a type of α_2 volume fraction enhancing element.

The prior β_0 grain boundaries (i.e. those formed during the 1270°C heat treatment) are coated with α_2 in all of the five alloys. This α_2 film is surrounded by a corresponding precipitate free zone on either side, of approximately equal depth to that of the α_2 film (see Figure 5.5c). In higher silicon level alloys, this α_2 film is dotted

with a series of fine (sub-micron) Ti_3Si_3 precipitates (see Figure 5.5d). As would be expected, the amount of grain boundary coverage provided by the silicide increases in the Ti-20-11-1.5 alloy.

Figure 5.6b shows a variety of less common microstructural characteristics on a grain boundary in the Ti-20-11-1.2 alloy. Apart from the small Ti_3Si_3 precipitates in the α_2 , which are shown in more detail in Figure 5.6d, in the centre of the micrograph, there is a much larger silicide particle, which has grown into a β_0 phase region on the grain boundary (Figure 5.6c). As the silicon solubility in β_0 is much lower than in α_2 (approximately 0.85at% at this temperature as opposed to 1.4at.% in the α_2), so any silicide particle which impinges on a β_0 area grows rapidly to reduce the supersaturation of silicon with respect to β_0 .

Also in this micrograph (at the top right hand side) is a large silicide particle, similar to the one shown in Figure 5.6a, which is surrounded by α_2 -precipitate free zone. The 'volume fraction enhancing' effect explain why in the matrix, where silicide particles have grown, there is a region around them that is α_2 free. When the system moves from a two phase region into a three phase one (Figure 5.7.), then the amount of silicon in the β_0 phase field is reduced as silicon is taken up by the silicide phase. This in turn changes the equilibrium so that silicon diffuses out of the α_2 phase, so reducing the volume fraction of α_2 by reducing the number of 'Aluminium Site' atoms which are available for α_2 production.

As with all of the other alloys examined in this work, the microstructure of the Ti-20-11-1.5 alloy aged at 1050°C is based on a two phase structure with the characteristic large second phase plates (α_2) on the grain boundaries and the precipitate platelets (α_2) in the β matrix away from the grain boundaries. There is no evidence of any β to β_0 transformation on cooling in the alloy. However, as in the Ti-23-11-1.5 alloy which will be discussed in Section 5.2.3, the α_2 phase is modified by the Nb content of the alloy to produce 'forbidden' reflections during X-ray diffraction. In these alloys this distortion is much greater, resulting in a truly orthorhombic structure. There is also a distribution of relatively large silicide particles throughout the alloy.

Figure 5.5.

SEM SEI micrographs of Ti-20Al-11Nb series alloys solution treated at 1270°C for 24 hrs, water quenched, then aged at 1050°C for 168hrs, water quenched.

Mechanically polished and deep etched with 3vol.%HF-10vol.%HNO₃ in water.

- (a) Ti-20-11-0.5. α_2 platelets (darker) in a β matrix.
- (b) Ti-20-11-1.2. The microstructure is similar to that shown in (c), though the volume fraction of α_2 is noticeably higher than in the alloy with the lower silicon content.
- (c) Ti-20-11-0.5. This shows a prior β grain boundary with an α_2 coating, which is characteristic of this type of alloy. Next to the grain boundary is an α_2 free zone surrounded with the conventional microstructure as shown in (a).
- (d) Ti-20-11-1.2. This micrograph shows a similar structure to that shown in (c), but with a set of small silicide particles (bright) along the grain boundary.

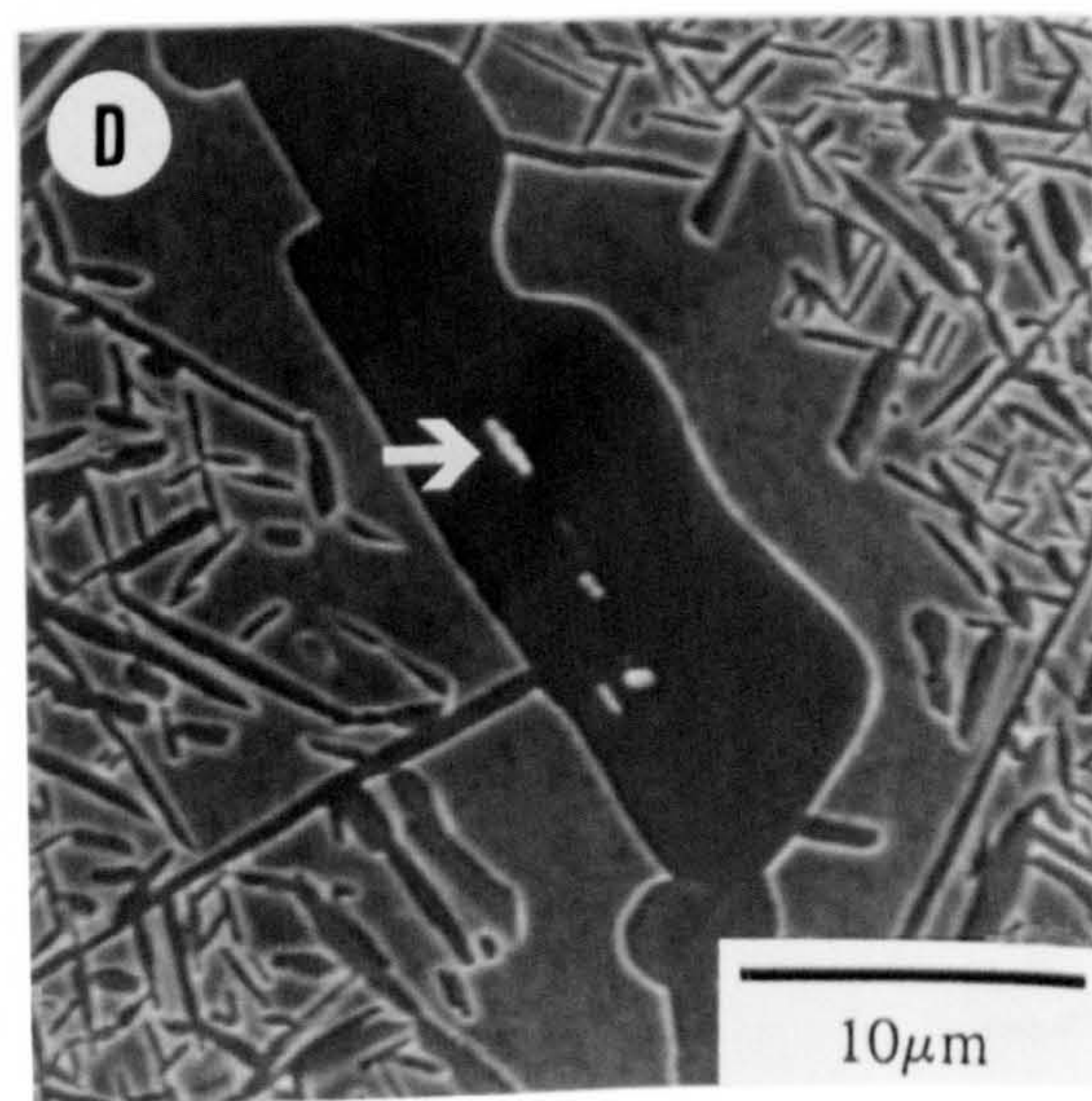
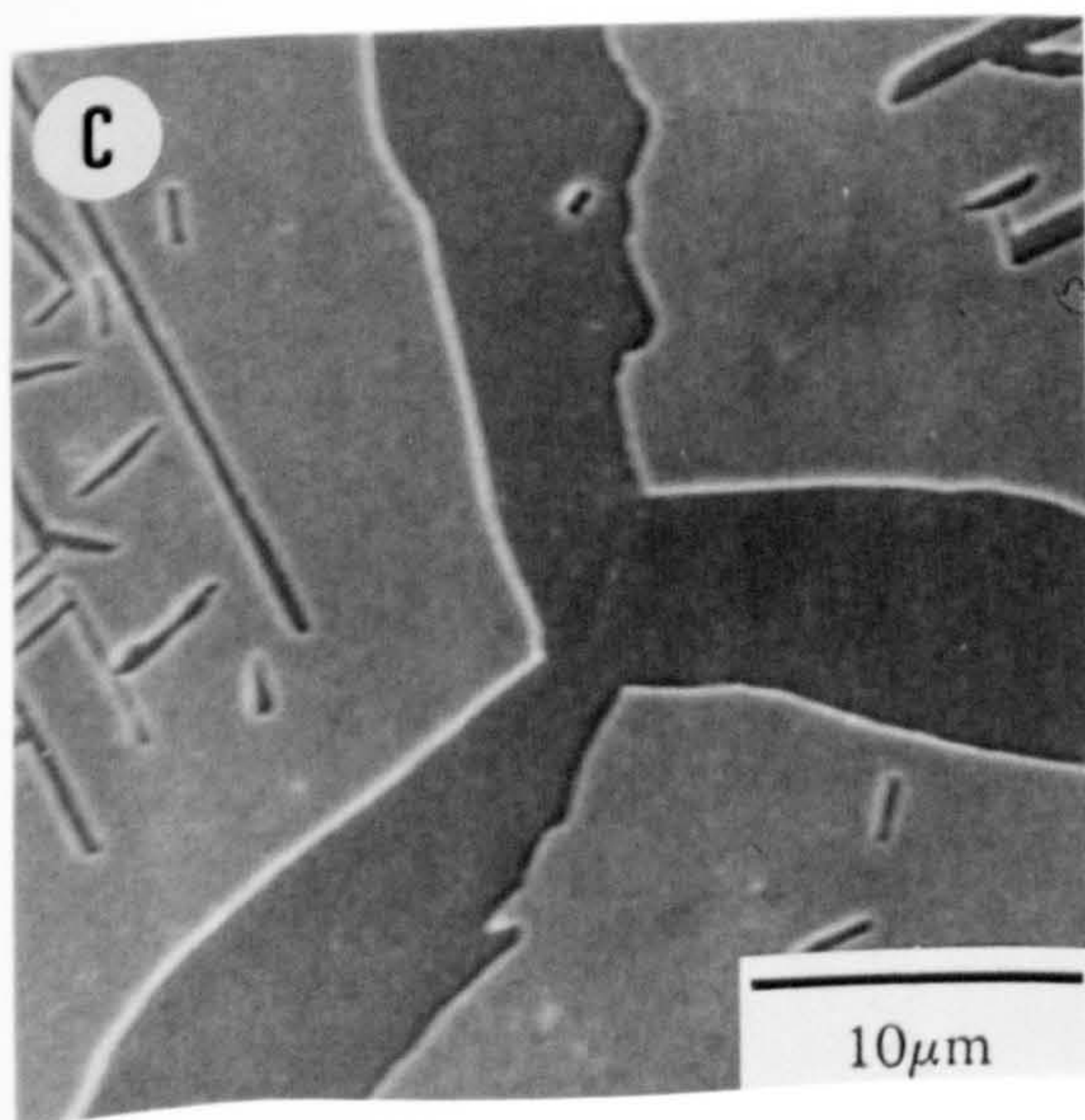
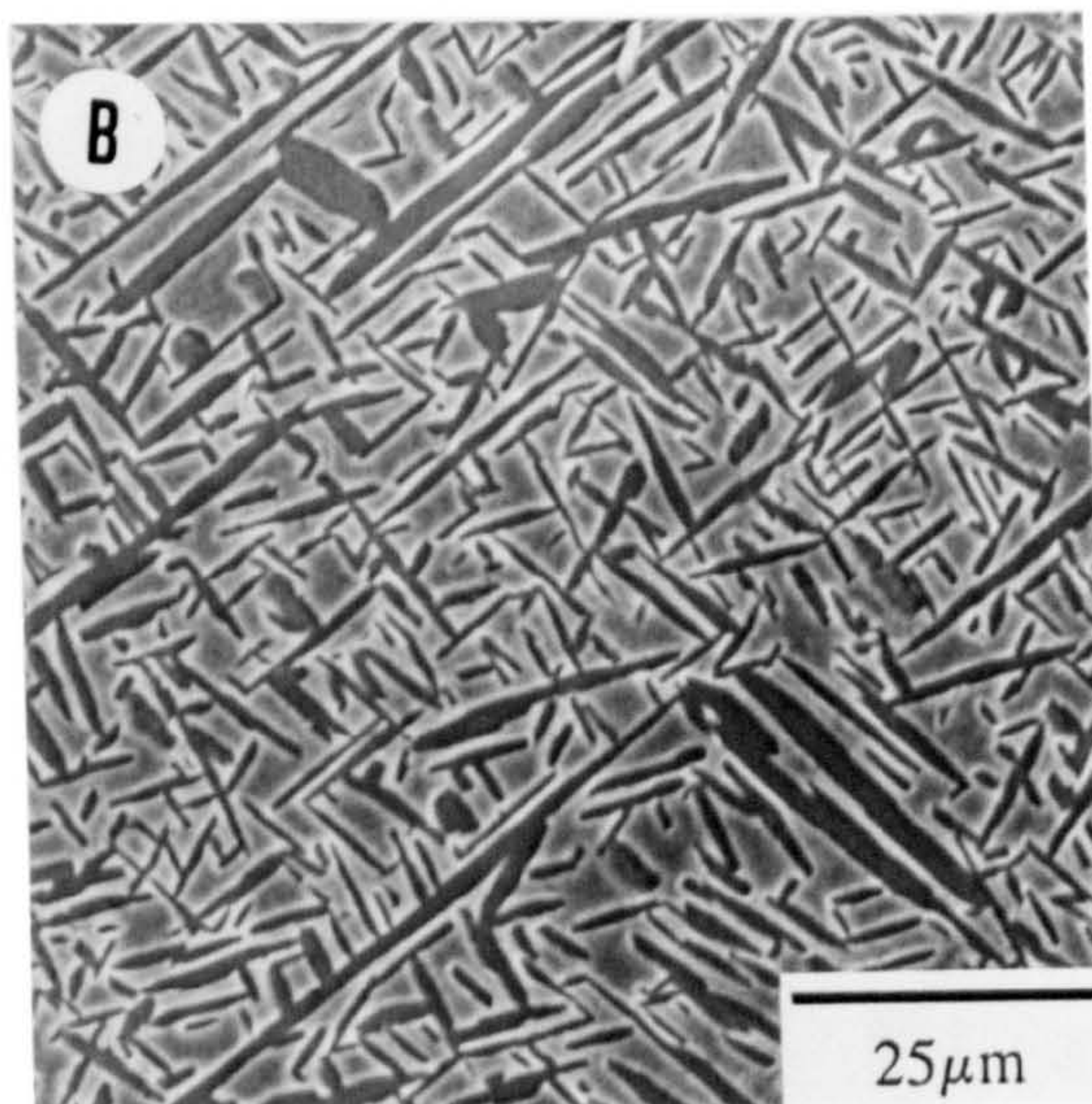
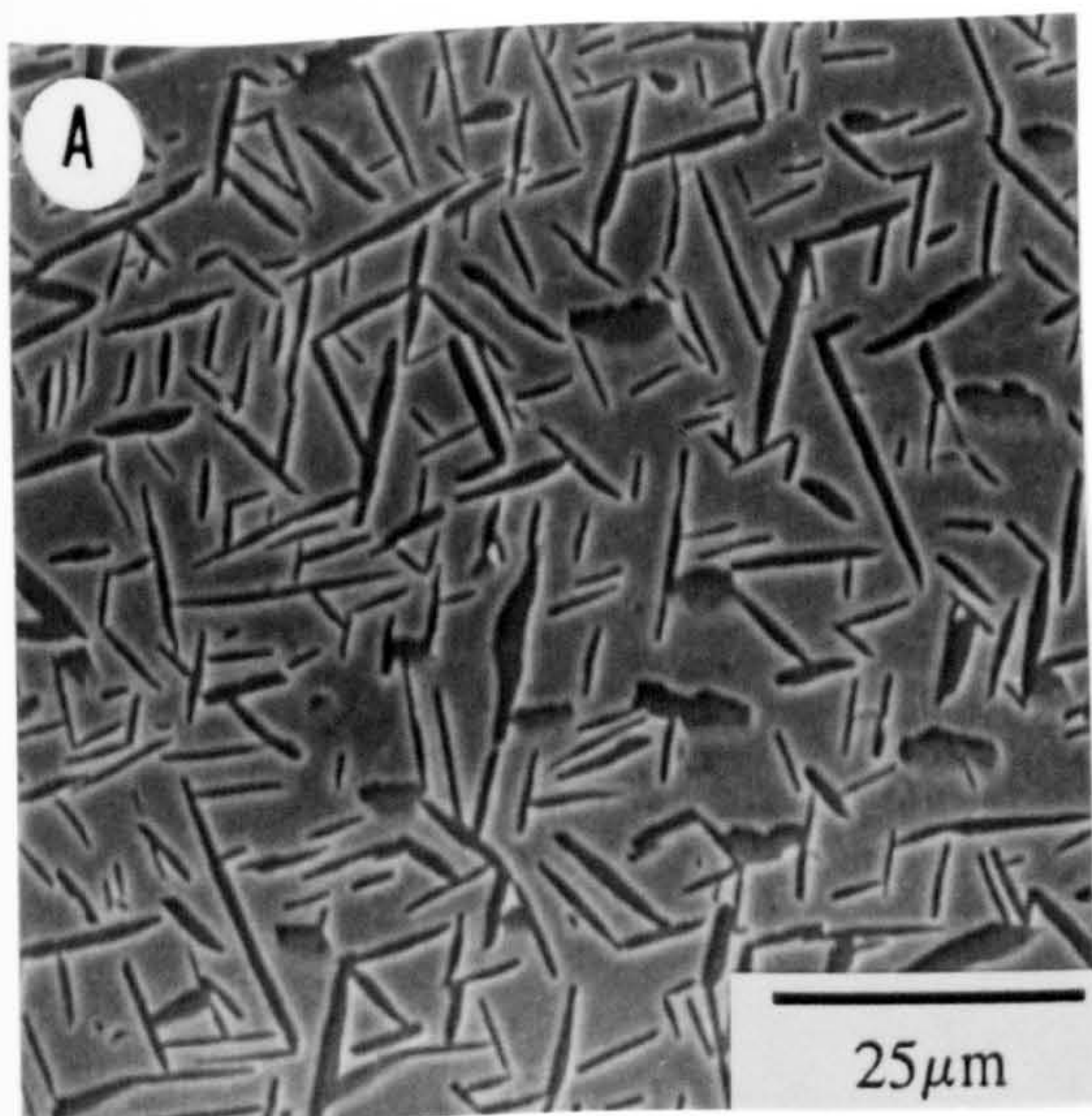
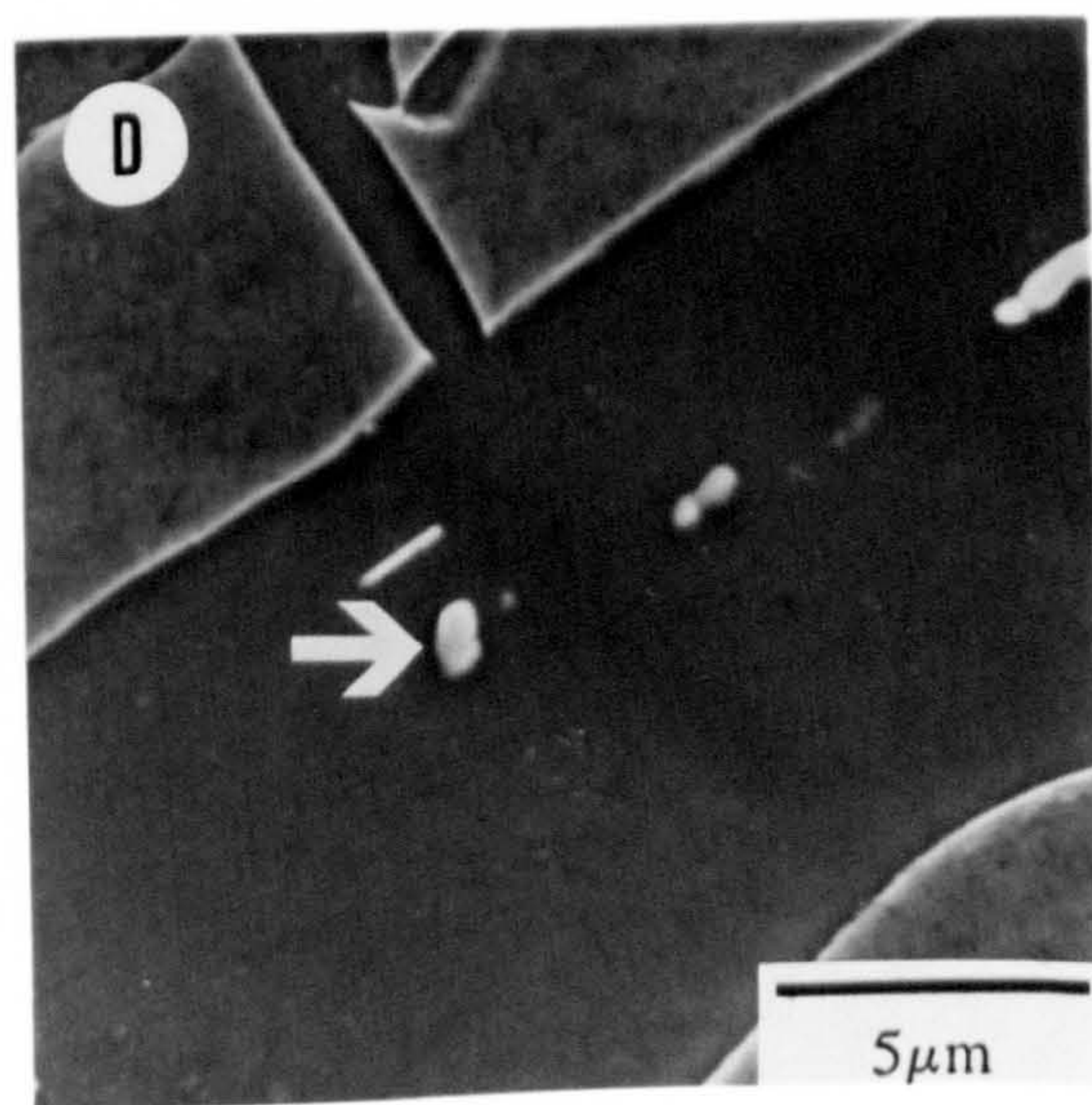
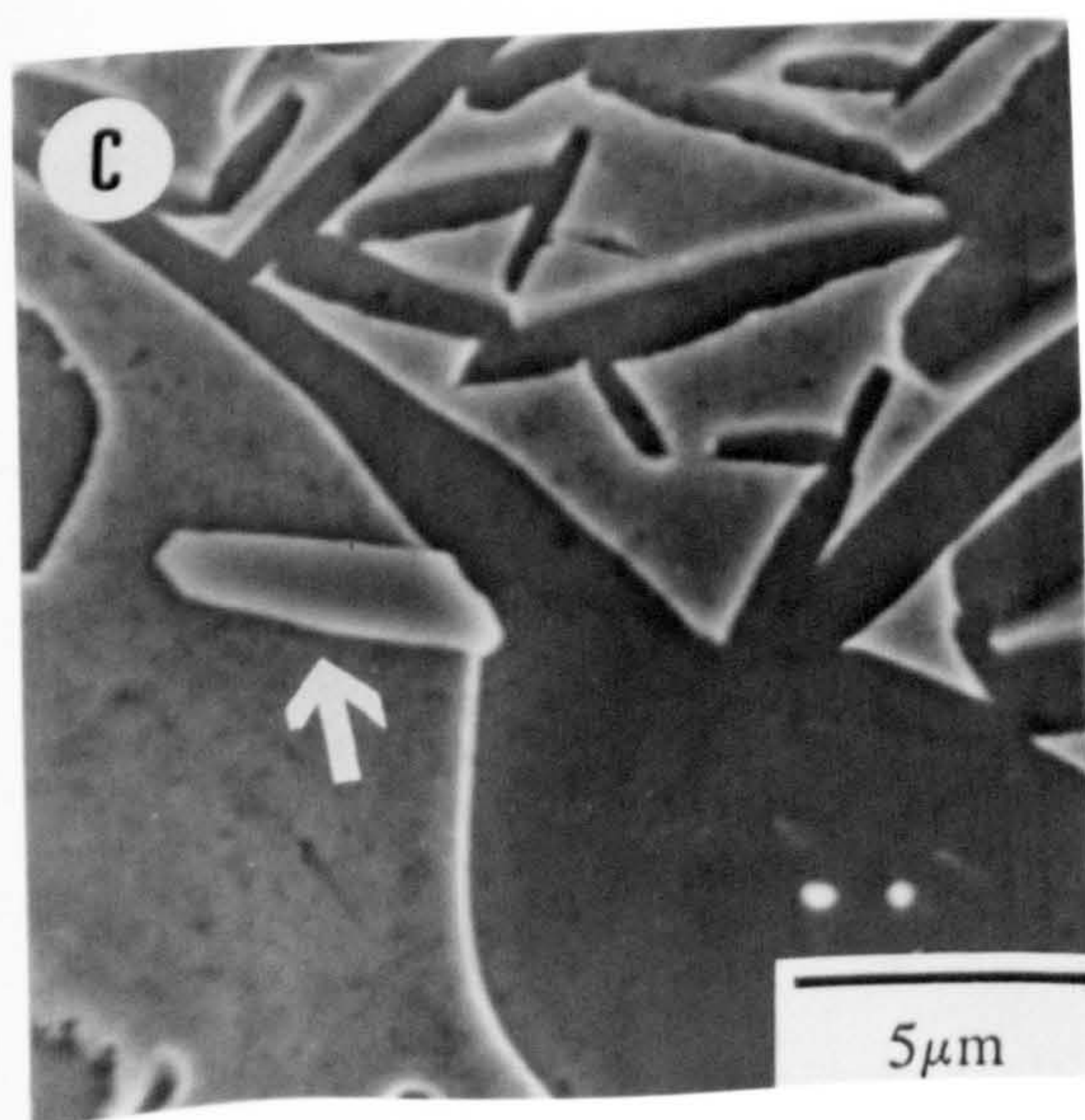
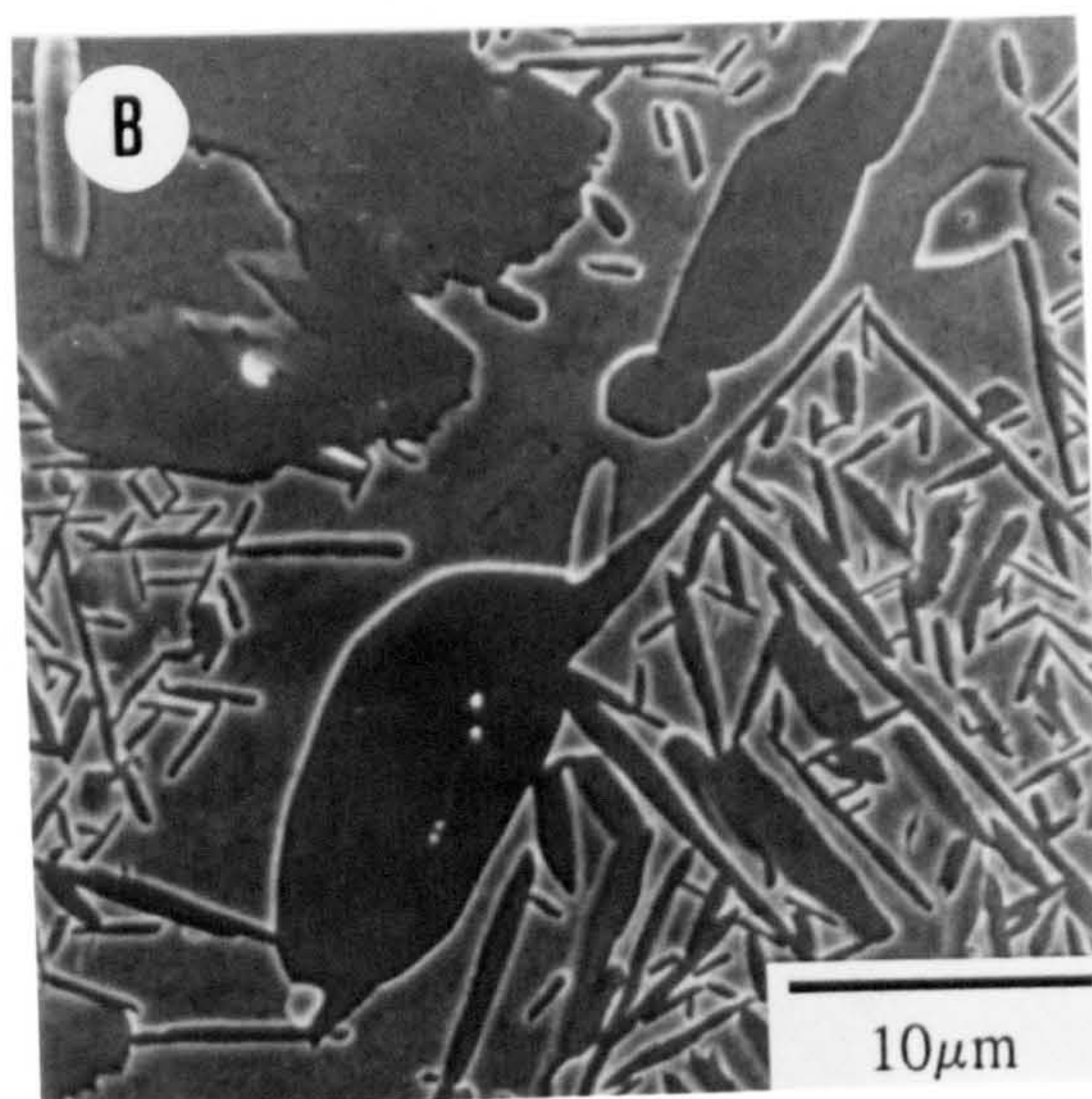
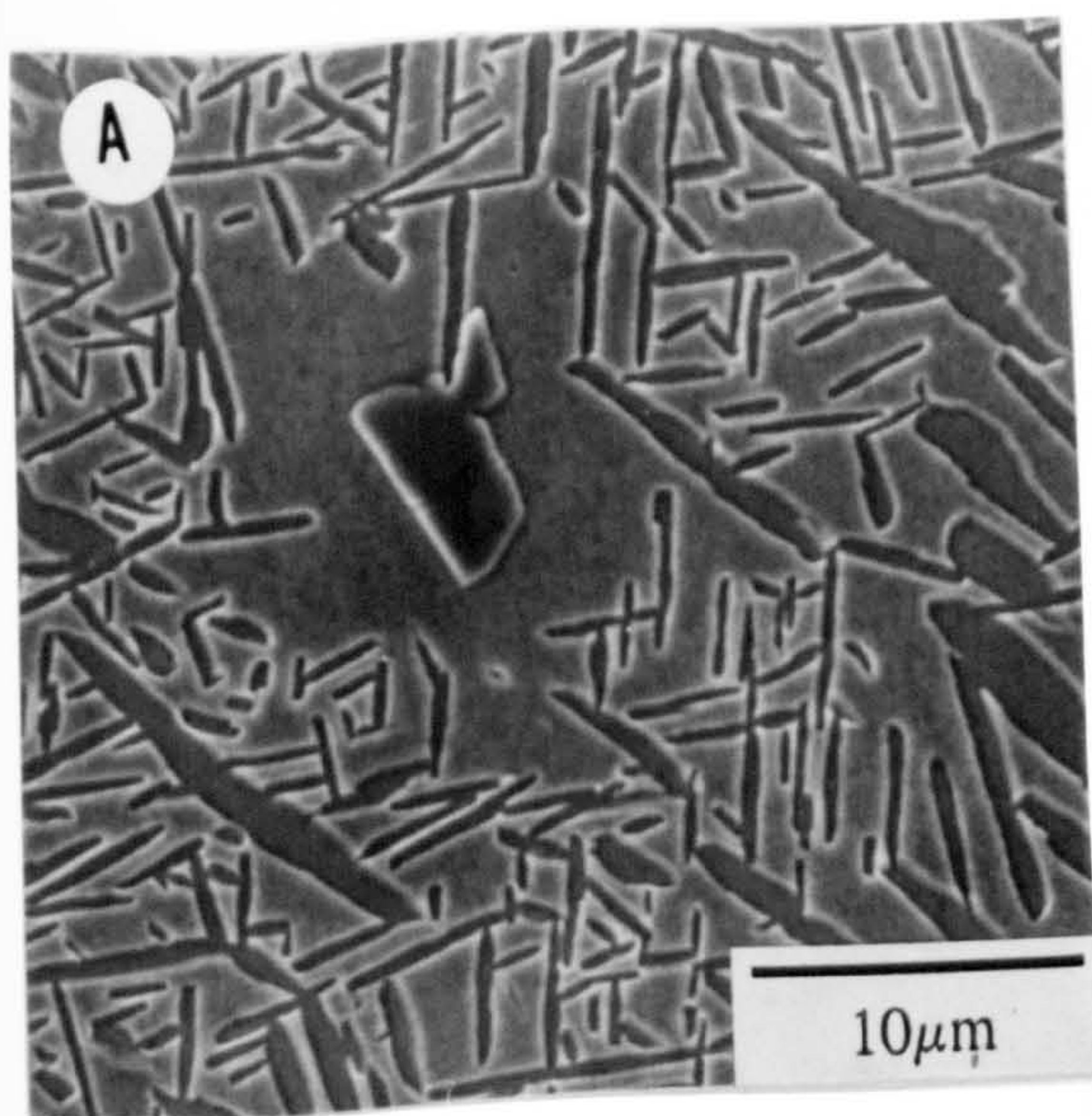


Figure 5.6.

SEM SEI micrographs of the Ti-20Al-11Nb-1.2Si alloy solution treated at 1270°C for 24 hrs, water quenched, then aged at 1050°C for 168hrs, water quenched.

Mechanically polished and deep etched with 3vol.%HF-10vol.%HNO₃ in water.

- (a) This micrograph shows a non-grain boundary silicide particle surrounded by an α_2 free zone
- (b) This shows a prior β grain boundary, mainly covered by α_2 , with silicide particles following it. This illustrates the two types of silicides present. Those precipitated in the α_2 phase are considerably smaller than those which form in the β phase. Note that chemically the two types of silicide are similar.
- (c) Detail of silicide precipitates in α_2 phase.
- (d) Detail of a silicide growing mainly within the β phase area.



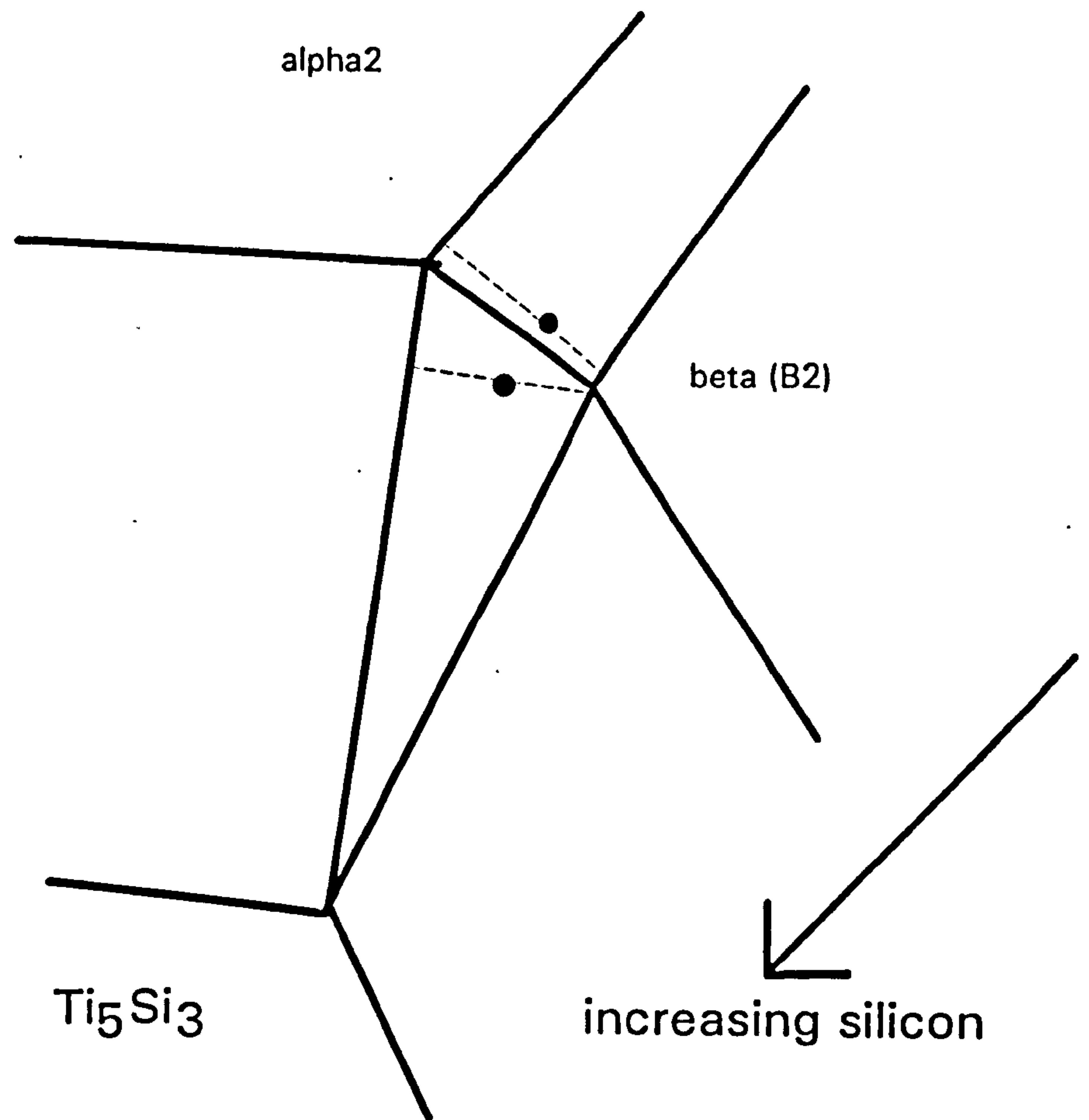


Figure 5.7. Schematic diagram showing the effect that moving from the two phase $\alpha_2 + \beta_0$ region to the three phase $\alpha_2 + \beta_0 + \text{Ti}_5\text{Si}_3$ field has in reducing the volume fraction of the β_0 phase.

5.2.3. Alloys based on Ti-23-X-Y with Higher Silicon Levels.

The three alloys Ti-23-11-1.5, Ti-23-15-1.5 and Ti-23-11-3 have been found to produce a different microstructure on quenching from the solution treatment temperature to that found in the other alloys (section 4), and thus may be expected to have a different structure to the other alloys when aged at 1050°C if the composition of the β_0 phase in the aged condition is also susceptible to martensitic transformations. Examination of the SEI micrographs shown in Figures 5.8a-f indicate that the morphology which exists is similar to that of the other alloys examined. However, X-ray diffraction indicates that the alloy consists of the two phases β and O in this condition. The compositions of the O phase in these alloys is very similar to that of the α_2 phase in similar alloys with lower silicon contents (see Table 5.1), the only difference being the higher silicon levels present in the O phase.

As discussed in section 5.2.1., in alloys based on Ti_3Al with Nb and Si additions, the effect of silicon on these alloys is to act as an α_2 stabilising element. When the solubility level for silicon in both the metallic phases is exceeded, then the addition of silicon would be expected to have little effect on the volume fractions of these two metallic phases. Raising the silicon content in the alloys still further beyond that which causes α_2 to transform to O appears to continue to raise the volume fraction of the O phase. This is clearly illustrated by a comparison of the microstructures present in both Ti-23-11-1.5 (Figures 5.8a&b) and Ti-23-11-3 (Figures 5.8c&d). These show a marked increase in the volume fraction of O phase in the Ti-23-11-3 alloy in comparison with the Ti-23-11-1.5 alloy. It is not clear if the effects of alloying additions on the volume fractions in $\alpha_2 + \beta_0$ alloys can be transferred to those in which the structure is based on O + β_0 , though in this case it appears to be valid.

The larger percentage of silicon in this alloy also produces an increase in the amount of Ti_5Si_3 which is formed. This has an effect on the morphology of the silicide which, as well as appearing as discrete blocks, is found in the form of 'chains' of particles which had formed along the grain boundaries and grown to the point at which they touched. This results in a series of chains of silicide which also appear along prior sub-grain boundaries, as illustrated in Figure 5.8c.

As would be expected, when a comparison is made between the 11 at.% and 15 at.% Nb containing alloys, the additional β stabilising effect of the Nb markedly increases the β volume fraction in the matrix (Figures 5.8a Vs 5.8e) The distribution of silicides on the grain boundaries (Figure 5.8f) remain the same as in the Ti-23-11-1.5 alloy.

5.3. 900°C Aged Microstructure

5.3.1. Alloys with a Nominal Silicon Content Below 0.9 at.%

When aged at 900°C, the microstructure of the different alloys undergoes a range of reactions. In most of the alloys examined which contain less than 1.5 at.% silicon, the microstructure formed is two phase $\alpha_2 + \beta_0$ of a considerably finer structure than that found when the alloys are heat treated at 1050°C. This structure is clearly illustrated in Figure 5.9a. X-ray diffraction shows that the Ti-23-11-0.9 alloy produces similar 'disallowed' reflections to those produced by some of the alloys aged at 1050°C. This may be an indication that the alloy has a composition very close to that in which the α_2 separates into 2 phases (α_2 and O).

The two phase structure is modified in the alloy of composition Ti-23-15-0.9. As can be seen in Figure 5.9b and c, which show SE and BE images of the alloy, it consists of three main phases. X-ray analysis and electron diffraction in a TEM indicate that this alloy consists of α_2 , β_0 and O phases (Figures 5.9d-g). The backscattered image indicates that the composition of the α_2 and O phases are similar. This is confirmed by the results of thin foil chemical analysis shown in Table 5.3. As with the alloys heat treated at 1050°C, the composition of the α_2 phase remains very close to the stoichiometric ratio. Interestingly, this is also true for the O phase, reinforcing the similarity between the two structures.

Phase	at.% Ti	at.% Al	at.% Nb	at.% Si	Ti + Nb : Al + Si Ratio
β_0	55.2	15.2	28.5	1.1	-
α_2	61.1	23.7	14.0	1.1	3.0:1
O	58.8	23.4	16.3	1.4	3.0:1

Table 5.3. Chemical Compositions of Phases in Ti-23-15-0.9 Aged at 900°C
Ascertained By Thin Foil EDS.

Figure 5.8.

Ti-23-X-Y alloys showing solution treated and then 1050°C /168hrs aged microstructure.

SE images of all alloys mechanically polished, etched in Kroll's Reagent.

- (a) Ti-23-11-1.5. Microstructure shows α platelets (etched) in a background of β at the bottom left. The large oval patches along the grain boundary are also formed of α phase. The dark raised section on the right hand side is a silicide particle (based on Ti_5Si_3).
- (b) Detailed view of grain boundary.
- (c) Ti-23-11-3. Microstructure shows α platelets (darker) in a background of β . Microstructure shows increased β stabilising effect of the added silicon. The silicon from the eutectic silicide structure found in the cast material which dissolved on solution treatment has resulted in the precipitation of a , more even distribution of Ti_5Si_3 within the matrix..
- (d) Detailed view of (c) showing silicides predominantly positioned on β phase.
- (e) Ti-23-15-1.5. Microstructure shows α (dark) platelets in a background of β . The α/β grain structure has markedly more β than the Ti-23-11-1.5.
- (f) Detail of the silicide on grain boundary between two large α grains.

