

THE EFFECT OF APPLIED TENSILE STRESS
AND OF AUSTENITIZING CONDITIONS ON THE
FORMATION OF MARTENSITE IN STEELS.

A Thesis
Submitted for the Degree of
DOCTOR OF PHILOSOPHY
in the
UNIVERSITY OF LONDON.

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December, 1960.

ABSTRACT

An investigation has been made to study the effect of applied tensile stress and of austenitizing conditions on the formation of martensite in En 23 steel containing 0.3 % C, 3 % Ni and 1 % Cr. The results were obtained using an apparatus that has been designed and built to measure simultaneously the temperature and electrical resistance of a thin wire specimen during continuous cooling; provision has been provided for the application of a dead weight tensile load to the specimen.

It has been found that increasing the austenitizing temperature increases the M_s temperature, and lowers the initial slope of the transformation curve, that is the percentage of martensite formed per $^{\circ}\text{C}$ decrease in temperature. These results have been discussed in terms of nucleation at structural heterogeneities, and a proposal has been made to account for the observations.

Both elastic and plastic stresses have been found to affect transformation to martensite. An elastic stress applied below the M_s temperature induces a burst of transformation as the load is applied, and M_s is raised slightly. Plastic deformation of the austenite in a limited temperature

range above M_s induces transformation to martensite while the specimen is deforming. Plastic deformation of the metastable austenite mechanically stabilizes the parent phase which is manifested in a depression of M_s . These observations have been discussed and a mechanism has been proposed to account for the enhanced deformation which has been observed to accompany transformation under stress.

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1. INTRODUCTION.

The name martensite was first introduced, in honour of Professor A. Martens, to describe the hard plate-like constituent found in quenched steels. In 1946, Troiano and Greninger¹ summarized the characteristics of the martensite transformation, and showed that it had much in common with the shear-like, or diffusionless transformations found in other alloy systems. Accordingly, the term "martensitic" is now generally used to denote the type of reaction rather than the character of the product.

The martensite transformation in steels is of great fundamental and technical importance, especially in the heat treatment of steels, and in certain fabrication processes when rapid cooling rates develop. The technological background to the present problem is the hard-zone cracking in welded steels, in which it was thought that stress and austenitizing conditions might be important. This investigation was undertaken to determine the fundamental effects of applied tensile stress and of austenitizing treatments on the formation of martensite in a low alloy steel.

2. MARTENSITIC TRANSFORMATIONS.

(i) The Nature of Martensitic Transformations.

There are a number of excellent review²⁻¹¹ articles on martensitic transformations. The crystallographic aspects have been treated comprehensively by Bilby and Christian⁵ and in their paper a definition of martensitic transformations is proposed. The general characteristics of the transformation showed that they differ markedly from those of nucleation-and-growth reactions. But these characteristics are insufficient to provide a satisfactory basis for a division of the solid state reactions into two groups, since some of the characteristics have now been shown to be absent from particular transformations.

Bilby and Christian⁵ have used the characteristic "change of shape" revealed on a flat surface by the tilting of the regions transformed, as the most convenient experimental feature to use to identify a reaction as martensitic. Transformed areas may be recognised by etching or by the distortion produced on a prepolished surface. Fiducial scratch marks are sheared over, and a transformed region is tilted out of the plane of the polish. No diffusion is involved in the process and

consequently the transformation product must have the same composition as the parent phase. This has been supported by the observation that ordered phases remain ordered after transformation¹².

The observed displacements indicate that the transformation strain is homogeneous in any one plate, but it has been shown by Greninger and Troiano³ that this strain does not give the atom movements, since the atoms are not then in their final positions in the martensite lattice. It is then necessary to postulate the occurrence of some heterogeneous strain due to twinning or slip on a fine scale in the martensite, and this then accounts for the discrepancy between the lattice deformation, due to the homogeneous shear, and the total shape deformation.

From the above considerations, a formal definition of martensitic transformations was given as follows⁵:

"A structural transformation is classed as martensitic if the atoms on a primitive lattice defined by a selected unit cell of the parent structure move to positions on a primitive lattice defined by some unit cell of the product structure, in such a way that the displacements constitute a homogeneous deformation. This deformation may be different in adjacent small regions."

From this definition it is seen that there is a close analogy between martensite transformations and mechanical twinning, which may even be regarded as a special type of martensitic transformation.

In any martensitic transformation, one of the most important experimental observations is the orientation relations of the two phases, and the orientation of the habit plane. In steels, most of the reviews give three groups of orientations, described as Kurdjumov-Sachs¹³, Nishiyama¹⁴ and Greninger-Proiano³, respectively. The orientation relationship and the habit plane of the martensite needles or plates changes with the carbon content. For steels containing less than 0.4 % carbon the habit plane appears to be $\{111\}_\gamma$, and from 0.5 % carbon to 1.4 % carbon is $\{225\}_\gamma$, while for higher carbon contents the habit plane is $\{259\}_\gamma$.^{5,19} This is also the plane observed in iron-nickel alloys.

Another important crystallographic aspect of martensitic transformations is that the product is usually lenticular in shape due to the opposing stress field of the matrix. In a few transformations, the transformed region has been observed to extend across the whole cross-section of a single crystal^{15,16},

and the interface is then plane. The main interface is usually considered to lie parallel to the habit plane. The nature of the interface is very important, and must remain invariant, i.e. all directions in this plane are unrotated and unchanged in length when averaged over macroscopic distances. Consequently, the shear component of the macroscopic strain lies parallel with the habit plane (or interface), while the dilational component is normal to it. The interface must also provide a suitable connection between the two phases, so that, as it advances, atoms from the austenite are transferred to the martensite lattice in the right orientation. In general, if an interface with these properties exists at all, it has a complex orientation, and the habit plane is then irrational.

However, a good deal of progress has been made in rationalizing these crystallographic features by Bowles and Mackenzie¹⁷, and Wechsler, Lieberman and Read¹⁸. In these phenomenological theories, the habit plane, orientation relationships and macroscopic distortions of the austenite-martensite transformation may be predicted from a knowledge only of the crystal structures of the initial and final phases. Experimental verification

of certain assumptions made in the theories has recently been obtained by observation of thin foils by transmission electron microscopy¹⁹.

It has been proposed that both the homogeneous strain and the dilatation are accomplished at the interface as it spreads (rapidly or slowly) through the parent phase. Frank²⁰ first proposed that the interface may be considered to comprise dislocation arrays which travel along with the interface and produce the heterogeneous strain, and so perfect coherency does not occur at the interface, as suggested by Kurdjumov². Also, the orientation of the dislocation array (interface) that joins the two phases will depend on the mode of slip or twinning in the heterogeneous strain, and in turn on the temperature at which the martensite is generated. This is reflected by the change in habit plane with transformation temperature in carbon steels as shown in Fig.1.