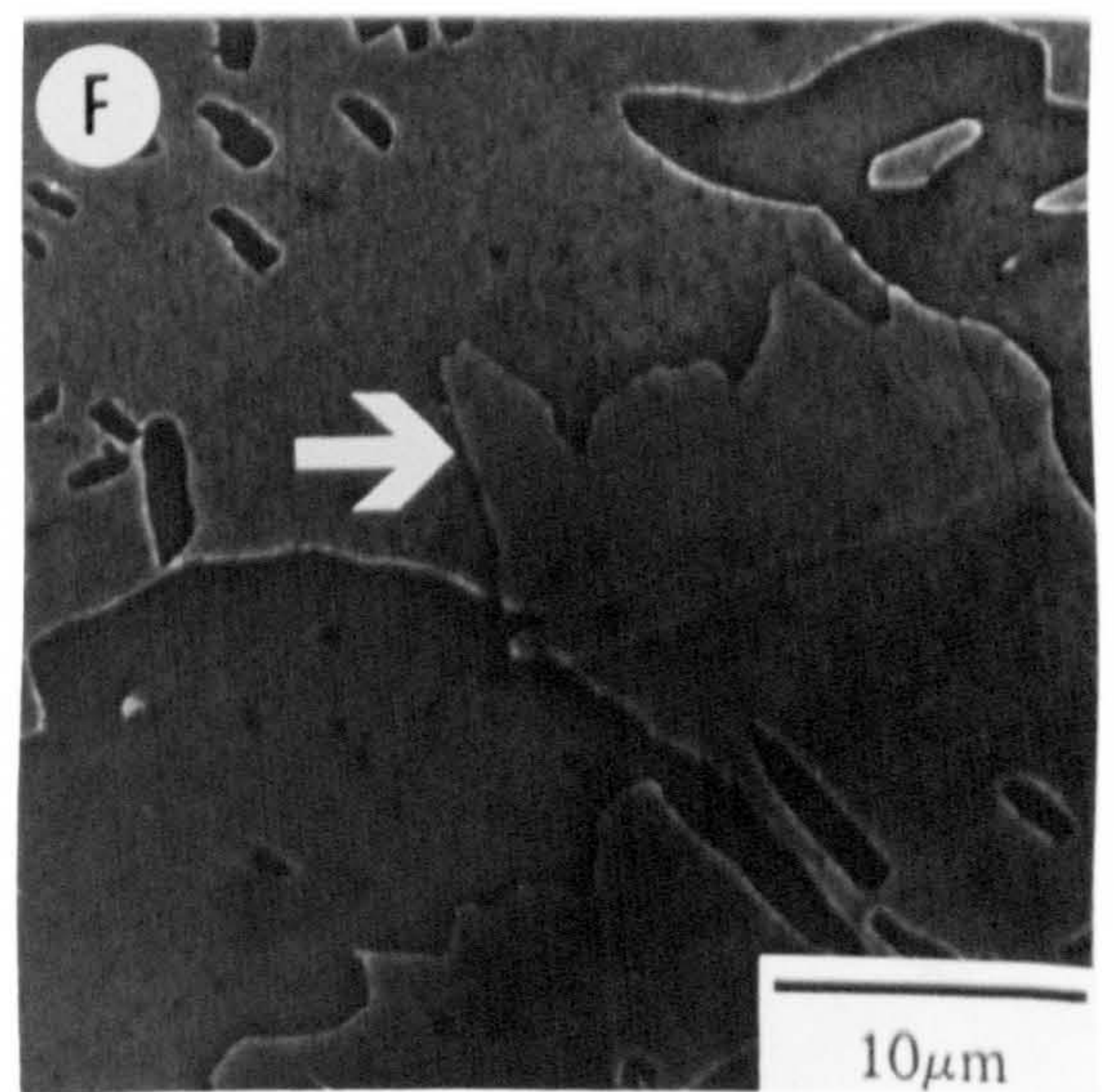
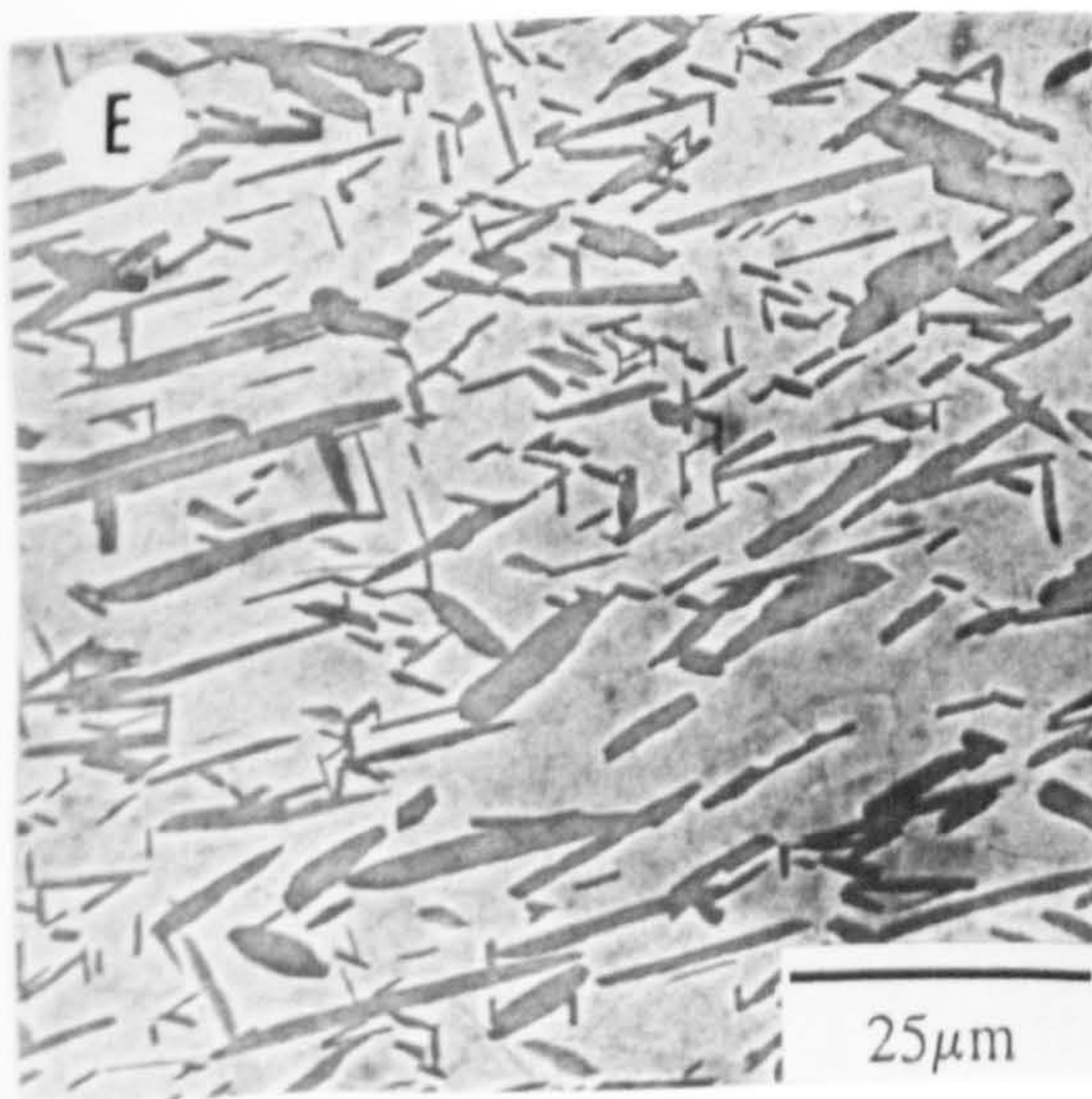
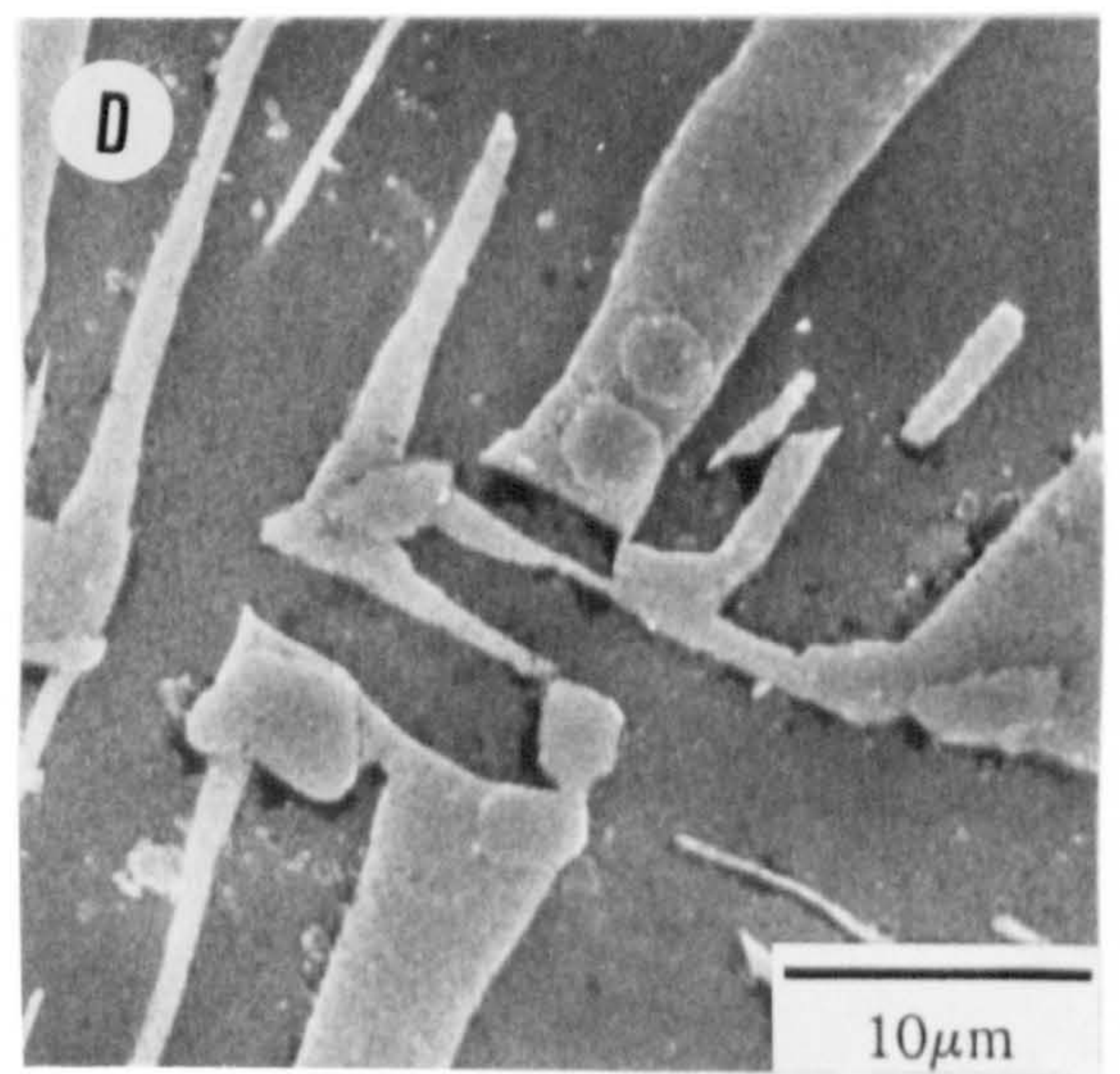
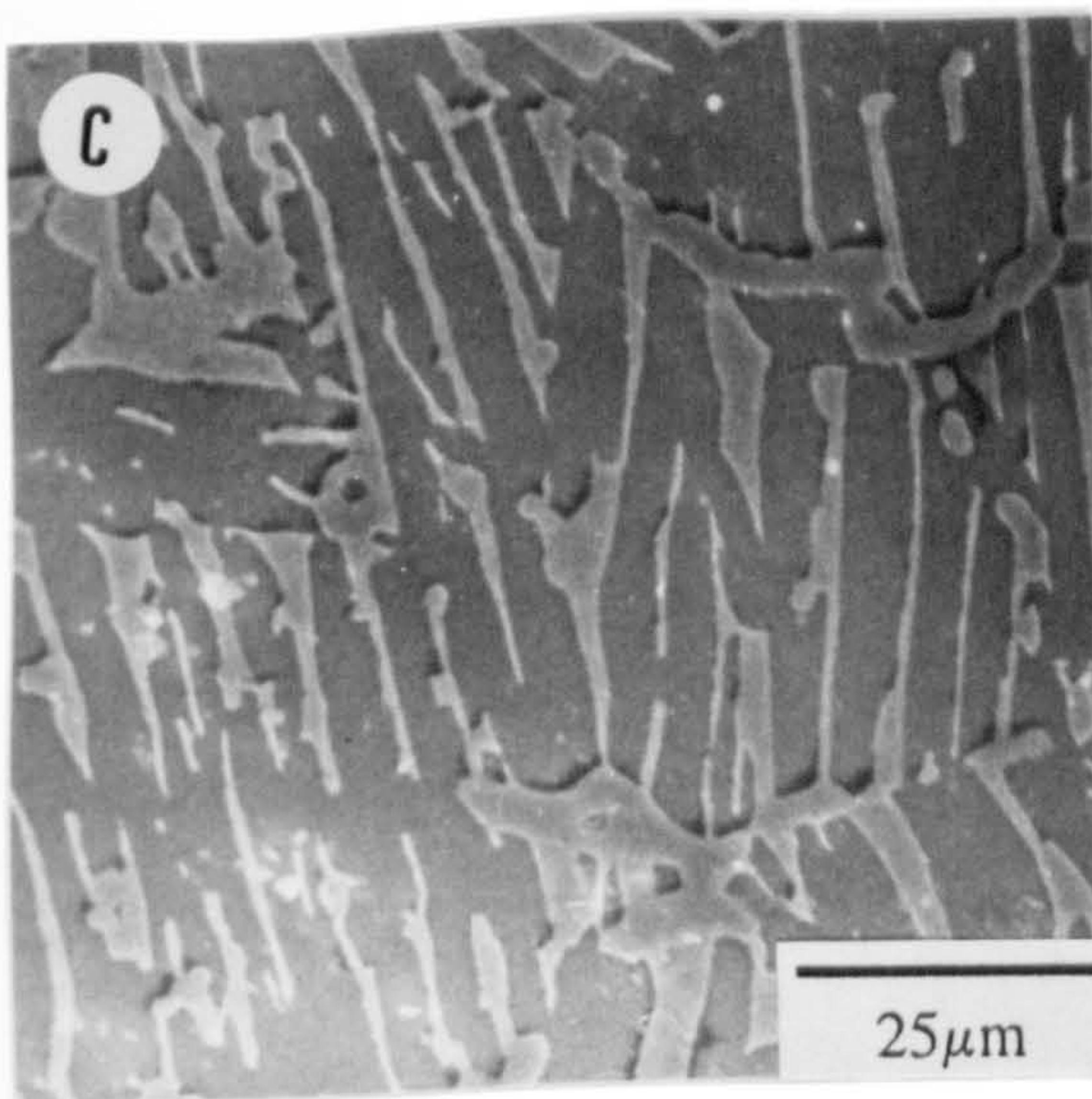
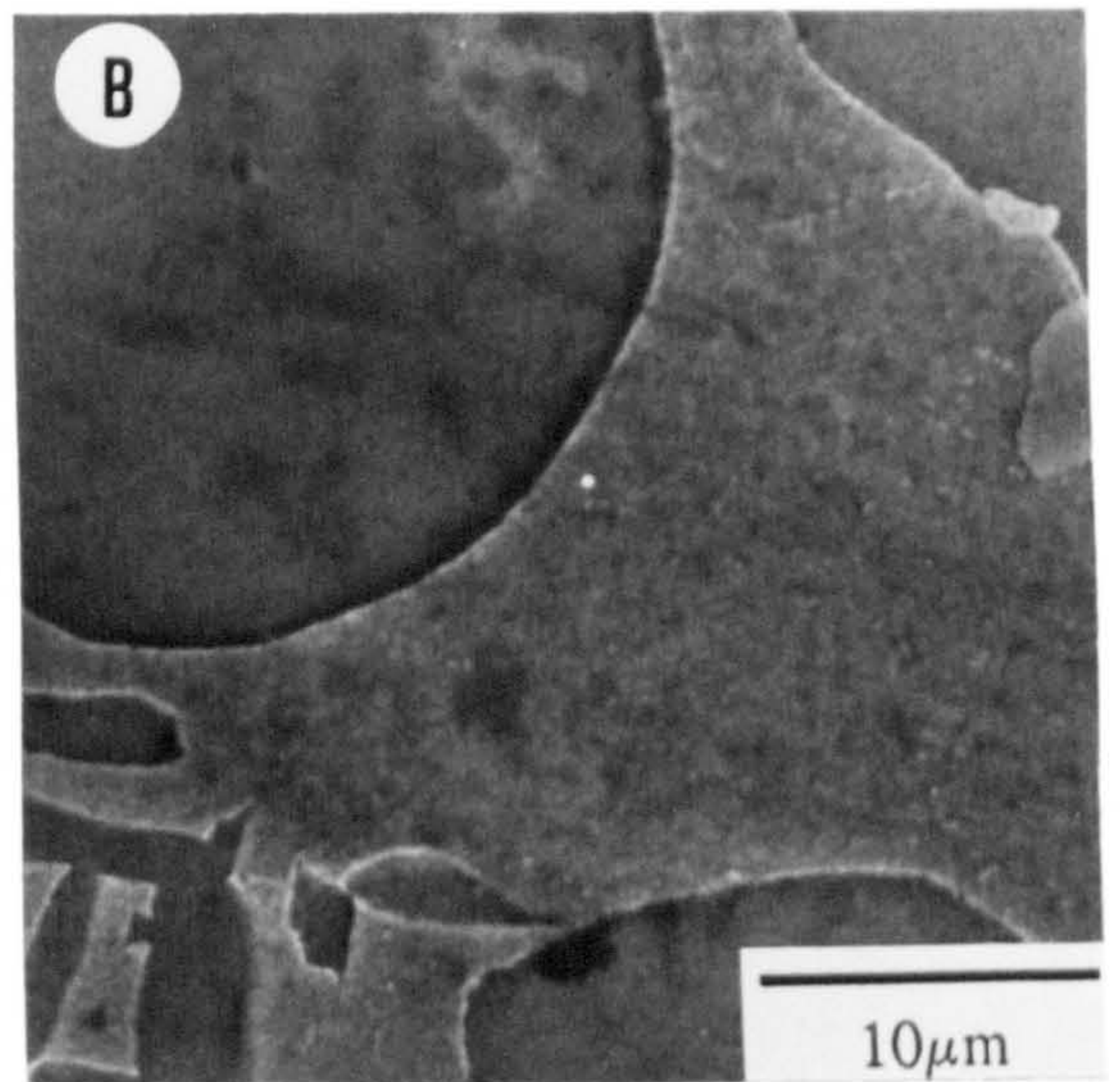
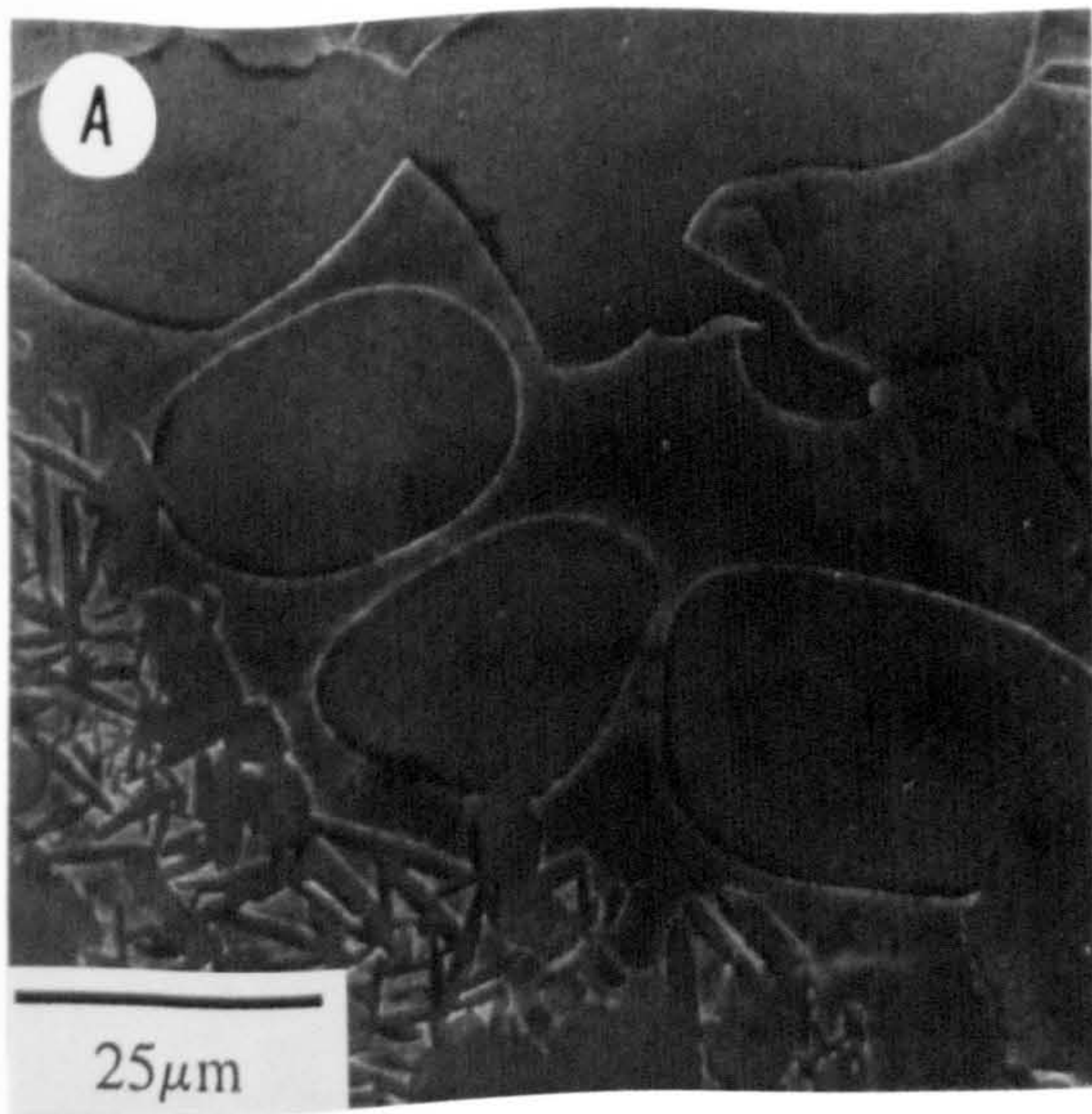
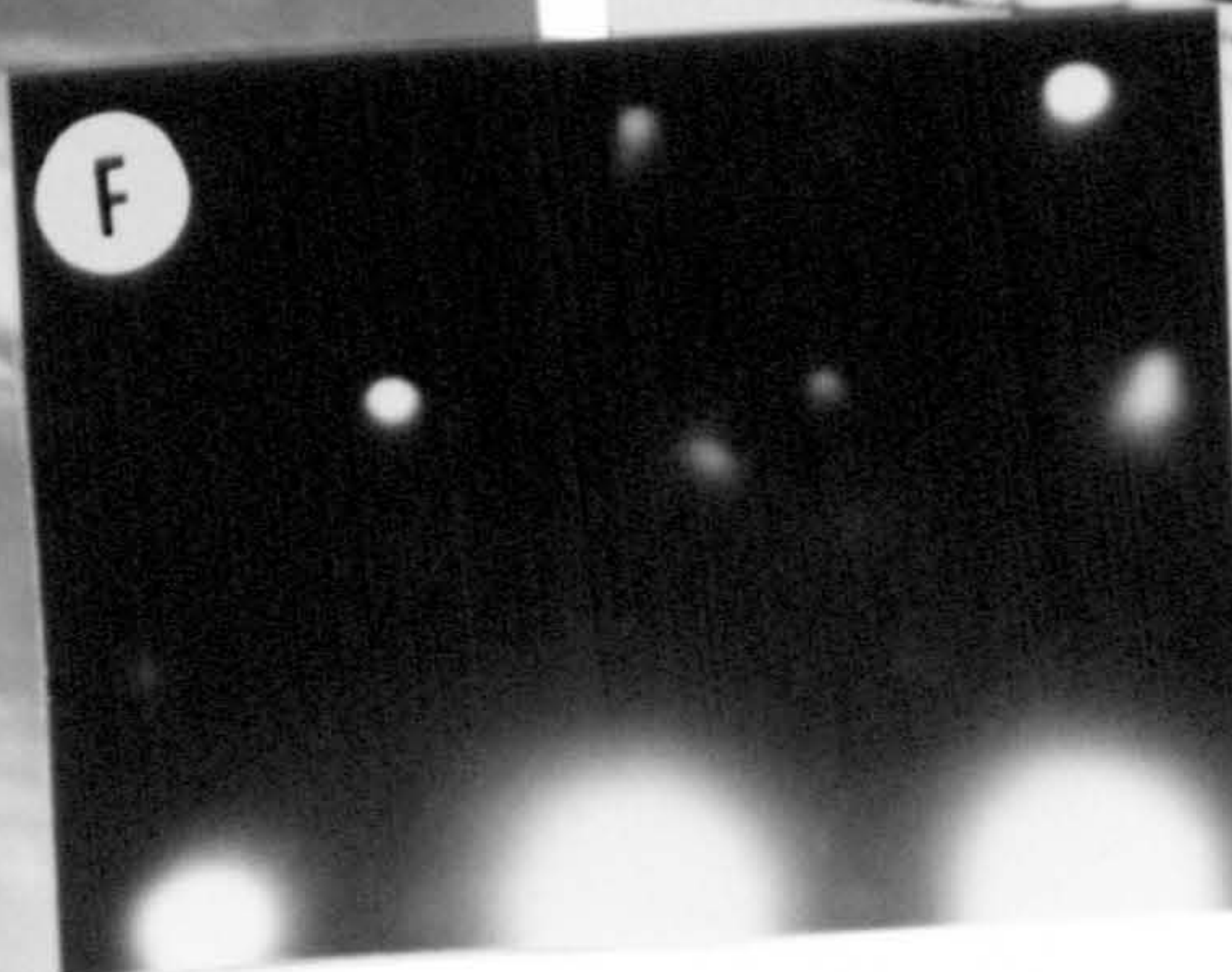
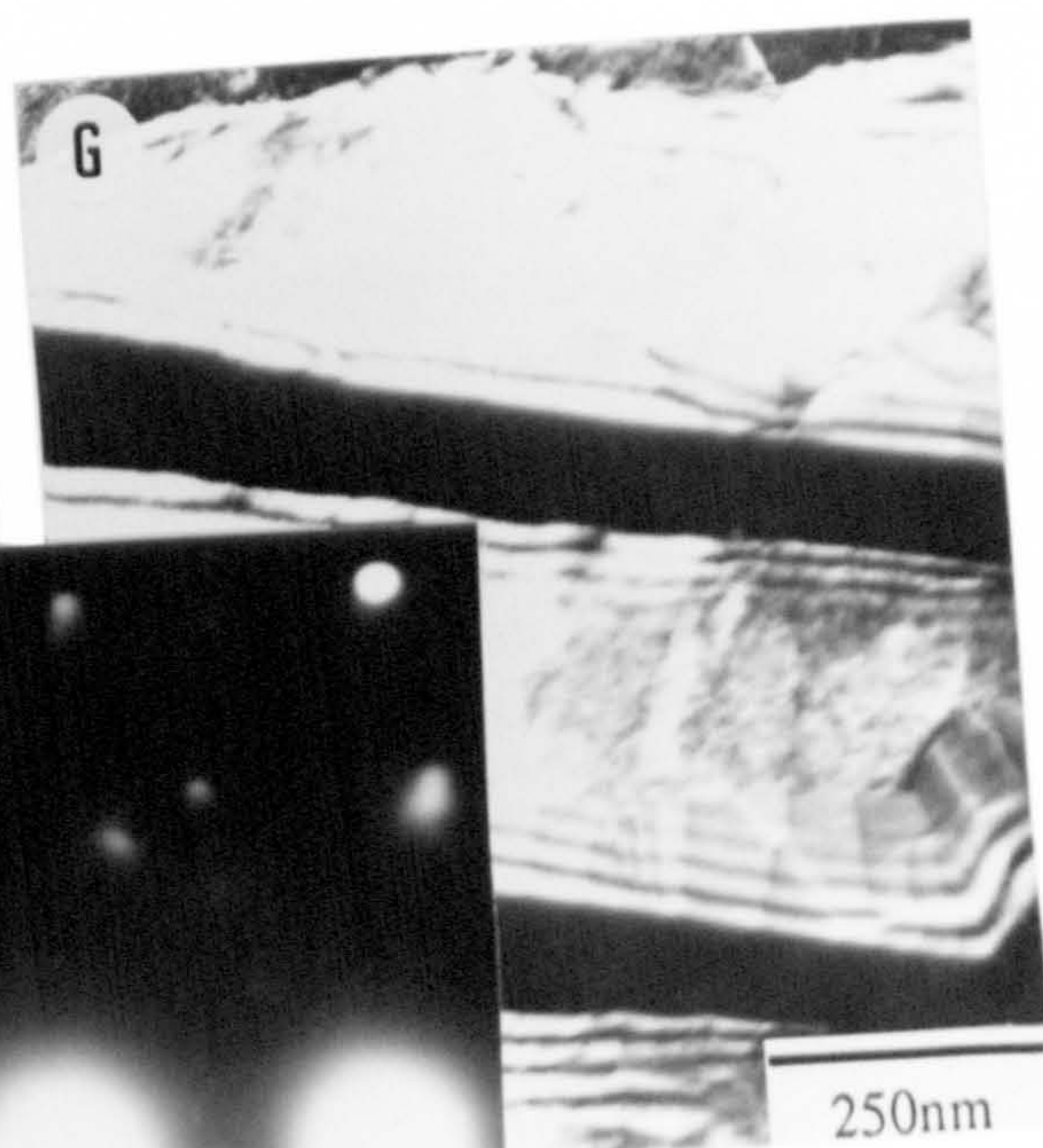
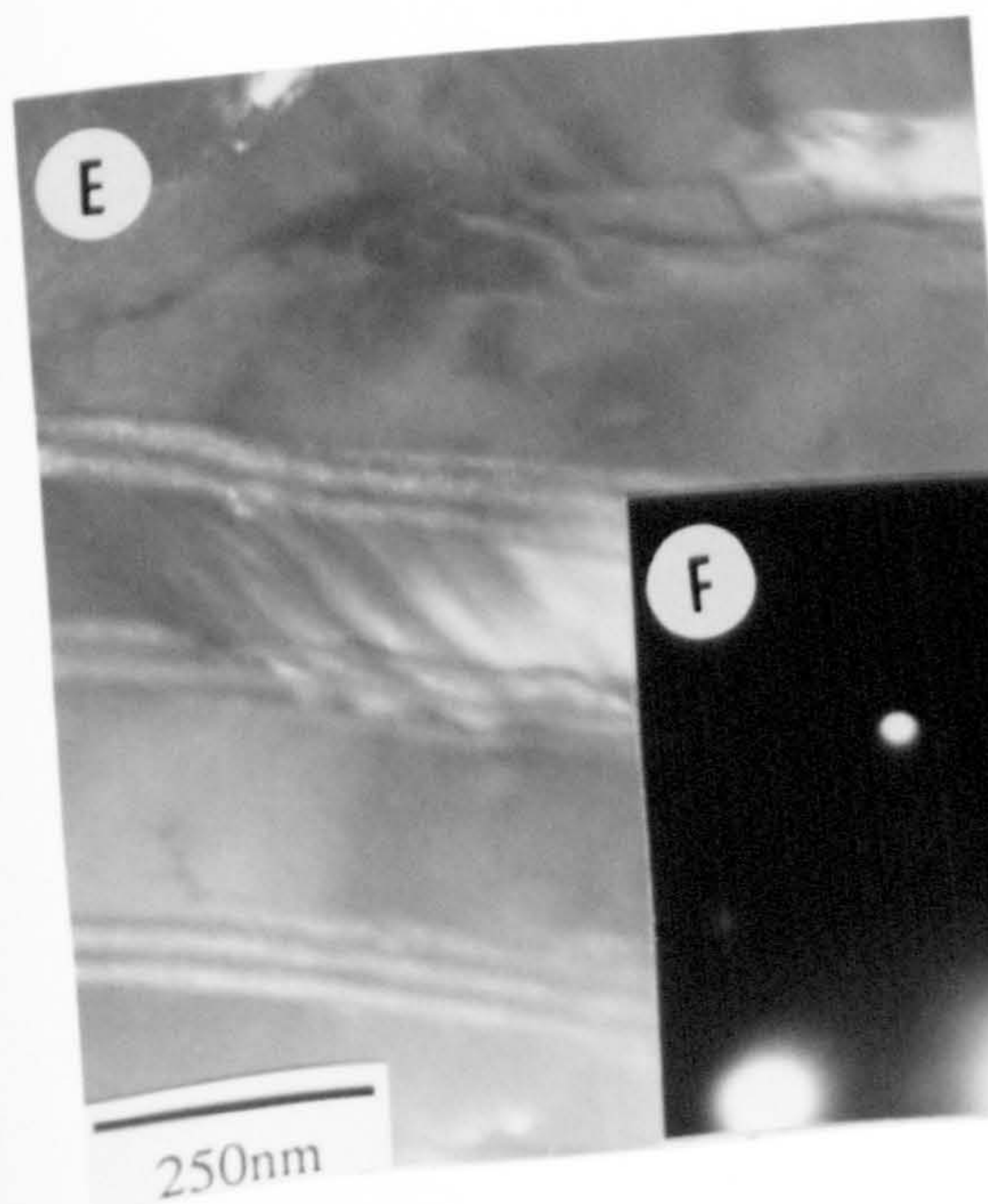
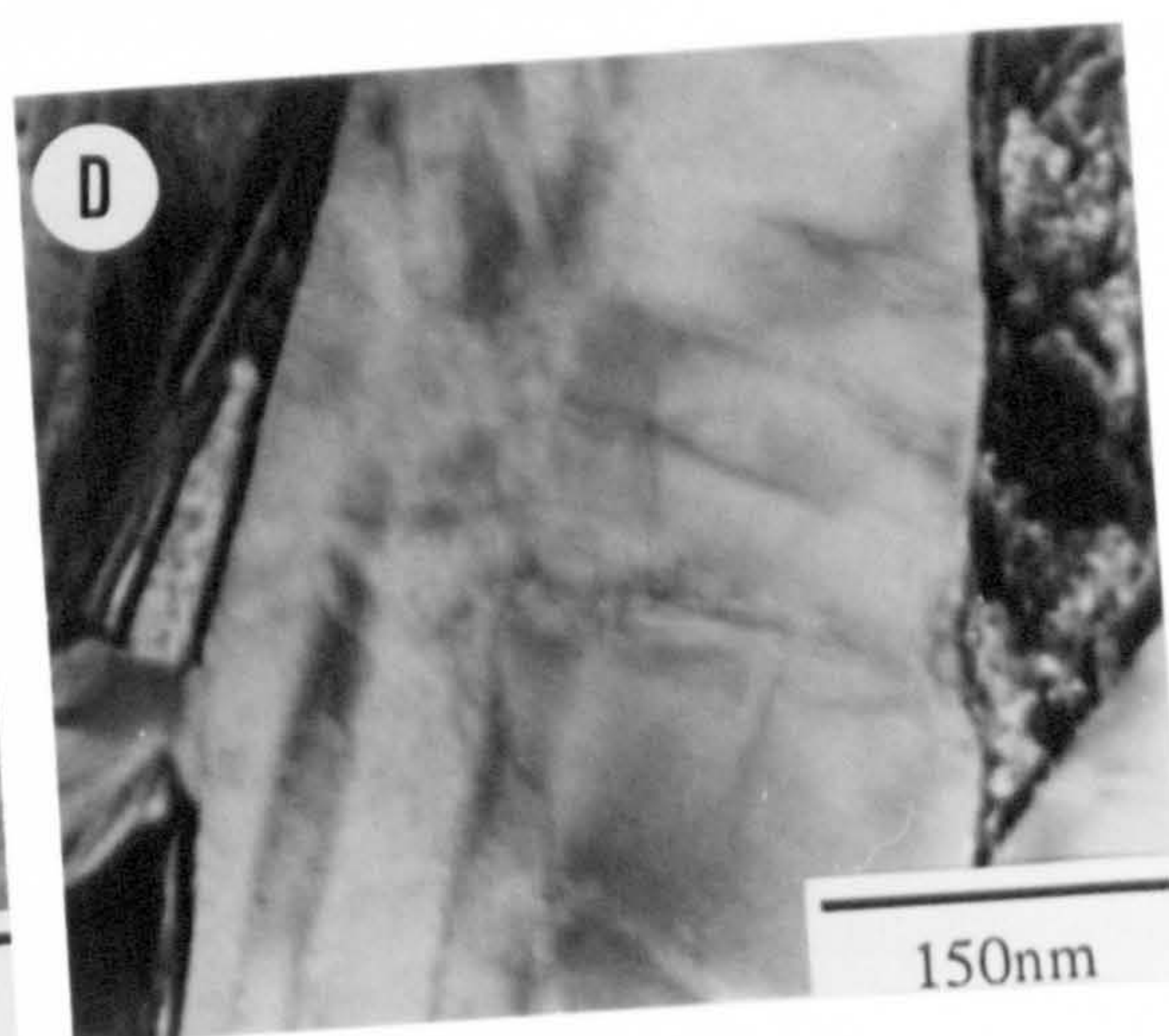
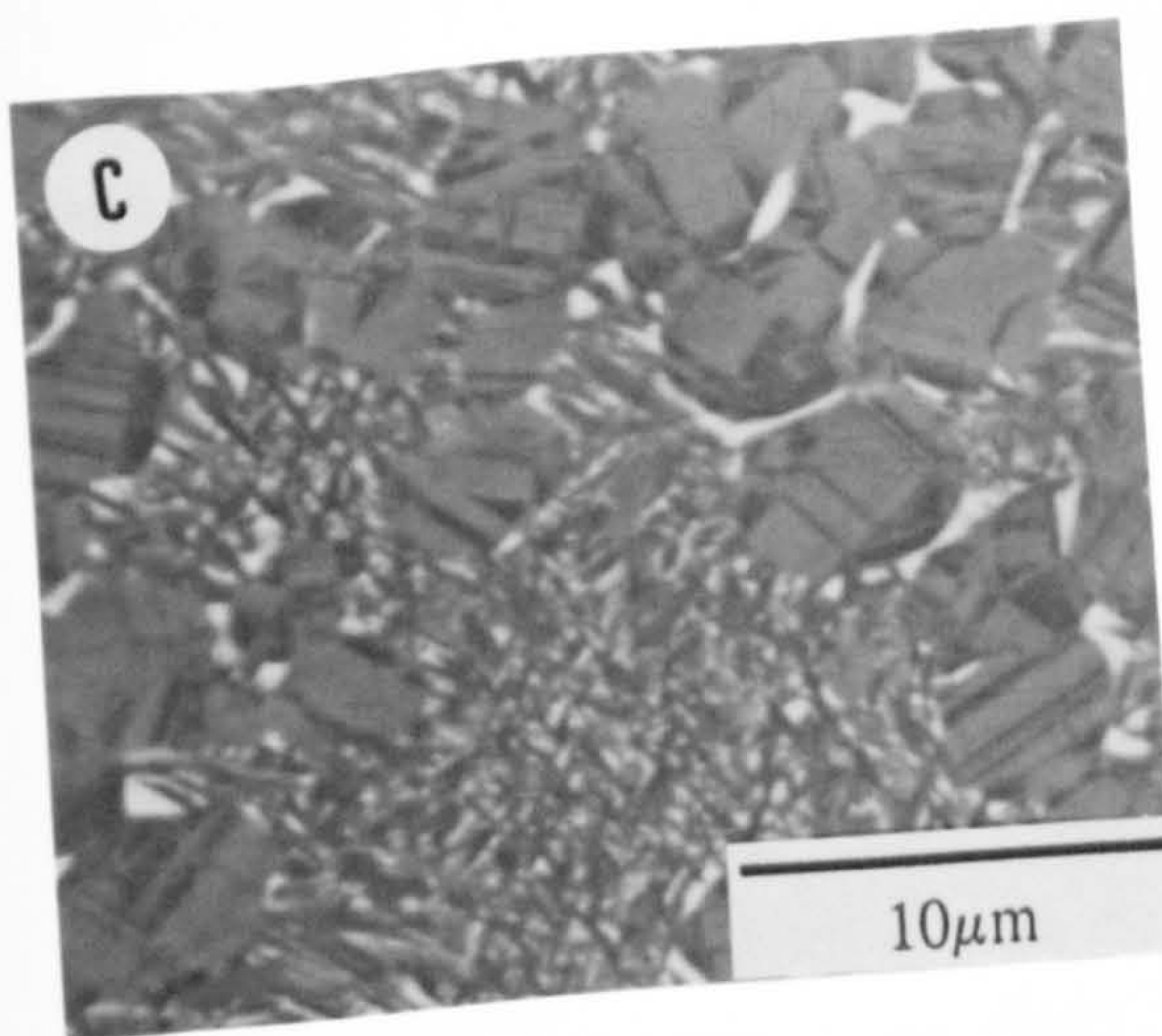
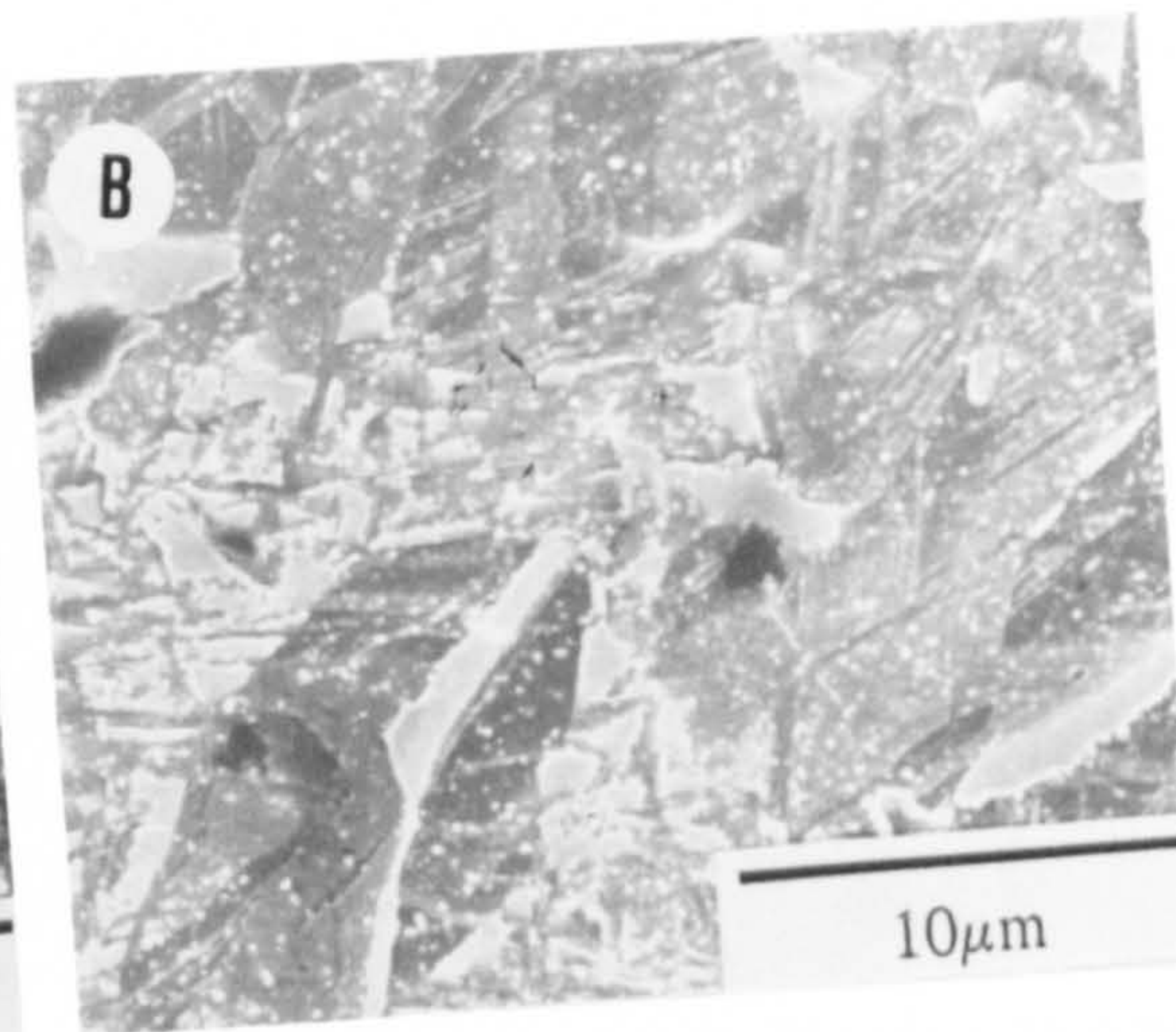
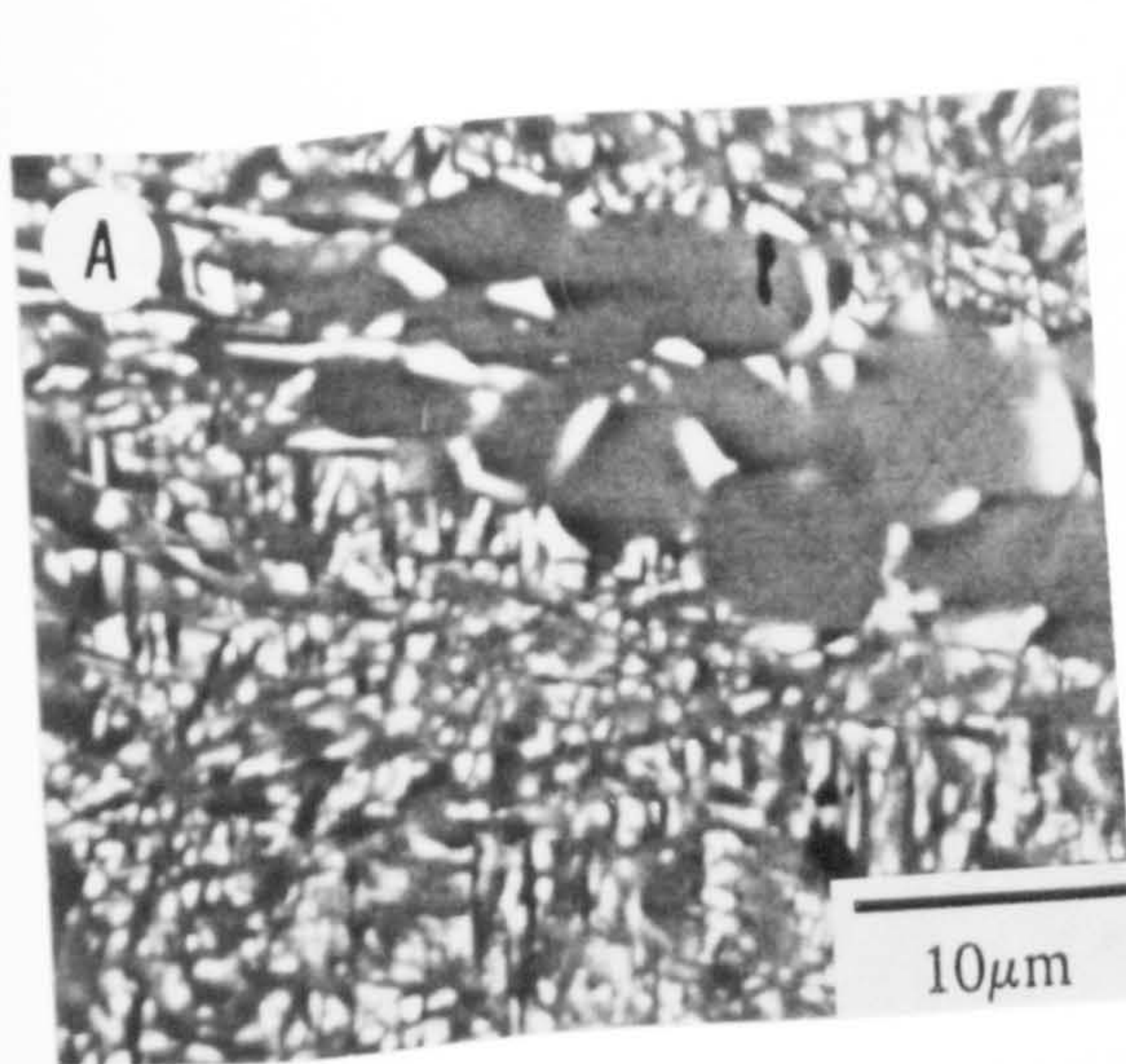


Figure 5.9

- (a) Alloy Ti-23-13-0.9 solution treated at 1270°C for 24 hrs, water quenched, then aged at 900°C for 168hrs, water quenched. This shows a BEI image of a grain boundary, with α_2 shown as the dark phase and β as the light phase.
- Alloy Ti-25-13-0.9 solution treated at 1270°C for 24 hrs, water quenched, then aged at 900°C for 168hrs, water quenched.
- (b) This shows a SE image of the alloy etched in Kroll's reagent. α_2 is shown as the darkest phase interspersed with a slightly lighter coloured phase (O) and β as the lightest phase.
- (c) This shows a BE image with α_2 shown as the darkest phase interspersed with a slightly lighter coloured phase (O) and β as the lightest phase.
- (d) TEM bright field micrograph showing three phase region.
- (e) Bright field image showing O grains within an α_2 grain with a small region of β at the top.
- (f) SADP showing β [110] and O [0001] orientations.



- (g) Darkfield image using the O diffraction spot.



The microstructure exists in a form such that the α_2 and O phases are found in parallel plates. This combined with the similarity in the composition and crystal structure leads to the idea that the two phase $\alpha_2 + \text{O}$ structure is formed by a decomposition of the α_2 phase. This is indicative of a transformation route as shown below:



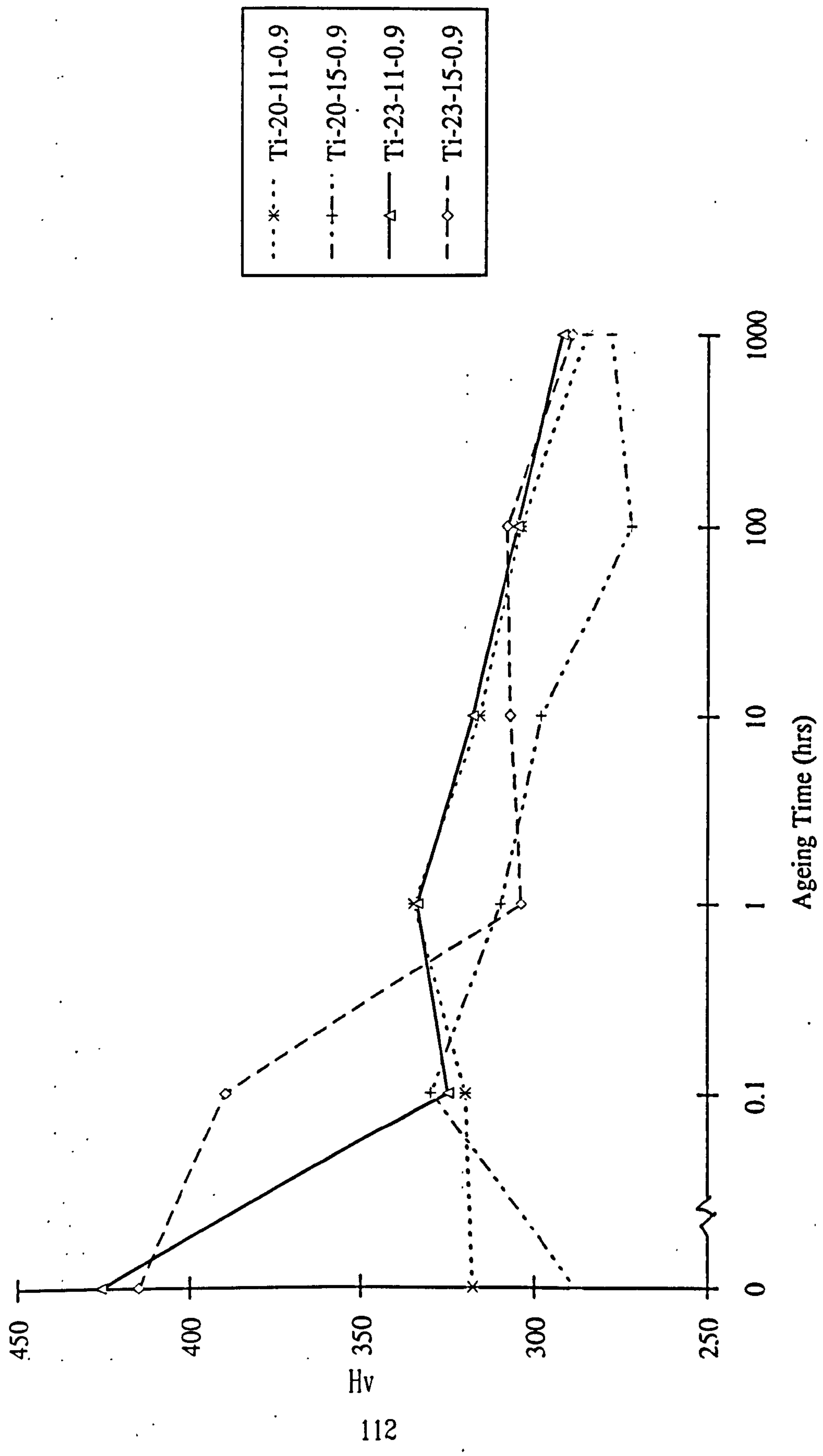
The similarity of the chemical composition of the α_2 and O phases indicates that should two distinct O phases exist, then the O phase found here is of the type identified by Banerjee et al [Ban87], and not the Ti_2AlNb phase identified by Bendersky [Ben89], as the transformation route which has been identified here is of a similar type to that of the Banerjee phase. The lattice parameters and chemical compositions are also closer to that of the Banerjee type phase.

Ageing curves (Figure 5.10) indicate that the hardness of the four main alloys converges after about 10 hrs, and shows no significant difference between the hardness of the $\alpha_2 + \beta$ alloys, and the three phase $\alpha_2 + \beta + \text{O}$ alloy. During the 900°C ageing process, no age hardening peak has been detected in the two phase alloys. The three phase Ti-20-15-0.9 alloy shows some increase in hardness to produce a peak after approximately 1 hour, which is likely to be the product of the O phase precipitation that does not occur in the other three alloys.

5.3.2. Alloys Containing More Than 0.9 at.% Silicon

When aged at 900°C the Ti-23-15.1.5 alloy exhibits a two phase structure. The matrix consists of the O phase, with a large distribution of silicide particles along the grain boundaries. Comparison of the microstructure (Figure 5.11a) with that found in the solution treated condition (Figure 4.5) indicates that the large silicide particles which are present, were formed during the solution treatment. These particles follow the boundaries of the large β grains which were present in the S.T. condition. The alloy also contains a more even distribution of finer particles of silicide, which, as can be seen in Figure 5.11b, are positioned along the O grain boundaries. It has not been possible to ascertain whether these silicides precipitated on the O grain boundaries, or if they acted to restrict the growth of the O phase. When

Figure 5.10. Ageing Curve for Alloys Heat Treated at 900°C



All hardness values are quoted to $\pm 2H_v$.

the microstructure of both the Ti-23-15-0.9 and Ti-23-15-1.5 alloys are compared, it is clear that the small change in alloy composition has a marked effect, moving the alloy from the three phase $\alpha_2 + \beta_0 + O$ field into the two phase $O + Ti_3Si_3$ field. A comparison of the compositions of the O phase in the Ti-23-15-0.9 alloy and the bulk composition in the Ti-23-15-1.5 alloy (Ti-23.4-16.4-1.4 vs. Ti-23-15-1.5) shows that the two compositions are very similar, indicating that the small change in composition in the system can have a marked effect on the final structure. It also shows the O phase stabilisation that the addition of silicon has on these alloys.