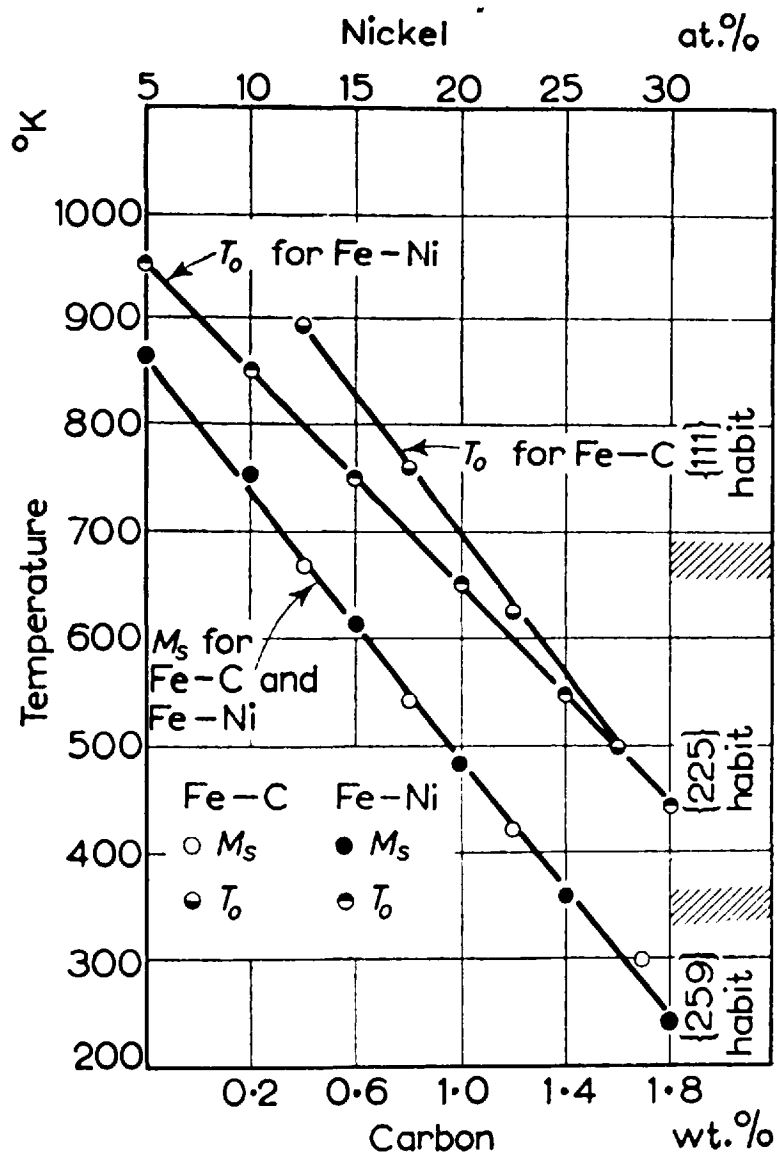


FIG.1. M_s AND T_0 FOR IRON-CARBON AND IRON-NICKEL ALLOYS. (AFTER KAUFMAN AND COHEN⁷).

(ii) Kinetics.

It was formerly considered that there were certain kinetic features characteristic of the martensite transformation, and these were summarized by Troiano and Greninger.¹ However, it has been found that there are exceptions to these generalizations. The basic features are discussed below:

(a) The growth of individual martensite plates is generally very rapid, with growth rates very much faster in the direction of the habit plane than in the direction normal to this plane. Exceptions are the transformations in gold-cadmium¹⁵, indium-thallium^{16,21}, and a number of others. An interesting example occurs in the uranium-chromium system, in which slow isothermal growth has been observed under the microscope. But it does appear that in these systems, although the overall growth rate of a plate is slow, the actual movement of the interface occurs in rapid discontinuous jerks²².

Bunshah and Mehl²³ have shown that the propagation rate of martensite in an iron-nickel alloy is about 10^5 cms/second and that individual plates form in about 10^{-7} second. The rates were found to be approximately the same for both athermal and isothermal transformation to martensite from -20°C

to -196°C . These observed growth rates are about one third of the speed of sound, which is the same as that observed for the propagation of cracks²⁴. The upper limiting velocity is that of the velocity of sound, the limiting rate of dislocation movement²⁵. These results are important in showing that the activation energy for the growth mechanism of martensite is effectively zero. Further evidence was provided in experiments by Kulin and Cohen²⁶, and Kaufman and Cohen²⁷, who found that an iron-nickel alloy transformed at temperatures as low as 4°K , at rates comparable with those observed at much higher temperatures.

(b) Transformation on cooling begins at a temperature called M_s , which may depend on the previous mechanical and thermal history and on grain size. The M_s temperature is usually unaffected by variation of cooling rate and the formation of martensite is not therefore suppressed by very rapid cooling. In most systems transformation, below the M_s point, occurs only on further cooling and ceases if held at a constant temperature; this type of reaction is called athermal. Steels and iron-nickel alloys, transform to martensite by the successive formation of new plates, each one growing very

rapidly to its final size. Therefore, the course of transformation with falling temperature depends on the nucleation of new plates, and not on the growth rate of existing ones. The transformation is complete at a temperature known as M_f , though in a number of systems a small amount of the high temperature phase is always retained.

There are, however, several exceptions to this characteristic, isothermal transformation having been noted in a number of alloys. Kurdjumov and Maksimova^{28,29} first reported completely isothermal martensite transformation and this has since been confirmed by other workers³⁰⁻³³. Several alloys have been shown to exhibit small amounts of isothermal transformation³⁴⁻³⁶.

Therefore, one of the original criterions of a martensitic transformation, that of insuppressibility of the M_s point, has now been discarded, although most transformations do show predominantly athermal kinetics.

Where isothermal reaction has been detected, it usually occurs below M_s , but there are a number of examples of isothermal transformation above M_s .^{28,31-33,35} Therefore, the presence of athermal martensite is not essential for isothermal formation.

But, since martensite transformations are strain sensitive and autocatalytic, the existence of athermal martensite may stimulate isothermal growth. Except for the uranium-chromium transformation³¹, all the isothermal reactions seem to proceed by the nucleation and growth of new plates, or by the rapid discontinuous growth of existing ones. The results show that nuclei may be formed by thermal activation, and that existing plates may become larger due to removal of stresses in the matrix, but that the growth is not thermally activated.