As would be expected in an alloy with a lower niobium content, the microstructure exhibited by Ti-23-11-1.5 shows a reduction in the amount of β (or O) phase stabilising effect which is caused by the reduction in the amount Nb in the alloy. This alloy consists of a large number of α_2 grains surrounded by transformed β (i.e. O) (see Figure 5.11e). There is markedly more silicide present. This is in the form of spheroidal particles which are distributed throughout the matrix, in contrast with the unevenly shaped grain boundary particles shown in Figure 5.11f. The prior silicide particles on the original grain boundaries show a large number of cracks around them (Figure 5.11f), which are likely to be extremely detrimental to the mechanical properties of the material. When the silicon content is increased further (in the Ti-23-11-3 alloy), the most obvious effect is to produce an increase in the volume fraction of the silicide particles present (Figure 5.11c). A more detailed examination (Figure 5.11d) shows more clearly the three phases present.

5.4. 800°C Aged Microstructure.

5.4.1. Low Silicon Content Alloys.

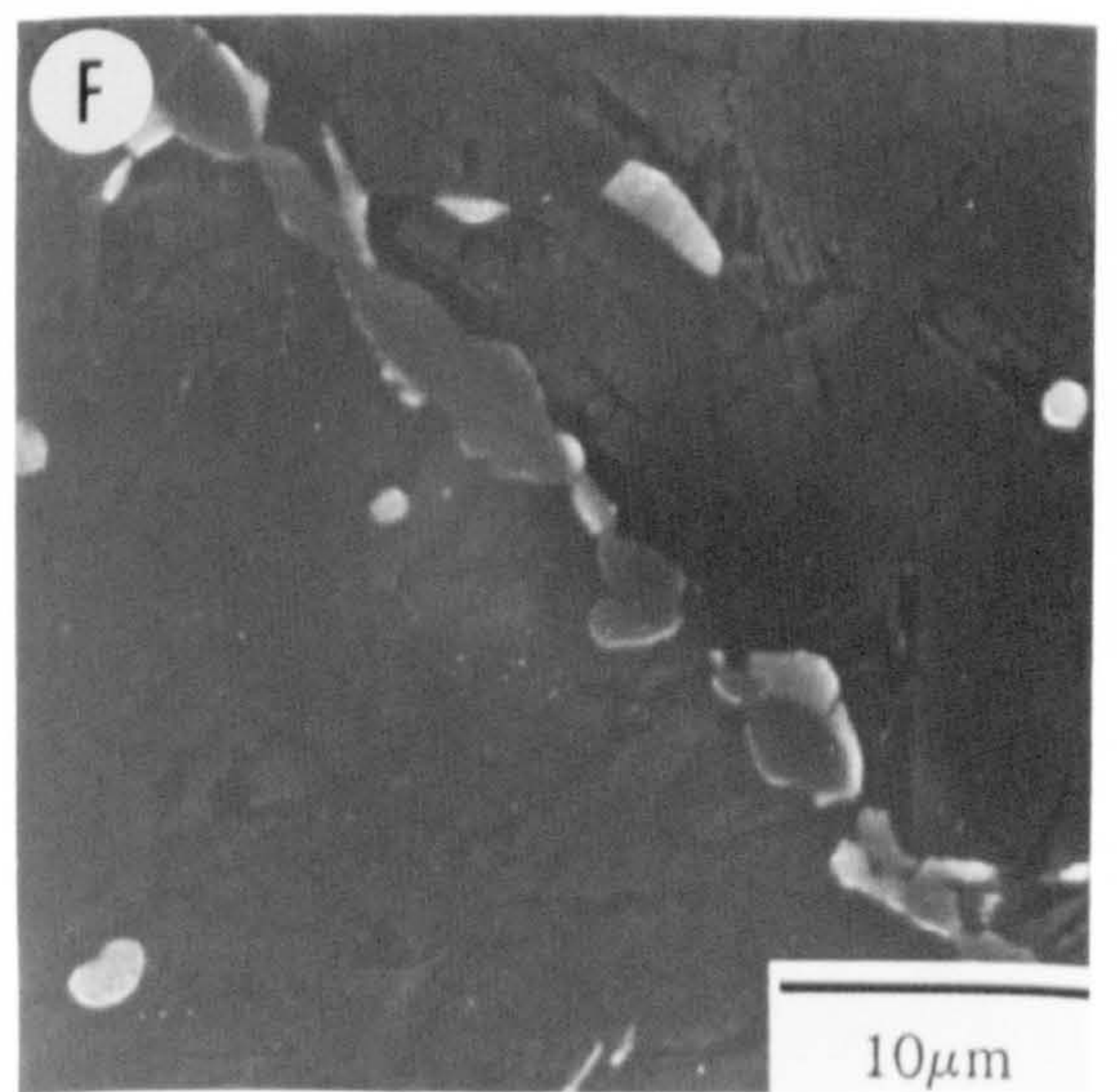
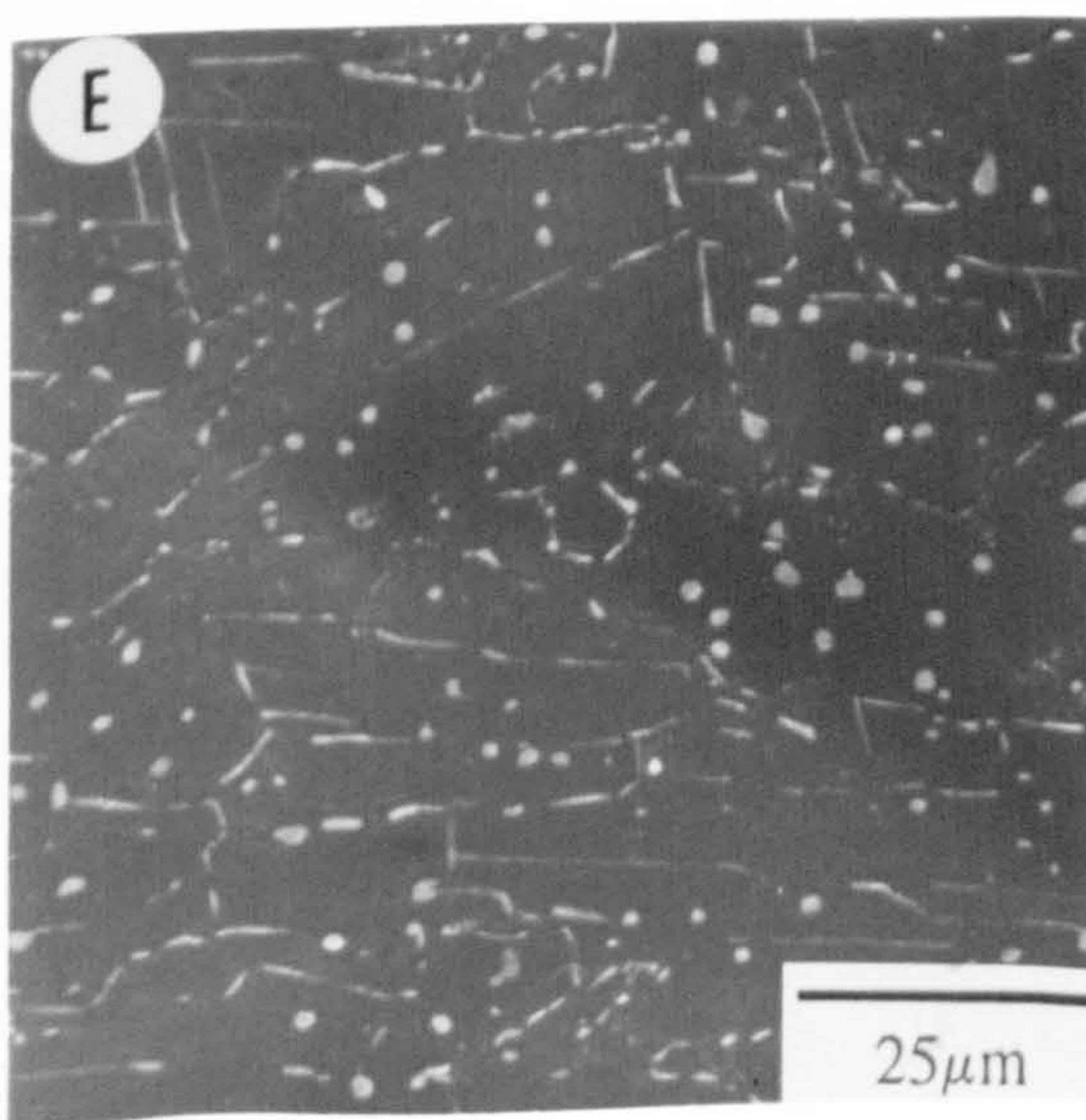
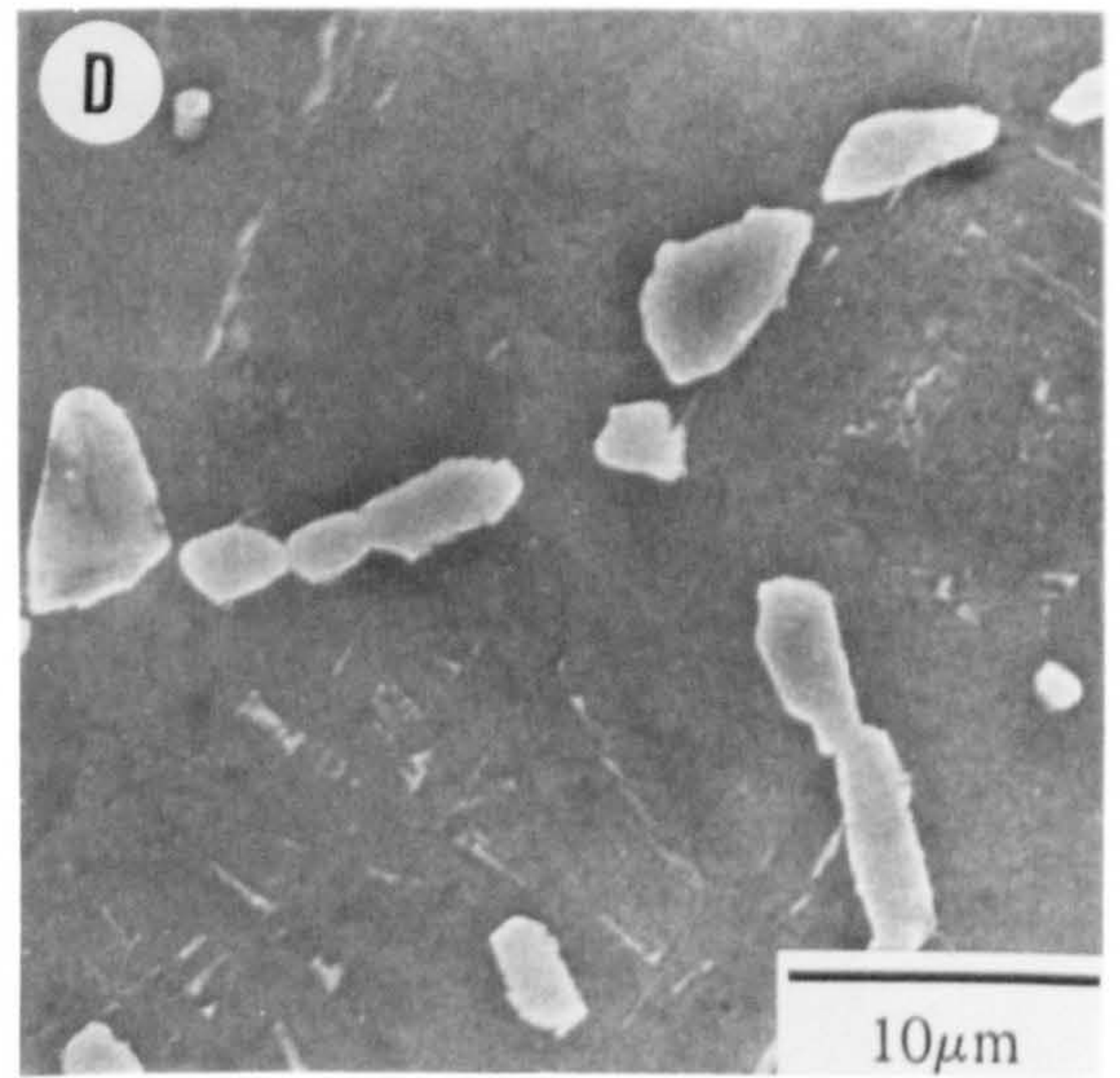
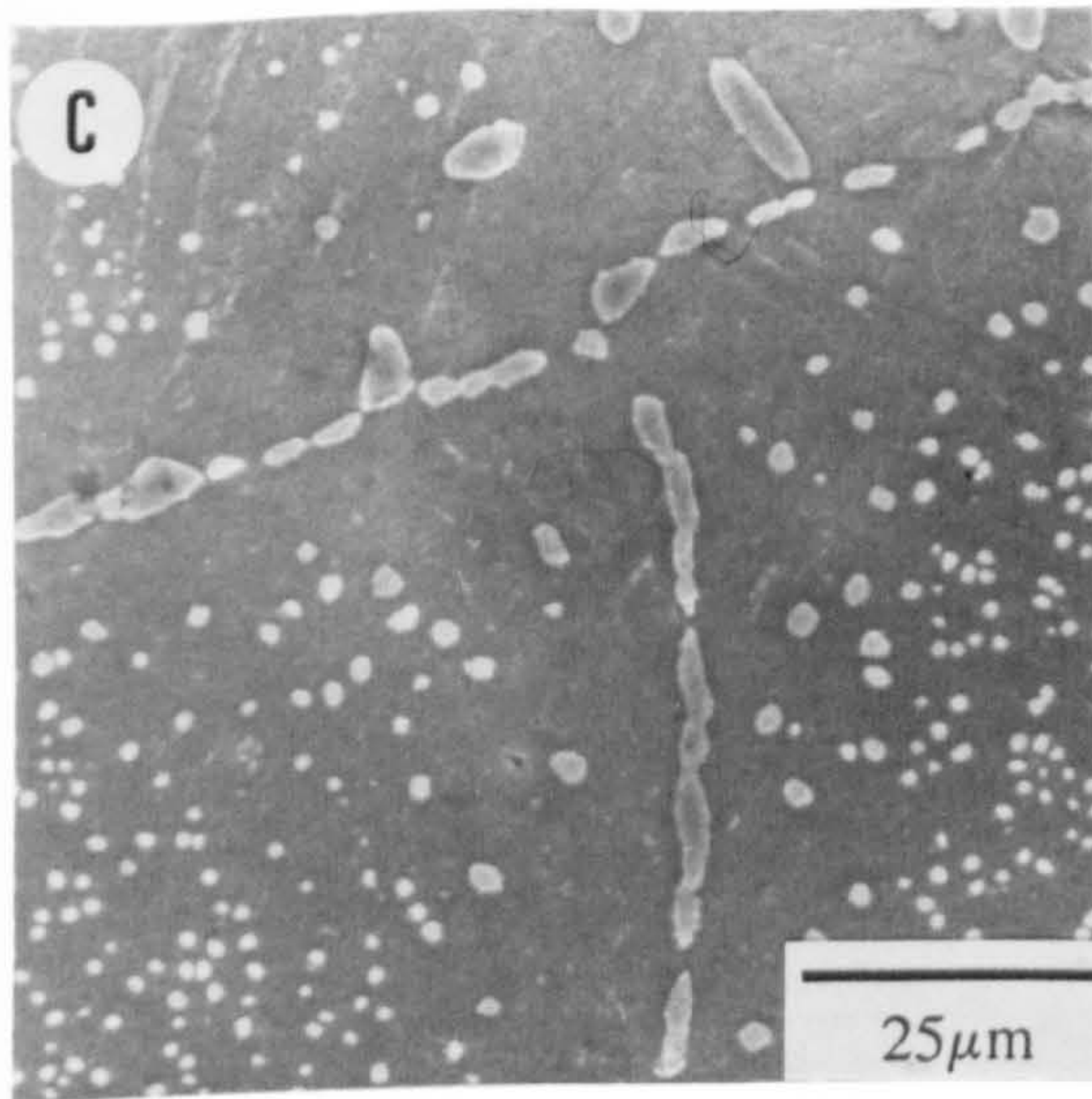
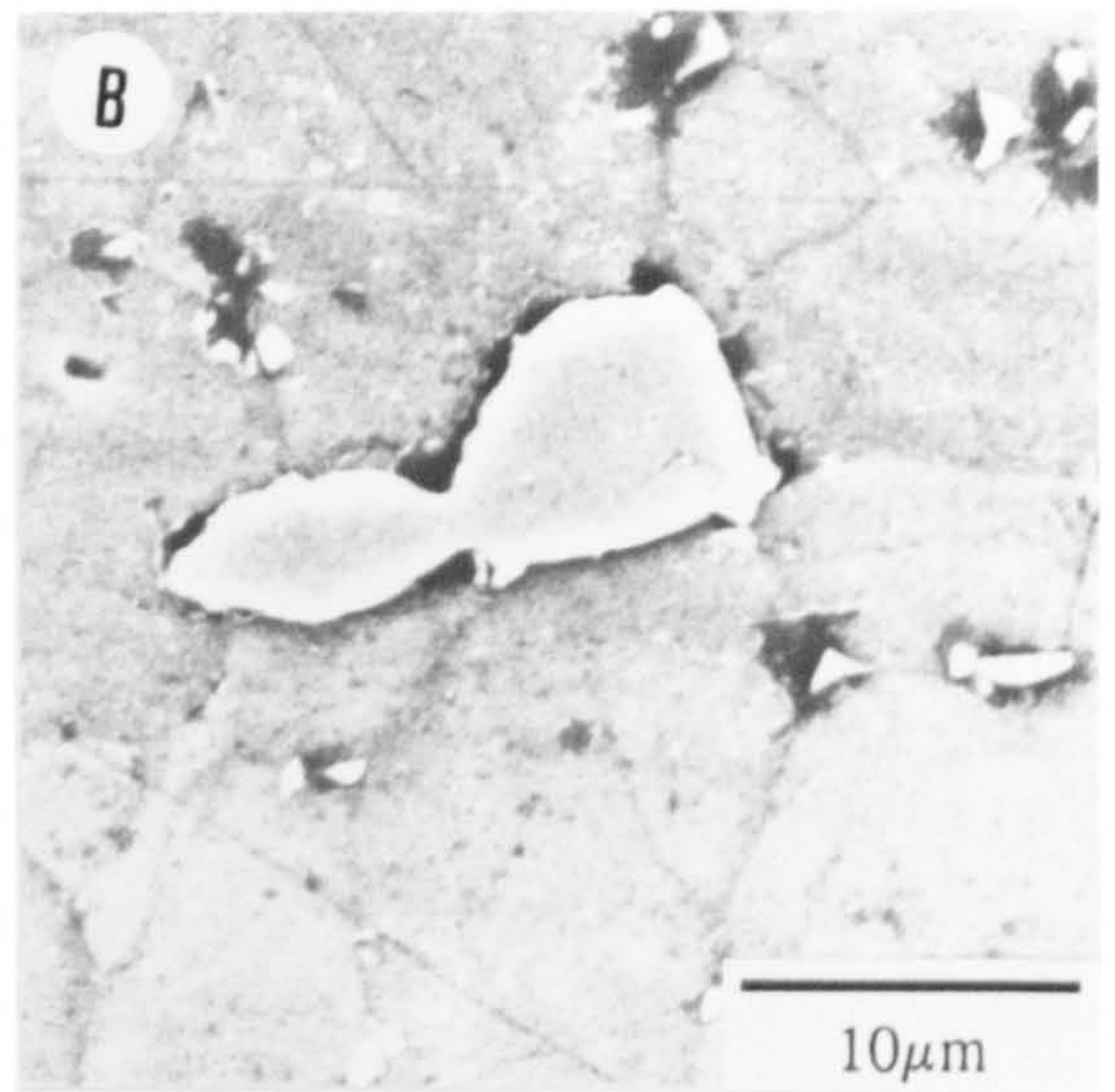
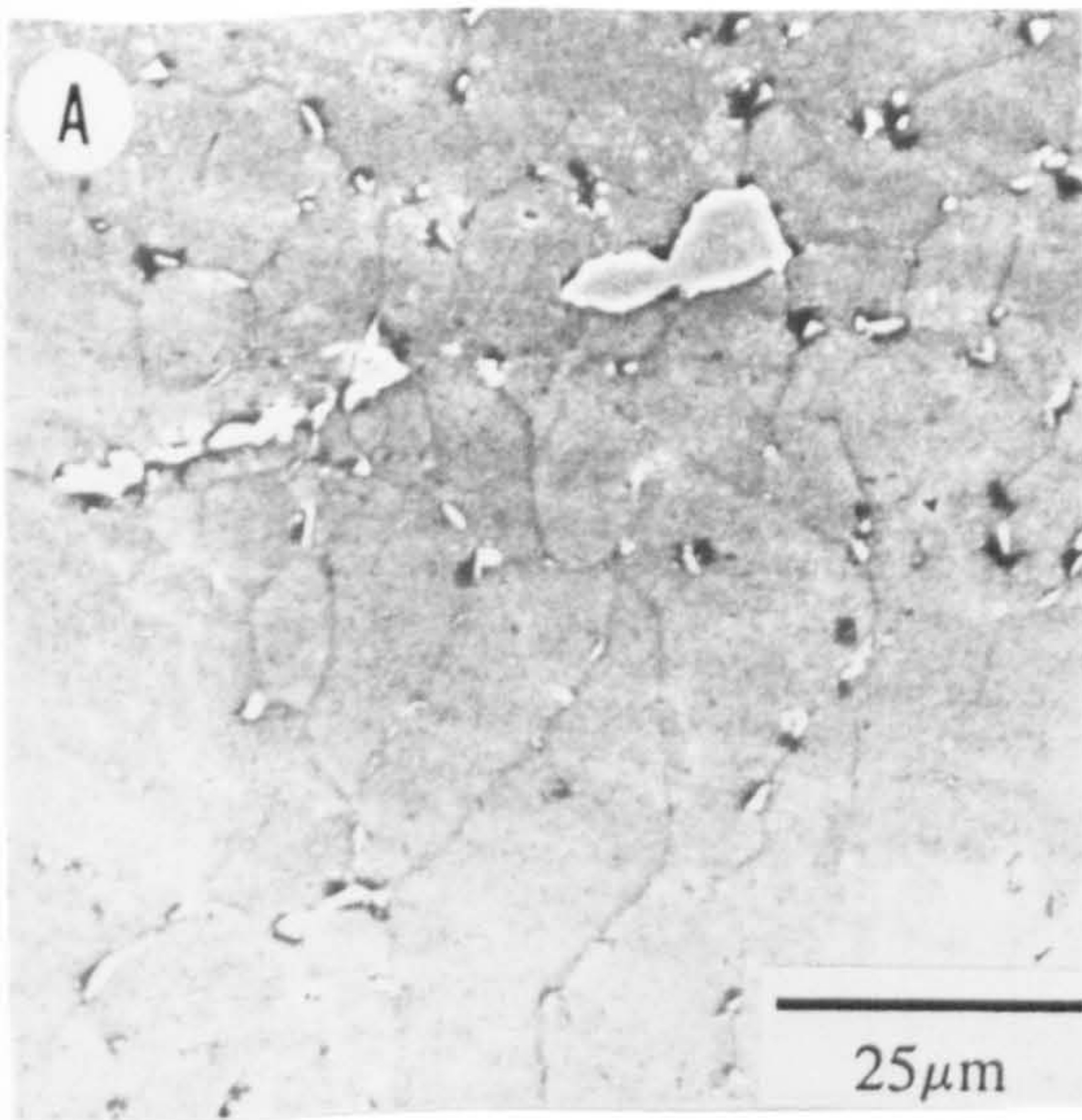
When aged at 800°C, the microstructure passes through two distinct forms. Initially the 'as quenched' microstructure is transformed by the precipitation of a fine distribution of α_2 platelets, which can be seen clearly in the Ti-20-11-0.9 alloy after 1hr ageing (Figure 5.12a). The two phases are identified as α_2 and β_0 in the diffraction pattern shown in Figure 5.12b. This $[001]\beta_0$ zone axis diffraction pattern confirms the conventional Burgers orientation relationship between the two phases. It also indicates by the presence of $(001)\beta$ diffraction spots that the β_0 phase is still

Figure 5.11.

Ti-23-X-Y alloys showing solution treated and then 900°C /168hrs aged microstructure.

SE images of all alloys mechanically polished, etched in Kroll's Reagent.

- (a) Ti-23-15-1.5. This shows the distribution of two morphologies of silicides. Firstly the large blocks at the top left, which were produced during the solution treatment, and secondly the much finer particles along the grain boundaries. The matrix is formed of α grains.
- (b) Detailed view of grain boundaries showing both types of silicide particle.
- (c) Ti-23-11-3. Microstructure shows α_2 platelets (darker) within a small amount of transformed β . Microstructure shows increased β stabilising effect of the added silicon. The two types of silicide shown in (a) are clearly visible in this alloy, with a large regular distribution of fine Ti_5Si_3 particles. Note that there is also a precipitate-free zone around the prior grain boundaries which are marked by the larger silicides.
- (d) Detailed view of (c) showing grain boundary silicides.
- (e) Ti-23-11-1.5. Microstructure shows α_2 (dark) plates in a background of transformed β with an even silicide distribution.
- (f) Detail of the silicide on grain boundary between two large silicide grains. Also visible are a range of surface cracks, particularly around the precipitates.



ordered. Dark field micrographs (Figures 5.12c & d) using $(0\bar{1}10)\alpha_2$ and $(\bar{1}10)\beta_0$ illumination clearly identify the two phases.

After 1000 hrs, the microstructure has changed markedly. The α_2 platelets now have a more rounded shape (Figure 5.13a), and are surrounded by transformed β_0 (i.e. O) which appears to contain a large concentration of defects (Figure 5.13f), the microstructure also now contains discrete O grains. The diffraction pattern shown in Figure 5.13b shows intense diffraction spots from both the α_2 and O phases as well as a faint diffuse area where β spots would be expected. Due to the low intensity of the β diffraction spots it is not possible to determine if the β exists in the alloy, or whether the low intensity maxima are due to some other cause. Figures 5.13c&d show an α_2 grain in bright and dark field illumination. The grains of α_2 are considerably larger than those of the O phase, as can be seen in Figure 5.13e, which also shows the relatively low defect level present. Thin foil EDS analysis of the alloy (Table 5.4) shows that the composition of the O phase is markedly different from that of the O phase which is found after ageing at 900°C (Table 5.3.), and is indeed closer to that of the β_0 phase at 900°C, as would be expected from the transformation route described above. This is indicative that on equilibrium cooling from the $\alpha_2 + \beta_0 + O$ phase field into the $\alpha_2 + O$ field, the β_0 and O phases combine to form a phase of intermediate composition. At this temperature, the Ti + Nb : Al + Si ratio does not follow stoichiometry in alloys heat treated in this way.

Phase	at.% Ti	at.% Al	at.% Nb	at.% Si
α_2	68.0	22.1	9.9	0.9
O	61.9	12.2	25.9	0.9

Table 5.4. Phase Chemistry in Ti-20-11-0.9 Aged at 800°C/1000 hrs.

Ageing curves for the four base alloys (Figure 5.14.) show age hardening peaks at 0.1hrs for 23 at.% Al alloys, and at 1 hr for the lower Al alloys. Due to the combined effect of particle coarsening and the complex transformations taking place, it is difficult to ascertain whether the presence of the O phase in the alloy after long term ageing has any marked effect on the hardness of the material.

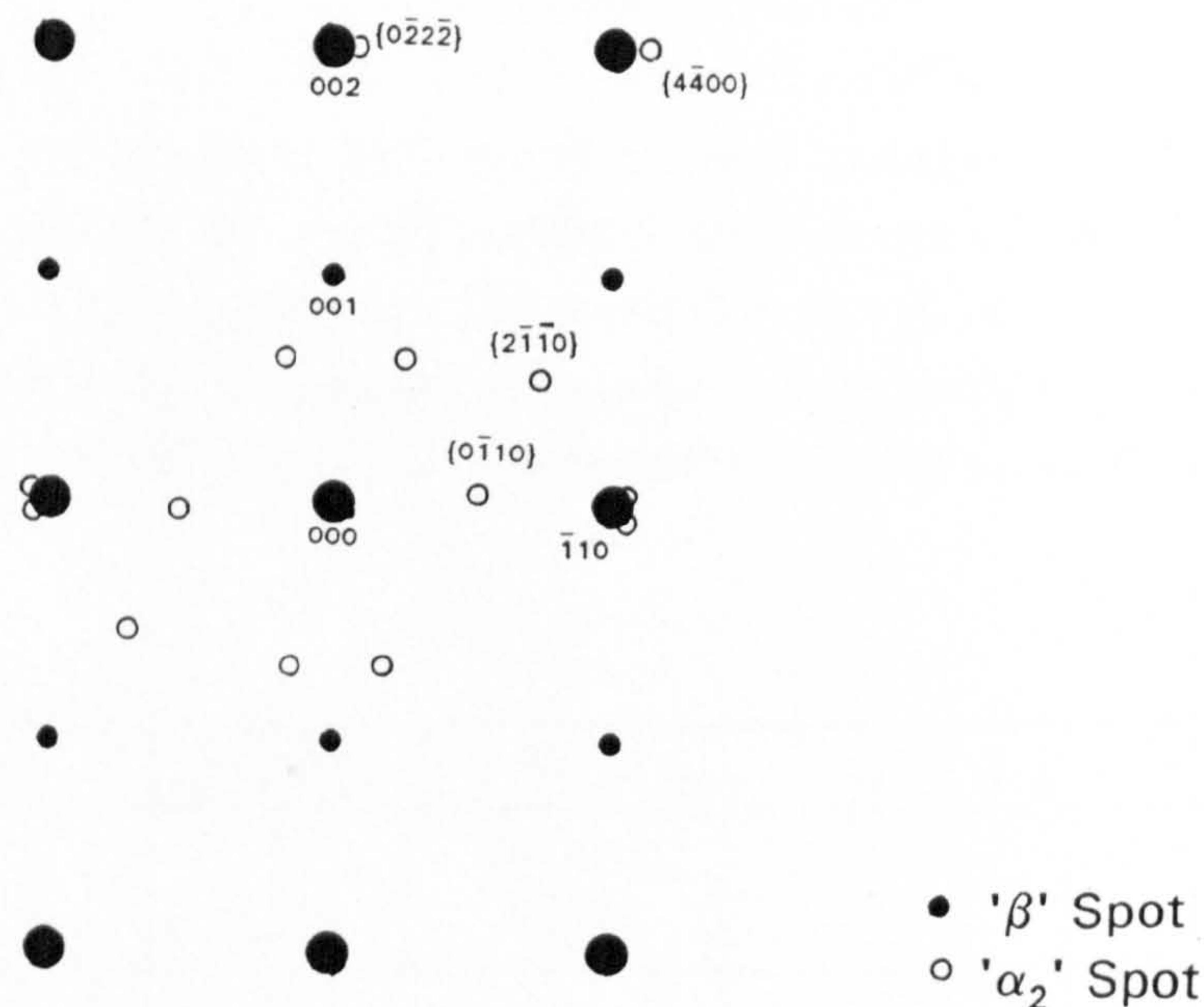
Figure 5.12.

Alloy Ti-20Al-11Nb-0.9Si (at.%), solution treated at 1270°C/24 hrs, water quenched, then aged at 800°C/ 1 hr, w.q.

TEM foils, electrochemically thinned in 7 vol.% H₂SO₄ in CH₃OH.

- (a) Bright field micrograph of α_2 platelets (bright) in small amount of β matrix (dark).
- (b) SADP with $[110]_{\beta_0}$ zone axis showing both α_2 and β_0 spots (see key). The presence of an $(001)_{\beta}$ spot indicates that the β is ordered B2 (i.e. CsCl structure) in this condition.

$$L\lambda = 6 \text{ cm}\text{\AA}$$



- (c) Dark field micrograph from $(0\bar{1}10)_{\alpha_2}$ spot showing α_2 platelets brightly, and indicating from the darker platelets at the top of the micrograph that more than one variant of α_2 has been precipitated.
- (d) Dark field micrograph from $(\bar{1}10)_{\beta}$ spot showing a bright background with a fine particulate distribution within.

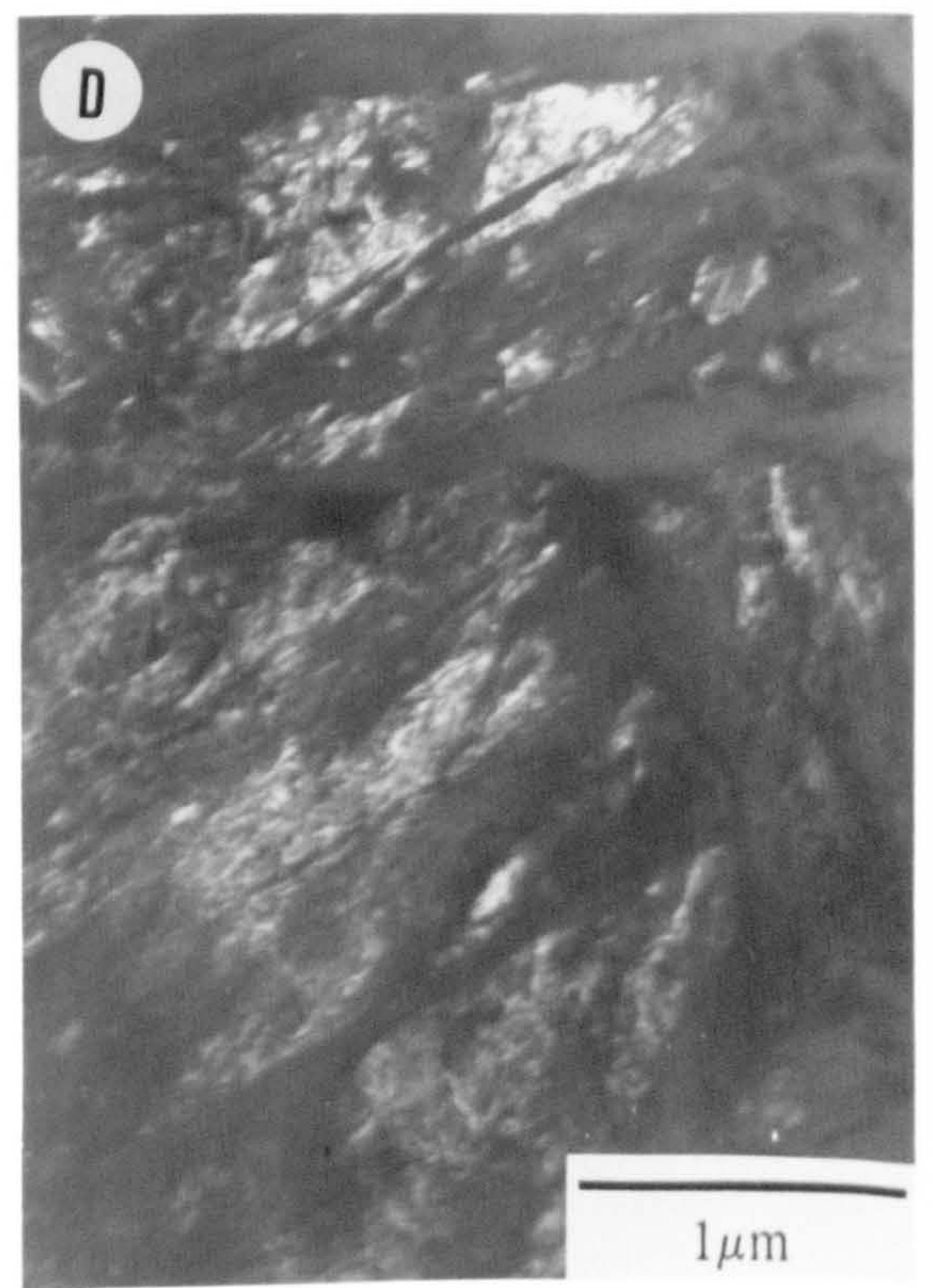
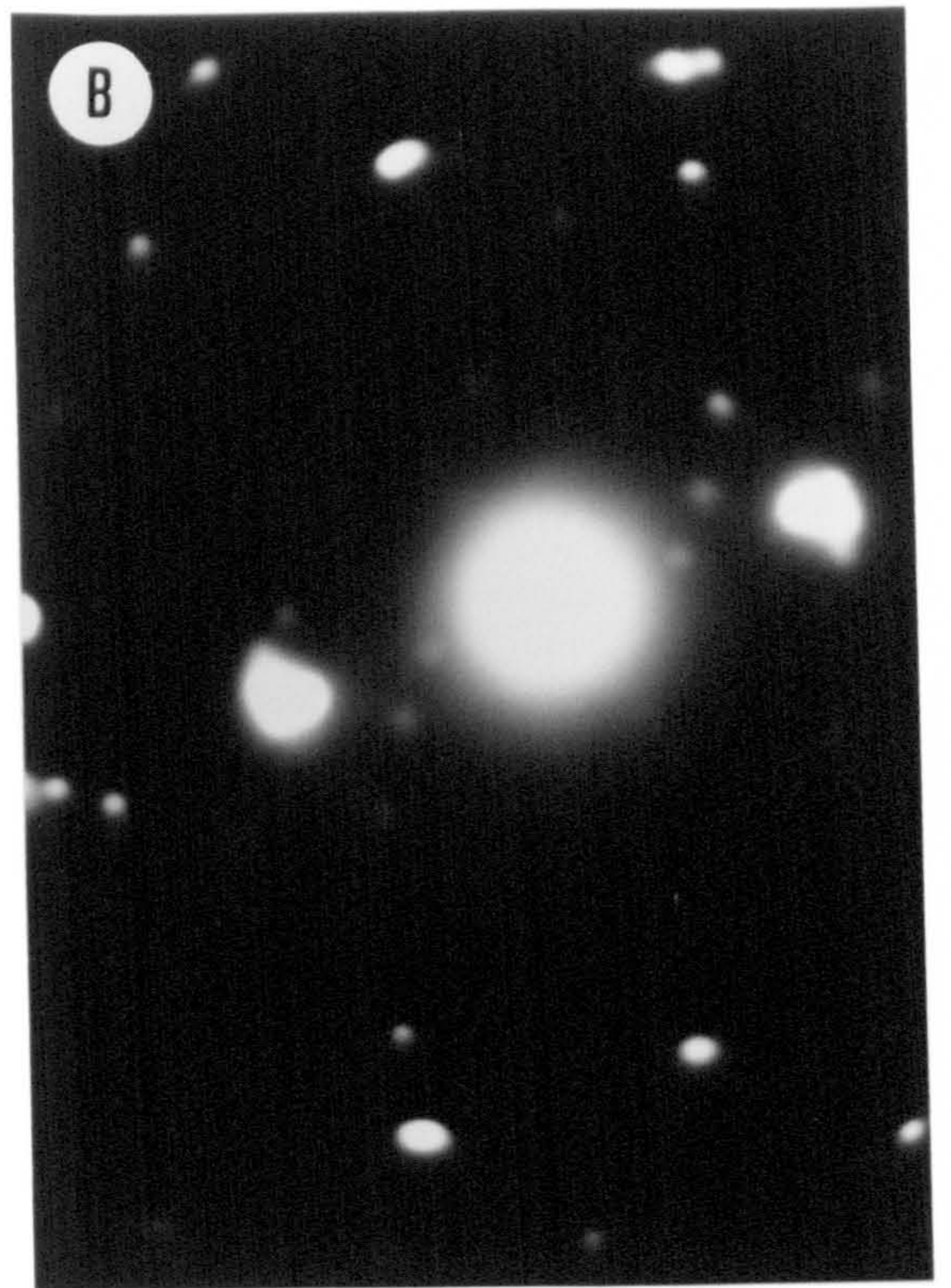
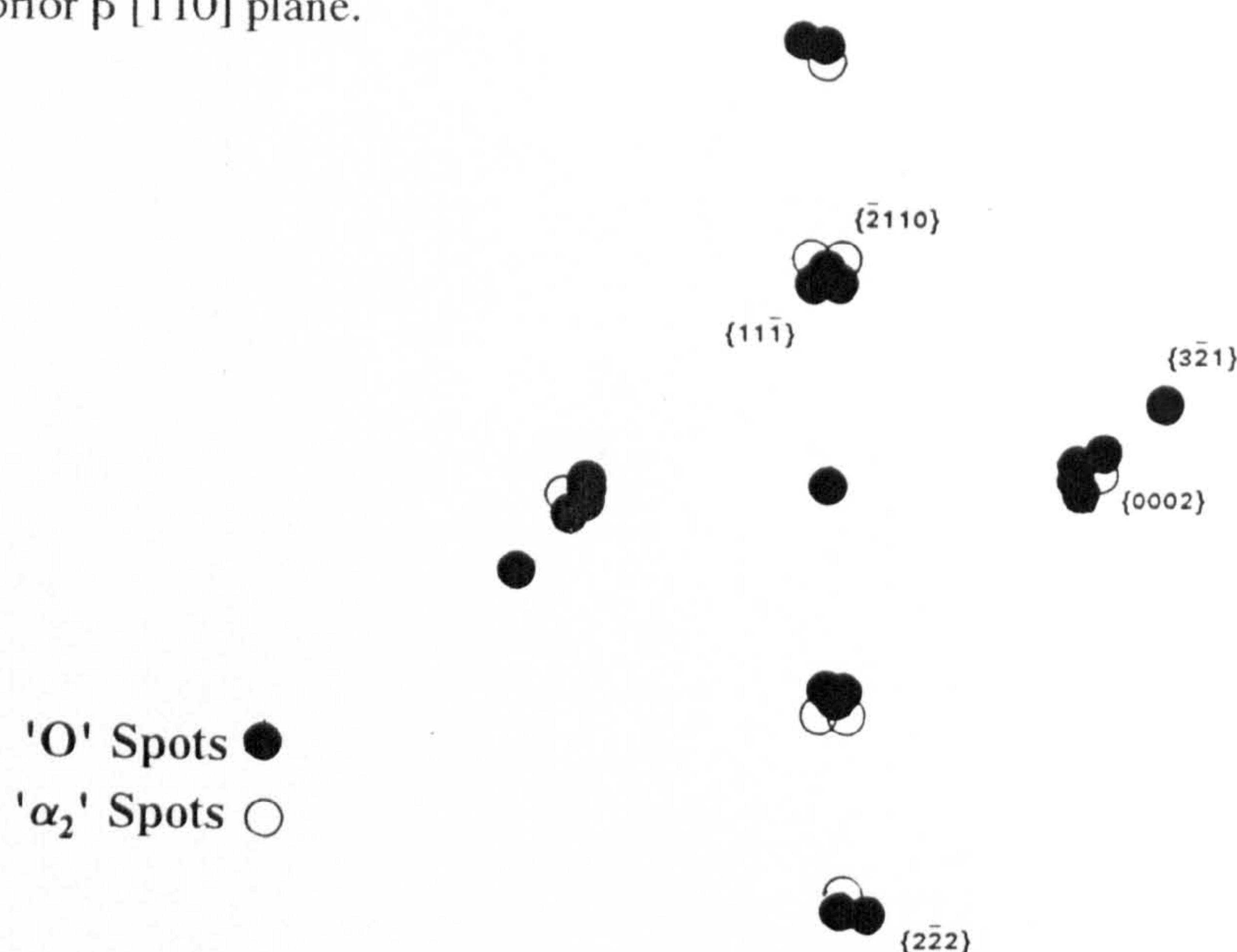


Figure 5.13.

Alloy Ti-20Al-11Nb-0.9Si (at.%), solution treated at 1270°C/24 hrs, water quenched, then aged at 800°C/ 1000 hrs, w.q.

TEM foils, electrochemically thinned in 7 vol.% H₂SO₄ in CH₃OH, ion thinned for 2hrs.

- Bright field image showing α_2 and O grains. Note also the small boundary layers of O phase surrounding the α_2 grain boundaries.
- SADP showing α_2 and O diffraction spots in with a zone axis parallel to the prior β [110] plane.



- Bright field image of a heavily faulted O grain surrounded by α_2 phase.
- Dark field image showing the same O grain as in c).
- Bright field image showing α_2 grains with transformed β (i.e. O phase) along the grain boundaries.
- Detail of α_2 grain (centre) with heavily faulted O grain on left. Note the small amounts of O phase between the α_2 grains on the left hand side of the micrograph.

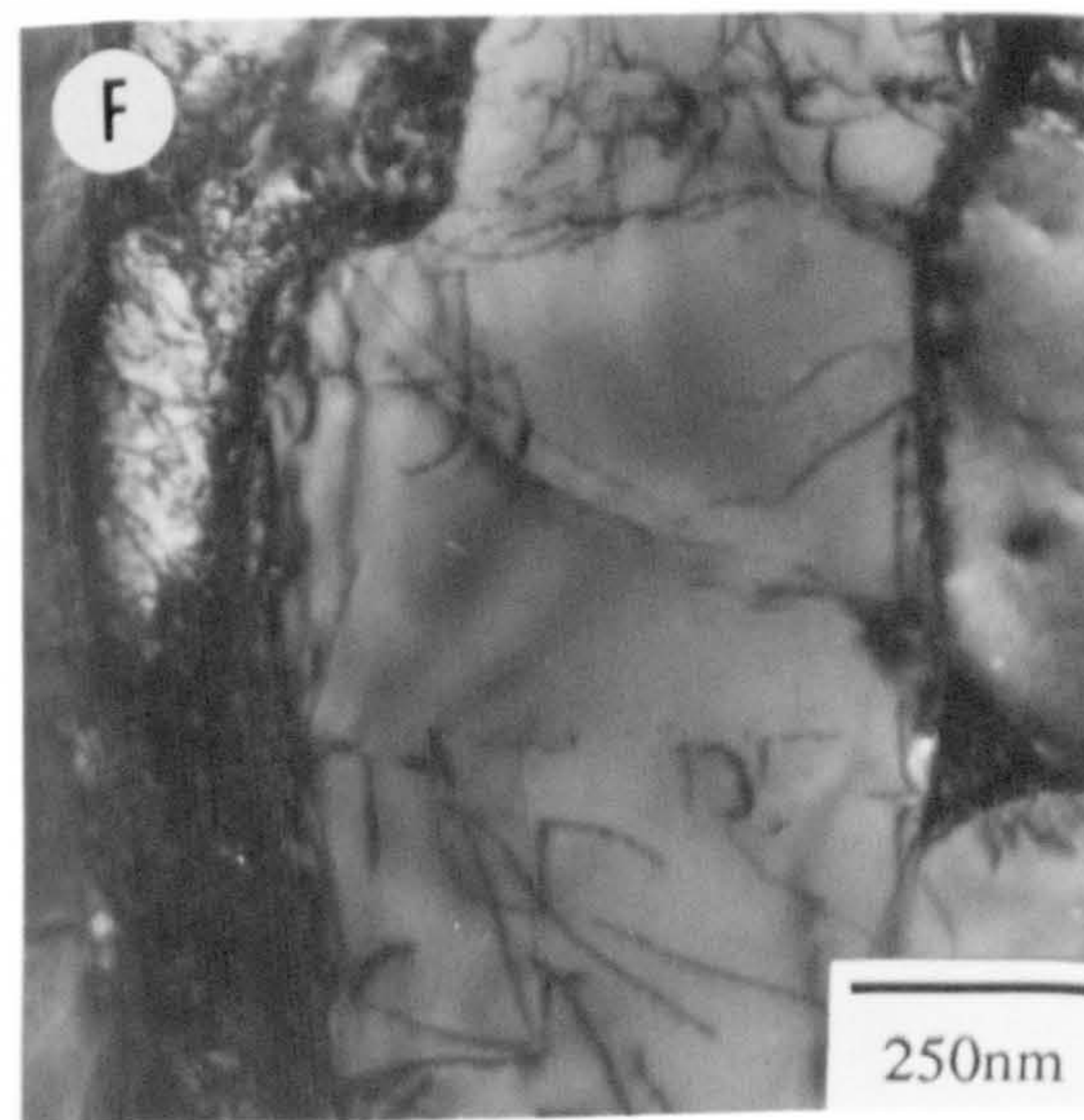
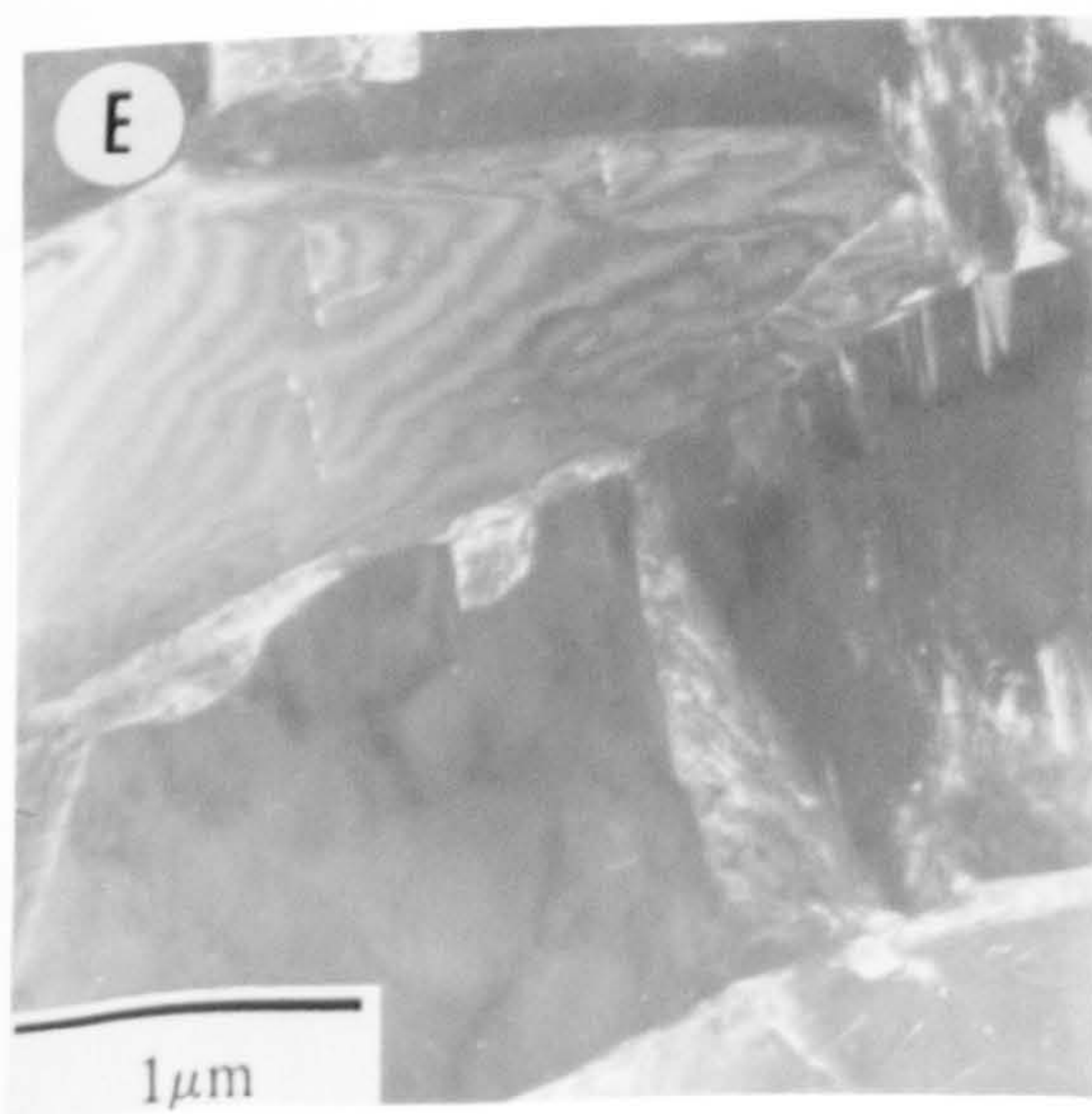
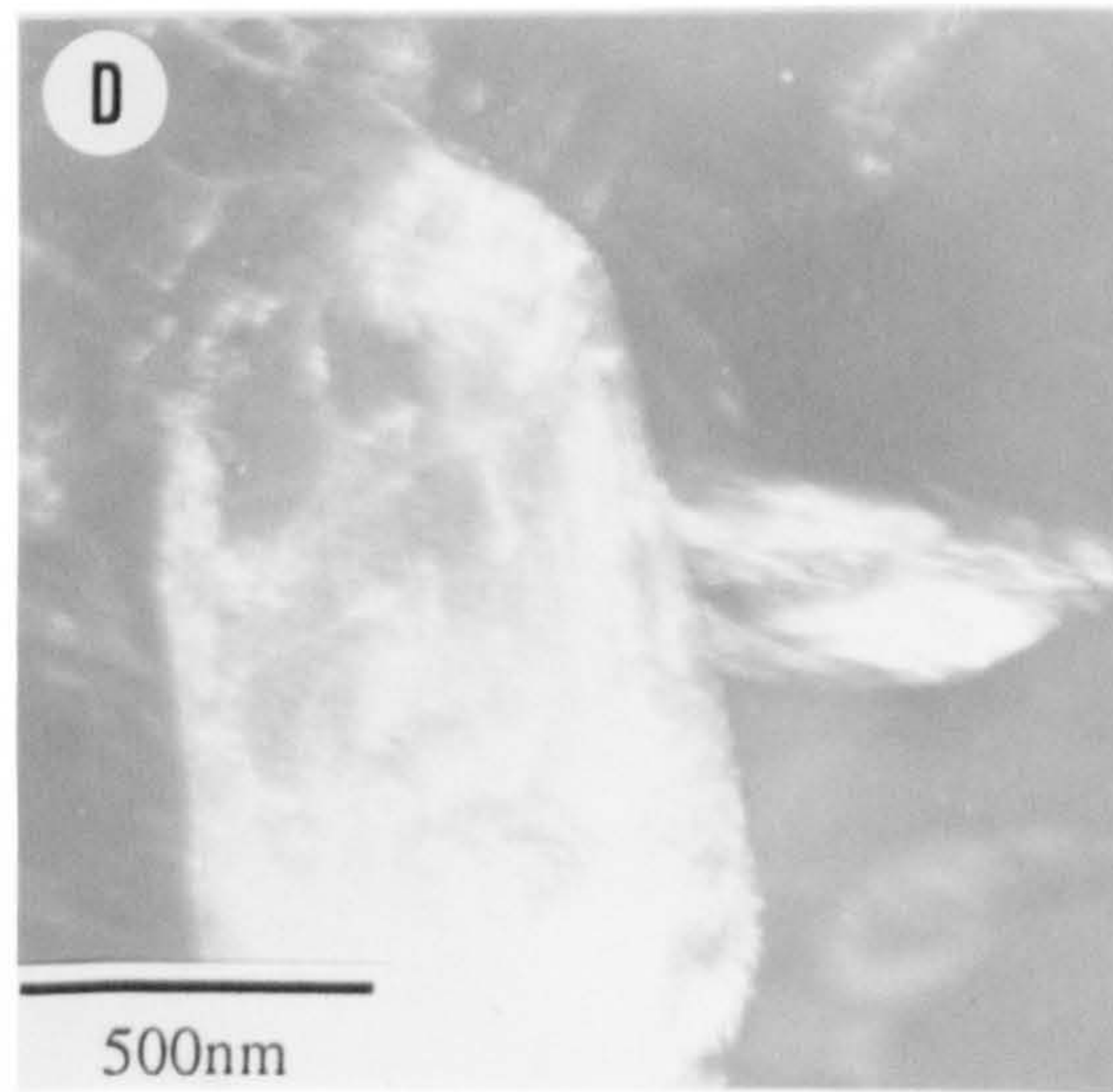
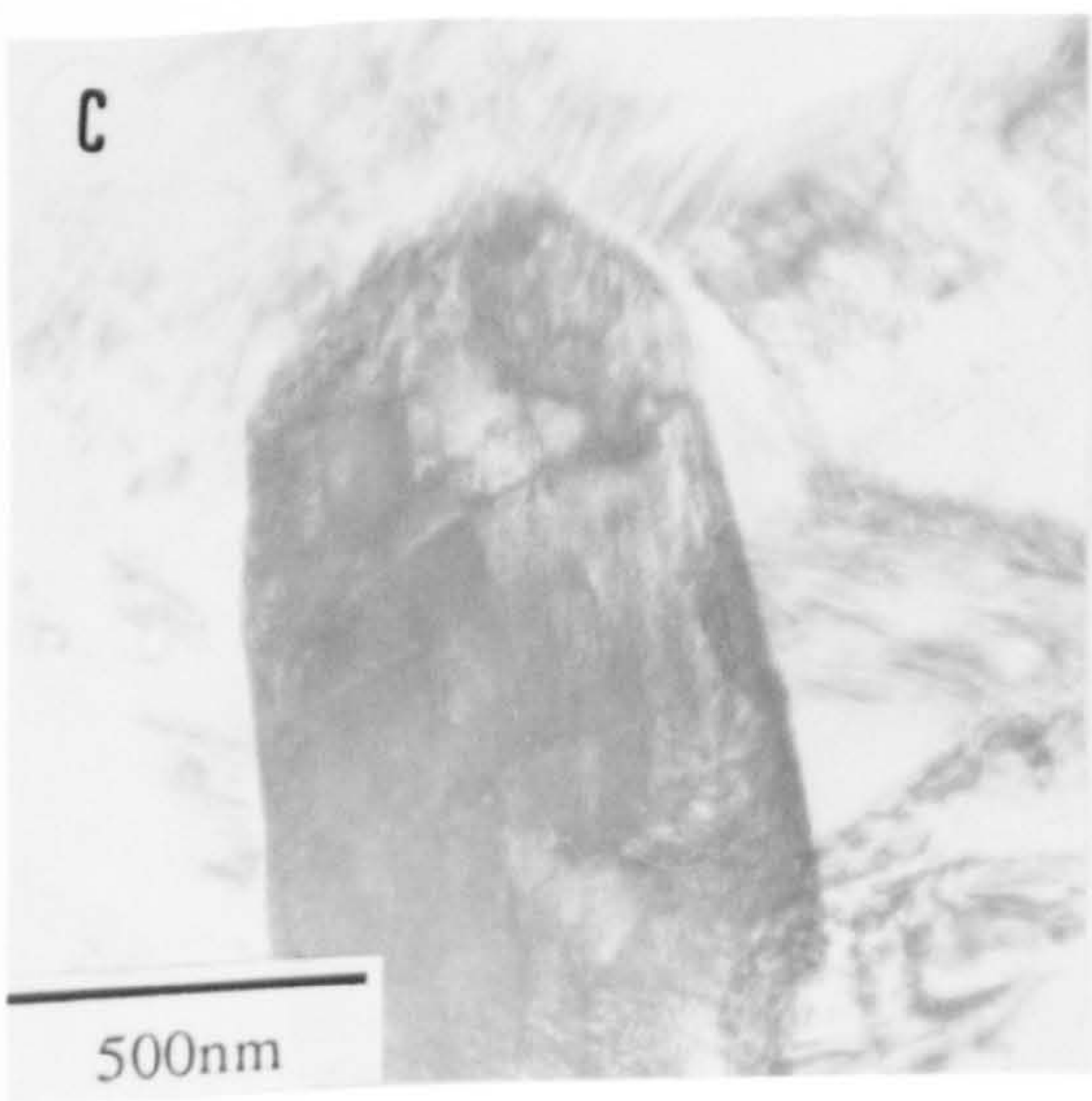
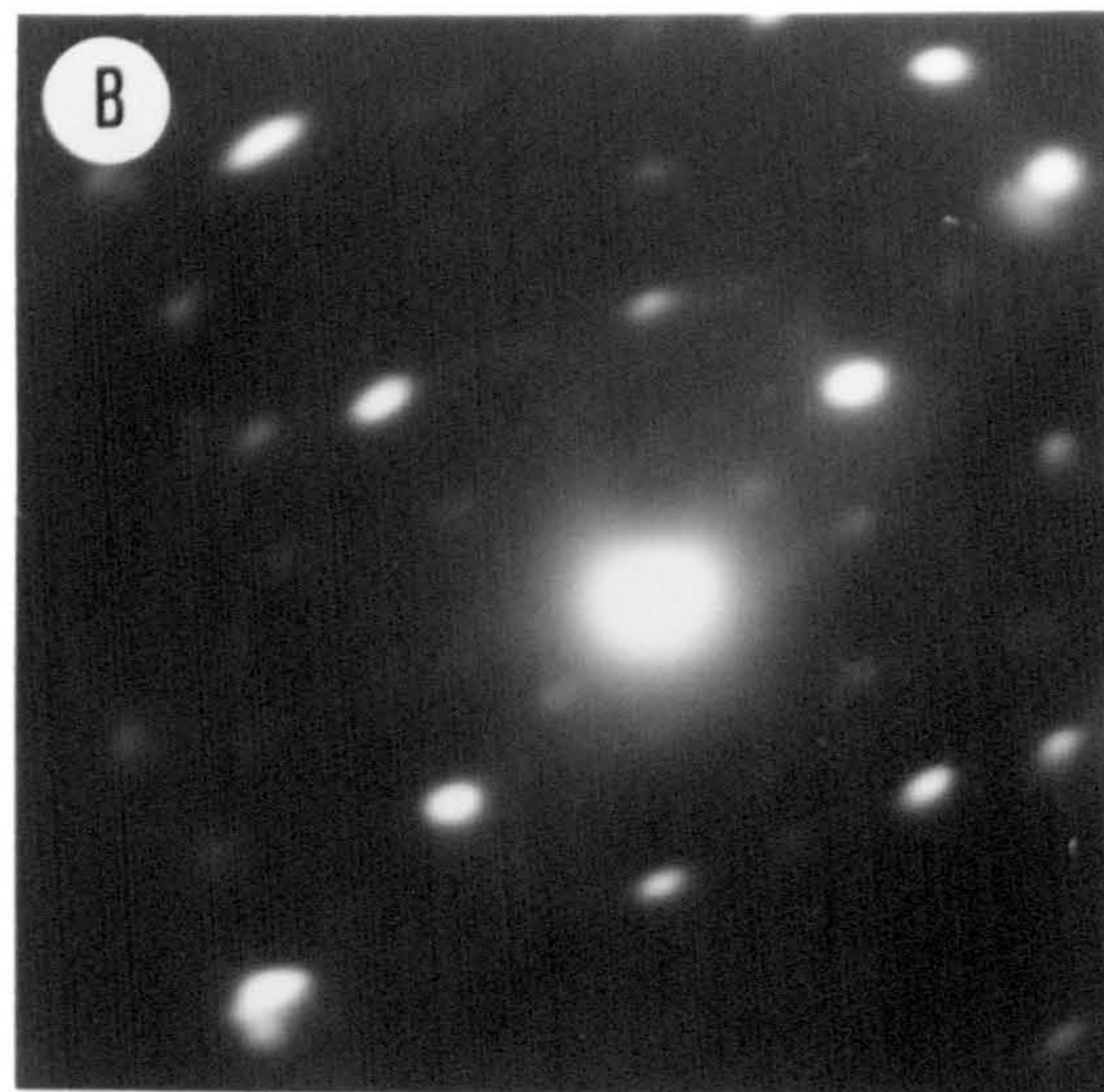
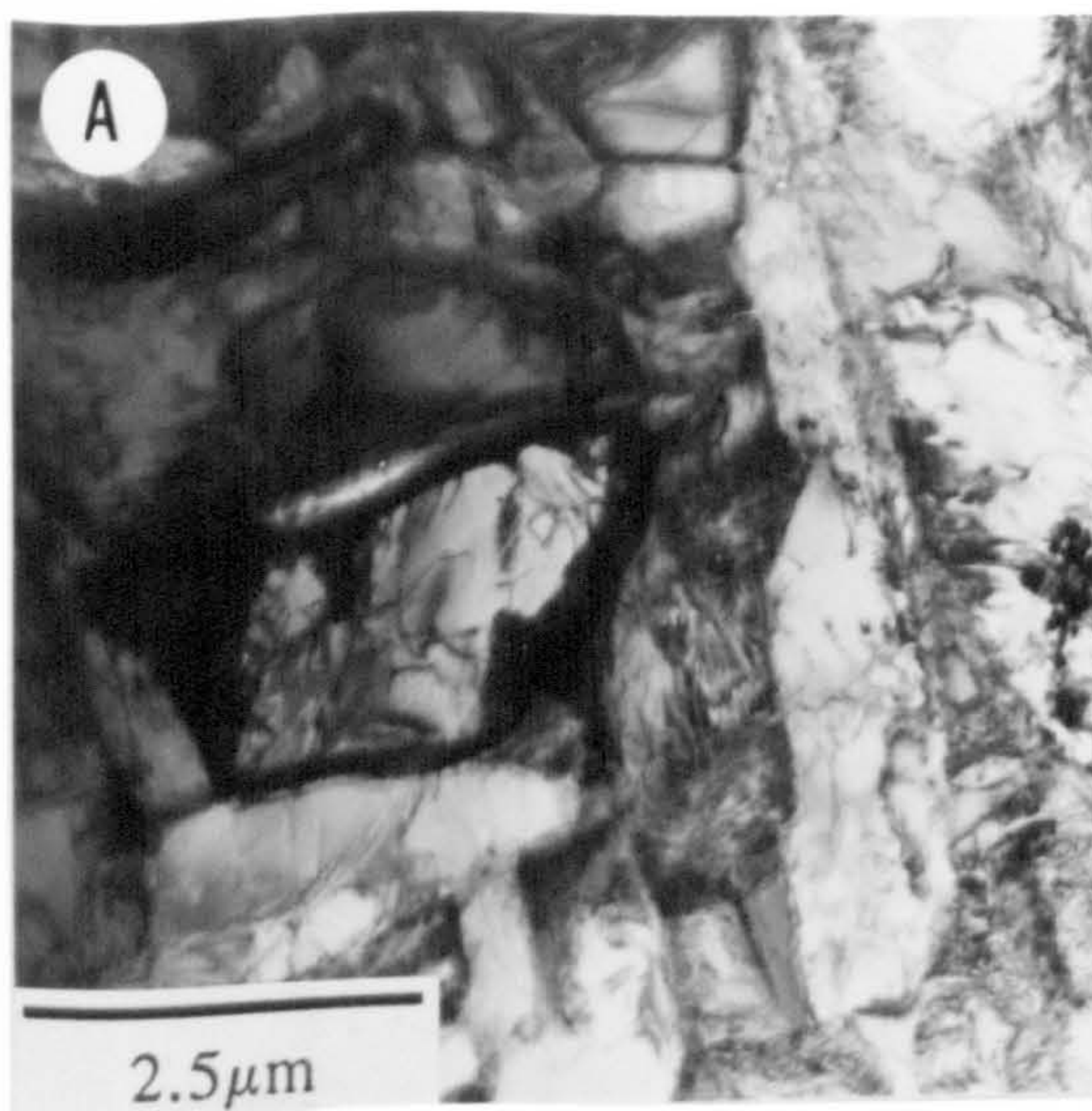
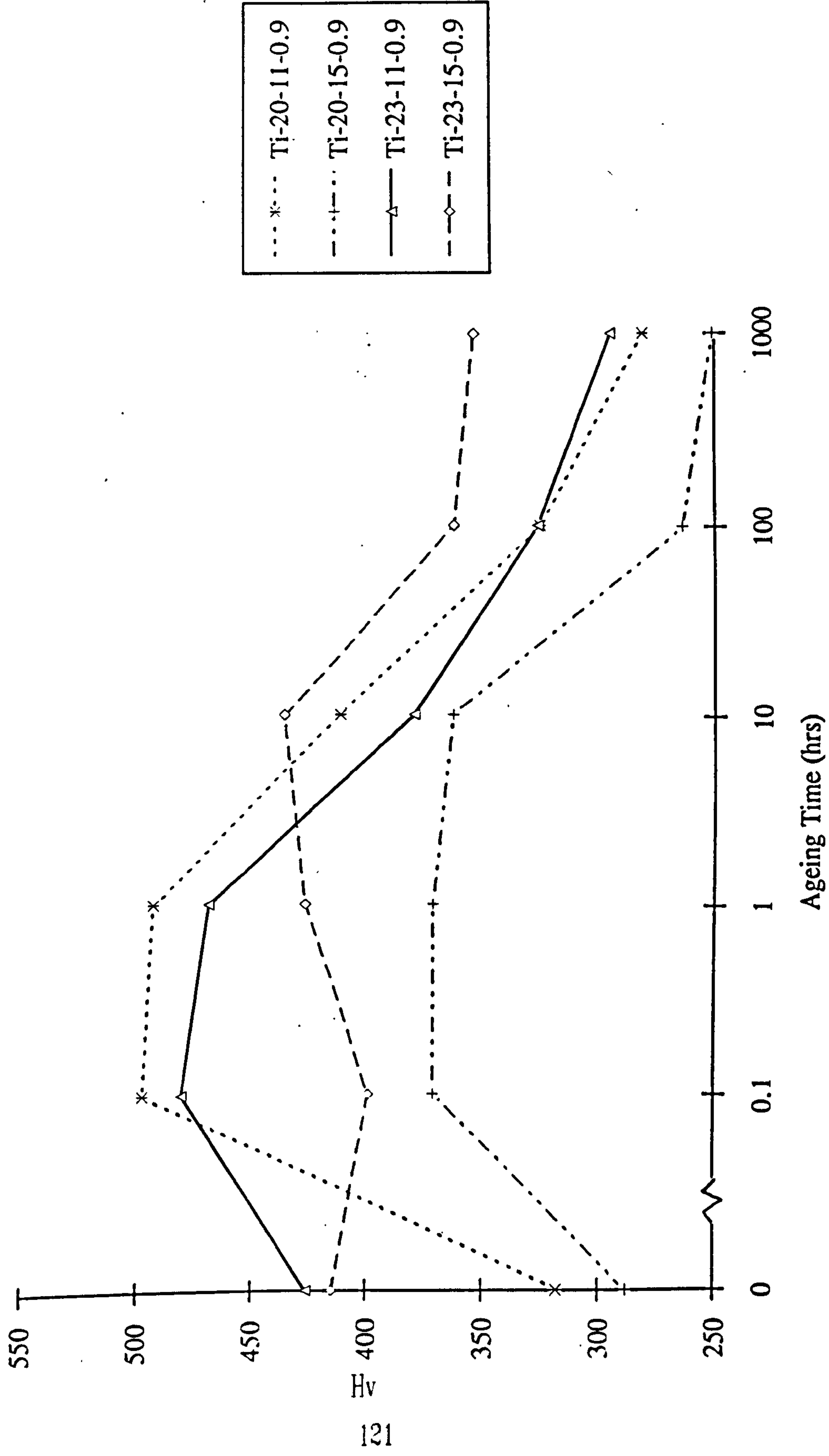


Figure 5.14. Ageing Curve for Alloys Heat Treated at 800°C



5.4.2. Alloys Containing More Than 0.9 at.% Silicon

A comparison of the microstructures of the alloys heat treated at 800°C and 900°C shows that the main difference in the structures present is that, as would be expected, the structures found at 800°C are much finer (Figures 5.15a,b,e & f). Secondary silicide precipitation in particular is on a much finer scale than at 900°C. This is clearly shown by the microstructures of Ti-23-15-1.5 shown in Figures 5.15e and 5.15f. This simple reduction in the scale of the structure does not hold entirely true for Ti-23-11-3, illustrated in Figure 5.15c. The structure exhibited by this alloy is very similar to that which it exhibited in the solution treated condition, with the main difference being the precipitation of fine scale $O + \alpha_2$ particles in the areas which did not undergo the martensitic transformation, as shown in Figure 5.15d. TEM studies were not carried out on this alloy, and it is not clear from X-ray diffraction data if the O phase precipitated during ageing has the same lattice parameters as that produced during the quench from the solution treatment temperature, or whether it is of a similar type to that formed in the other alloys during the ageing process.

5.5. 650°C Aged Microstructure

When aged for 1hr, the microstructure of the alloys is formed of a series of parallel laths of α_2 in the β_O phase (Figure 5.16a). When viewed in a transmission microscope, the α_2 phase appears heavily mottled (Figure 5.16b) in the same way as O phase does after 800°C ageing.

Unlike in the alloys aged at 800°C, extended ageing does not produce any O phase. The only phase transformational effect which occurs is the disordering of the β phase in the Ti-20-11-0.9 alloy shown after 1000hrs ageing, as can be seen in the $[110]_\beta$ zone axis diffraction pattern shown in Figure 5.16c. The conventional Burgers orientation between the phases after the ageing treatment is clearly shown in Figure 5.16d. The spacing of the platelets of α_2 is much wider than after shorter ageing times.

The very fine microstructure which occurs in the alloys at this temperature, even after 1000 hrs appears to have affected the chemical compositions produced by thin foil EDS, due to the limiting factor of the size of the electron beam used in the analysis. The EDS analysis of Ti-20-11-0.9 shown below in Table 5.5 shows the

Figure 5.15.

Ti-23-X-Y alloys showing solution treated and then 800°C /168hrs aged microstructure.

SE images of all alloys mechanically polished, etched in Kroll's Reagent.

- (a) Ti-23-11-1.5. Microstructure shows α_2 (dark) plates in a background of transformed β with grain boundary silicide and a smaller distribution of precipitated silicide.
- (b) Detail of the silicide on grain boundary between two large matrix grains.
- (c) Ti-23-11-3. Microstructure shows O platelets (darker) within a small amount of retained β . Microstructure shows increased O/ β stabilising effect of the added silicon. The structure has not changed markedly from that of the solution treated condition, in that the O platelets retain the prior morphology. In the parts of the structure which had not previously transformed has now produced a very fine O + β structure between the O 'arms'.
- (d) Detailed view of (c) showing grain boundary silicides.
- (e) Ti-23-15-1.5. This shows the grain boundary silicides. There is also a very fine distribution of silicide particles. The matrix is formed of O grains.
- (f) Detailed view of grain boundaries showing both types of silicide particle.

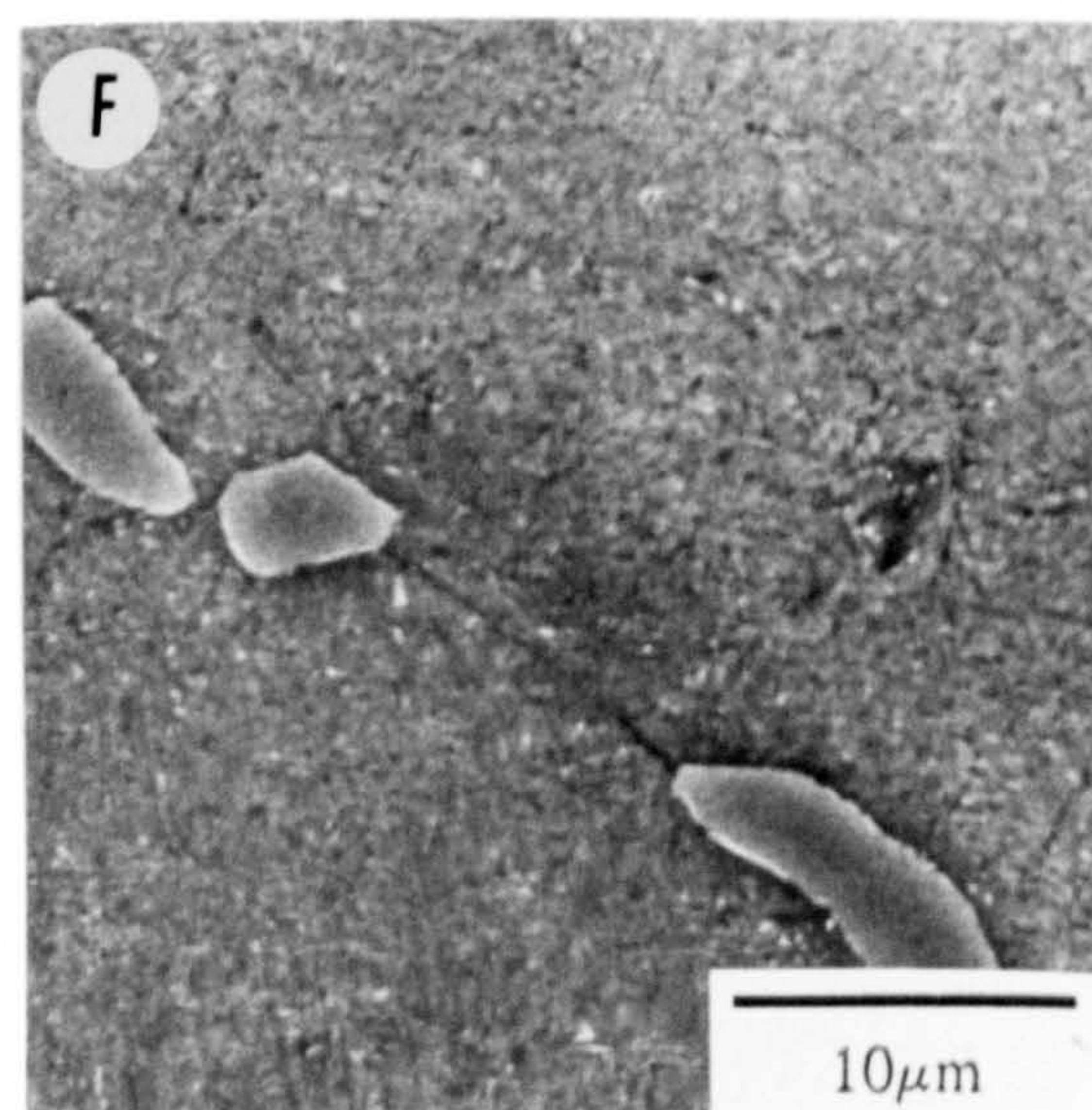
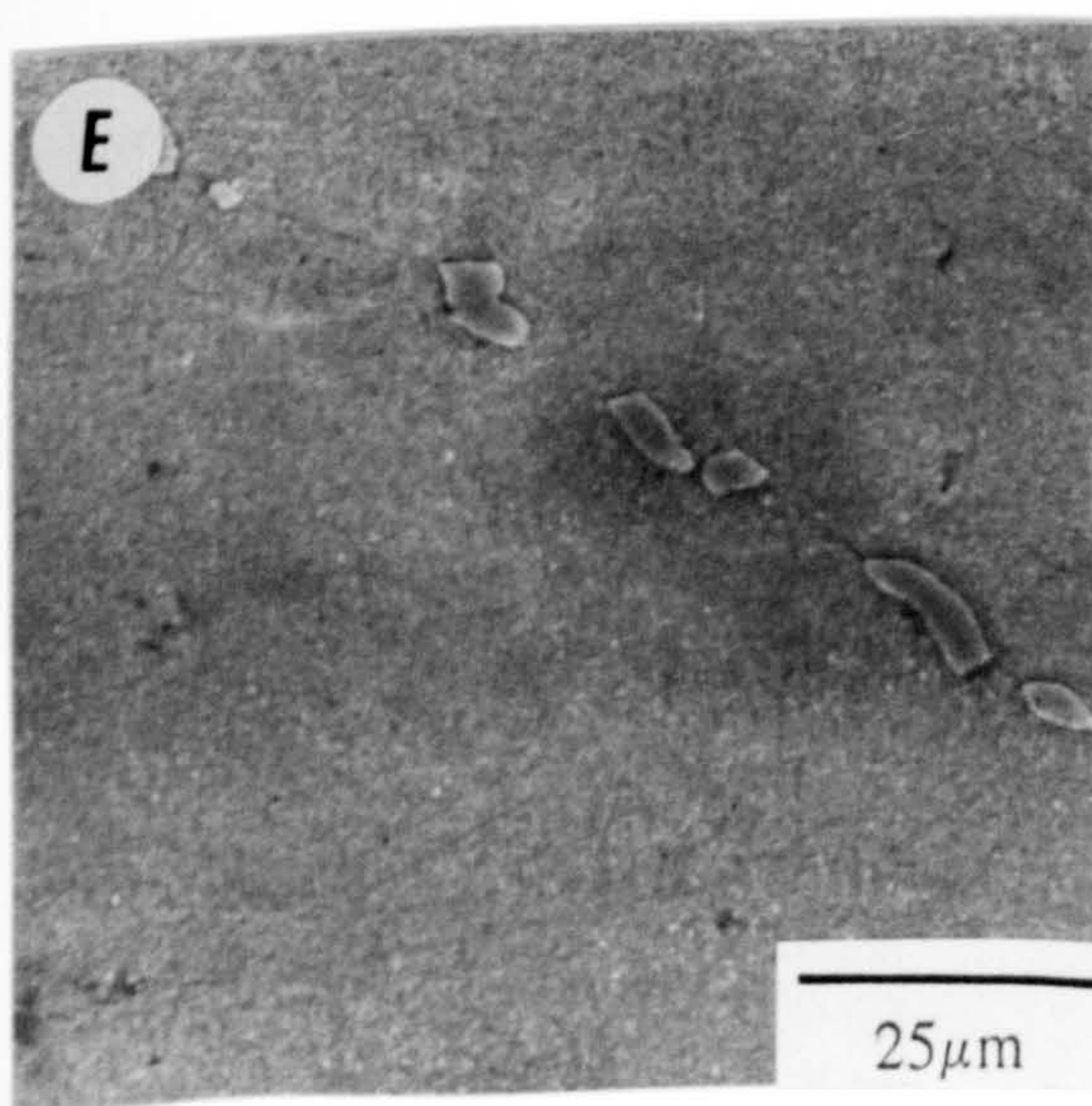
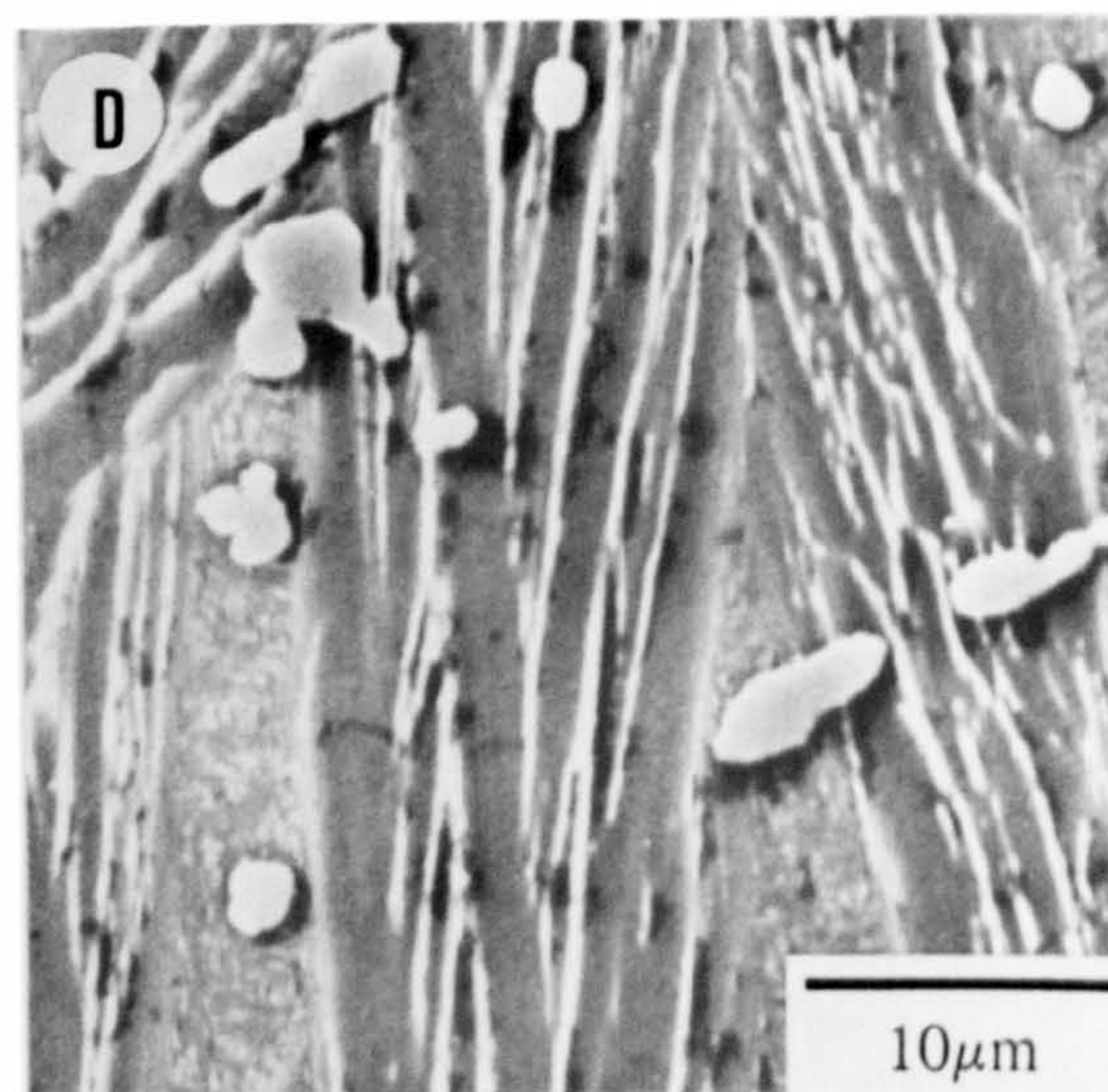
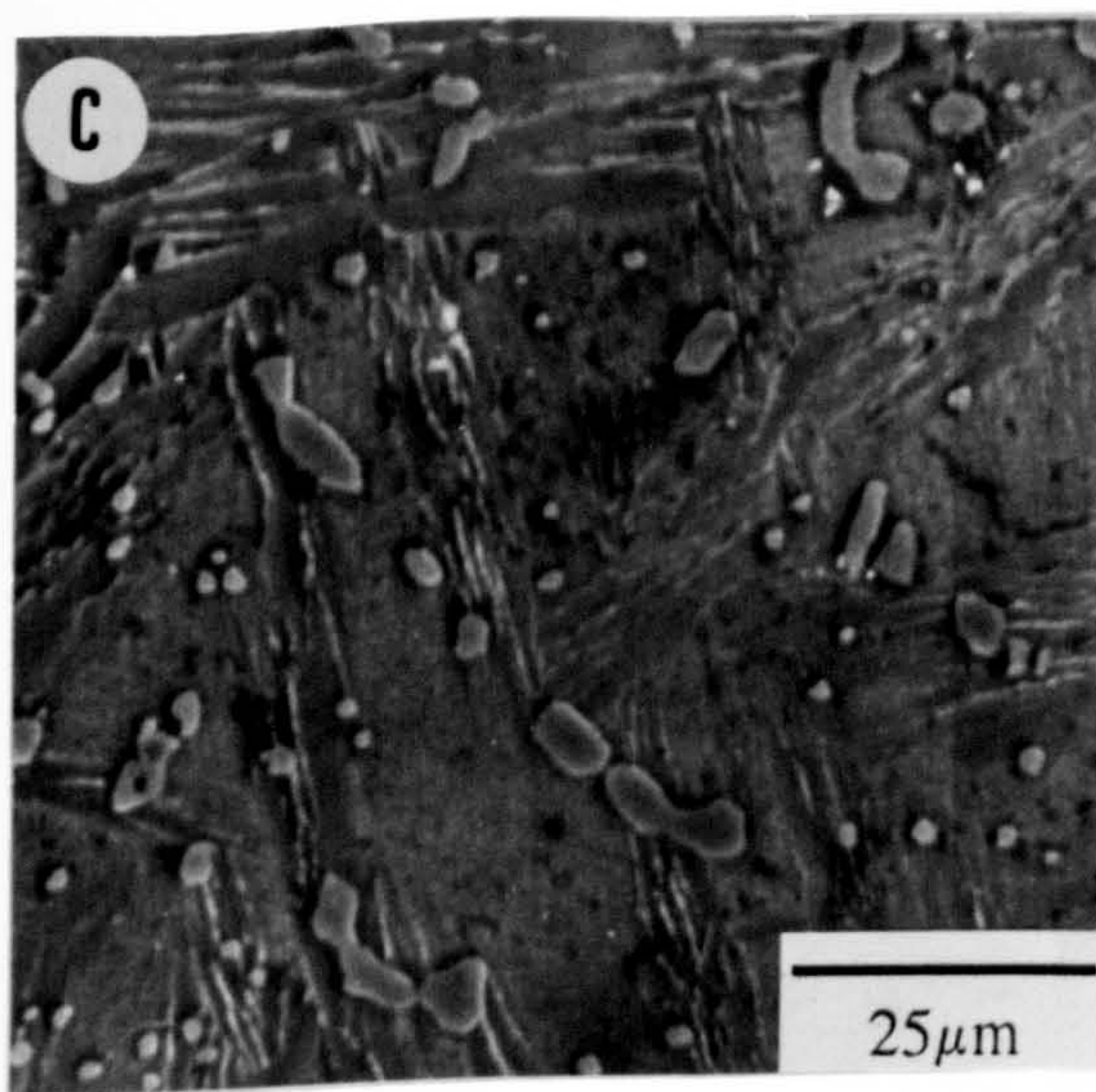
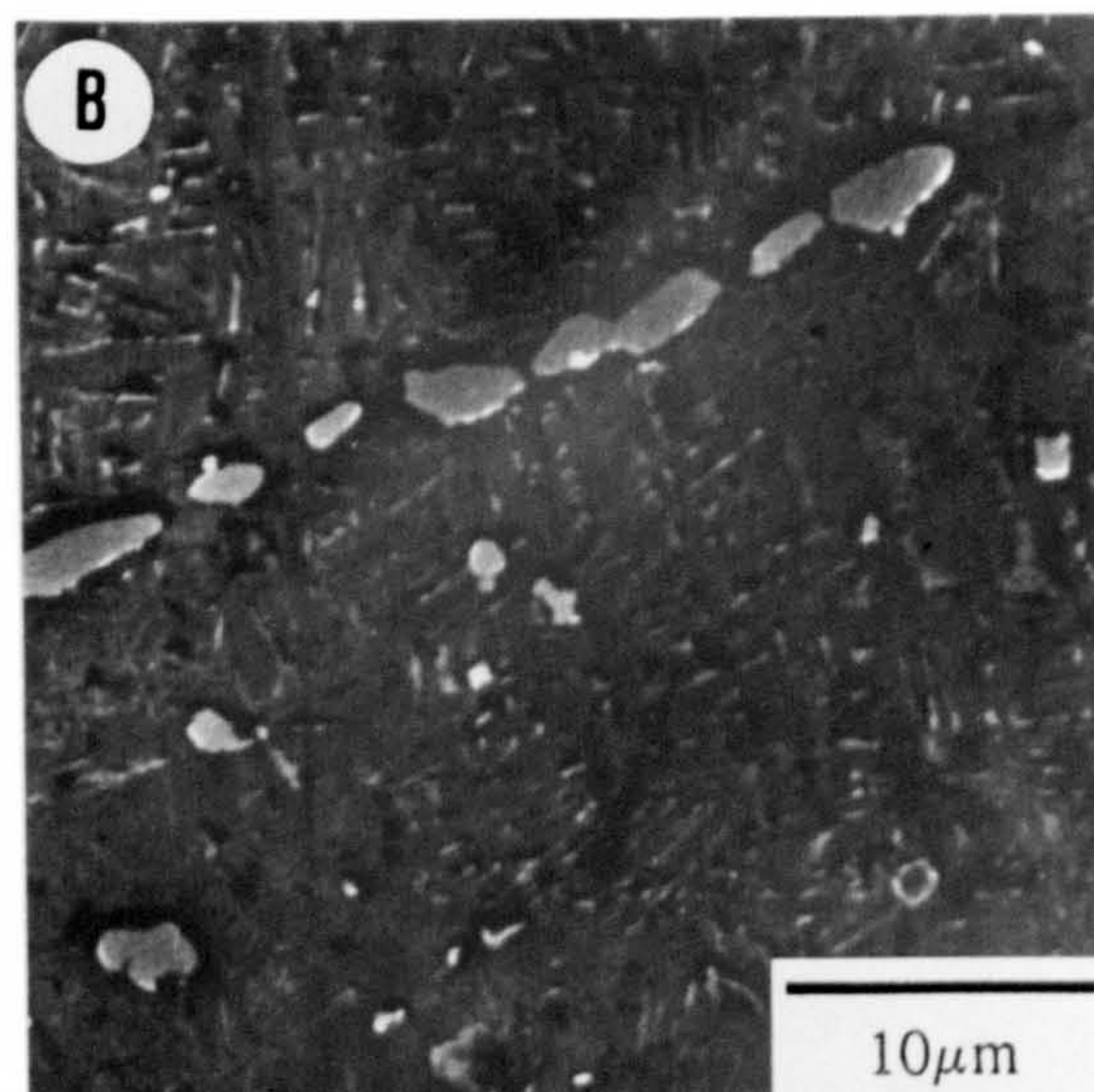
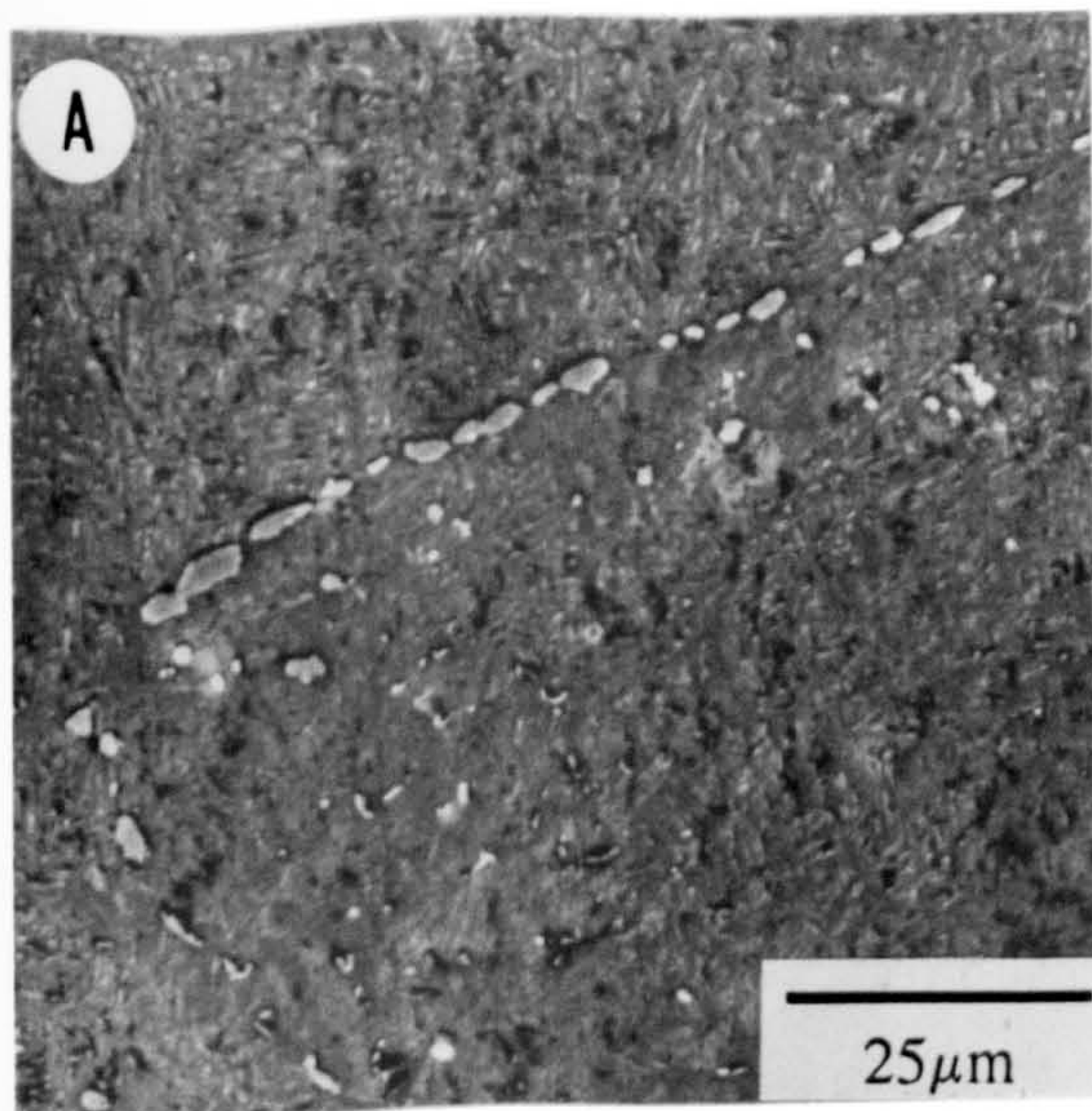


Figure 5.16.

Alloy Ti-20Al-11Nb-0.9Si (at.%), solution treated at 1270°C/24 hrs, water quenched, then aged at 650°C/ 1 hr, w.q.

TEM foils, electrochemically thinned in 7 vol.% H₂SO₄ in CH₃OH.

(a) Bright field image of parallel series of α_2 laths (dark) in light β matrix showing precipitation orientation.

(b) Detail of α_2 laths showing mottled surface finish.

Alloy Ti-20Al-11Nb-0.9Si (at.%), solution treated at 1270°C/24 hrs, water quenched, then aged at 650°C/ 1000 hrs, w.q.

TEM foils, electrochemically thinned in 7 vol.% H₂SO₄ in H₂O.

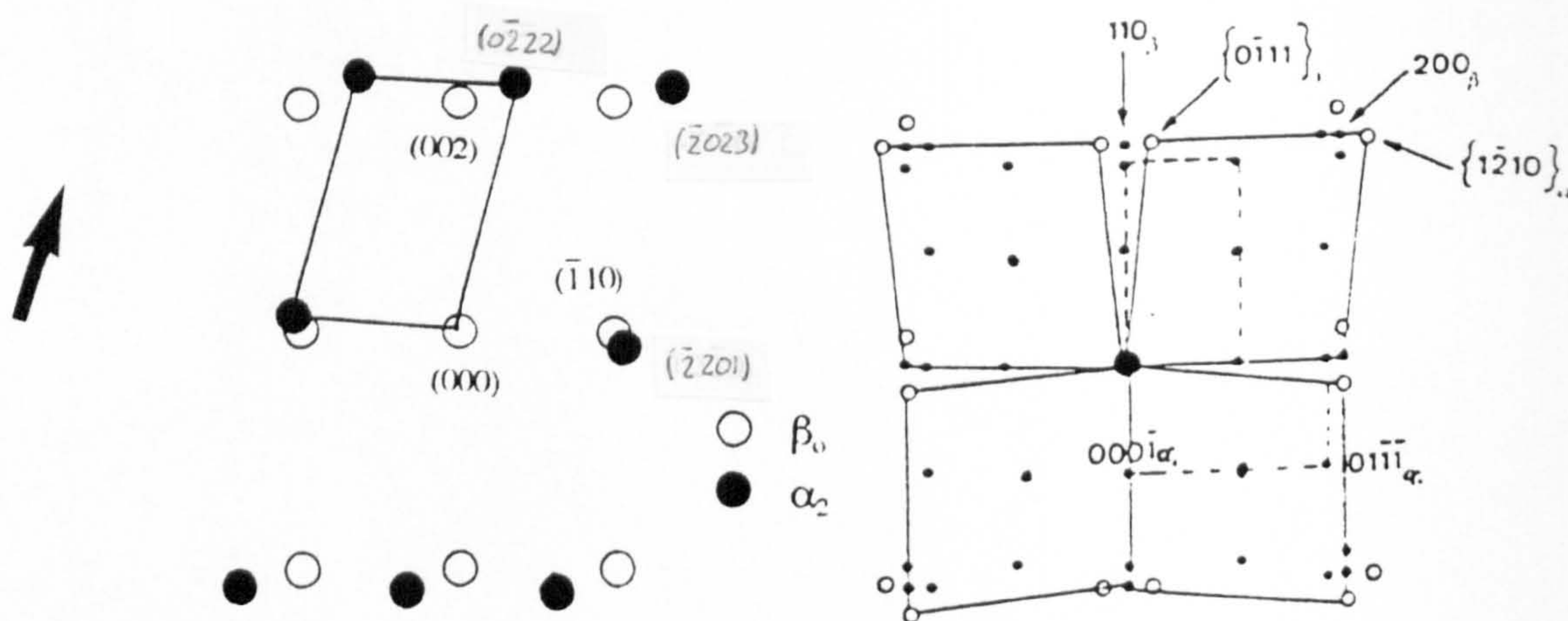
(c) SADP showing $[110]_\beta$ diffraction spots. After this ageing treatment the β phase has disordered, as can be seen from the lack of (001) diffraction spots, which are present in alloys aged at higher temperatures.