Once a martensite transformation has started, either athermally or isothermally, the subsequent course of the transformation may be greatly influenced by autocatalysis. Orowan³⁷ has suggested that the accommodation stresses round a martensite plate may favour the growth of another plate with a different shear plane, thereby producing the zig-zag pattern of needles that is often observed. Machlin and Cohen³⁸ have shown that in iron-nickel alloys, a large burst of transformation may occur accompanied by an audible click. The burst is preceded by a small amount of transformation, so that the stresses produced by one martensite plate assist in the nucleation of another plate, usually near the tip of the existing one.

(c) Most martensitic transformations are reversible, and show a temperature hysteresis between the cooling and heating reactions. The hysteresis is small, when the range of transformation is also small. In iron base alloys the hysteresis is large and may amount to as much as 300 - 400°C. This characteristic will be discussed further in later sections.

(d) Plastic deformation and even elastic stress in some systems may induce transformation above M_s , and increase the amount of transformation below M_s . There is a temperature, termed M_d , above which plastic deformation will not induce transformation. If the parent phase is deformed above M_d or even below M_d , the matrix may become mechanically stabilized against further transformation on subsequent cooling. This stabilization and also the stimulation of transformation are discussed more fully in the section on the effect of stress on the martensite transformation.

(e) If an alloy is cooled slowly or held at a constant temperature, the phenomenon of 'thermal stabilization' may be operative. In this case, the amount of transformation on further cooling is reduced. Many examples of stabilization have been reported, when the cooling is interrupted below M_s ,

but if the temperature of holding is above M_s , evidence of stabilization is not yet conclusive³⁰, 39-52.

If an alloy is held in a suitable temperature range, then on further cooling to any temperature, the amount of transformation is reduced. This effect has now been well established when the temperature of holding is below M_s ^{30,40-47}. For a constant amount of prior transformation, the amount of stabilization increases to a certain maximum with time⁴⁸. Stabilization has been reported to impede the isothermal^{36,51} as well as the athermal transformation, and also the reversible heating transformation⁴⁹. After stabilization the transformation on further cooling often proceeds at an accelerated rate, and even in bursts. Instances have been reported of stabilization occurring after interrupted cooling above M_s , but the evidence is rather conflicting.

A number of explanations have been proposed to account for the many examples of stabilization, which, of course, may not be all attributable to the same mechanism. Recently it has been found that small amounts of impurity atoms play a major part in the stabilization process⁵¹ in iron-nickel alloys. When carbon and nitrogen were removed from

the alloys, no evidence of stabilization was found. It was suggested that the interstitial diffusion controlling the stabilization occurred within the martensitic embryo, rather than in the matrix, the atoms moving towards the interface and thereby immobilizing it, by locking the dislocations comprising the interface. It has also been suggested that stabilization results from a strengthening of the parent phase, caused by the formation of Cottrell atmospheres⁴⁴ at dislocations, or by precipitation⁵³, again perhaps on dislocations, thereby making the matrix more resistant to further transformation in a manner analogous to mechanical stabilization.

Further evidence that interstitial atoms play a large part in the stabilization process has been provided by Imai and Izumiyama⁵². They observed that steels containing aluminium and titanium, which have a strong affinity for nitrogen, were less easily stabilized than those containing only silicon and manganese, or nickel and tin, respectively. No stabilization of the austenite was noted for a decarburized iron-nickel alloy.

Again it has been proposed that the close-coupling of the interface may be destroyed by time-dependent plastic yielding or relaxation⁵⁴ of the

elastic stresses surrounding an existing plate⁴⁸. It has been suggested that there may be a connection between stabilization and the first stage of tempering⁴⁸.

(iii) The Free Energy Change.

(a) The Chemical Free Energy Change.

Since martensitic reactions are essentially diffusionless, the composition of the austenite and the product, martensite, will be the same, and therefore lend themselves more easily to a thermodynamic treatment than do diffusion controlled transformations. Each phase has a chemical free energy that varies with temperature, and there may be a temperature T_0 , at which the two free energies are equal. At any other temperature the difference in free energy may be expressed :

$$F^{\gamma} - F^{\alpha'} = \Delta F^{\alpha' \rightarrow \gamma} \text{ cal/mol ... (1)}$$

When martensite is more stable than austenite, that is below T_0 , this quantity is positive and its value gives a quantitative measure of the driving force of the reaction. Fig.2. is a schematic representation of $F^{\alpha'}$ and F^{γ} as a function of temperature.