(d) SADP on $[100]_\beta$ zone axis. This pattern illustrates the classic Burgers Orientation Relationship between the β and α_2 phases, such that;

$$(110)_\beta // (0001)_{\alpha_2}; [111]_\beta // [\bar{1}1\bar{2}0]_{\alpha_2}.$$

(c)

(d)

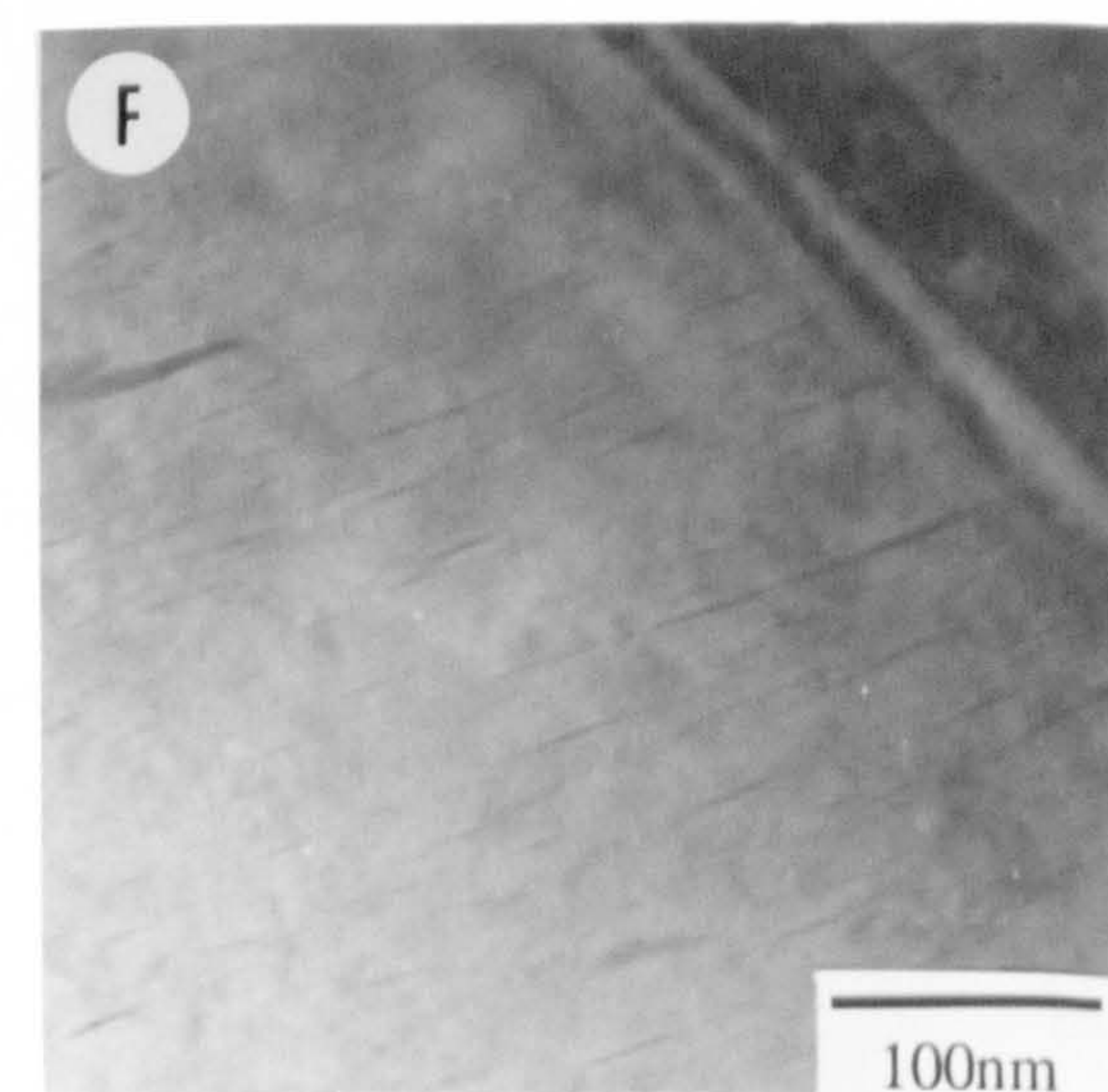
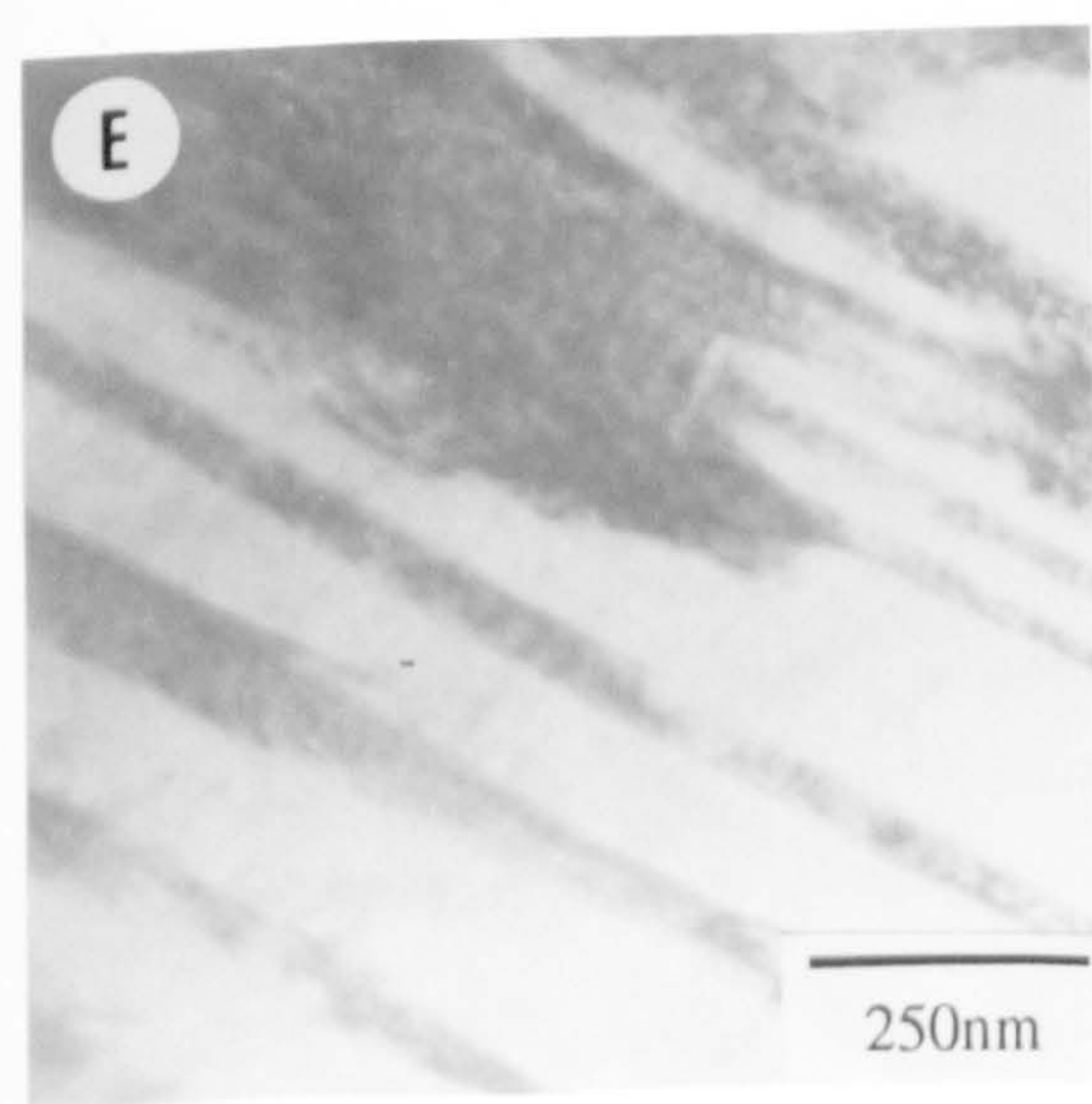
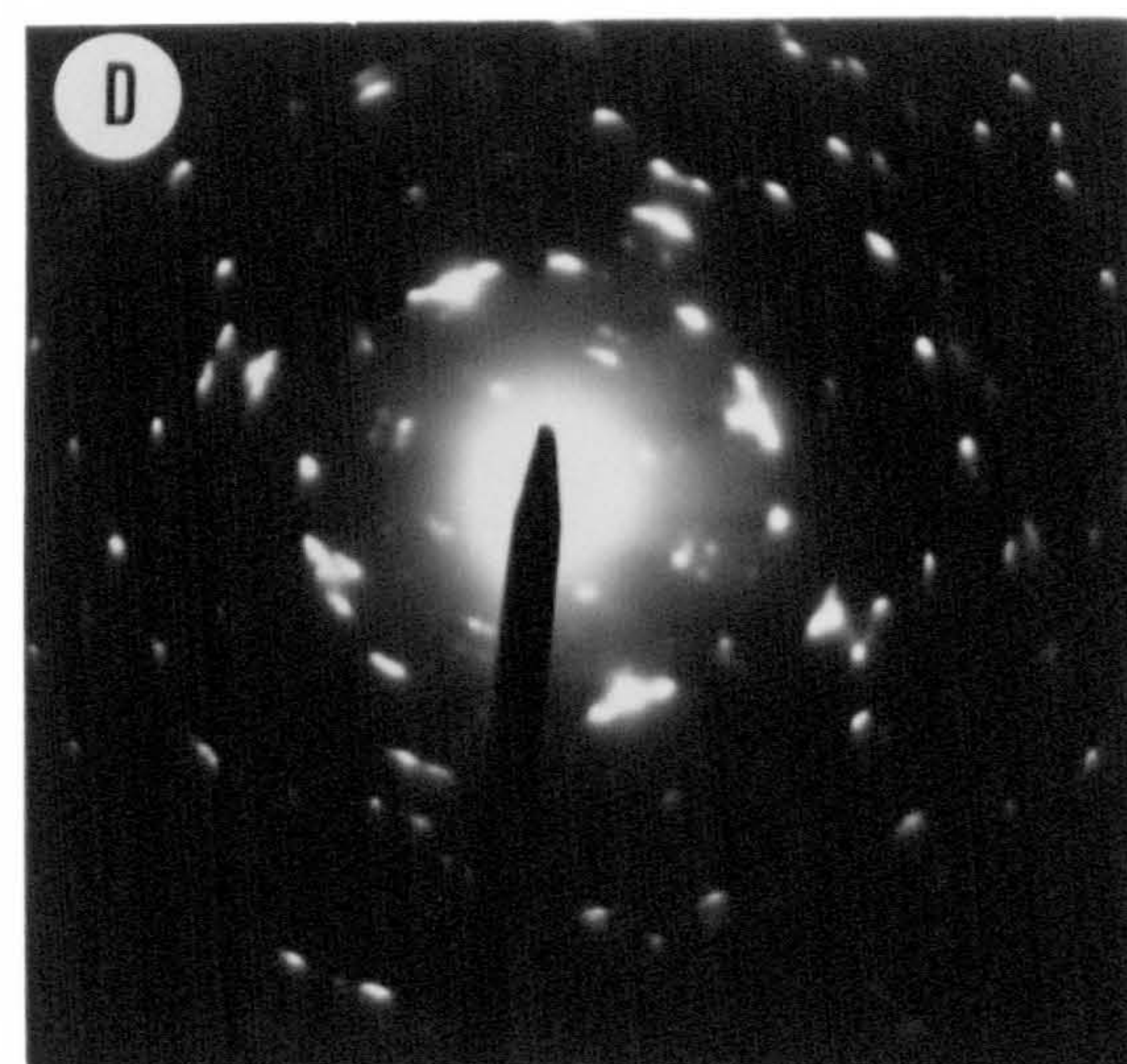
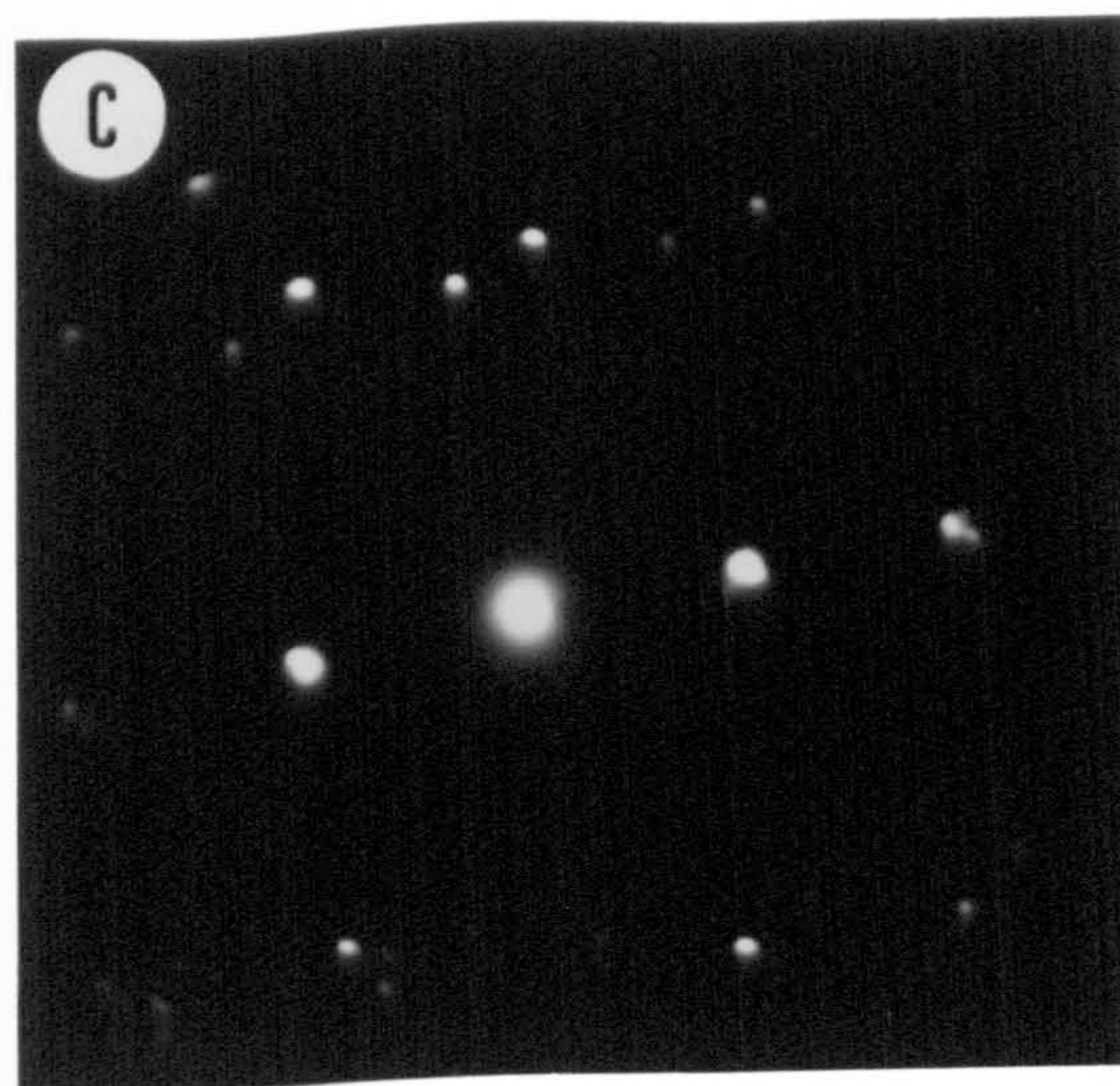
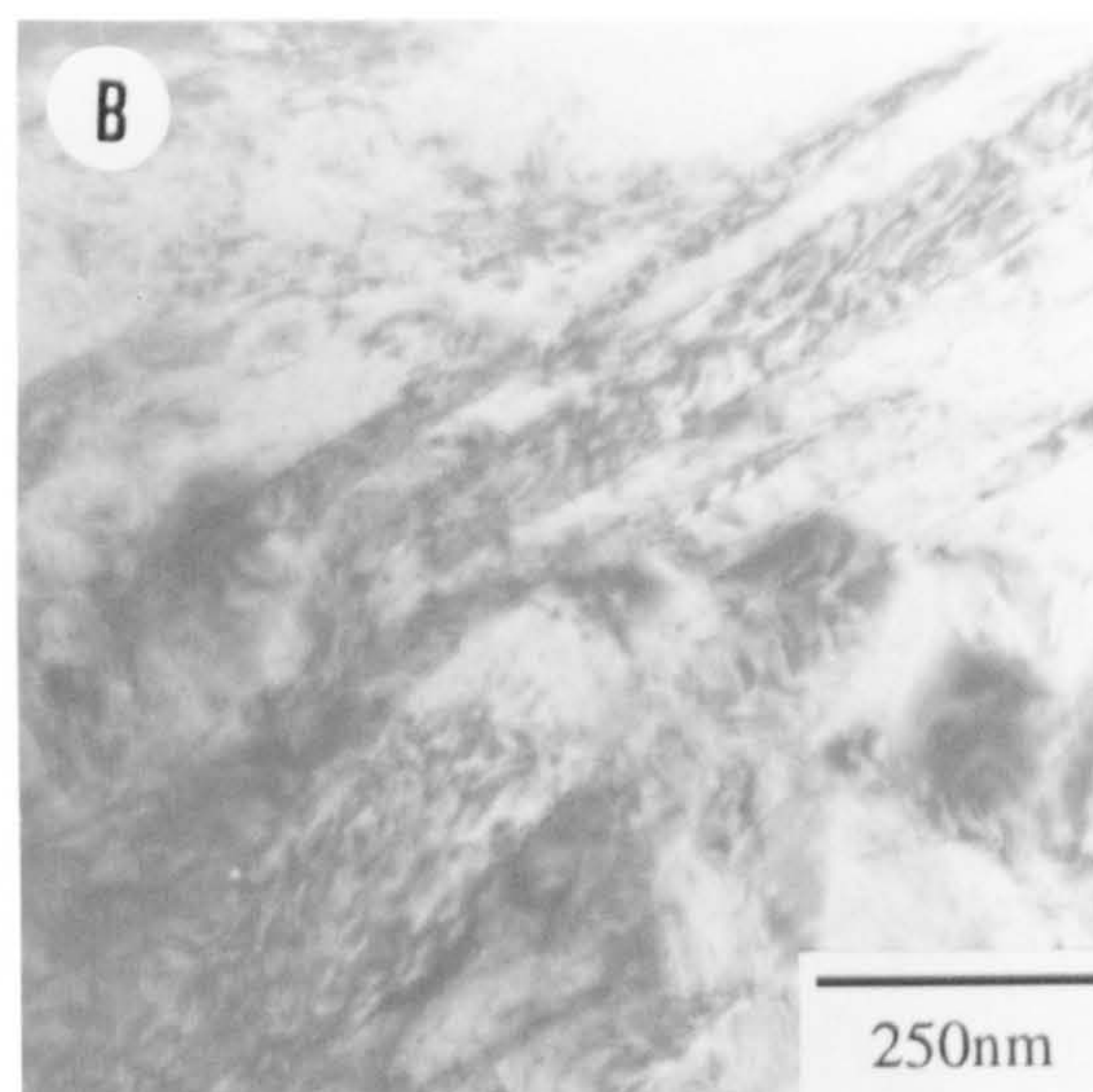
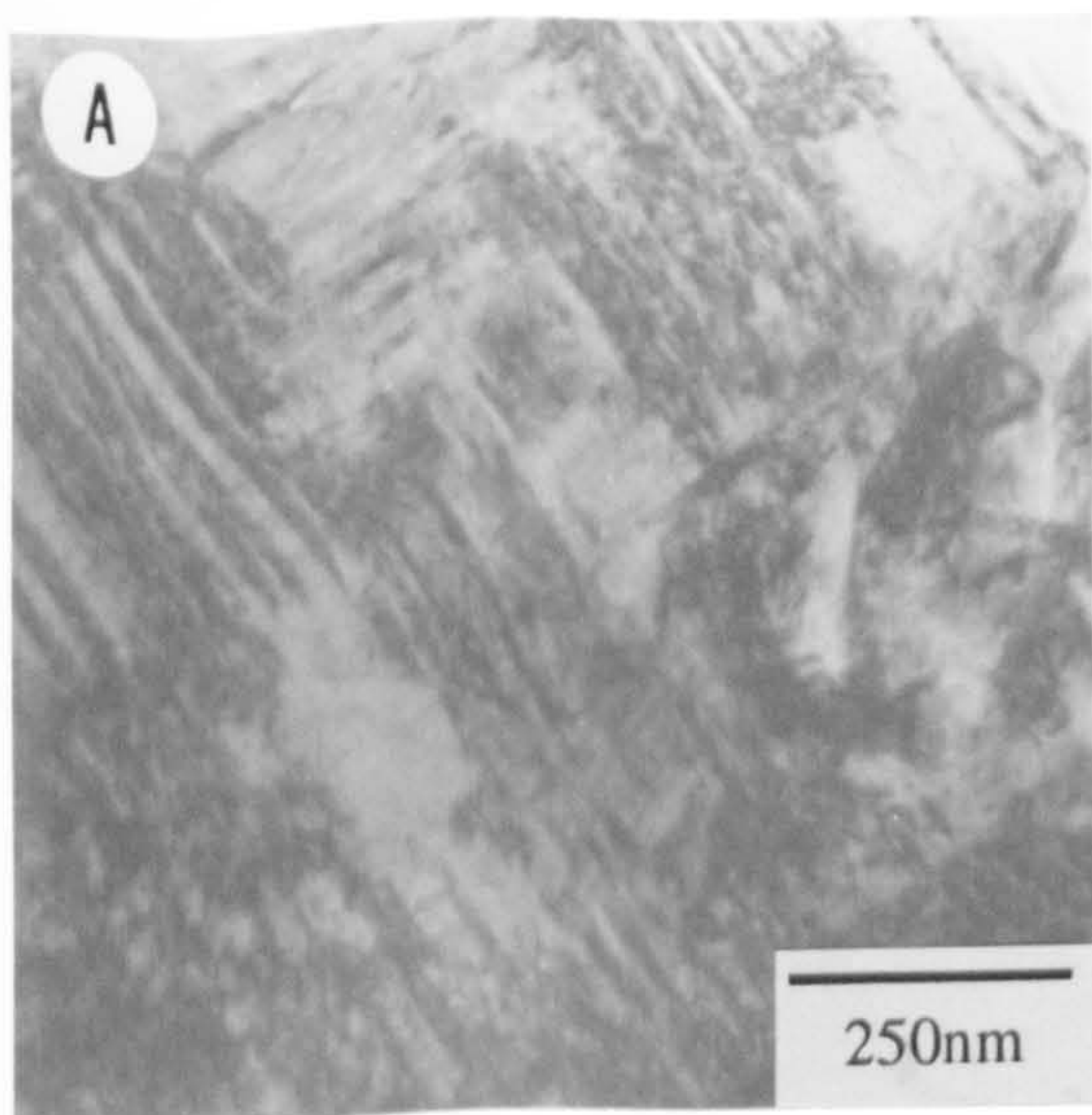


$L\lambda = 3.5 \text{ cm}\text{\AA}$ Z.A. $[41\bar{3}6]_{\alpha_2}$

$L\lambda = 2.3 \text{ cm}\text{\AA}$

(e) Bright field image showing coarsened α_2 laths in the β matrix.

(f) Bright field image which shows a series of very fine precipitates which occur between the major α_2 laths.



compositions at 650°C. This should be compared with those of the α_2 and O phases when aged at 800°C, as shown in Table 5.4.

Phase	at.% Ti	at.% Al	at.% Nb	at.% Si
α_2	67.3	20.9	10.8	0.9
β	65.1	18.3	15.4	0.9

Table 5.5. Phase Chemistry in Ti-20-11-0.9 Aged at 650°C/1000 hrs.

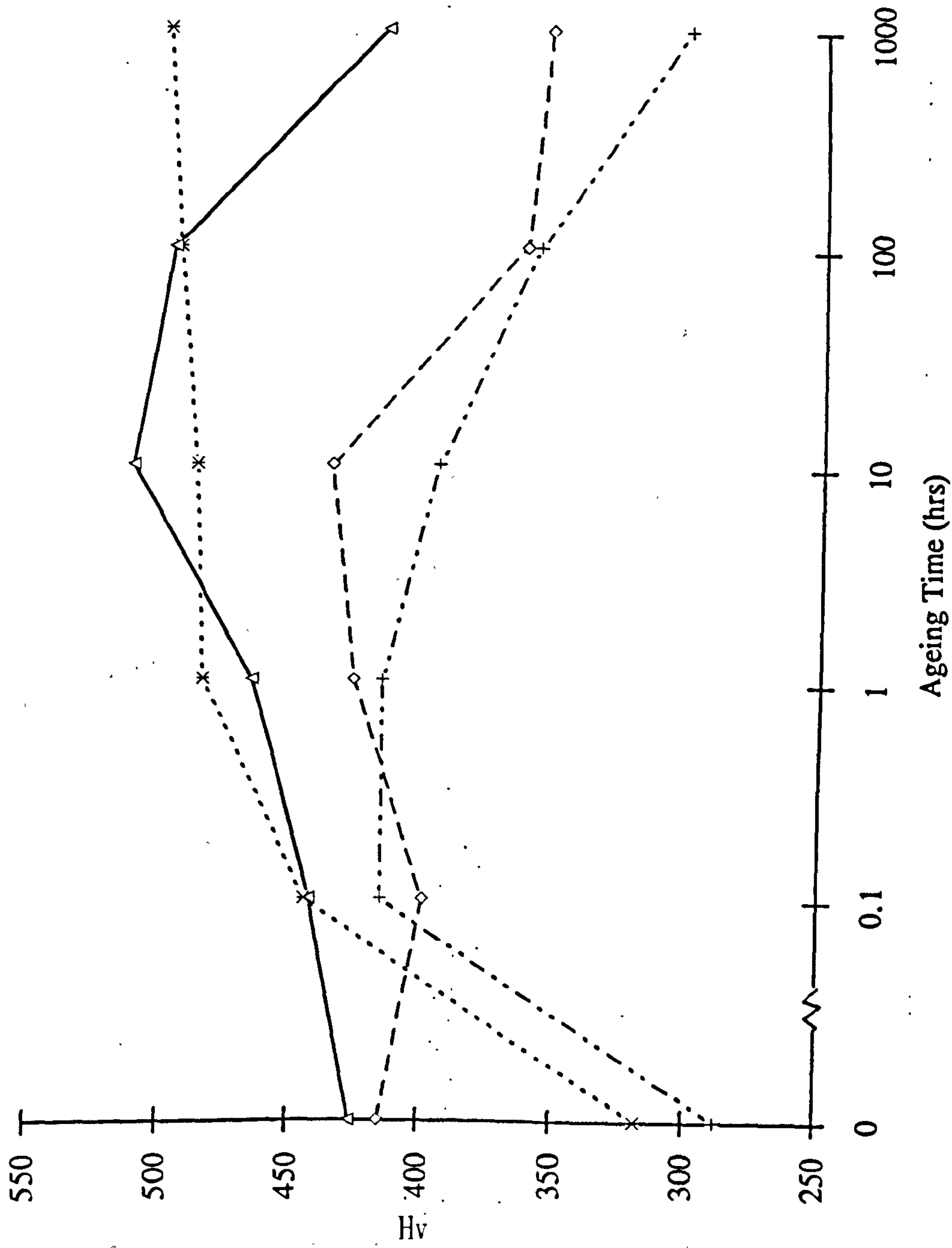
As would be expected from the increasing time for transformations which is evident when the ageing curves for the alloys aged at 900 and 800°C, at 650°C age hardening takes significantly longer to occur than at higher temperatures, occurring at around 0.1 hr for the Ti-23-11-0.9 alloy and at 10 or more hrs with other alloys (Figure 5.17). Unlike the higher temperature ageing curves, at 650°C, the alloys show significantly different hardnesses after long ageing times. Ti-20-11-0.9 shows no significant drop in hardness after 1000 hrs. The hardnesses of the other three alloys reduce by differing degrees. For a fixed niobium content, lowering the aluminium content ^{may} raise the hardness, and for a fixed aluminium content, lowering the niobium content raises the hardness.

5.6 Temperature Dependence of Terminal Hardness

When the hardness of the alloys in their longest term aged condition (i.e. after 1000 hours) is compared with respect to their ageing temperatures, clear trends are visible (Figures 5.18-21, the values in each are estimated to be within $\pm 5\text{Hv}$), which correspond to the phase transformation data, at least at high temperatures. At low temperatures (650°C and below), the values are affected by the relatively slow rate at which diffusional transformations take place, and thus the 1000 hrs aged hardness values are affected by age hardening mechanisms which are at different stages. This can be seen clearly in the preceding ageing curves (Figures 5.17 for 650°C, and 4.9 for 380°C).

The most noticeable effect of temperature is that throughout the temperature range 1270 to 800°C (900°C for Ti-23-15-0.9), the peak hardness recorded in the alloys *increases* with increasing temperature. Thus, with increasing β_0 and decreasing

Figure 5.17. Ageing Curve for Alloys Heat Treated at 650°C



All hardness values are quoted to $\pm 2H_v$.

Figure 5.18. Temperature Dependence of 1000 hrs Aged Hardness in Ti-20-11-0.9

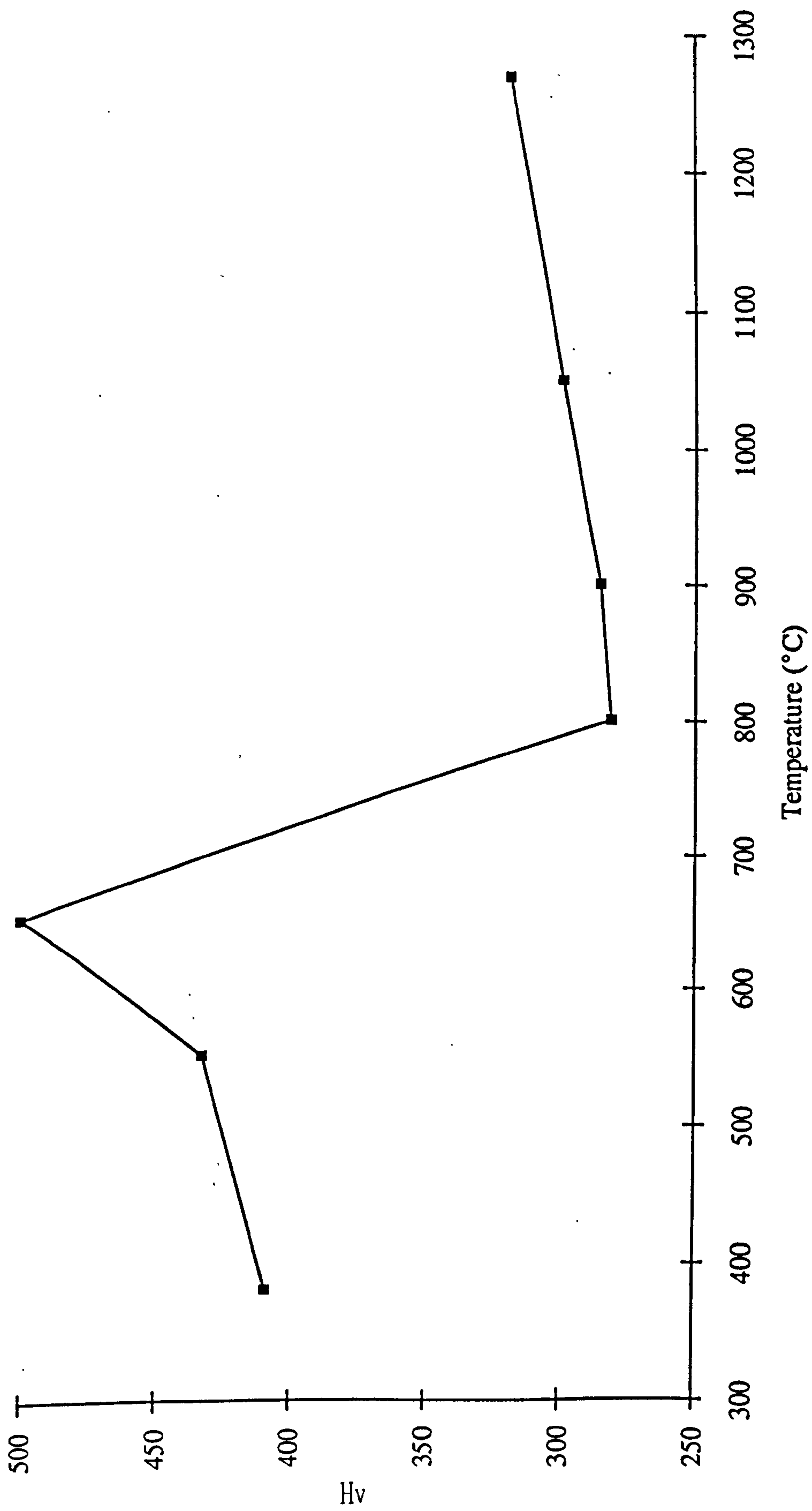


Figure 5.19. Temperature Dependence of 1000 hrs Aged Hardness in Ti-20-15-0.9

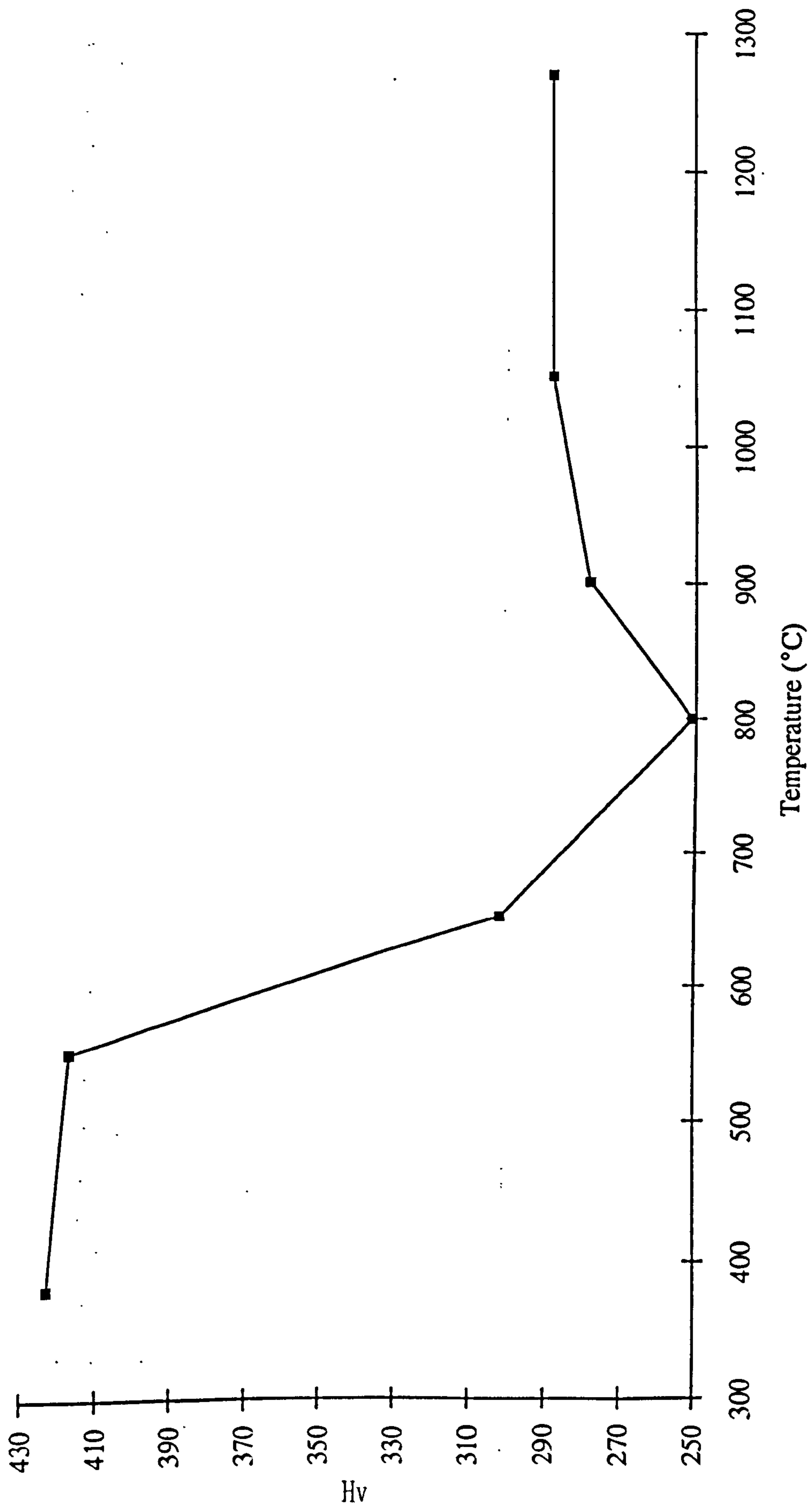


Figure 5.20. Temperature Dependence of 1000 hrs Aged Hardness in Ti-23-11-0.9

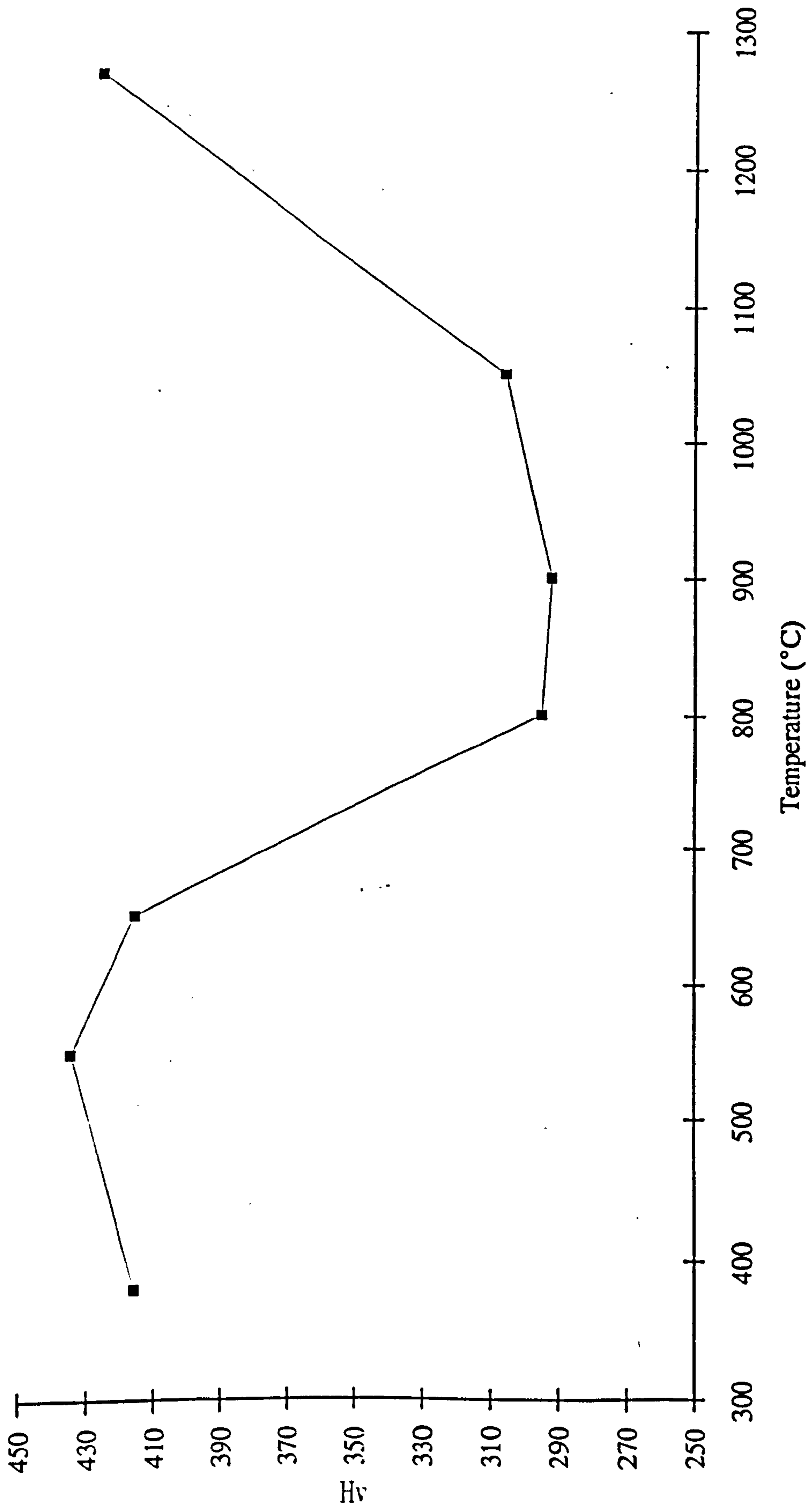
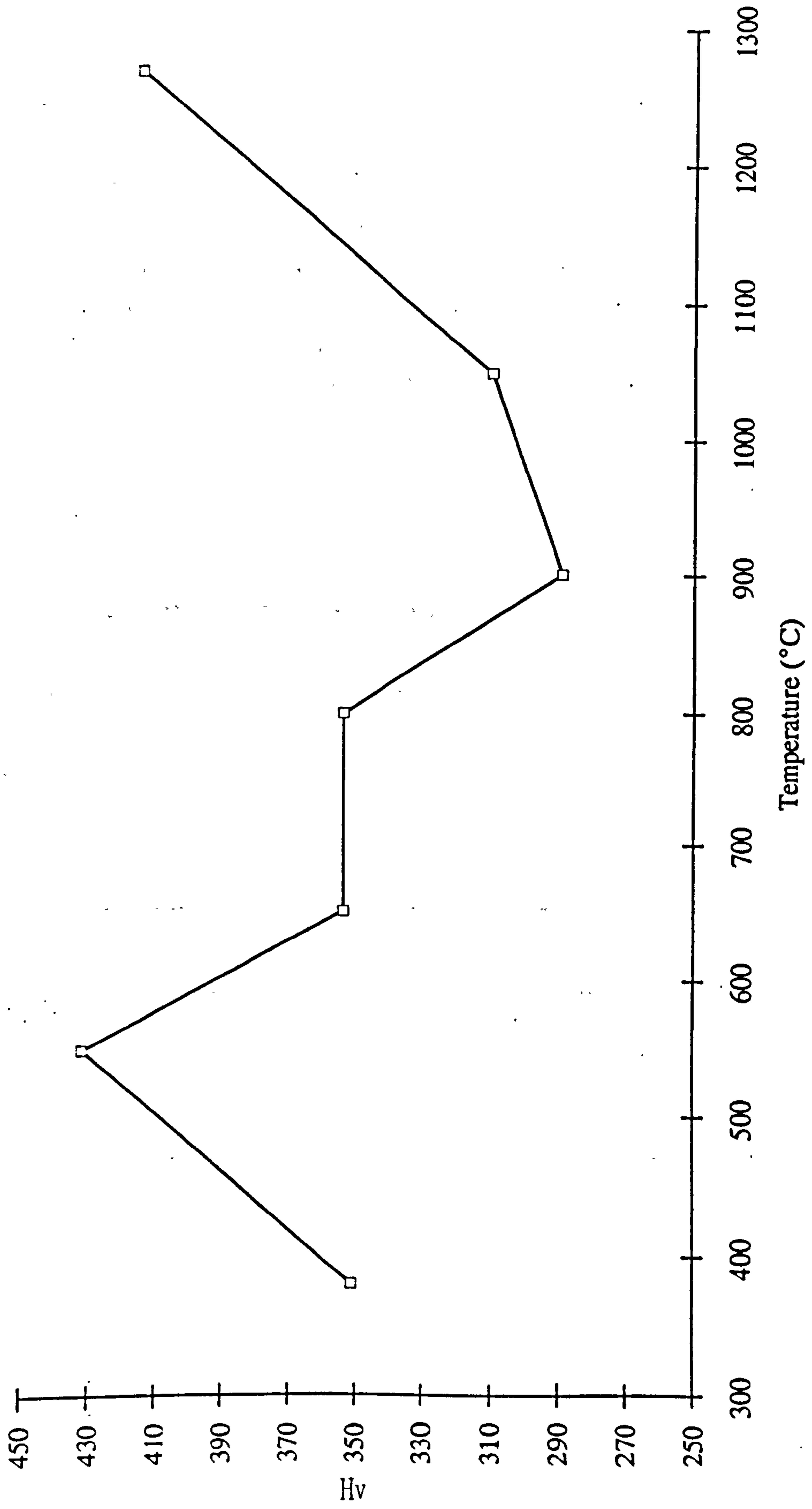


Figure 5.21. Temperature Dependence of 1000 hrs Aged Hardness in Ti-23-15-0.9



α_2 volume fractions, the hardness increases. This implies that the β_0 phase is harder than the α_2 phase, which would not be expected given that the α -based phases are generally harder and stronger than β based phases. Though it is possible that the increased hardness is produced by the increase in ω phase or tweed which the quenching produces.

The substitution of the O phase for the β_0 phase at 800°C does not appear to have any effect on the overall hardness of the alloys, whose decrease in hardness remains roughly constant between 1050 and 800°C, particularly in the 11 at.% Nb alloys. The only marked deviation from this behaviour is exhibited by the Ti-23-15-0.9 alloy, which shows a jump in hardness of approximately 55 Hv at 800°C, relative to the value found at 900°C. The differing behaviour is probably attributable to the fact that this alloy is within the three phase $\alpha_2 + \beta_0 + O$ region at this temperature, and the other three are within the two phase $\alpha_2 + O$ region.

5.7. Summary of Phases Present in Aged Alloys

The tables below show the phases which have been identified in each alloy after the longest ageing treatment which was used, which for most of the alloys is 1000 hrs (approx. 6 weeks).

Alloy	Ageing Time (hours)	β_0	α_2	O	Ti ₅ Si ₃
Ti-20-11-0.9	24	Yes			
Ti-20-15-0.9	24	Yes	Yes		Yes
Ti-23-11-0.9	24	Yes	Yes		
Ti-23-15-0.9	24	Yes	Yes		

Table 5.6. Phases Present at 1100°C.

Alloy	Ageing Time (hours)	β_0	α_2	O	Ti ₅ Si ₃
Ti-20-11-0.9	1000	Yes	Yes		
Ti-20-15-0.9	1000	Yes	Yes		
Ti-23-6-0.9	168	Yes	Yes		
Ti-23-11-0.9	1000	Yes	Yes		
Ti-23-13-0.9	168	Yes	Yes		
Ti-23-15-0.9	1000	Yes	Yes		
Ti-20-11-0.5	168	Yes	Yes		
Ti-20-11-1.2	168	Yes	Yes		Yes
Ti-20-11-1.5	168	Yes	Yes		Yes
Ti-23-6-1.5	168	Yes	Yes		
Ti-23-11-1.5	168	Yes		Yes	Yes
Ti-23-15-1.5	168	Yes		Yes	Yes
Ti-23-11-3	168	Yes		Yes	Yes

Table 5.7. Phases Present at 1050°C

Alloy	Ageing Time (hours)	β_0	α_2	O	Ti ₅ Si ₃
Ti-20-11-0.9	1000	Yes	Yes		
Ti-20-15-0.9	1000	Yes	Yes		
Ti-23-6-0.9	168	Yes	Yes		
Ti-23-11-0.9	1000	Yes	Yes		
Ti-23-13-0.9	168	Yes	Yes		
Ti-23-15-0.9	1000	Yes	Yes	Yes	
Ti-23-6-1.5	168	Yes	Yes		Yes
Ti-23-11-1.5	168		Yes	Yes	Yes
Ti-23-15-1.5	168			Yes	Yes
Ti-23-11-3	168		Yes	Yes	Yes

Table 5.8. Phases Present at 900°C

Alloy	Ageing Time (hours)	β_0	α_2	O	Ti ₅ Si ₃
Ti-20-11-0.9	1000		Yes	Yes	
Ti-20-15-0.9	1000		Yes	Yes	
Ti-23-11-0.9	1000		Yes	Yes	
Ti-23-13-0.9	168		Yes	Yes	
Ti-23-15-0.9	1000		Yes	Yes	
Ti-23-11-1.5	168		Yes	Yes	Yes
Ti-23-15-1.5	168			Yes	Yes
Ti-23-11-3	168		Yes	Yes	Yes

Table 5.9. Phases Present at 800°C

Alloy	Ageing Time (hours)	β_0	α_2	O	Ti ₅ Si ₃
Ti-20-11-0.9	1000		Yes	Yes	
Ti-20-15-0.9	1000		Yes	Yes	
Ti-23-11-0.9	1000		Yes	Yes	
Ti-23-15-0.9	1000		Yes	Yes	

Table 5.10. Phases Present at 650°C

5.8. Air Cooled Conditions

5.8.1. β Solution Treated and Aged Alloys

A series of alloys based on the ternary composition Ti-20Al-11Nb were examined in a solution treated and aged condition to study the effect of the addition of silicon on the microstructure. The set of five alloys coded as 5 to 9 (see Table 3.2) were provided by D.R.A. having been previously heat treated as follows; β solution treated for 1 hour at 1150°C, gas cooled in an argon stream at a cooling rate equivalent to air cooling. Aged at 625°C for 2 hours and again gas cooled.

5.8.1.1. Microstructure of Base Alloy

In the heat treated condition described in section 5.8.1, the microstructure of the base Ti-20-11 alloy consists of a series of fine α_2 platelets in a retained β background (see Figure 5.22a.). This microstructure is retained in alloys with up to 0.9at% Si added (see figures 5.22b & c). An important detail to note is that there is a distribution of α_2 along the prior β_0 grain boundaries (see Figure 5.22c) which is likely to be detrimental to the mechanical properties of the bulk material. Examination of this alloy when quenched from the β_0 solution treatment temperature and then aged at 650°C for a similar period of time (see section 5.5) produces a microstructure which is very similar to that found here, indicating that the precipitation of the α_2 platelets probably occurs during the ageing treatment, and is not a product of the relatively slow cooling from the β_0 solution treated condition.

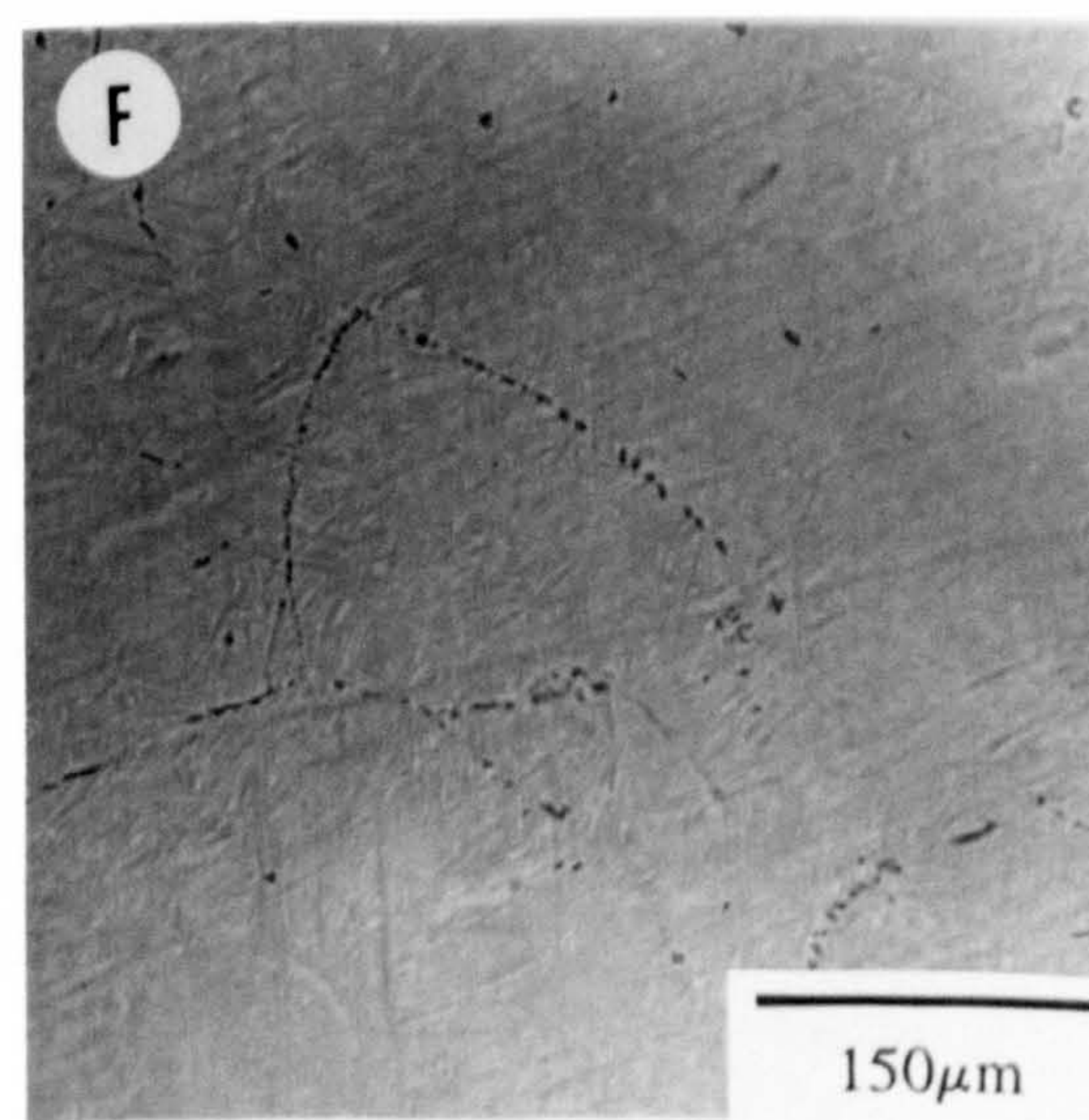
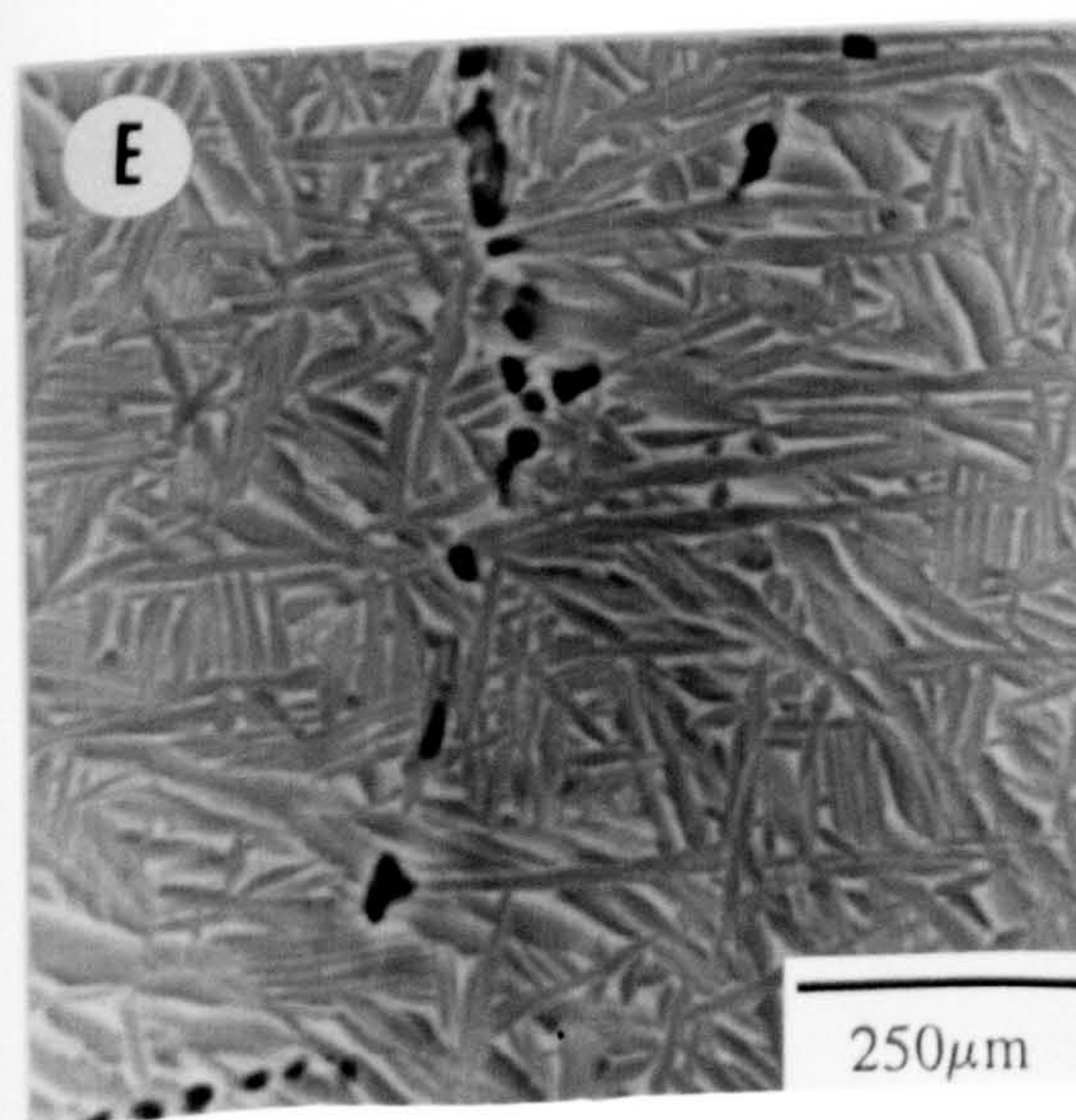
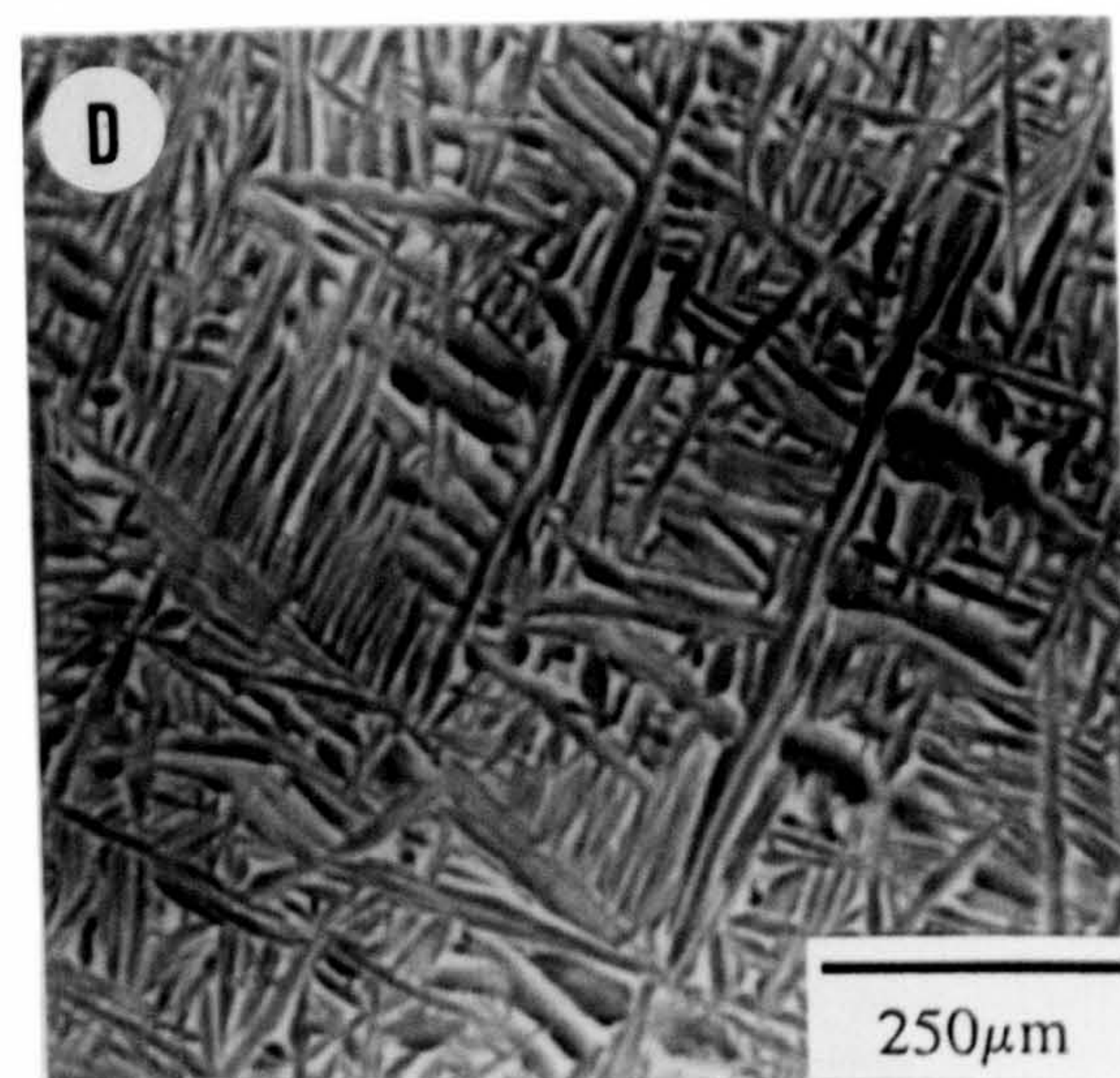
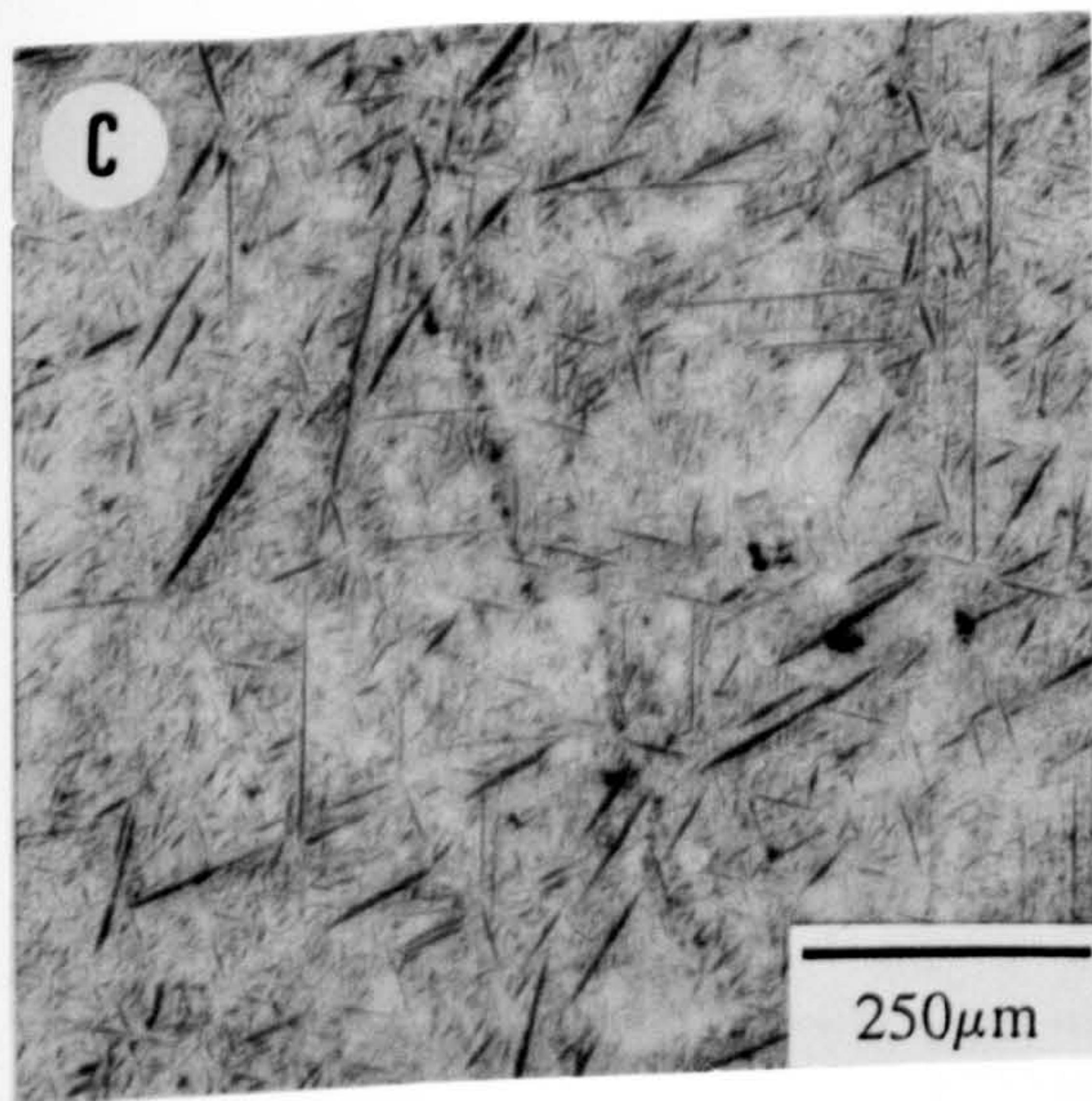
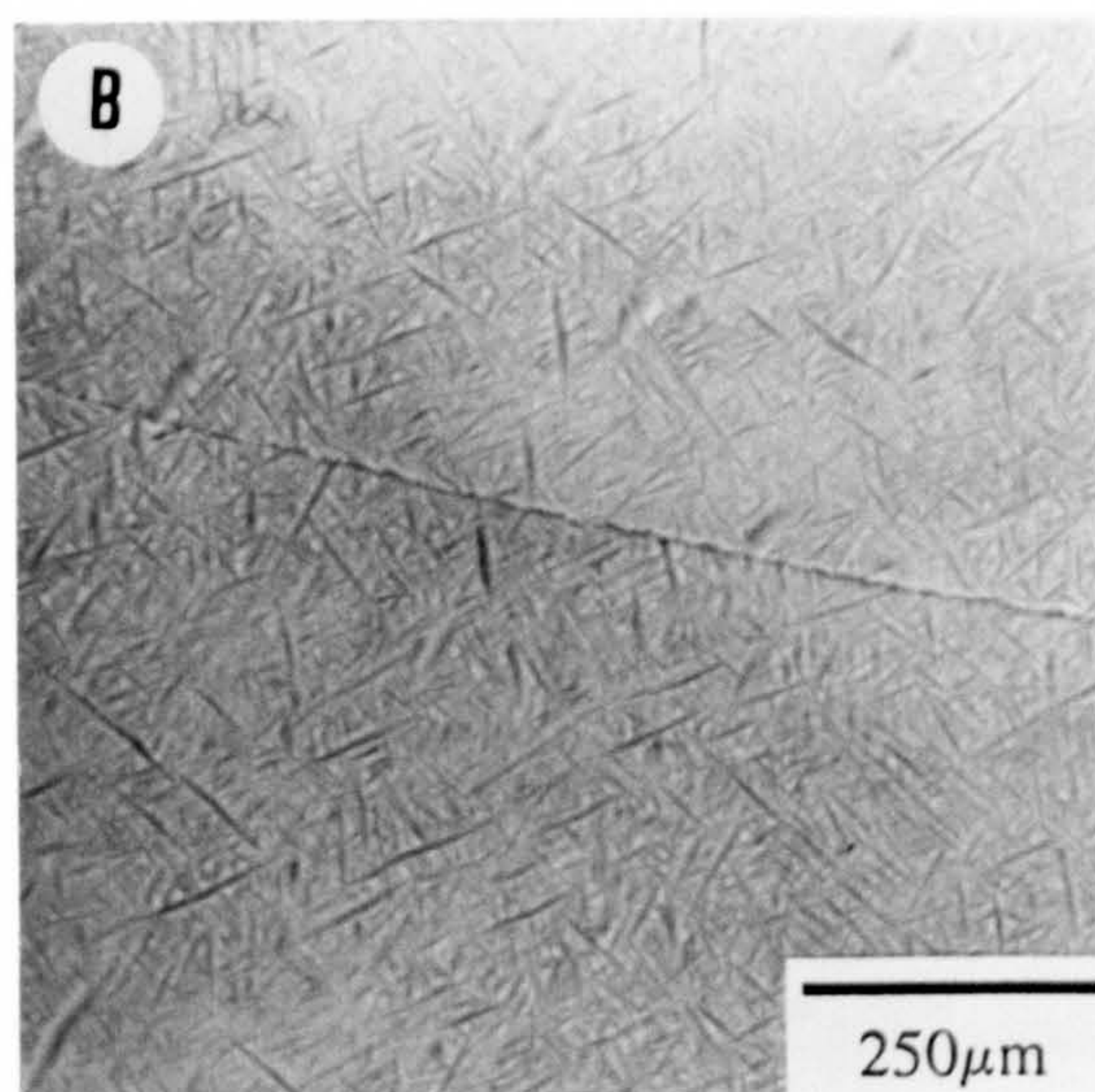
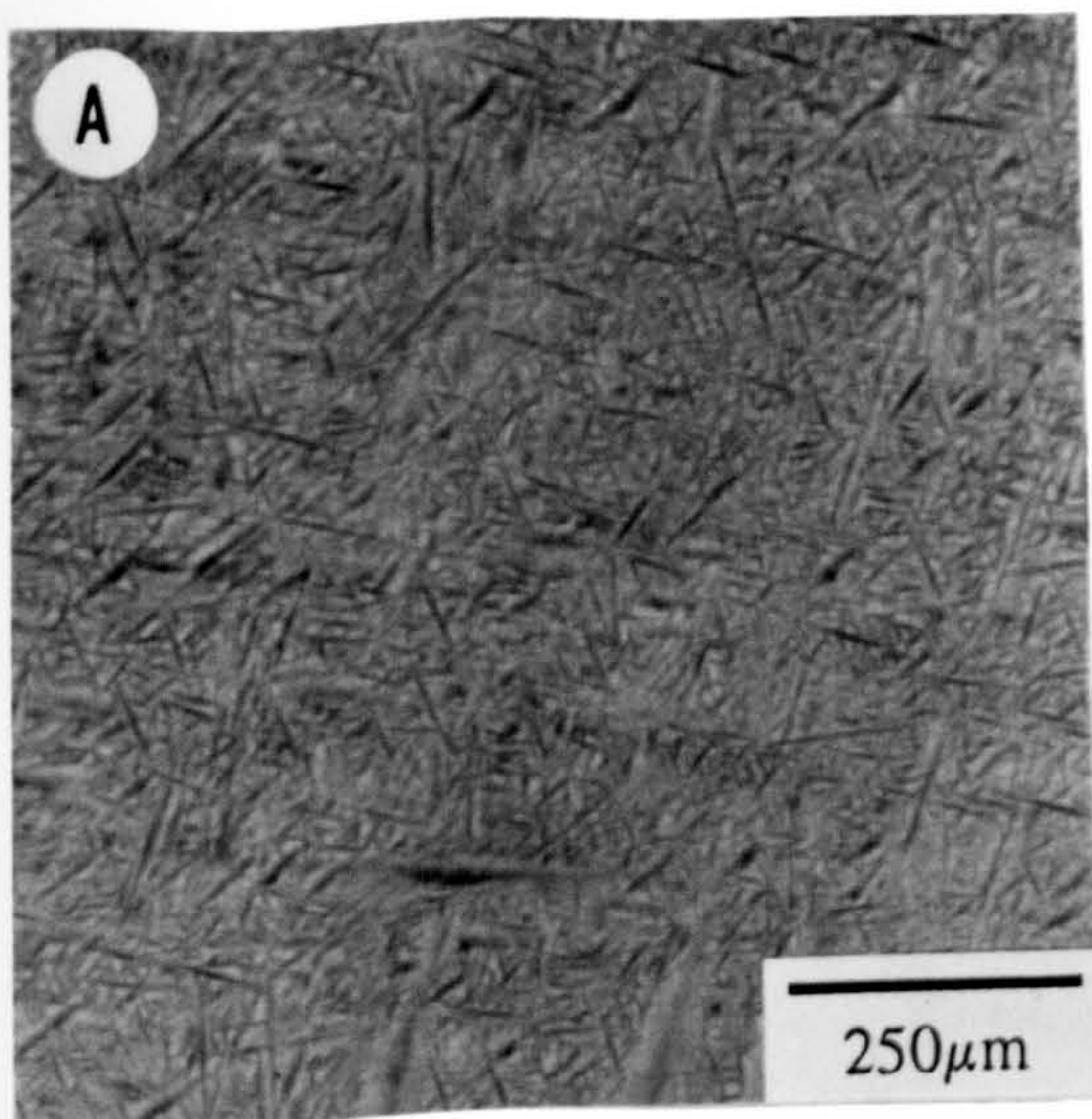
5.8.1.2. Microstructure of Higher Silicon Content Alloys.

When the silicon content of the alloys is raised above a level determined as approximately 1at.%, the microstructure of the alloy changes markedly. This is shown clearly in Figure 5.22d. As can be seen in this micrograph, the structure has been coarsened noticeably. The darker coloured platelets are still produced by the precipitation of α_2 , but the background, which in the lower silicon content alloys was formed from untransformed β_0 , is now made up of a series of very fine particles of

Figure 5.22.

SEM BEI micrographs of Ti-20Al-11Nb series alloys solution treated 1150°C/1hr, aged at 625°C/2hrs, mechanically polished and deep etched with 3vol.%HF-10vol.%HNO₃ in water.

- (a) Alloy Ti-20-11. Dispersion of fine α_2 platelets (dark) in a β matrix.
- (b) Alloy Ti-20-11-0.5. Fine dispersion of α_2 platelets (dark) in a β matrix. This microstructure is of the same form and scale as that shown in (a).
- (c) Alloy Ti-20-11-0.9. This micrograph shows that with 0.9at.% silicon added, the microstructure of the alloy in this condition remains the same.
- (d) Alloy Ti-20-11-1.2. When the silicon content is raised to 1.2at.%, the microstructure is markedly changed. The structure is coarsened noticeably. The darker platelets are still α_2 as in the ternary alloy, but the background phase has transformed from β to O.
- (e) Alloy Ti-20-11-1.5. The microstructure remains similar to that shown in (e), but with the addition of silicides along the prior β grain boundaries (shown as the darkest phase).
- (f) Alloy Ti-20-11-1.5. This low magnification micrograph shows the distribution of the silicide particles along the grain boundaries, as well as a distribution of particles inside the prior β grains.



the phase described as O. This phase was first reported by Banerjee [Ban87], and has since been found in a variety of alloys based on the ternary addition of between 10 and 25at.% niobium to Ti_3Al based alloys. The structure of the O platelets can be seen in Figure 5.24b, and should be compared with the structure of the β_0 shown in Figure 5.24a.

As can be seen from Table 5.11. the b lattice parameter of the orthorhombic phase is noticeably distorted from that of the α_2 phase. If α_2 is indexed as an orthorhombic crystal then the b parameter would be 1003pm (to change the indexing method, the b parameter of the hexagonal structure is multiplied by $\sqrt{3}$). This distortion is greater than that reported in most other orthorhombic structures of similar compositions (see Table 2.2). The probable reason for this will be detailed later.

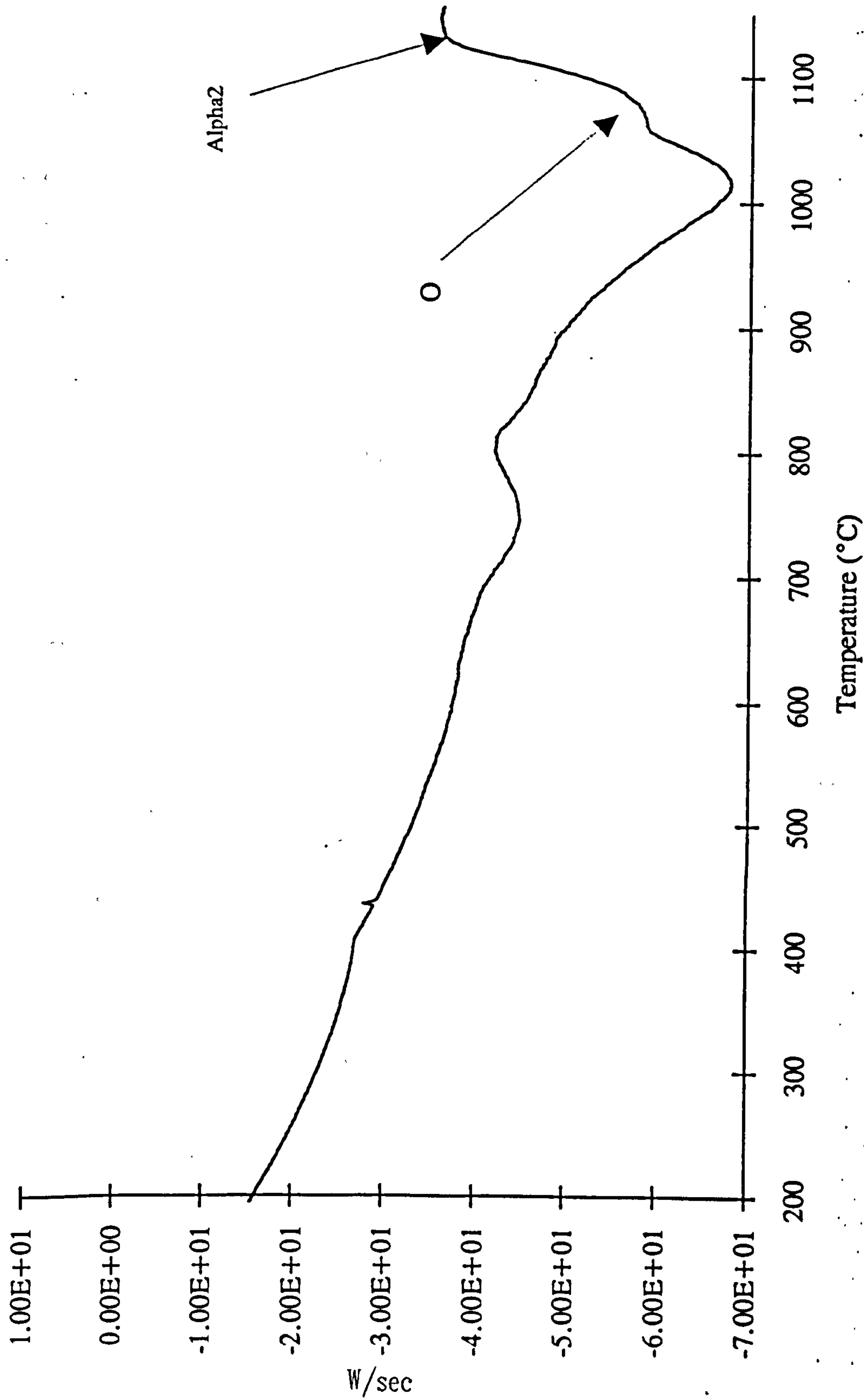
Si Content	α_2		β_0		O	
	a	c	a	a	b	c
				-	-	-
0	579	466	326			
0.5	579	465	326	-	-	-
0.9	579	465	326	-	-	-
1.2	579	465	-	585	975	466
1.5	579	465	-	585	975	466

Table 5.11. Lattice Parameters (in pm)

To identify the difference between the phase transformations which occur to produce the $\alpha_2 + \beta_0$ structure and those for the $\alpha_2 + \text{O}$ structure, a series of D.S.C. (Differential Scanning Calorimetry) experiments were undertaken. Samples of each of the five alloys in the aged condition were heated at 30°C / minute up to 1200°C. From this it is possible to identify the phase transformations which occurred during the cooling of the samples, and the approximate temperatures at which they occurred. A detailed explanation as to the identification of the peaks is given in the appendix, but the transformation from β_0 to O which occurs in these alloys is identified in Figure 5.23. From this, and examination of other alloys it is clear that the transformation from β_0 to O occurs during the air cooling from the solution treated condition. This explains why

the microstructure is much coarser than in the $\alpha_2 + \beta_0$ alloys in which the α_2 is produced at a much lower temperature.

Figure 5.23. D.S.C. Curve Showing the start of transformation of beta to alpha2 and O on cooling.



As was discussed in Section 4.1., the addition of Nb to Ti₃Al increases the stability of the β phase with respect to any martensitic transformations on quenching. There is also no formation of α_2 during the quenching process. When silicon is added to one of these β stabilised alloys it has a large effect on the transformations which occur during rapid cooling. When the alloy (in this case Ti-20Al-11Nb-1.2Si) cools below approximately 1000°C, the rapid transformation of β_0 to O begins. The composition of O phase (see Table 5.12.) is markedly different from the composition of β_0 in the single phase β_0 phase field prior to the transformation, which has a nominal composition of Ti-20Al-11Nb-1.2Si. When the transformation occurs, the composition of the remaining β_0 is markedly poorer in Nb and richer in Al than previously, and thus is less strongly β stabilised. It is suggested that this induces a transformation from β to α_2 during the cooling of the alloy.

Alloy	Structure	Composition (at.%)			
		Ti	Al	Nb	Si
Ti-20Al-11Nb-0.9Si	α_2	67.6	21.1	10.3	1.0
	β_0	66.0	11.1	22.1	0.0
Ti-20Al-11Nb-1.2Si	α_2	66.6	21.5	10.2	1.7
	O	67.6	11.7	21.8	0.4

Table 5.12. Composition Of Alloys in 1150°C Solution Treated, 625°C Aged Condition (from thin foil EDS)

When the silicon level in the alloy is raised further, to 1.5at.%, the solubility of silicon in the matrix phases is exceeded, and silicide precipitates based on the stoichiometric structure Ti₃Si₂ are produced. These silicides are formed during the β_0 solution treatment as precipitates on the grain boundaries. This marking of the grain boundaries clearly shows that, in the higher silicon content alloys, α_2 does not grow along the β_0 grain boundaries (see Figure 5.22e & f). It is suggested that this is because the β_0 to O transformation occurs *before* the α_2 begins to be produced⁵⁰ there are no β_0 grain boundaries for the α_2 to grow on.

5.8.2. $\alpha_2 + \beta$ Solution Treated and Aged Alloys

Two of the alloys discussed above were also heat treated in the $\alpha_2 + \beta$ phase field at 1050°C and then aged to allow a comparison between the microstructural effects of the two solution treatments on the material when aged. Figure 5.24c shows the typical microstructure for this heat treatment. The microstructure shows a relatively even distribution of 'blocky' α_2 in what, at 1050°C is a β_0 background (see Section 5.2.2). After ageing the β_0 phase has transformed to a $\alpha_2 + \beta_0$ structure similar in morphology, though finer in scale than that of the β solution treated alloy. When the silicon content is raised to a higher level, the microstructure remains the same with the addition of silicide particles (Figure 5.24d). It should be noted that the increase in the silicon level does not produce a modification of the microstructure such as that found in the β heat treated material, as no O phase has been found.

As the O phase is reported to be based on the stoichiometric composition Ti_2AlNb it is probable that a compositional shift away from this point would reduce or prevent its formation. Thus the effect of modifying the composition of the β_0 (by the large scale precipitation of α_2) in the 1050°C solution treated condition away from that in the 1150°C condition is probably preventing the $\beta_0 \Rightarrow \text{O}$ transformation from taking place.

Figure 5.24.

TEM micrographs of Ti-20Al-11Nb series alloys solution treated 1150°C/1hr, air cooled, aged at 625°C/2hrs, air cooled.

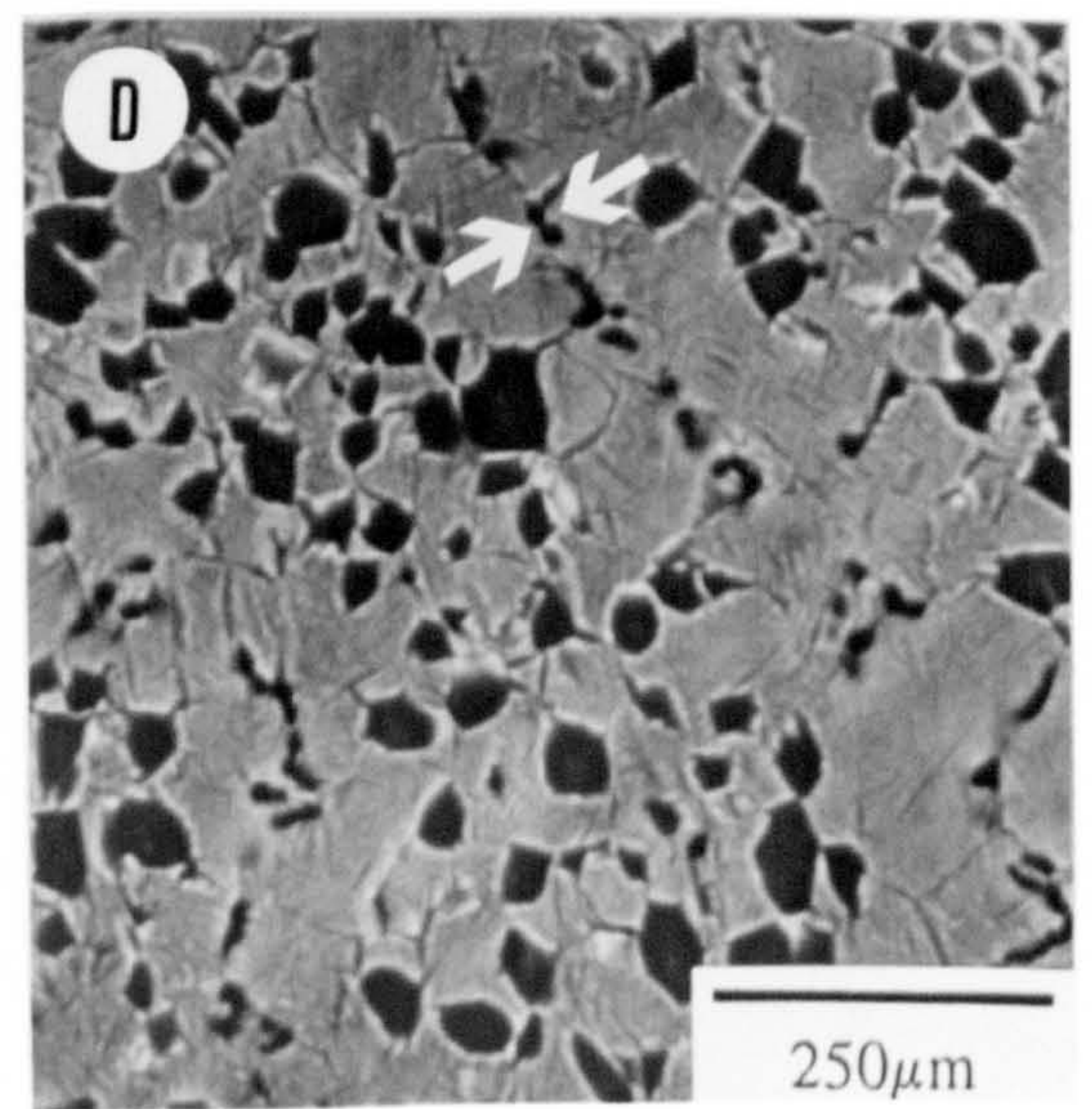
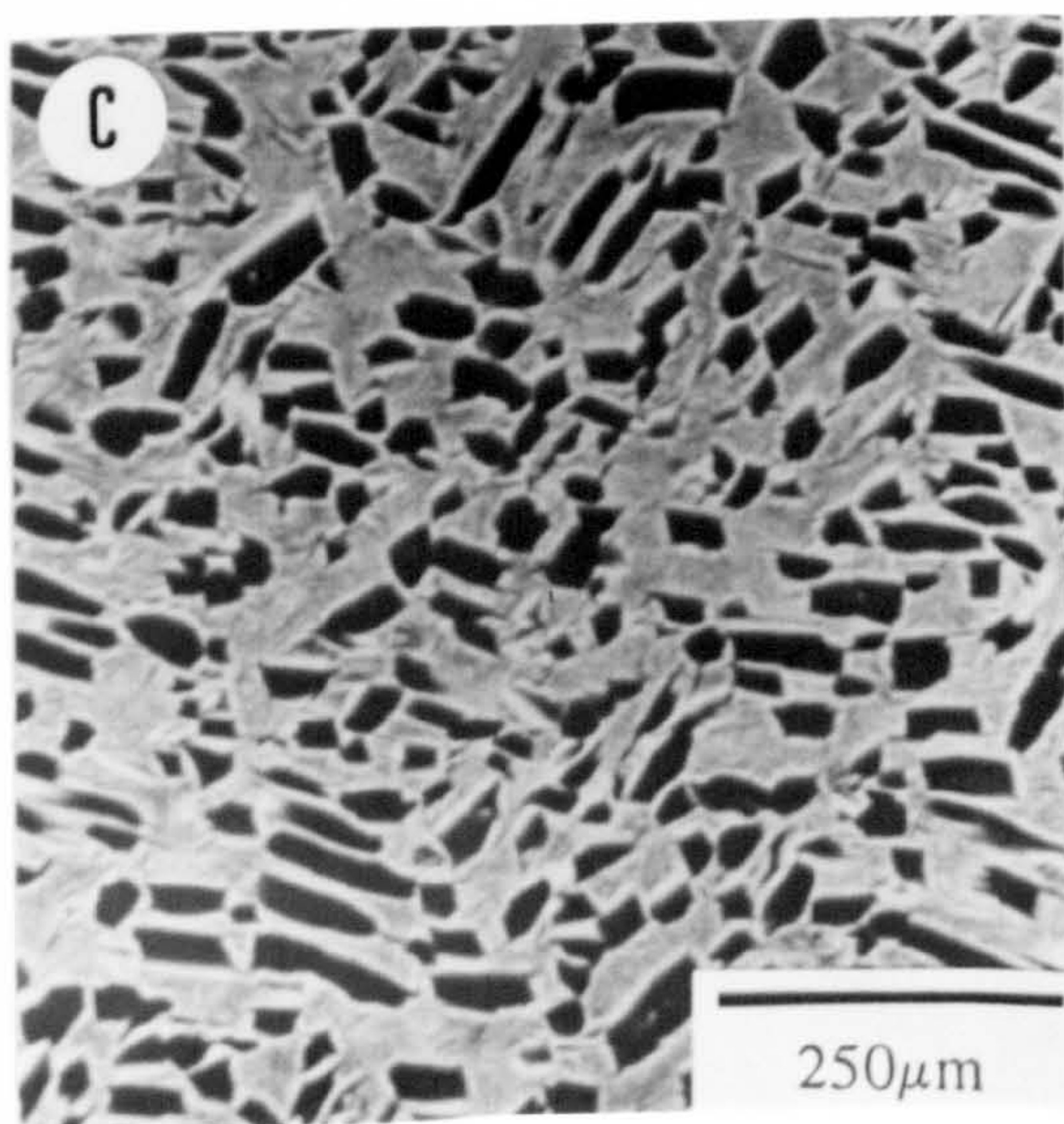
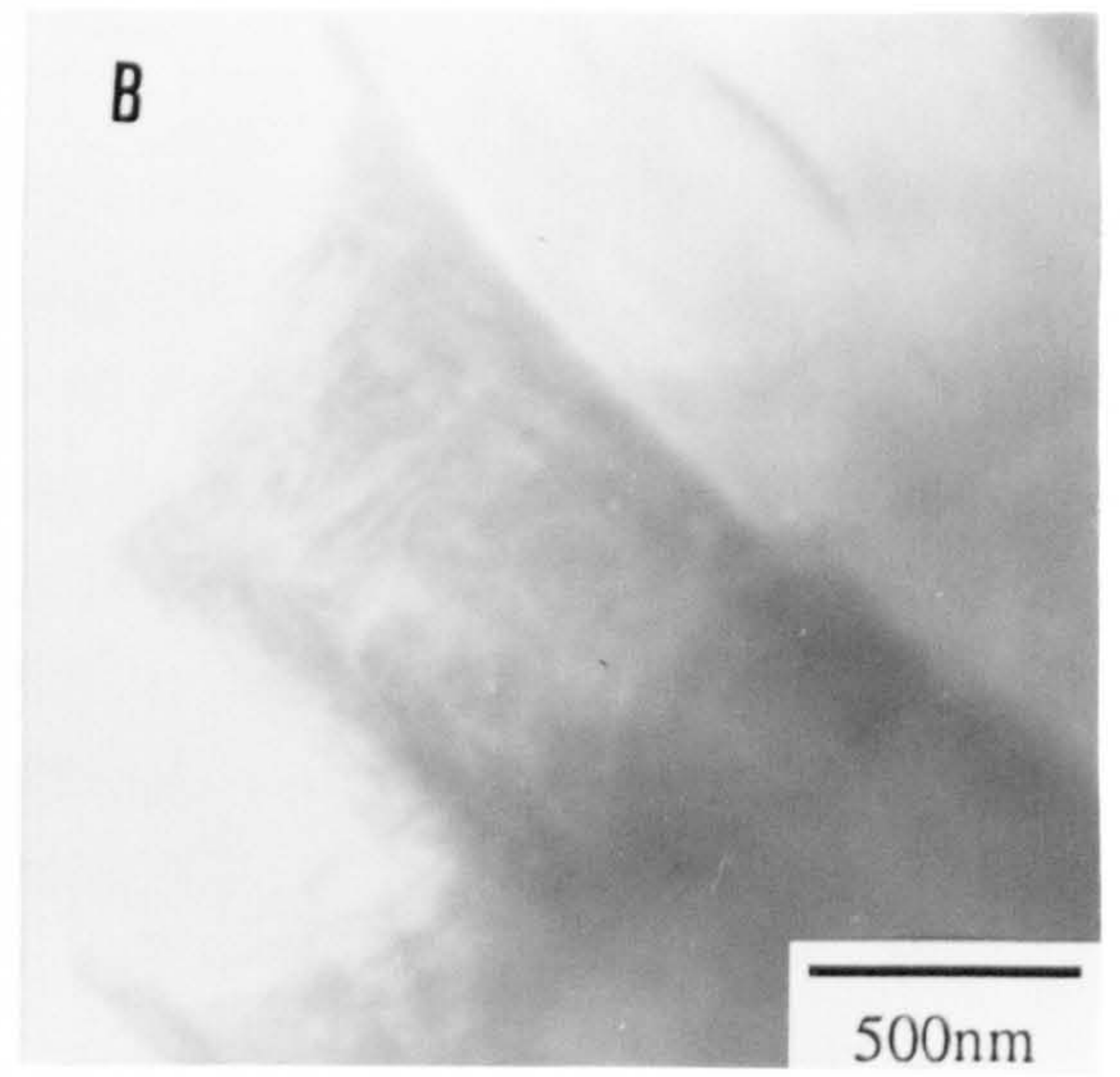
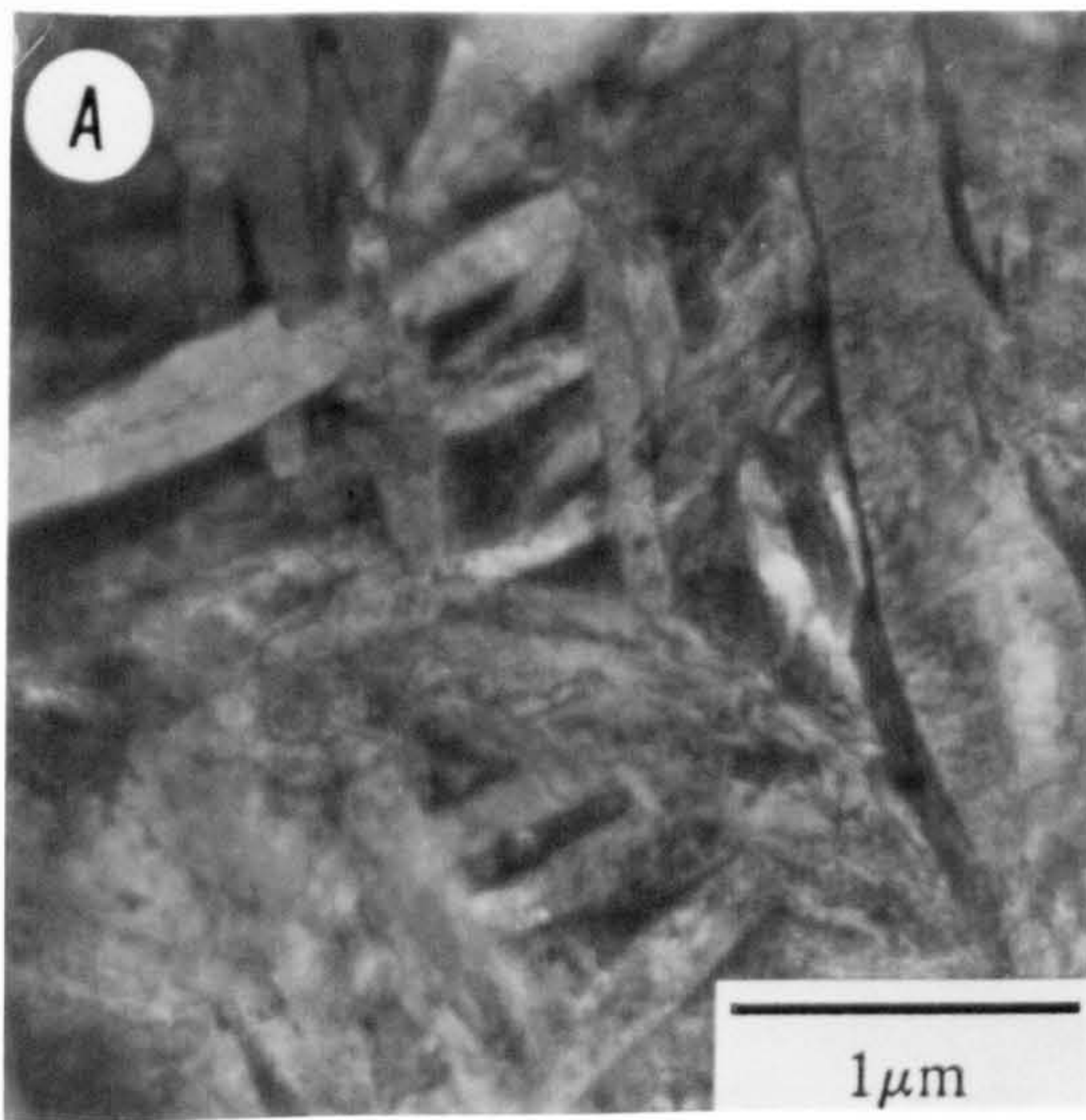
TEM foils, electrochemically thinned in 10 vol.% H₂SO₄ in CH₃OH.

- (a) Ti-20-11-0.5. This bright field micrograph shows α_2 platelets (light) in a background of β (dark).
- (b) Ti-20-11-1.2. This bright field micrograph shows detail of the very fine laths in an O grain (darker) surrounded by α_2 .

SEM SEI micrographs of Ti-20Al-11Nb series alloys solution treated at 1050°C for 1 hr, air cooled, then aged at 625°C for 2hrs, air cooled.

Mechanically polished and deep etched with 3vol.%HF-10vol.%HNO₃ in water.