In the cooling of any given alloy, M_s lies

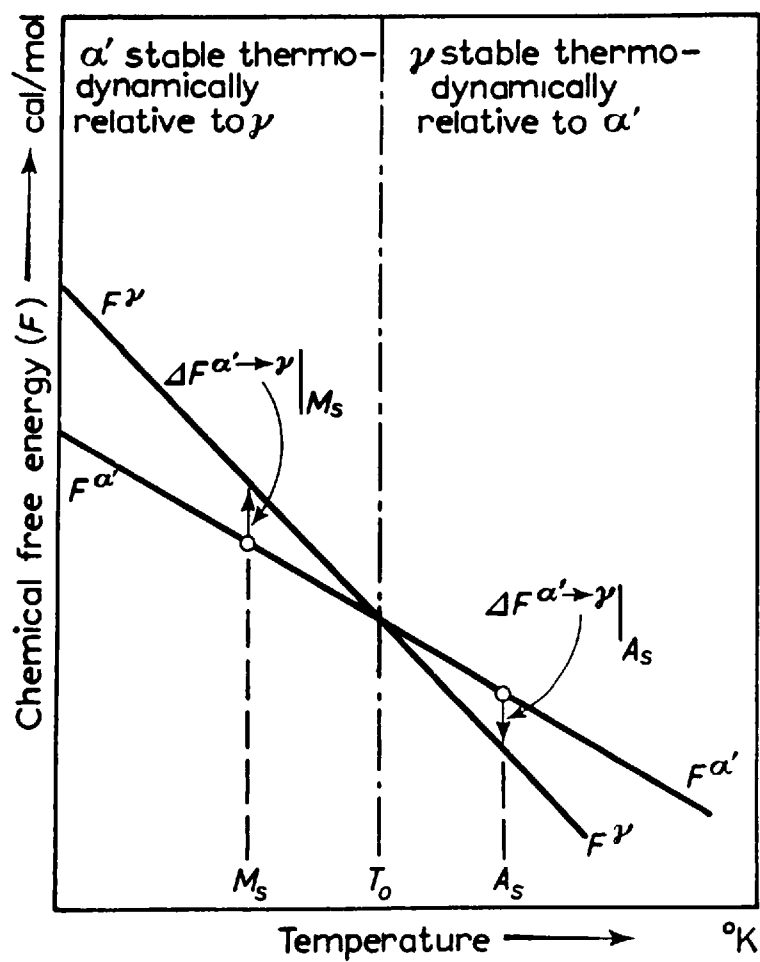


FIG. 2. SCHEMATIC REPRESENTATION OF $F^{\alpha'}$ AND F^{γ} VS. TEMPERATURE FOR AN IRON-BASE ALLOY. (AFTER KAUFMAN AND COHEN⁷).

below T_0 , because the austenite-to-martensite reaction does not necessarily start immediately the thermodynamic conditions become favourable. The supercooling results from the non-chemical restraining forces, which will be discussed later, that is, the interfacial energy of the new particle and its associated strain energy. The start of the reverse transformation, the A_s temperature, often requires superheating as shown in Fig.2, and usually lies approximately as far above T_0 as M_s is below.

There is not much thermodynamic data available for systems having a martensitic transformation. One of the difficulties is that diffusionless transformations often occur at a low temperature where equilibrium cannot be achieved. However, there is a good deal of such data available in the iron-carbon⁴² and iron-nickel^{7,49} systems, and much progress has been made, mainly by Kaufman and Cohen⁷, in the calculation of T_0 in these systems from thermodynamic data. Fig.3 shows the change in chemical free energy attending the martensite reaction in iron-carbon alloys as a function of temperature and carbon content. The driving force at M_s or $\Delta F^{\alpha \rightarrow \gamma}$, is independent of the carbon content, and is 290 cal/mol.