- (c) Ti-20-11-0.5. This micrograph shows a distribution of α_2 grains (dark), which are similar to those in the alloy without secondary ageing. These are surrounded by a structure which in the 1050°C condition is β , but which after the secondary ageing has transformed to a structure of α_2 platelets in a β background similar to that found in the β solution treated then aged condition.
- (d) Ti-20-11-1.5. In this alloy the structure is similar, but with a distribution of silicide particles (marked on micrograph).



5.9. Summary

At 1050°C, the equilibrium microstructure is $\alpha_2 + \beta_0$ for most of the alloys. In alloys based on Ti-23-X-Y when the silicon content is 1.5 at.% or more, the α_2 phase is replaced by O. At 900°C, the microstructure of the base alloys is similar to that at 1050°C, only refined. The Ti-23-15-0.9 alloy moves into a three phase field, introducing O grains of a similar composition to the α_2 ones, only with a slightly higher niobium content. The α_2 phase at both 900 and 1050°C is stoichiometric $(\text{Ti+Nb})_3(\text{Al+Si})$. When added to Ti-Al-Nb in the $\alpha_2 + \beta_0$ phase field, the silicon acts on an isothermal basis as an α_2 stabilising element, even though it does not have this effect when considered over changing temperature.

Increasing the silicon content of the alloys induces an orthorhombic stabilising effect to the extent that in moving from Ti-23-15-0.9 to Ti-23-15-1.5, the structure transforms from $\alpha_2 + \beta_0 + \text{O}$ to $\text{O} + \text{Ti}_3\text{Si}_3$.

In Ti-20-11-X alloys air-cooled from 1150°C and then aged at 625°C, the microstructure consists of $\alpha_2 + \beta_0$ when the alloy contains less than 1 at.% silicon. When the silicon level is raised above that level a coarser structure of O laths with α_2 is formed. When the composition exceeds 1.5 at.% Si, silicide particles are also present.

Chapter 6.

Phase Transformations and Crystal Structures.

6.1. Introduction

This section brings together the evidence provided by microstructural features along with D.S.C. data and lattice parameter information to interpret the phase transformations which occur in the Ti-Al-Nb-Si system within the composition range studied.

As the system under examination contains four components, to represent a true isobaric section (constant pressure), it is necessary to utilise four spatial dimensions for the three compositional and one temperature axes. Due to this quaternary systems are generally represented by isothermal tetrahedra. As these are also difficult to interpret, the phase diagram sections discussed here have been simplified further. In alloys in which the silicon content is less than that which induces silicide formation (i.e. the alloys containing 0.9 at.% Si or less), ternary isothermal sections with axes representing titanium, niobium and a combined aluminium plus silicon content are plotted. Though the silicon content in the alloys does vary between the α_2 and the β phases, the change (~ 0.5 at.%) was considered small enough that a meaningful ternary section, ignoring this variation, could be produced. This has not been possible for the silicide containing alloys as the silicon level in the silicide (~ 30 at.%) modifies the ternary section by a very large degree.

When it is necessary to illustrate the effect of temperature on the system, clarity is lost when projecting the transformations onto a triangular prism. Thus it has been decided that pseudo-binary sections should be used to represent the transformations which occur. These are highly schematic, as no account is taken of any variations in the distribution of the other elements not directly represented within the diagram. Thus when interpreting the pseudo-binary sections provided, it should be noted that the phase boundaries are not placed accurately in the horizontal plane, and only indicate that a phase transformation occurs between the marked alloy compositions which it bisects. Some phase fields have not been identified microstructurally and have been inserted for compliance with the conventional rules for phase diagram production.

6.2. Constant Silicon Content Sections.

At the solution treatment temperature used throughout this work (1270°C), each of the alloys examined consists of either single phase β_0 (see Figure 6.1.) or a two phase structure consisting of Ti_3Si_3 particles within a β_0 matrix. At this temperature the maximum solid solubility of silicon in β_0 is approximately 1.1 at.%. In the alloys in which the silicide does not form, on quenching the alloy contains retained β_0 with a tweed structure [Str88] and some ω type precipitates. A type of orthorhombic martensite formation is formed in the higher silicon level alloys. This has been discussed in section 4.

At 1050°Cⁱⁿ the isothermal section illustrated in Figure 6.2., the alloys plotted all lie within a two phase α_2 plus β_0 phase field. Over most of the composition range studied the boundaries of both the α_2 and the β_0 phase lie parallel to the constant Al+Si contours. As described in section 5, the α_2 phase extends stoichiometrically within the system towards the Nb-rich regions. It is important to note that in the most highly alloyed samples, there is a deviation from this behaviour, as the phase boundaries swing towards the aluminium corner. If the curve of the β_0 boundary is extrapolated beyond the alloy compositions examined, it follows a line which would encompass a region in which the nominal compositions of both the β_0 and O phases occur, within the β_0 single phase field. Fully ordered β_0 as described by Banerjee [Ban87] and the orthorhombic phase characterised by Mozer [Moz90] both have the same nominal composition of Ti_2AlNb , though they exist over different temperature ranges.

When the temperature is lowered to 900°C (Figure 6.3), the compositions of the two phases are not changed significantly from those found at 1050°C in the $\alpha_2 + \beta_0$ phase field. The appearance of a three phase field ($\alpha_2 + \beta_0 + \text{O}$), within the alloy range studied does produce a significant increase in the separation of the compositions of the α_2 and β_0 phases. While the α_2 phase has split into two phases of similar composition with slightly varying Nb content, the β_0 phase shifts its composition markedly. As would be expected, for the β_0 phase field to exist at lower temperatures, the composition must be more highly β_0 stabilised than at higher temperatures. So the β_0 phase in equilibrium with α_2 and O moves to compositions much richer in Nb as temperature decreases, and the relative thermodynamic stability of α_2 and O with respect to β_0 increases.

Figure 6.1. Ternary section in Ti-Al-Nb Phase Diagram at 1270°C with Constant 0.9 at.% Si Content

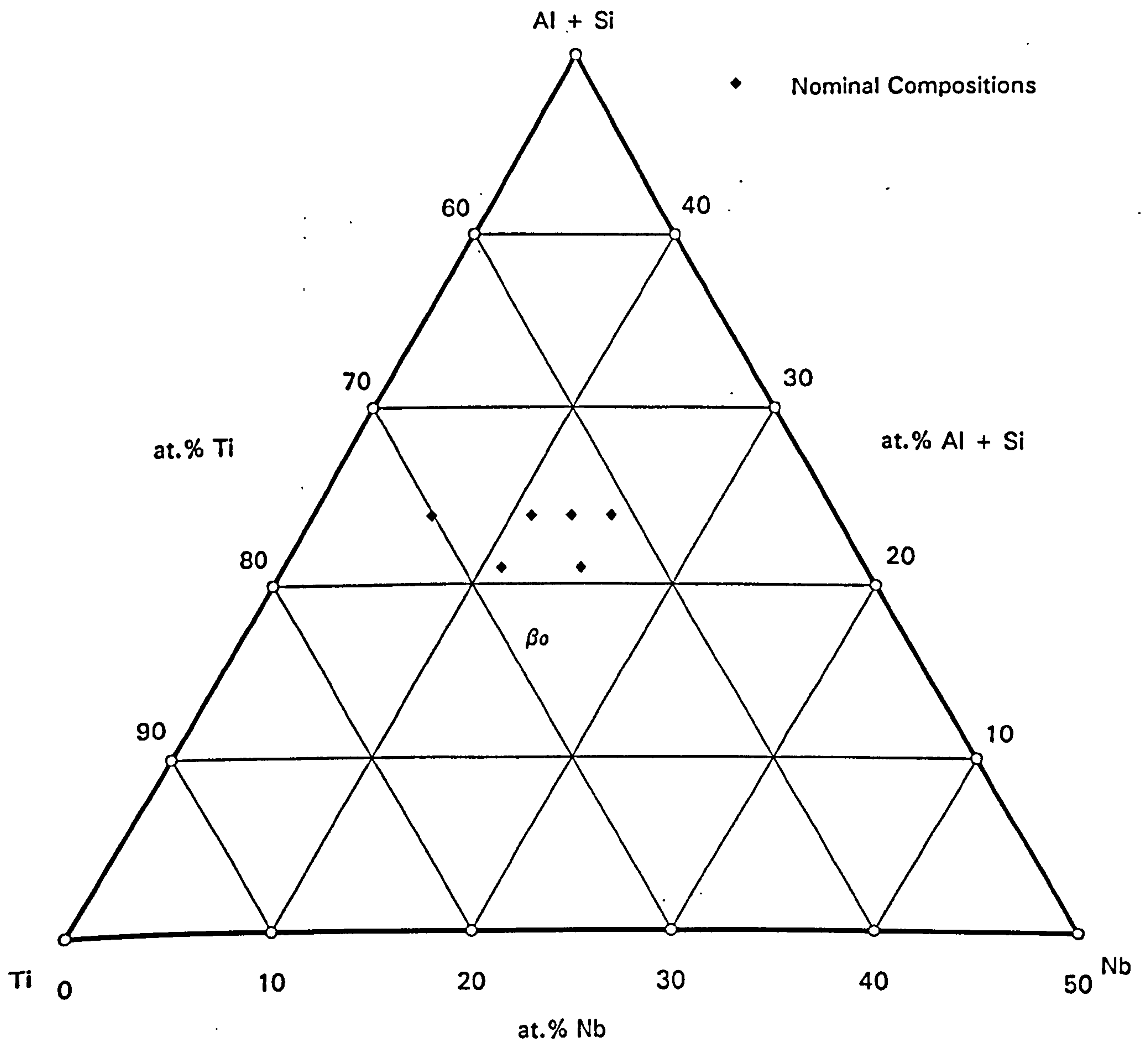


Figure 6.2. Ternary section in Ti-Al-Nb Phase Diagram at 1050°C with Constant 0.9 at.% Si Content

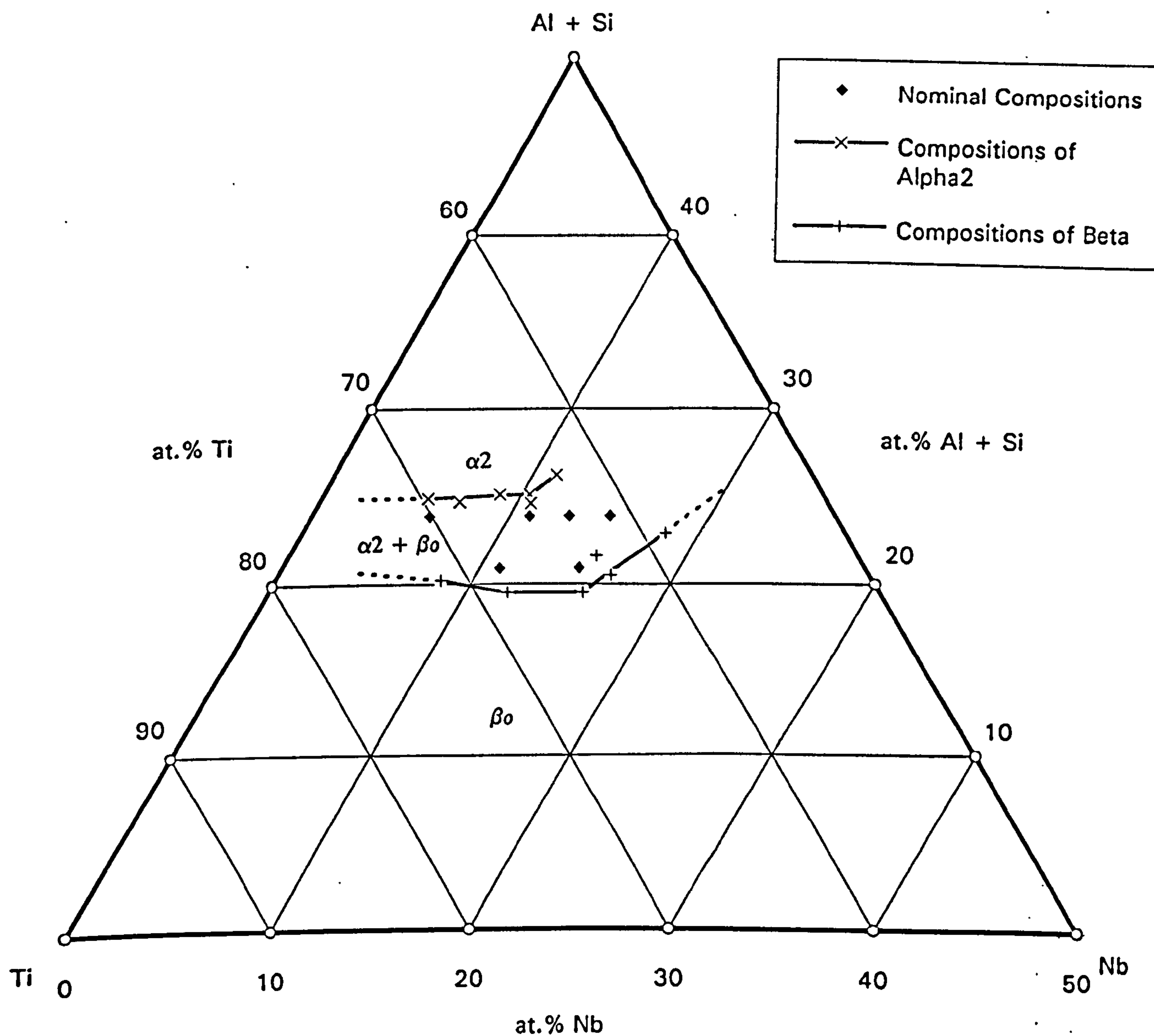
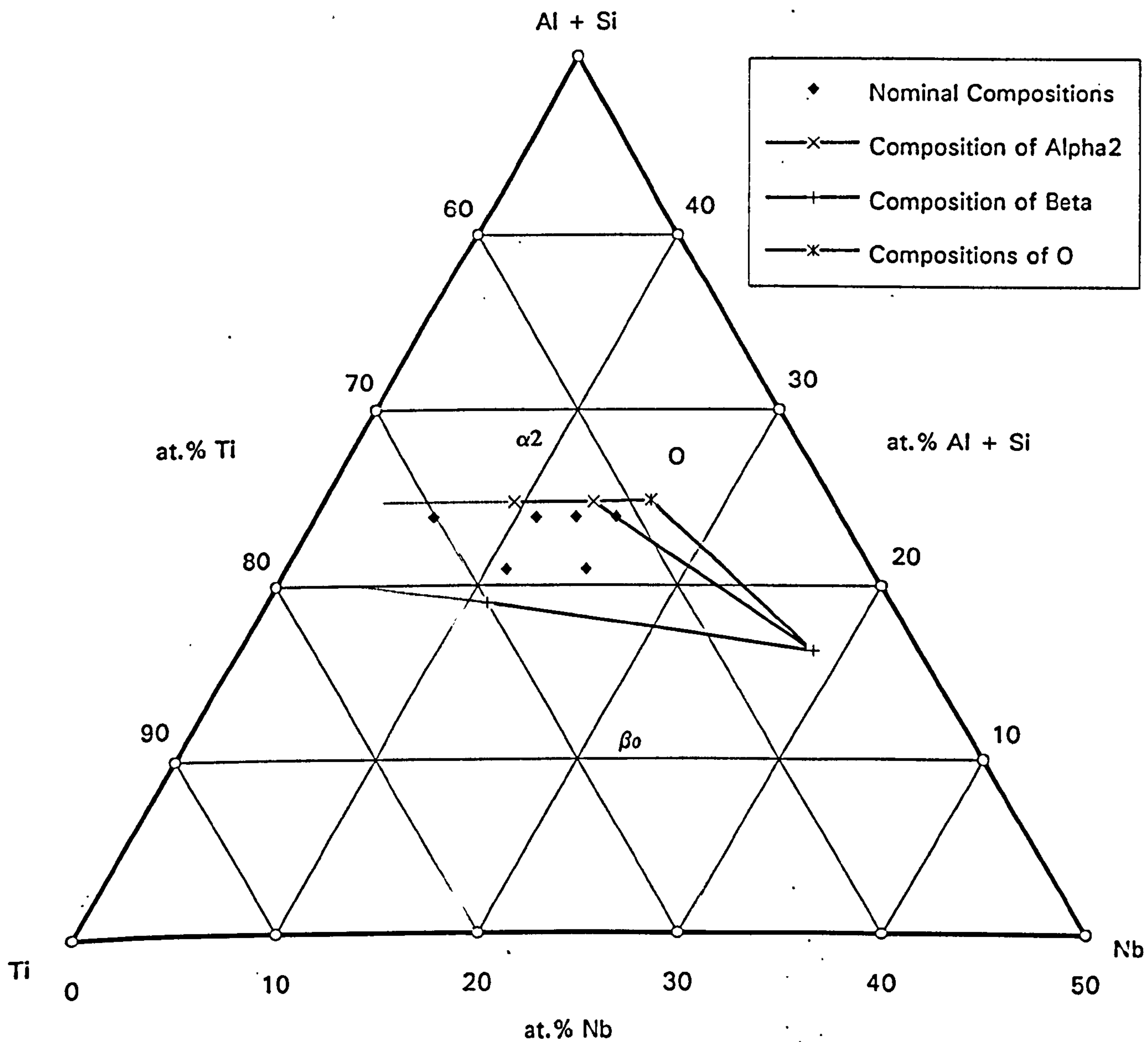


Figure 6.3. Ternary section in Ti-Al-Nb Phase Diagram at 900°C with Constant 0.9 at.% Si Content



A comparison of the diagram sections at 1050 and 900°C, and the microstructure of the Ti-23-15-0.9 alloy at 900°C indicates that the transformation from two to three phases via the opening up^{of} a miscibility gap in the α_2 and the formation of α_2 and O platelets. The composition of the O phase is similar to that of the orthorhombic phase identified by Banerjee [Ban87]. If this miscibility gap were to extend to a high enough temperature, then a ternary peritectoid formation ($\beta_0 + \alpha_2 \rightarrow O$) would be produced, as suggested by Banerjee [Ban88].

The current work has produced no conclusive evidence either way, but for convenience the pseudo-binary vertical sections are shown with an intermediate structure between a peritectoid and eutectoid formation present. The recent work of Thomas [Tho92] clearly shows that the β_0 transus is linear for alloys of similar compositions to those examined here, which indicates a peritectoid formation.

The vertical section in Ti-20-X-0.9 shown in Figure 6.5. shows that the phase region which at 900°C was $\alpha_2 + \beta_0$, has now changed to $\alpha_2 + O$. The O phase present is of a markedly different composition to that found at 900°C, and is very similar to that of the β_0 phase at 900°C, while the α_2 composition has remained at a similar level to that found at 900°C.

Previous examinations have identified O phase within two largely different compositional regions for alloys of ternary compositions similar to the alloys studied here. To explain why this occurs (at least in quenched and aged alloys such as these) it is necessary to consider the transformations which occur while the alloy is being heated from room temperature to the ageing temperature. To do this it is necessary to study the pseudo-vertical sections of the phase diagram. These were identified by a combination of microstructural information and D.S.C. curves, samples of which are shown at the end of this section along with identification of the transformations occurring and their identifying characteristics. A summary of the transformation temperatures for the four base alloys is shown below in Table 6.1.

Transformation	Alloy			
	Ti-20-11-0.9	Ti-20-15-0.9	Ti-23-11-0.9	Ti-23-15-0.9
meta. $\beta \Rightarrow$	375	393	407	411
$\alpha_2 + \text{meta. } \beta$				
meta. $\beta + \alpha_2$	710	725	714	731
$\Rightarrow \alpha_2 + \text{O}$				
$\alpha_2 + \text{O} \Rightarrow$	844	831	842	826
$\alpha_2 + \text{O} + \beta$				
$\alpha_2 + \text{O} + \beta \Rightarrow$	884	890	896	912
$\alpha_2 + \beta$				
$\alpha_2 + \beta \Rightarrow \beta$	1102	1102	1142	1159

Table 6.1. Transformation Initiation Temperatures For Alloys During Heating in °C.

Microstructural examination failed to detect a three phase $\alpha_2 + \beta_{\text{O}} + \text{O}$ field in three of the alloys (Ti-20-11-0.9, Ti-20-15-0.9 and Ti-23-11-0.9), though examination of D.S.C. curves has provisionally identified the boundaries of the three phase field. Note - to follow the rules for phase diagram construction it is necessary to assume that these alloys must pass through a three phase field, as otherwise the phase diagram must include a 'surface' at which three phases meet, i.e. on this vertical section three phases will meet at a point. The phase rule only permits an even number of phases to meet at such a point (or 'surface' in four dimensions) [Gib06].

The phase sections incorporating this data are shown in Figures 6.8, 6.9, 6.11 and 6.12. The dashed lines on the phase sections mark the limits of metastability of the α_2 and β_{O} phases at low temperatures. The lower temperature line indicates the temperature at which α_2 phase begins to precipitate from the metastable β_{O} structure during heating. The higher temperature dashed line indicates the transformation of the remaining metastable β to the O phase. Examinations of the effect of ageing on the quenched microstructure in section 5 show that, for example an alloy aged at 800°C will transform in the following manner during the heating up to 800°C, and the isothermal ageing process;



Thus, the diffusional formation of α_2 during the heating process will change the composition of the β_{O} markedly, moving it towards the Nb rich corner of the phase

diagram and thus stabilising it with respect to any β to α or α_2 transformations. During the ageing process for alloys heat treated at 800°C, as would be expected, the heating rate within the furnace slows as the sample temperature gets closer to the equilibrium level. As can be seen from the heating curve shown in Figure 6.4., for heat treatments which are nominally 0.1 hrs at 800°C, most of the time is spent in the heating process, the rate of which begins to slow at around 650°C. As it is known from the 650°C / 0.1 hr ageing treatment that a decomposition reaction occurs in alloys aged at that temperature



it is likely that this will also occur during the heating of the alloys up to 800°C. When the temperature is close to the equilibrium 800°C level, the transformation of β_o to O takes place (the temperature at which the $\alpha_2 + \beta_o \Rightarrow \alpha_2 + O$ transformation finishes is within 25°C of the 800°C equilibration temperature even when the heating rate is as high as 50°C/min, which is higher than that which occurs in these alloys when the temperature is close to the equilibrium furnace temperature). Thus the resulting O phase is of a composition similar to that of the O phase found by Bendersky et al [Ben89]. The interpretation of a true equilibrium phase diagram for this system is made more complex by this apparent compositionally invariant transformation of one phase into another ($\beta_o \Rightarrow O$, with the α_2 composition apparently being unmodified), as in equilibrium terms the composition of the alloy in which the phases transform is determined not by the overall alloy composition, but by the composition of the individual phases. The compositionally invariant transformation from β_o to O also explains why the O phase boundary is able to move so that its composition is no longer similar to that of the α_2 phase.

It can be seen in Table 6.1. that the aluminium and niobium content of the alloys changes the temperatures of the transii in the system. As niobium is a β stabilising alloying addition in titanium it would be expected to reduce the transus temperature. Conversely, the addition of aluminium should raise it. It is interesting to see that the addition of aluminium does indeed raise the $\beta \Leftrightarrow \alpha_2 + \beta$ transus (Figures 6.11 and 6.12) by approximately 13°C / at.% Al, however, raising the niobium level *does not* lead to a reduction in this temperature. What it does do is lower the minimum temperature at which the β_o phase is stable (i.e. the $\alpha_2 + \beta_o \Leftrightarrow \alpha_2 + O$ or

Figure 6.4. Heating Rates For Samples Aged On Pre-Heated Blocks

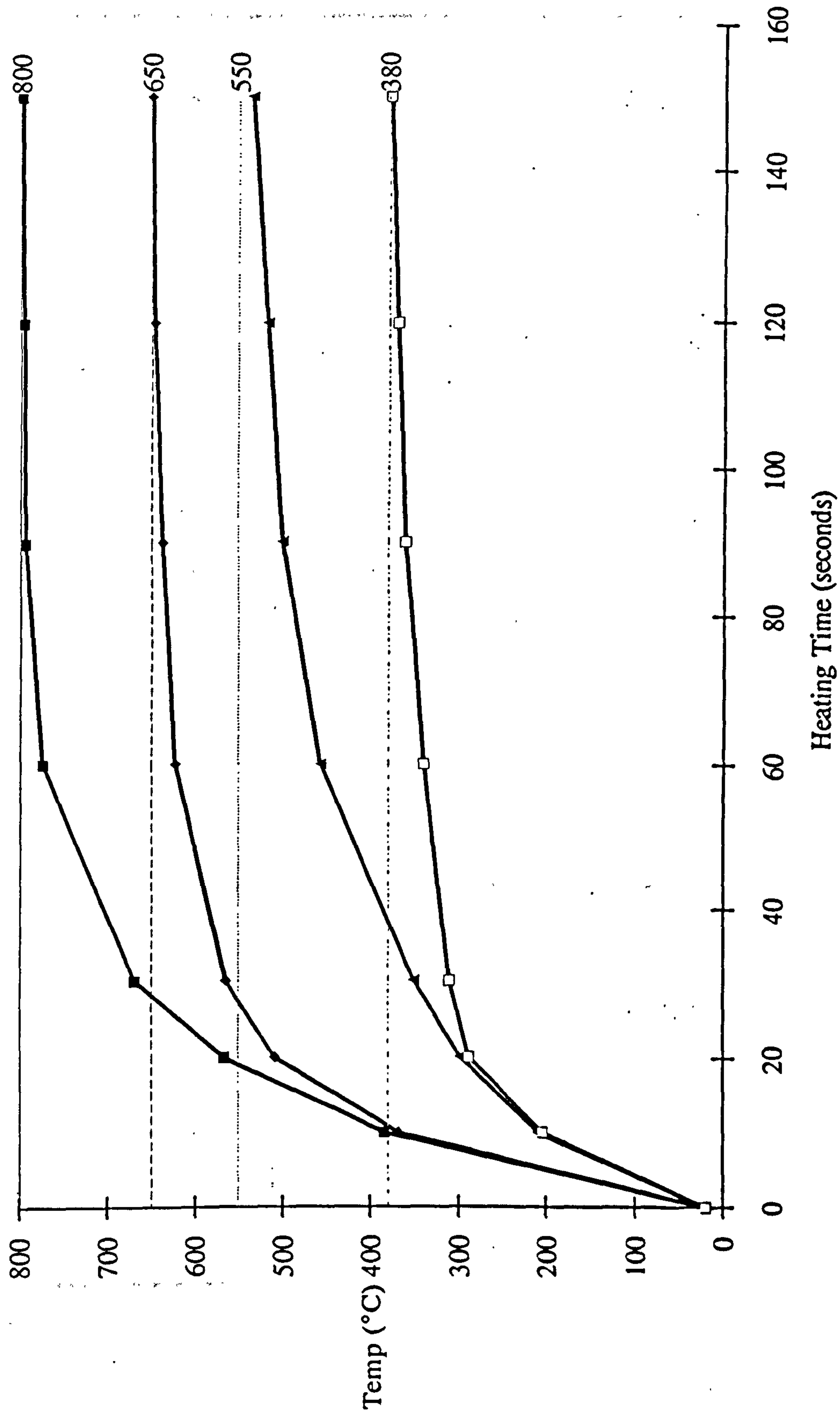


Figure 6.5. Binary Section in Ti-20-11-X Alloys varying Silicon

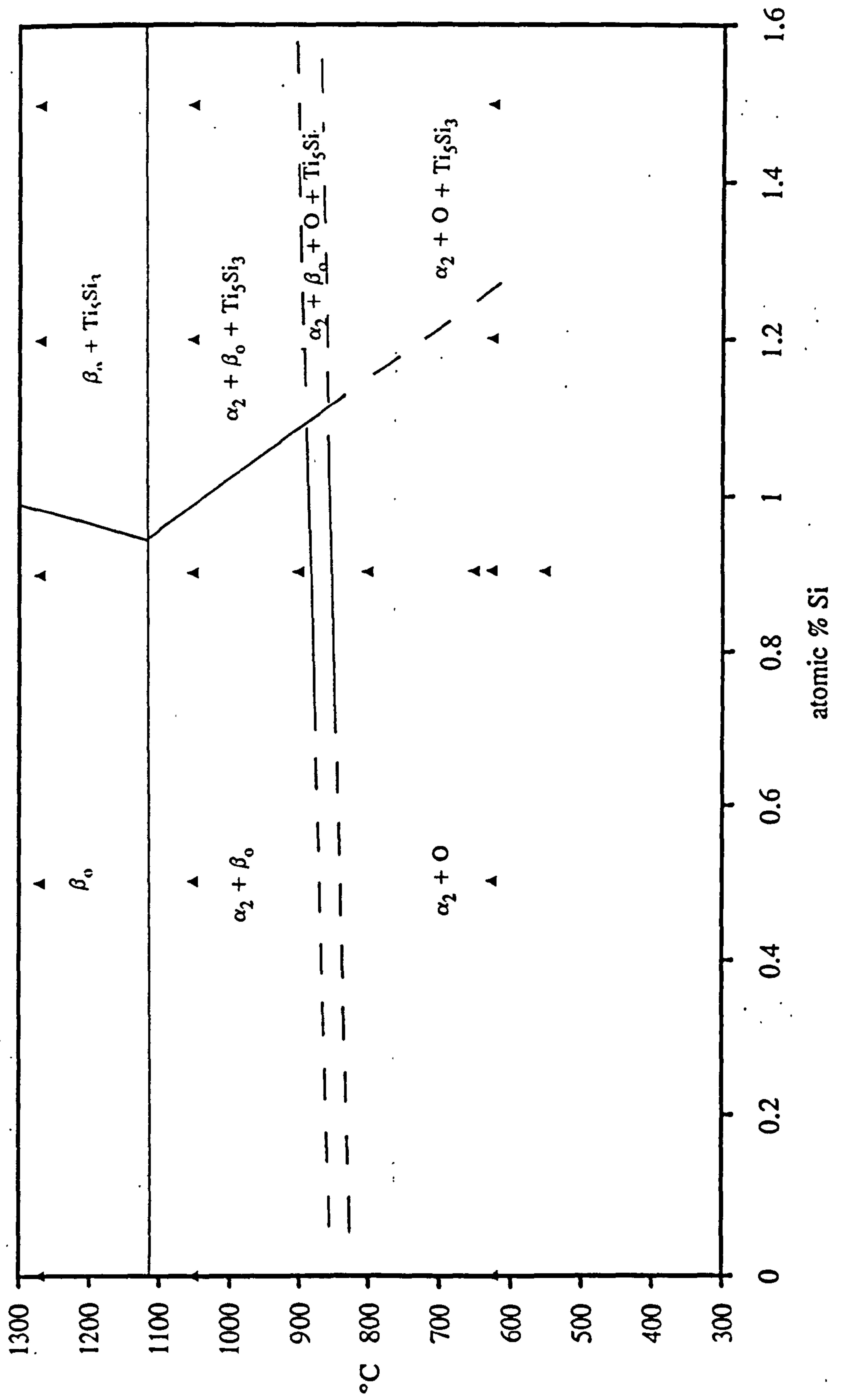


Figure 6.6. Binary Section in Ti-23-11-X Alloys varying Silicon

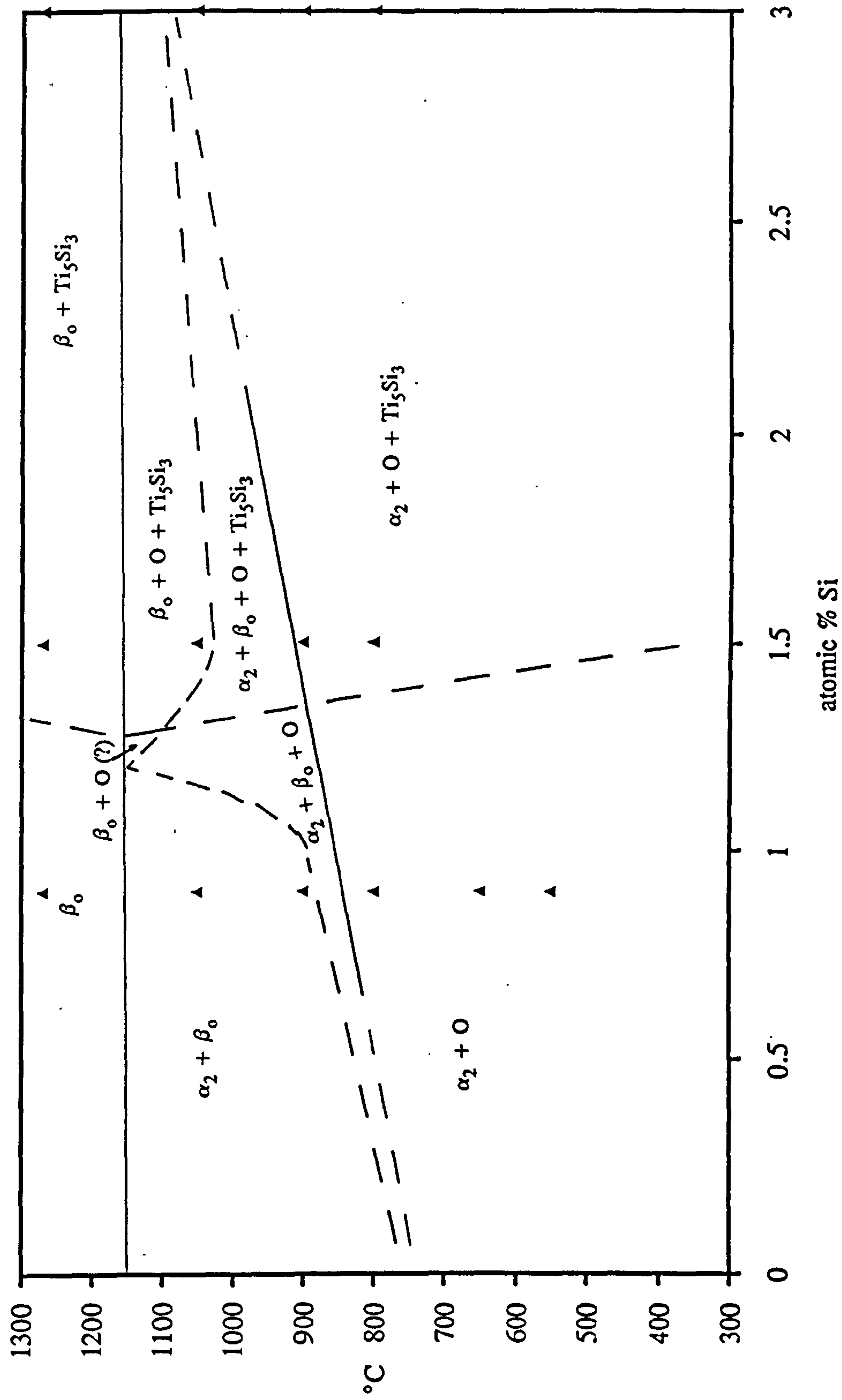


Figure 6.7. Binary Section in Ti-23-15-X Alloys varying Silicon

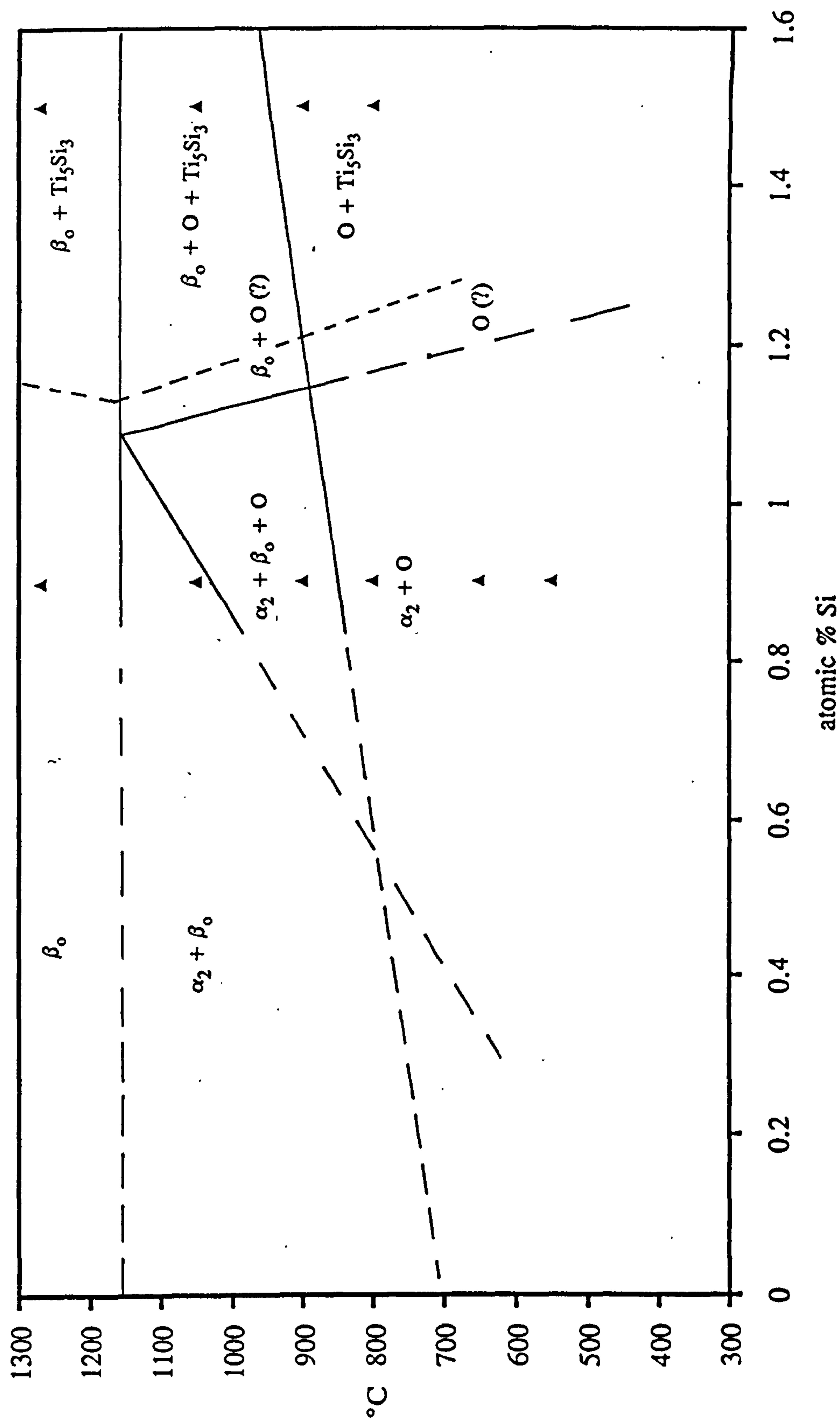


Figure 6.8. Binary Section in Ti-20-X-0.9 Alloys varying Niobium

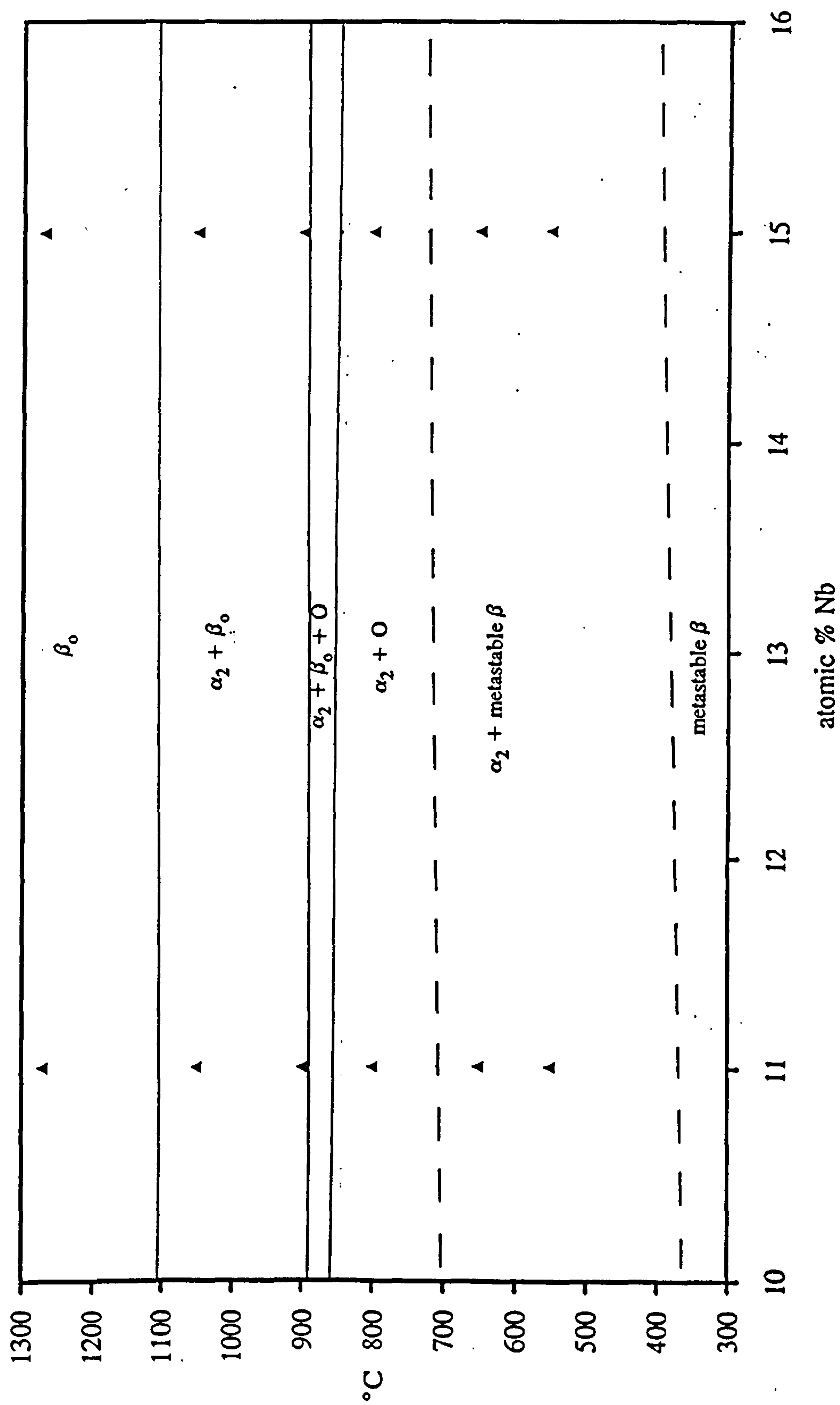


Figure 6.9. Binary Section in Ti-23-X-0.9 Alloys varying Niobium

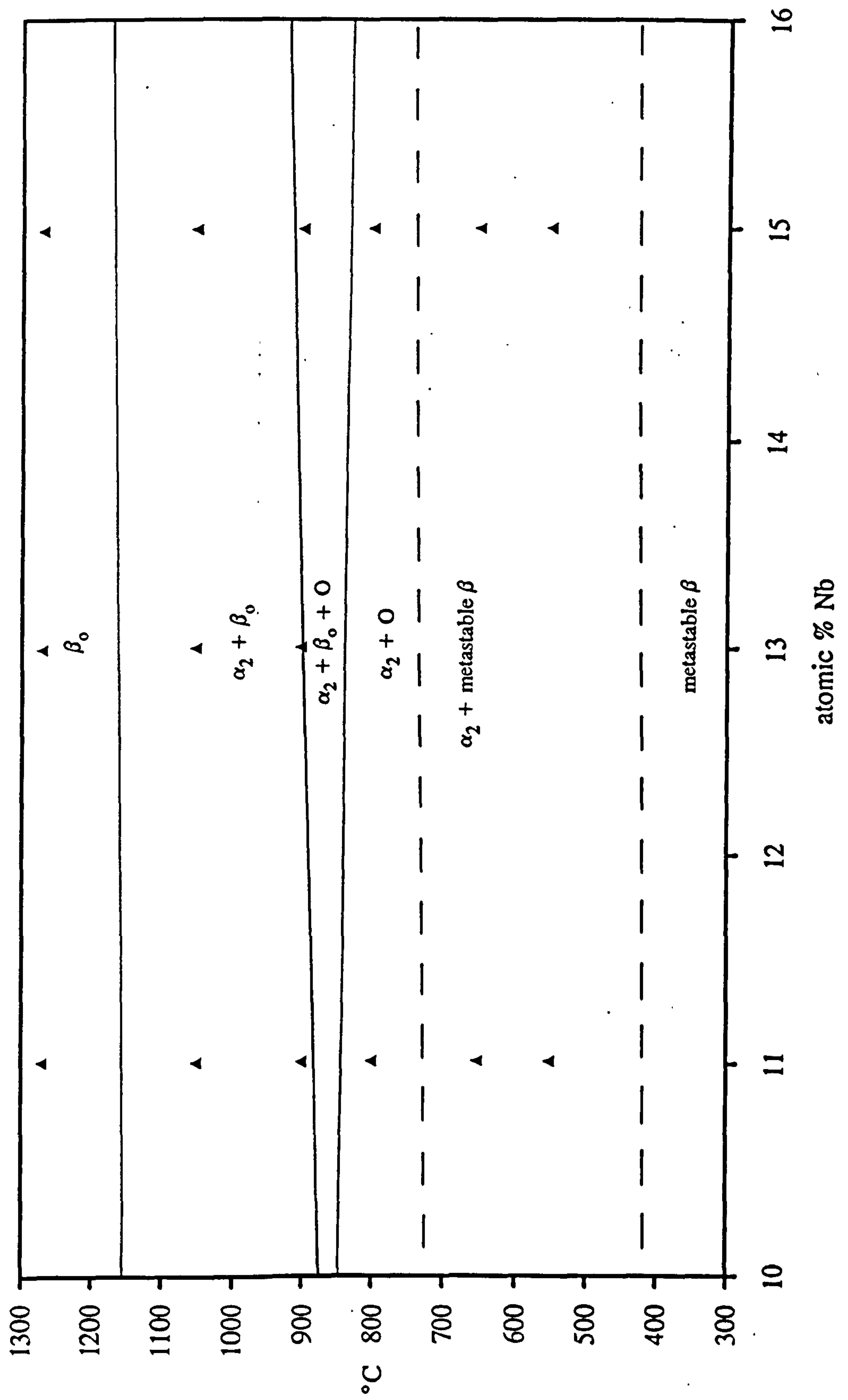


Figure 6.10. Binary Section in Ti-23-X-1.5 Alloys varying Niobium

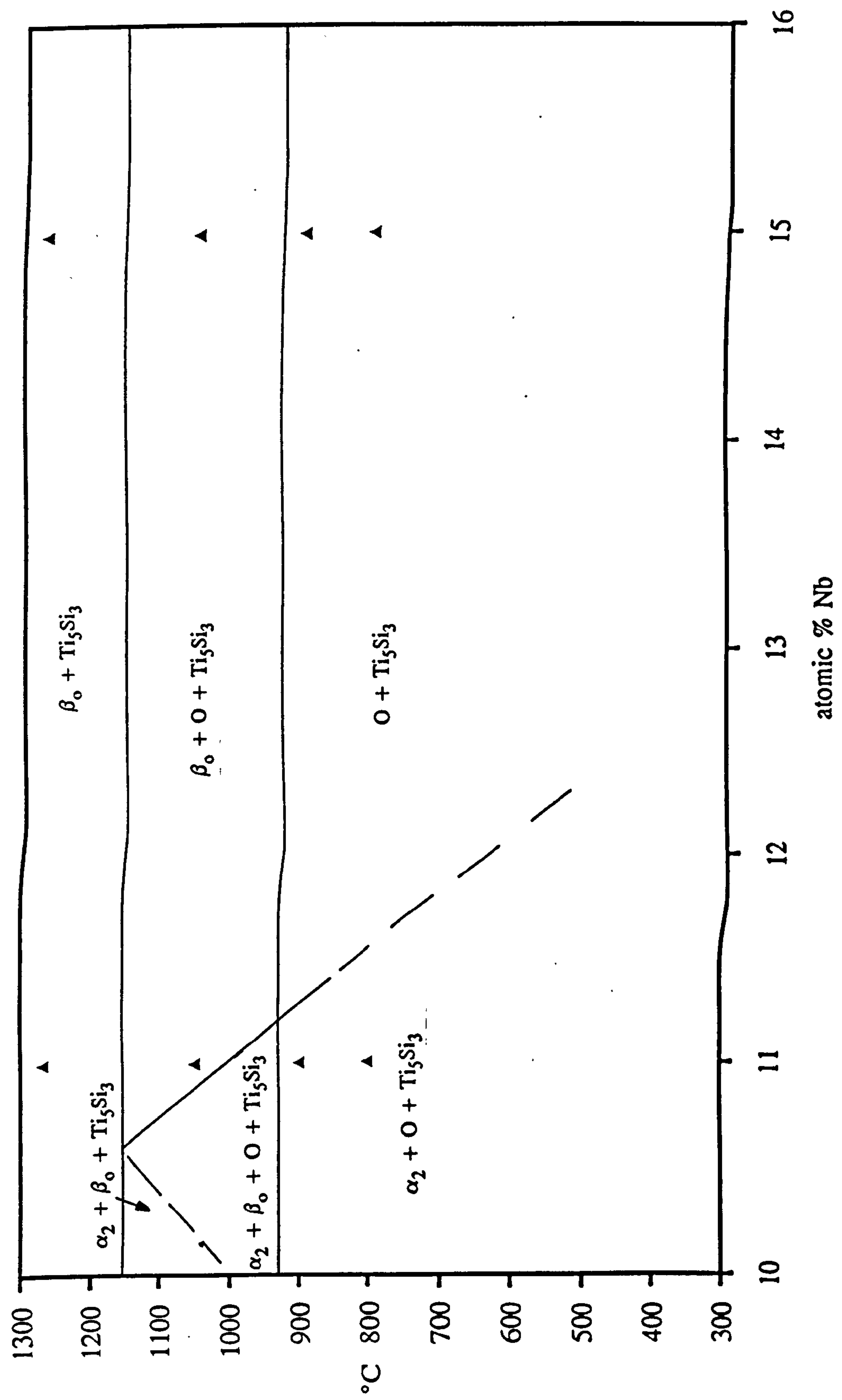


Figure 6.11. Binary Section in Ti-X-11-0.9 Alloys varying Aluminium

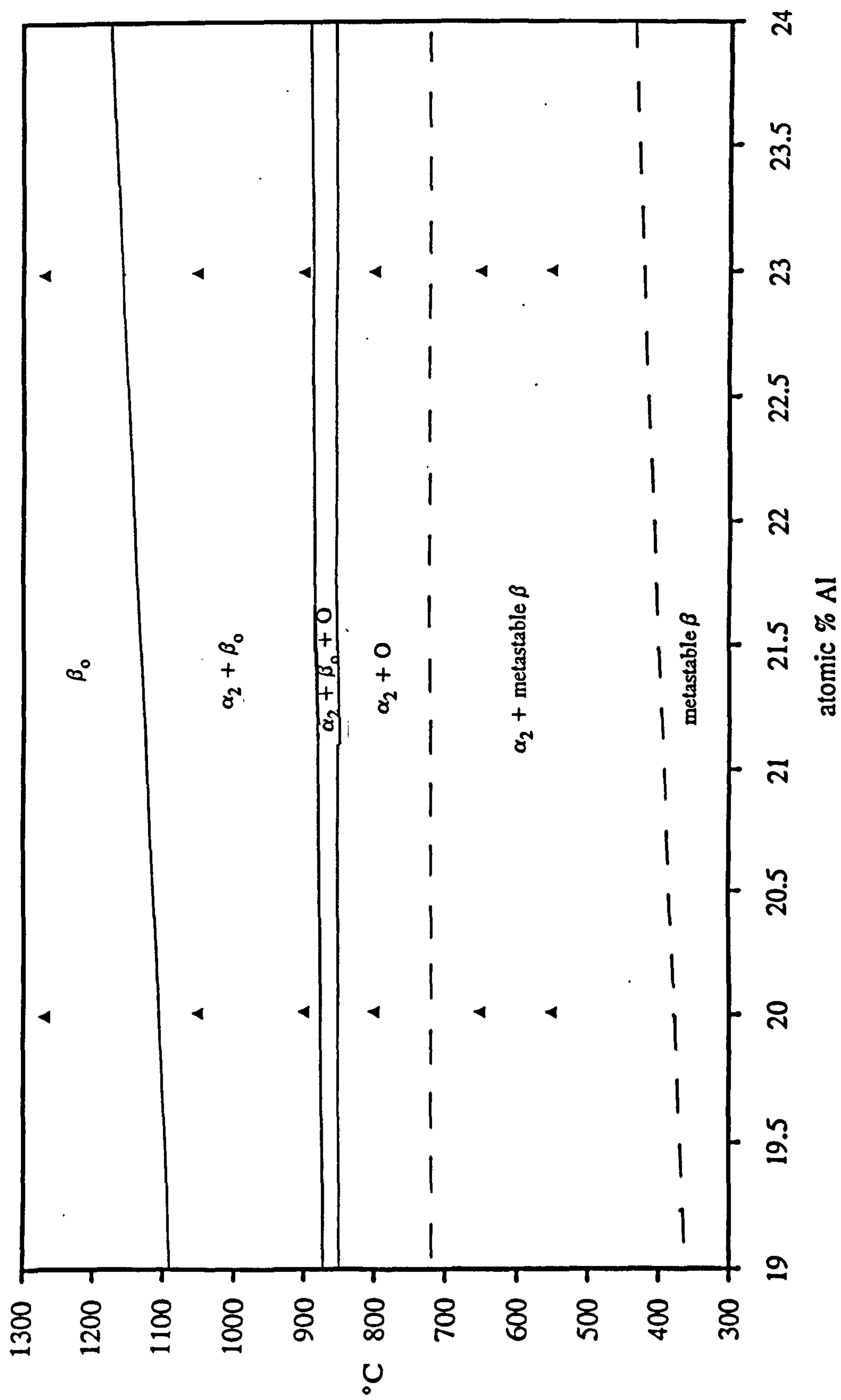
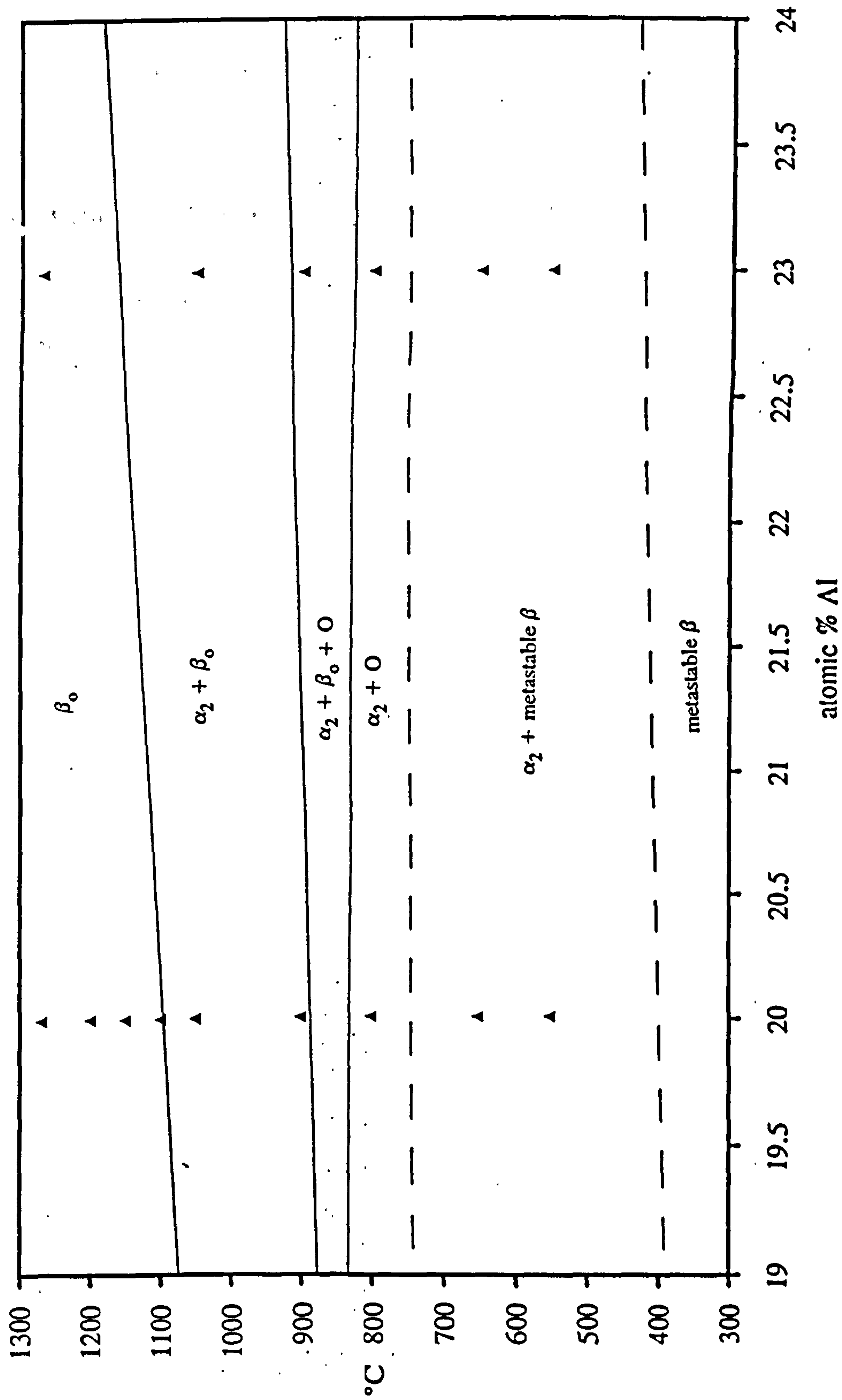


Figure 6.12. Binary Section in Ti-X-15-0.9 Alloys varying Aluminium



$\alpha_2 + \beta_0 + O \rightleftharpoons \alpha_2 + O$ transformation temperatures). Thus the addition of either aluminium or niobium extends the range over which the phase it stabilises can exist over, but does not affect the stability of the other phase.

6.3. The Effect of Silicon on The Quaternary Phase diagram.

As was discussed in section 6.1., it is difficult to represent the effect of silicon more accurately than by simple schematic diagrams, so the phase sections represented here do not attempt to accurately map the phase boundaries.

The first and most obvious effect of raising the silicon content is that when the silicon content reaches approximately 1 at.%, the solubility limit is exceeded, and silicide particles based on the stoichiometric composition Ti_5Si_3 are produced. The solubility of silicon in the β_0 phase is approximately 1 at.% at 1270°C, dropping to 0.8 at.% at 900°C. The solubility is higher in both α_2 and O, at approximately 1.4 at.%.

Although silicon is a β eutectoid former in titanium-based alloys, the effect of its addition in these alloys is rather different. As can be seen in Table 5.1., the solubility of silicon in the β phase is approximately 0.8-0.9 at.% at 1050°C. However, in α_2 it is markedly higher, at a level of around 1.4 at.%. The amount of silicon present in the α_2 rises as the silicon content in the alloy as a whole is increased. As silicon is believed to substitute onto aluminium sites in this stoichiometric phase in preference to the aluminium atoms, this would be expected to cause some of the aluminium to be 'rejected' from the aluminide were it to remain stoichiometric, which it does for all of the alloys examined at 900 and 1050°C. To maintain the equilibrium between the α_2 and β_0 phases, the silicon has the effect of producing a larger volume fraction of α_2 phase. Thus the silicon acts on an isothermal basis as a type of α_2 volume fraction enhancing element. It is this adherence of the α_2 phase to stoichiometry that produces the large compositional changes in the β_0 phase which have been described above (section 6.2.).

The second major effect of the addition of silicon is to induce a rapid β_0 to O transformation during air cooling. This has been discussed previously (in section 5.7.), as has the de-stabilisation of the metastable β_0 on quenching that occurs in alloys containing 1.5 or more percent silicon.

The third, and possibly the most significant effect of silicon is the strong orthorhombic stabilising effect of relatively small additions of silicon. For example at 1050°C, changing the silicon level in Ti-23-11 from 0.9 to 1.5 at.% moves the alloy from the $\alpha_2 + \beta$ phase field into one containing O and β (Figure 6.6). The compositions of the α_2 and the O phase are very similar, differing only in their silicon content. This variation should be contrasted with that of adding niobium to the alloys. It is the addition of approximately 11 at.% or more of Nb to the binary Ti_3Al system that causes the O phase to form. At 1050°C, the addition of 4 at.% Nb to the Ti-23-11-0.9 alloy does not produce a change from α_2 to O (Figure 6.9), whereas only 0.6at.% Si does.

The effect of the silicon level is particularly noticeable in the Ti-23-15-X alloys (Figure 6.7.). As can be seen in the pseudo-binary section illustrated, the heat treatments undertaken have identified 7 different phase fields., with up to four more being possible. In this section, the silicon solubility boundary is marked with a dotted line. This is because data has not been obtained as to which side of the $\alpha_2 + \beta_O + \text{O}$ phase field boundaries that the silicon solubility occurs. What is shown in the phase section illustrates only $\beta_O + \text{O}$ and $\beta_O + \text{O} + \text{Ti}_3\text{Si}_3$ fields bounding each other. It is also possible that an $\alpha_2 + \beta_O + \text{O} + \text{Ti}_3\text{Si}_3$ field exists, as well as the three phase $\alpha_2 + \beta_O + \text{Ti}_3\text{Si}_3$ field which has been identified in some other alloys (i.e. Ti-20-11-1.5 at 1050°C and Ti-20-15-0.9 at 1100°C). When the two alloys shown in Figure 6.7. are compared, it is clear that in addition to the silicide formation, the alloy forms the $\beta_O + \text{O}$ phases also identified in Ti-23-11-1.5. More importantly, at 900°C, the $\alpha_2 + \beta_O + \text{O}$ phase field which is present in Ti-23-15-0.9 has transformed to a two phase structure of $\text{O} + \text{Ti}_3\text{Si}_3$. An examination of the compositions of the O phase in both alloys indicates that they are very similar in composition.

If the phase section along the constant Al (23 at.%), constant Si (1.5 at.%), varying Nb section (Figure 6.10.), is examined, then it can be seen that the $\alpha_2 + \text{O}$ field spreads underneath the $\beta_O + \text{O}$ field at the lower Nb end. This shows that the boundary of the $\alpha_2 + \text{O}$ field is at a relatively low Nb level, which suggests that the composition of the O phase identified at 800°C (see Table 5.4.) in the lower Si content alloys is not a truly equilibrium structure. The suggested route by which these transformations occur is shown in Figure 6.13.

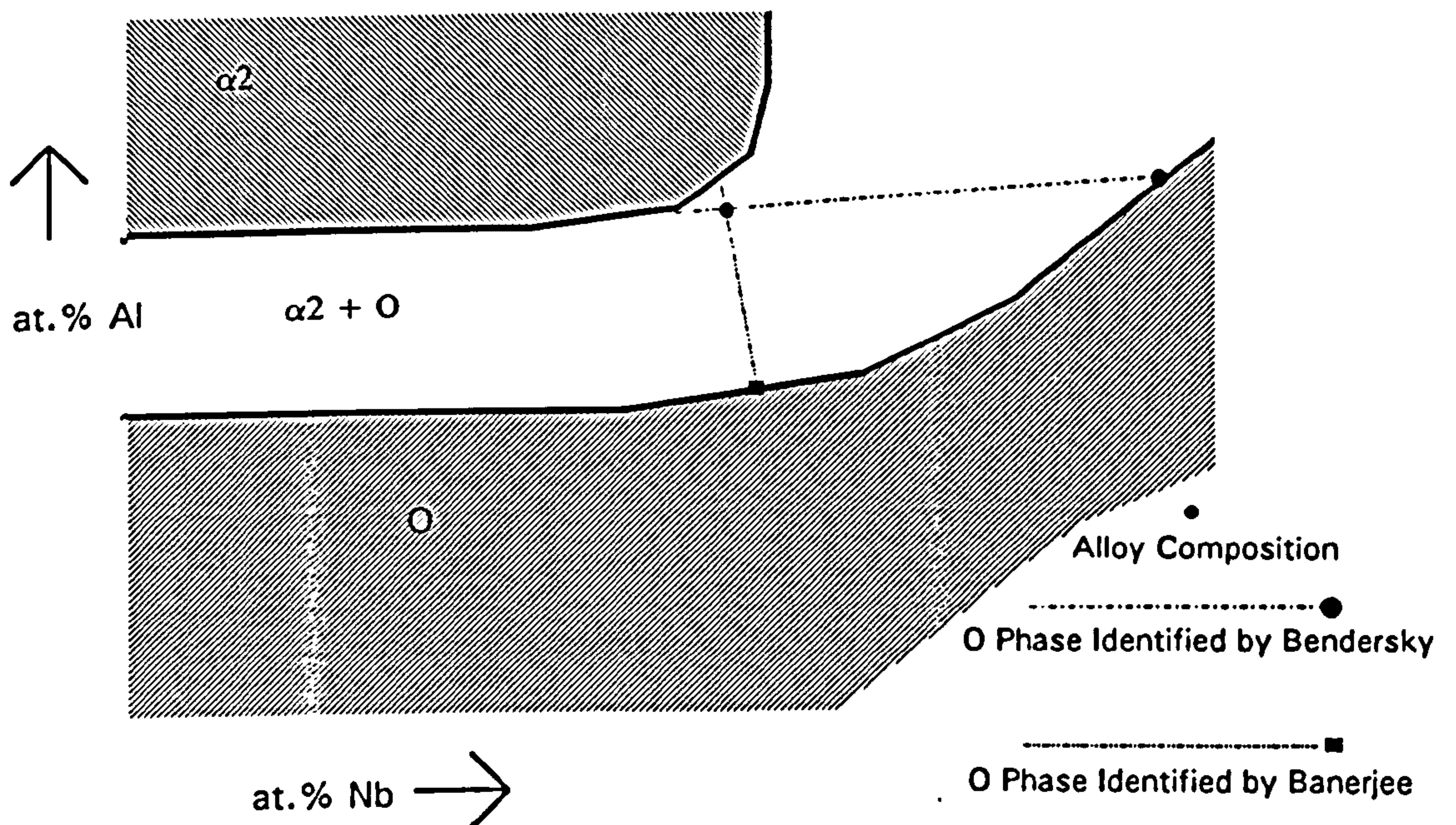


Figure 6.13. Schematic diagram showing how a slight change in the composition of the α_2 phase can produce O phase of a composition similar to those found by Banerjee and Bendersky.

6.4. Crystal Structures Found In Alloys.

The lattice parameters of each of the alloys examined have been calculated from X-ray diffraction data, and are summarised below in Tables 6.2-5.

Alloy	Structure	Lattice Parameters		
		a	b	c
Ti-20-11-0.9	β_O	323	-	-
	ω	458	-	281
Ti-20-15-0.9	β_O	323	-	-
	ω	458	-	281
Ti-23-11-0.9	β_O	323	-	-
	ω	458	-	281
Ti-23-15-0.9	β_O	323	-	-
	ω	458	-	281
Ti-23-11-1.5	β_O	324	-	-
Ti-23-11-3	β_O	325	-	-
			-	
Ti-23-15-1.5	β_O	324	-	-
			-	

Table 6.2. Lattice Parameters (in pm) for Alloys Solution Treated at 1270°C. (excluding silicides)

Alloy	Structure	Lattice Parameters		
		a	b	c
Ti-20-11-0.9	β_0	324	-	-
	α_2	578	-	465
Ti-20-15-0.9	β_0	324	-	-
	α_2	579	-	465
Ti-23-11-0.9	β_0	324	-	-
	α_2	579	-	465
Ti-23-15-0.9	β_0	323	-	-
	α_2	579	-	465
Ti-23-13-0.9	β_0	324	-	-
	α_2	579	-	465
Ti-23-11-1.5	β_0	325	-	-
	O	585	973	468
Ti-23-11-3	β_0	326	-	-
	O	585	973	469
Ti-23-15-1.5	β_0	324	-	-
	O	585	973	470
Ti-23-6-0.9	β_0	325	-	-
	α_2	578	-	465
Ti-23-6-1.5	β_0	325	-	-
	α_2	578	-	465
Ti-20-11	β_0	324	-	-
	α_2	579	-	465
Ti-20-11-0.5	β_0	324	-	-
	α_2	579	-	465
Ti-20-11-1.2	β_0	324	-	-
	α_2	579	-	464
Ti-20-11-1.5	β_0	325	-	-
	α_2	579	-	464

Table 6.3. Lattice Parameters (in pm) for Alloys Solution Treated at 1270°C, the Aged at 1050°C. (excluding silicides)

Alloy	Structure	Lattice Parameters		
		a	b	c
Ti-20-11-0.9	β_0	325	-	-
	α_2	579	-	465
Ti-20-15-0.9	β_0	326	-	-
	α_2	579	-	465
Ti-23-11-0.9	β_0	326	-	-
	α_2	579	-	465
Ti-23-15-0.9	β_0	326	-	-
	α_2	579	-	465
	O	592	975	466
Ti-23-13-0.9	β_0	326	-	-
	α_2	579	-	465
Ti-23-11-1.5	β_0	326	-	-
	O	592	975	466
Ti-23-11-3	β_0	326	-	-
	O	592	975	466
Ti-23-15-1.5	β_0	326	-	-
	O	592	975	466

Table 6.4. Lattice Parameters (in pm) for Alloys Solution Treated at 1270°C, then Aged at 900°C. (excluding silicides)

Alloy	Structure	Lattice Parameters		
		a	b	c
Ti-20-11-0.9	α_2	579	-	463
	O	590	971	465
Ti-20-15-0.9	α_2	579	-	464
	O	595	970	464
Ti-23-11-0.9	α_2	580	-	466
	O	590	970	465
Ti-23-15-0.9	α_2	579	-	467
	O	594	971	467
Ti-23-13-0.9	α_2	579	-	466
	O	592	971	466
Ti-23-11-1.5	β_0	326	-	-
	O	590	970	466
Ti-23-11-3	β_0	326	-	-
	O	590	970	466
Ti-23-15-1.5	O	594	973	466

Table 6.5. Lattice Parameters (in pm) for Alloys Solution Treated at 1270°C, then Aged at 800°C. (excluding silicides)

As can be seen from the tables above, the a parameter of the α_2 phase is unaffected (within the errors of the diffractometer used) by any changes in composition or temperature within the range examined. This is also true for the 'c' parameter at temperatures of 900°C and above. At 800°C there is a small change in lattice parameter with both increasing aluminium and niobium leading to an increase in lattice parameter. An example of the X-ray diffraction peaks produced in a typical α_2 phase (in Ti-20-11-0.9 at 1050°C) are shown in Table 6.6. When the crystallographic data is compared with the compositional data for the α_2 phase (and not for the bulk alloy composition), it can be seen that the lattice parameters remain constant while the α_2 phase remains stoichiometric, as it does at 900 and 1050°C. At 800°C, the composition of the α_2 phase moves towards a lower Al+Si level, when the c parameter changes.

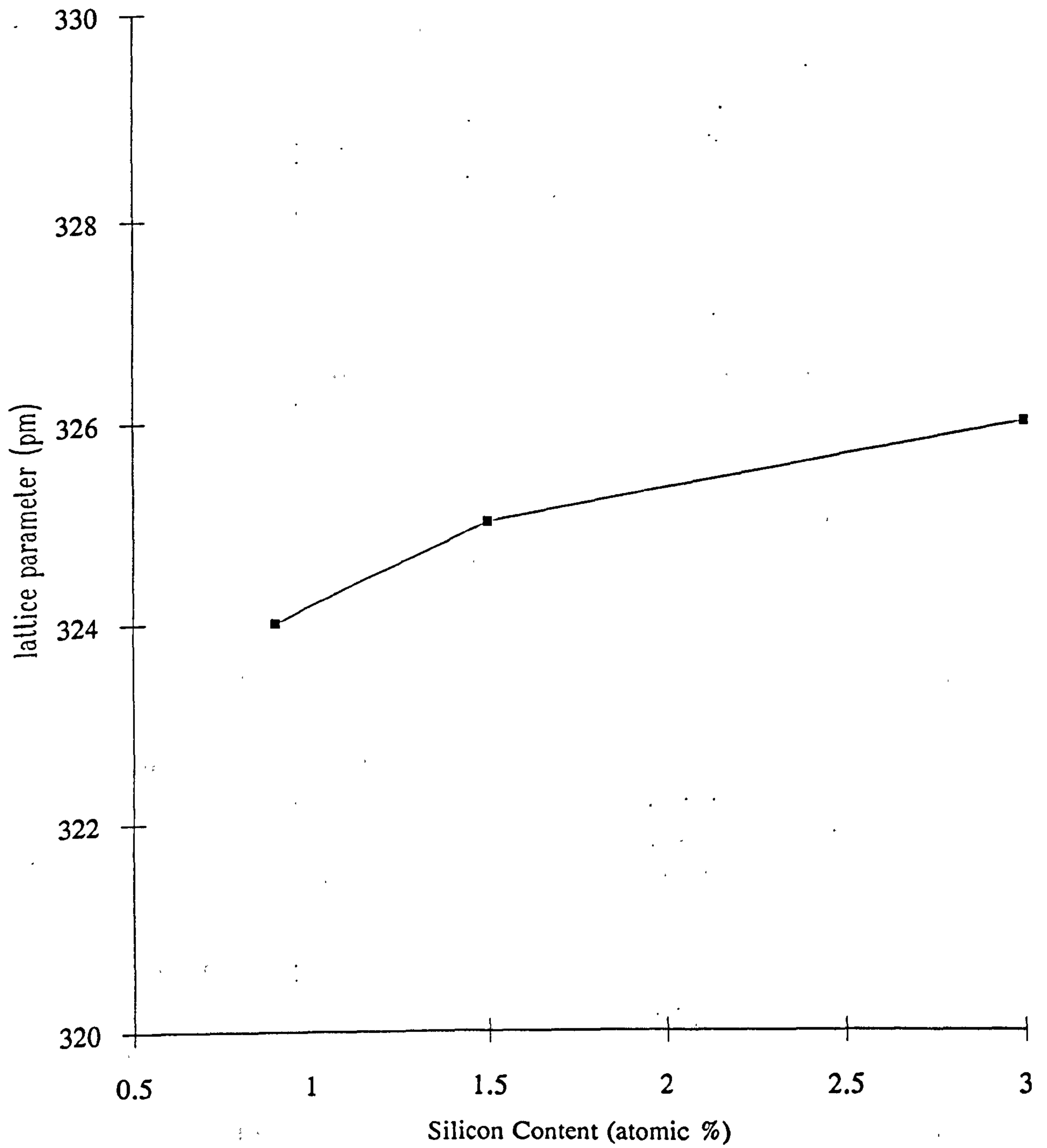
Crystal Plane	Plane Spacing (pm)
(10 $\bar{1}$ 0)	50.1
(10 $\bar{1}$ 1)	34.1
(2 $\bar{1}$ $\bar{1}$ 0)	28.9
(20 $\bar{2}$ 0)	25.1
(2 $\bar{1}$ $\bar{1}$ 1)	24.6
(0002)	23.3
(2 $\bar{2}$ 01)	22.1
(10 $\bar{1}$ 2)	21.1
(3 $\bar{2}$ $\bar{1}$ 0)	18.9
(2 $\bar{1}$ $\bar{1}$ 2)	18.2

Lattice Parameters are a : 579 pm and c : 466 pm.

Table 6.6. X-ray Diffraction Peaks for α_2 Structure Found in Ti-20-11-0.9 at 1050°C.

In the β phase, the converse temperature dependence occurs. At 900°C, the composition has no effect on the lattice parameters, but does have an effect at 1050°C. It should be noted that in all but one alloy the increase in temperature reduces the lattice parameter by varying degrees. As with the temperature dependence of the α_2 phase, that of the β_0 phase is governed by compositional changes. Examination of the ternary sections at 900, 1050 and 1270°C (Figures 6.1-3) show that the composition of the β_0 phase becomes increasingly niobium-rich as the temperature is reduced. As the niobium atom has a larger diameter than the titanium one which it substitutes for [Ban88], it would be expected to produce an enlargement of the lattice parameters, and indeed this is the case. In the Ti-20-11-X alloys the lattice parameter is only modified by the highest silicon addition level, changing from 324pm to 325pm. In the Ti-23-11-X alloys the change in lattice parameter is greater, though this is over a much larger silicon addition range. In these alloys the lattice parameter increases from 324 to 326 with 0.9 to 3 at.% silicon addition. This is shown in Figure 6.14a. There is a marked effect when the niobium level is varied. Increasing the Nb level reduces the lattice parameter by 5 pm over the composition range from 11 to 15 at.% in Ti-23-X-0.9 alloys, as illustrated in Figure 6.14b. Variations in aluminium content in the alloys do not appear to affect the lattice parameters. Example d spacings from X-ray diffraction are given below in Table 6.7.

Figure 6.14a. Effect of Silicon Addition Level on beta lattice parameters in Ti-23-11-X Alloys



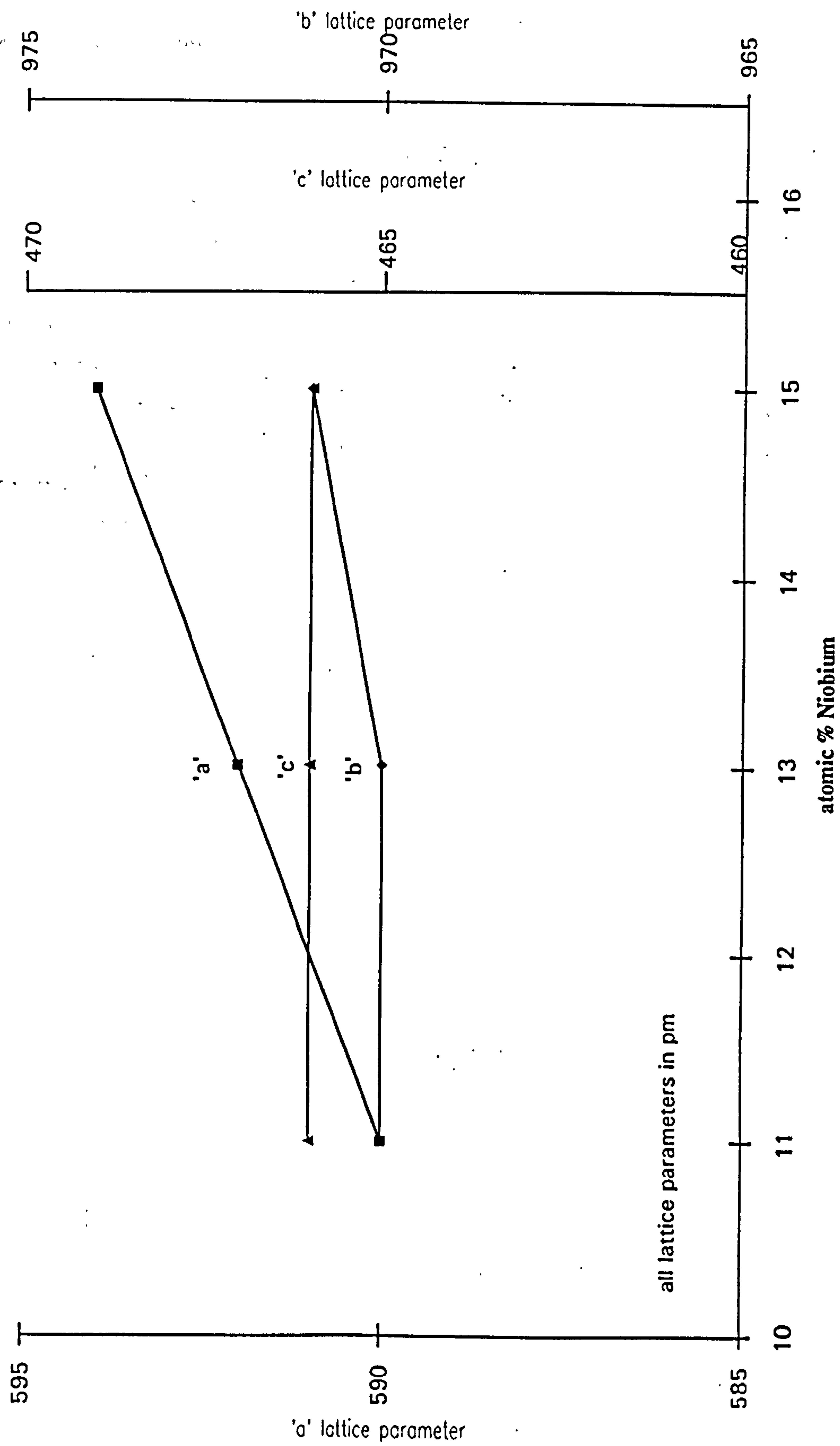
Crystal Plane	Plane Spacing
(100)	32.4
(110)	29.1
(111)	18.7
(200)	16.2
(210)	14.5
(211)	13.2
(300)	11.5
(310)	10.8
(311)	10.8
(222)	10.2
(320)	9.8
(321)	9.4
(400)	9.0

Lattice Parameter is a: 324 pm

**Table 6.7. X-ray Diffraction Peaks for β
Crystal Structure Found in Ti-20-15-0.9 after
Solution Treatment at 1270°C.**

The lattice parameters in the O phase have been found to be much more susceptible to compositional variation than the other two phases, which explains the wide range of lattice parameters reported by other authors (see table 2.2). At 1050°C, the O phase shows no difference in lattice parameters between those in alloys containing 11 at.% Nb and the one containing 15 at.% Nb. When the alloys are aged at 900°C, a comparison of the lattice parameters again shows that the composition of the base alloys does not affect the lattice parameters. They have, however, been modified by the change in ageing temperature, with the orthorhombicity increasing significantly, as the a parameter is increased and the b parameter decreased. Lowering the ageing temperature to 800°C produces another change in the lattice parameters, with the orthorhombicity again being increased. At this temperature the range of alloys in which the orthorhombic phase is produced is greatly increased, and this increased range now shows a compositional dependence for the lattice parameters. This clearly shows that increasing the niobium content in the alloys increases the a parameter of the O phase. Changing the aluminium and silicon content does not appear to cause any significant change in the lattice parameters. As can be seen in Figure 6.14b.,

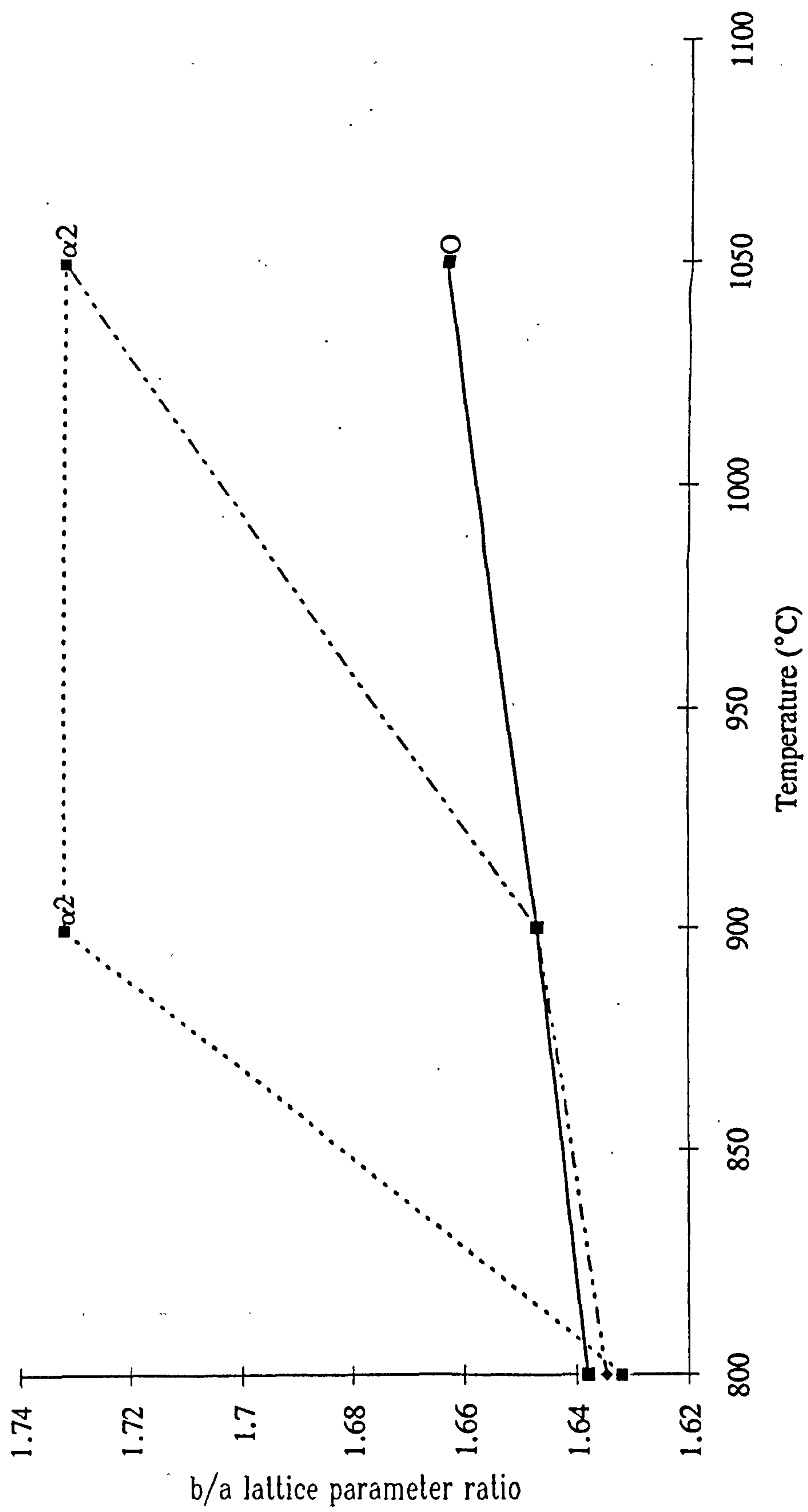
Figure 6.14b. Effect of Niobium Additions on Orthorhombic Phase Lattice Parameters at 800°C



increasing the niobium content by 1 at.% produces an increase in the a parameter of approximately 10pm.

As has been discussed previously (section 6.2.), the composition of the orthorhombic phase changes markedly as the temperature is lowered, moving towards the niobium-rich corner of the phase diagram, which, as suggested by Kestner-Weykamp [Kes89], increases the orthorhombicity of the phase. To provide a measure of the amount of distortion from the hexagonal α_2 structure which the orthorhombic phase exhibits, a comparison of the b/a lattice parameter ratio should be used. When the hexagonal structure is indexed as an orthorhombic crystal, the b/a ratio is found to be $\sqrt{3}$. Thus any change in ratio from this can be used as a measure of orthorhombic distortion. The temperature dependence of the orthorhombic distortions of two sample alloys is given in Figure 6.15. Typical X-ray diffraction peaks for the orthorhombic phase are shown in Table 6.7.

Figure 6.15. Temperature Dependence Of Orthorhombicity



Crystal Plane	Lattice Parameter
(010)	980
(100)	592
(110)	507
(020)	490
(011)	422
(120)	377
(111)	343
(021)	338
(030)	326
(200)	296
(121)	294
(130)	286
(210)	283
(031)	267
(220)	253
(040)	245
(131)	244
(211)	242
(002)	233
(012)	227
(140)	226
(221)	227
(230)	219
(102)	217
(041)	217
(112)	212
(022)	211
(141)	203

Lattice Parameters are: $a=592$, $b=980$, $c=467$ (all values in pm)

**Table 6.7. X-ray Diffraction Peaks For O Crystal Structure
Found in Ti-23-11-1.5 Solution Treated at 1270°C**

6.5. Summary

The alloys examined here consist of a combination of 4 different phases, α_2 , β_0 , O and Ti_3Si_3 . The silicide phase forms when the silicon content of the bulk alloy exceeds approximately 1.1 at.%. The β_0 phase produced by the initial quenching process is stable at temperatures down to at least 900°C, and is found in a metastable form at temperatures up to approximately 780°C. As the temperature is lowered, the niobium content, and hence the β -stabilising content of the phase rises. The α_2 phase is present in most of the alloys at temperatures of between approximately 400 and 1100°C. It does not form at higher temperatures in alloys with a silicon content of 1.5 at.% or more. The composition of the α_2 phase corresponds to that of a stoichiometric phase of $(\text{Ti}+\text{Nb})_3(\text{Al}+\text{Si})$ over a wide range of compositions in the $\alpha_2 + \beta_0$ phase field. The orthorhombic phase has been identified within two distinct compositional regions. At higher temperatures it has a composition similar to that of α_2 , and at lower temperatures it transforms directly from relatively highly niobium stabilised β_0 , producing a composition which is distinct from that of the higher temperature α_2 phase. Phase fields have been identified in which two of the metallic phases exist in equilibrium. The boundaries for a three phase $\alpha_2 + \beta_0 + \text{O}$ field at 900°C have also been identified.

In a constant aluminium, constant silicon section, the phase diagram is of a form which is intermediate between the peritectoid and eutectoid forms. In a constant aluminium, constant niobium section, the addition of silicon to the alloy produces a peritectoid structure similar to that found in the low aluminium Ti-Al-Si phase diagram [Cro58].

The lattice parameters of the α_2 and β_0 phases have been found to be relatively independent of temperature, but those of the O phase show increasing orthorhombicity with decreasing temperature due to the large changes in composition which occur in that phase.

Chapter 7.

Conclusions.

- (1) The β_0 phase in Ti-(20-23)Al- (11-15)Nb-0.9Si is ordered at all temperatures below 1270°C. Fine scale anti-phase domain boundaries are not generally present in the alloys examined indicating that the ordering does not occur on quenching.
- (2) Throughout the temperature range in which the $\alpha_2 + \beta_0$ phase field exists (900-1100°C) the α_2 phase has been found to be stoichiometric with the composition of $(\text{Ti}+\text{Nb})_3(\text{Al}+\text{Si})$. The niobium content in the phase ranges between 5.4 and 11.2 at.%. The silicon is present at a level of up to 1.5 at.%.
- (3) The silicon in the α_2 phase substitutes onto the aluminium sites and appears to act as an aluminium equivalent.. Thus silicon acts as an α_2 volume fraction enhancer.
- (4) The orthorhombic 'O' phase has been identified over a wide range of compositions. In Ti-23-15-0.9 at 900°C it has been identified within a three phase $\alpha_2 + \beta_0 + \text{O}$ region. In this field the O phase has a composition which is stoichiometric $(\text{Ti}+\text{Nb})_3(\text{Al}+\text{Si})$ as is the α_2 phase, but with a higher niobium and silicon content (16.3 and 1.4 at.% respectively).
- (5) It appears from the microstructure that the O phase forms by decomposition of α_2 phase into a structure consisting of α_2 and O laths at high temperatures (800°C and above). The formation of O phase at 900°C in Ti-23-15-0.9 appears to occur without any interaction between the α_2 and β_0 phases.

- (6) At 1050°C, the O phase is only present in alloys containing 1.5 at. % silicon or more, where it replaces the α_2 phase that is present in alloys containing 0.9 at. % Si or less. The composition of the O phase is similar to that of the α_2 phase, except that the silicon content is higher. Silicide particles are also found at this temperature in the 1.5 at. % Si alloys. A three phase ($\alpha_2 + \beta_0 + O$) region has not been found at this temperature.
- (7) The terminal solubility of silicon is markedly higher in the α_2 phase (up to 1.4 at. %) than it is in the β_0 phase (0.8 at. %). This is indicative that the phase diagram section in the direction of increasing silicon is peritectoid in nature. In binary titanium - silicon alloys it is eutectic.
- (8) When solution treated at 1270 °C and then water quenched, the Ti-20-11,15-0.9 alloys produce a microstructure which consists of β_0 containing 'tweed', and there is evidence of some ω -type structure.
- (9) In the Ti-23-15-0.9 alloy, after solution treatment and water quenching the microstructure is similar to that for the lower aluminium content alloys, except that plates of α_2 are produced throughout the matrix. The hardness of the higher aluminium alloys is significantly higher (by approximately 130Hv) than that found in the 20 at. % aluminium alloys due to the hardening effect of the α_2 plates.
- (10) The $\beta_0 +$ tweed microstructure remains in a metastable form up to approximately 390°C, with only the precipitation of more ω phase occurring below that temperature.
- (11) At temperatures of 390°C and above, α_2 is precipitated, which produces a microstructure based on $\alpha_2 +$ metastable β (disordered). Due to the change in composition caused by the α_2 formation, the β phase remains in a metastable form (with respect to the $\beta_0 \rightarrow O$ transformation) at temperatures up to approximately 750°C.
- (12) At $\sim 750^\circ\text{C}$, the microstructure transforms to $\alpha_2 + O$. The O phase is of a composition similar to that of the highly stabilised β which exists at slightly lower temperatures.

- (13) O phase has been found with two markedly different compositions, at 800°C it has a composition of Ti-12.2Al-25.9Nb-0.9Si (at.%) and at 900°C it is of a composition of Ti-23.4Al-16.3Nb-1.4Si (at.%).
- (14) Lower temperature (800°C) O phase is of a markedly different composition to that of higher temperature (>900°C) forms because of the transformations which occur during the heat treatment process. Thus, there is only one type of O phase, but its' composition varies due to the processing route employed.
- (15) Alloys which contain higher levels of silicon (1.5 at.% and above), when solution treated at 1270°C and water quenched have a markedly different structure to that of the alloys with a lower silicon content. The 1.5 at.% Si alloys have a microstructure which apart from the matrix structure also contains particles of a silicide with a composition of $(\text{Ti}+\text{Nb})_{5.1}(\text{Si}+\text{Al})_3$. Apart from the distribution of silicide particles, the microstructure has also been found by backscattered electron imaging, to contain a martensitic type structure.
- (16) When aged at 900°C and below, Ti-23-15-1.5 is found to consist of two phase O + silicide. The O phase is of a composition very similar to that of the O phase found in the three phase $\alpha_2 + \beta_0 + \text{O}$ field in Ti-23-15-0.9, but with a slightly lower niobium content. The increase of 0.6 at.% Si in the alloy produces a shift in the phase diagram towards the single phase O region, i.e. it acts as an O phase stabilising element.
- (17) In Ti-20-11 alloys with silicon contents from 0 to 1.5 at.%, air-cooled from 1150°C, then aged at 625°C, the microstructure consists of $\alpha_2 + \beta_0$ in alloys with less than 1 at.% silicon. Above that the structure is transformed to a coarser structured $\alpha_2 + \text{O}$ phase. When the silicon content is raised to 1.5 at.% silicide particles are also present.
- (18) Increasing the niobium content in the alloys increases the temperature range stability of O phase.
- (19) Increasing the aluminium content increases the temperature range of stability of α_2 phase, but does not increase the lowest temperature at which the β_0 phase is found.

- (20) In alloys in which only the niobium content is varied, the 'vertical' phase section ~~has~~ appears to exhibit behaviour that is intermediate between eutectoid and peritectoid transformational behaviour.

Chapter 8.

Further Work.

Certain areas of study in this work have brought to light a range of questions which have not been addressed here, and should be answered. Some of the points considered to be most important are described below;

- (1) The 'vertical' (i.e. temperature variant) sections which have been identified in this work have some phase boundaries which are open to a variety of interpretations given the microstructural information which has been identified during this work. Of particular interest is the question as to whether a four phase $\alpha_2 + \beta_o + O + Ti_5Si_3$ field exists, and its' extent. Certain phase fields (specifically the three phase $\alpha_2 + \beta_o + O$ field) have only been identified by D.S.C. in some of the alloys, and thus alloys should be heat treated within the reported temperature ranges to confirm the existence of these fields.
- (2) The examination of the 1050°C aged, air cooled, 625°C aged alloys indicated that solution treatments in phase fields other than the β_o field can modify the microstructure markedly, which may be used to improve the microstructural properties, such as removing the large areas of α_2 precipitation on β_o grain boundaries in 1050°C aged alloys.
- (3) The current work did not conclusively identify whether the nature of the reaction to produce the O phase was eutectoid or peritectoid (in the varying niobium section). A more detailed D.S.C. examination of the $\beta_o / \alpha_2 + \beta_o$ phase boundary is recommended to provide more information as to this reaction.
- (4) It is recommended that slow cooling of some of the alloys to examine the $\alpha_2 (+ \beta_o) \rightarrow \alpha_2 + O (+ \beta_o)$ transformation should be carried out, as it is not entirely clear as to how this transformation occurs.

Further Work

- (5) The martensitic transformations which occurred in the 1.5 at.% Si alloys when solution treated and cooled should be examined in more detail. Examination of TEM foils is particularly recommended, as this was not carried out during the current work.
- (6) From the binary Ti-Si phase diagram, it would be expected that along with the Ti_5Si_3 particles reported, particles based on the Ti_3Si stoichiometric compound would also be found. However, this compound forms slowly, and thus to identify whether this compound does occur it is recommended that slow cooling of one or more of the 1.5 at.% alloys should be carried out.

Appendix

Interpretation of Transformational Data From Calorimetry.

Transformational data provided by D.S.C. (Differential Scanning Calorimetry) can provide valuable information regarding transformation temperatures, but individual transformations can be difficult to interpret in systems which contain a large number of transformations, such as the currently investigated system. The figure below shows a typical heating curve for a sample of Ti-20-11-0.9 solution treated at 1270°C for 24 hrs and water quenched. The transformations which are identified in this curve will be those which occur in the alloys in the aged conditions discussed previously. It was decided to concentrate on heating curves to tie in with the microstructural data provided by the aged alloys, as the transformational routes which the alloy follows on cooling from the β_0 phase field during the D.S.C. examinations will differ from those found in the alloys in the conditions in which they have been heat treated, which would complicate the interpretation of the calorimetry data.

As the heating rate used in D.S.C. can change the temperatures at which the transformations are indicated (specifically by superheating and temperature gradients within the samples), the transformation temperatures reported are those at which the gradient of the line starts to deviate from that which it had been following.

The first transformation (marked A in the figure) which occurs is the precipitation of α_2 within the metastable β_0 matrix, which, as it is represented as a peak is endothermic. This large peak is particularly susceptible to a variation in the heating rate, as the diffusional processes which occur during the transformation are slow at the low temperature (~375°C) at which it begins. This interpretation of transformation occurring at this temperature is confirmed by the microstructural examinations at 380 and 650°C discussed previously. Moving to higher temperatures there is a gradient change (marked B), which if the gradients above and below it are extrapolated, they intersect at approximately 650°C. This is *not* a transformation in the alloy. As can be seen in the lower line, which shows a D.S.C. curve 'dry run', i.e. one in which no sample is loaded into the calorimeter, the baseline is not linear due to an amplification in the errors inherent in the equilibration mechanism employed in the calorimeter at higher temperatures, and a pronounced curve occurs where the gradient changes in the figure.

The next gradient change which is *not* caused by the baseline deviation is the beginning of a trough which occurs at approximately 710°C (marked C). The transformation being identified by a trough indicates that the reaction is exothermic. As the structure of the alloys is known to be $\alpha_2 + \beta$ at 650°C, and $\alpha_2 + O$ at 800°C, the transformation which occurs at this temperature has been identified as being;



The next trough (i.e. exothermic reaction), marked D on The figure, which starts at 844°C has been identified as marking the phase boundary between the $\alpha_2 + O$ and the $\alpha_2 + O + \beta_o$ phase fields. The three phase region has not been identified microstructurally in this alloy, but in the Ti-23-15-0.9 alloy, the three phase region has been identified within the temperature range identified by the corresponding D.S.C. curve.

At 884°C, the transformation from the three phase field into the two phase $\alpha_2 + \beta_o$ field begins (marked E on The figure.). This phase region produces the most clearly defined trough, which ends at 1102°C, where the transformation into the single phase β_o region occurs. The 2 phase $\alpha_2 + \beta_o$ region identified by D.S.C. corresponds to the microstructural evidence provided by the alloys aged at 900 and 1050°C. The 1270°C solution treated condition provides evidence as to the phases present above the 1102°C transformation point.

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