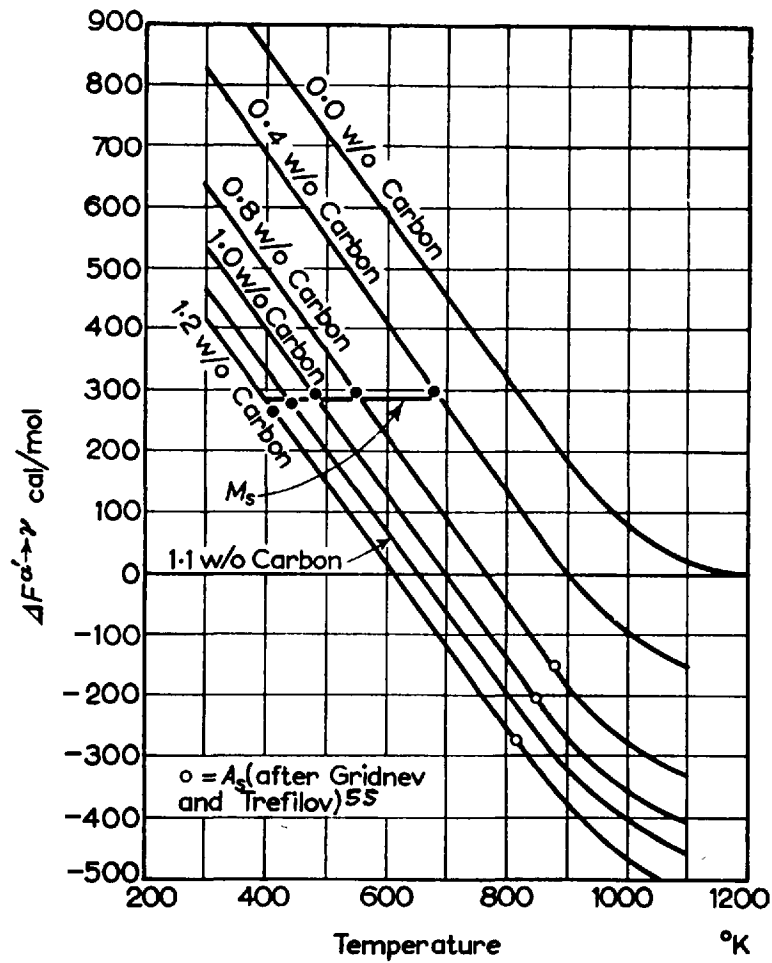


FIG.3. CHANGE IN CHEMICAL FREE ENERGY ATTENDING THE AUSTENITE-MARTENSITE REACTION IN IRON-CARBON ALLOYS AS A FUNCTION OF TEMPERATURE AND CARBON CONTENT. (AFTER COHEN, MACHLIN AND PARANJPE⁴²).

The experimental determination of T_0 depends on bracketing it between M_s and A_s . In iron-base alloys the hysteresis may be as large as 400°C. In iron-carbon alloys, the reverse transformation is not easily observed because of the interference of tempering reactions until high heating rates are achieved. Recently, Gridnev and Trefilov⁵⁵ have reported A_s values in steels, lying 300° - 400°C above M_s , rapidly heated at >600°C/sec., but there is some doubt that a true reverse martensitic transformation was observed and tempering completely suppressed. In all alloys exhibiting martensitic transformations a reverse transformation has been observed, except where some intermediate decomposition product is formed.

In general the hysteresis gap can be narrowed by plastic deformation. M_s is then raised becoming M_d and A_s is lowered, to A_d . M_d is defined as the highest temperature at which the austenite-to-martensite reaction may be induced by plastic deformation. The gap was almost completely closed in cobalt-nickel alloys by Hess and Barrett⁵⁶, using this method. If M_d and A_d cannot be brought together, then T_0 is taken as $\frac{1}{2}(M_d + A_d)$. This procedure has been used by Kaufman and Cohen⁴⁹ for

the determination of T_0 in iron-nickel alloys, and T_0 turns out to be about $\frac{1}{2}(M_S + A_S)$ for this system. There are some alloys, for example, indium-thallium¹⁶ and gold-cadmium⁵⁷, in which the hysteresis is so small, that plastic deformation is unnecessary to determine T_0 .

The determination of T_0 by plastic deformation is a kinetic effect; the deformation stimulates the nucleation of the thermodynamically more stable phase where transformation would not normally take place on cooling. But the possibility does arise of raising the equilibrium temperature T_0 by elastic stresses. Burkart and Read¹⁶ have shown that in an indium-thallium alloy M_S and A_S (and consequently T_0) are raised by elastic stress. M_S in iron-nickel alloys has also been shown, by Patel and Cohen,⁵⁸ to be influenced by elastic stresses. This change in the equilibrium temperature T_0 due to mechanical factors is a thermodynamic effect in agreement with Le Chatelier's principle, in contrast to the kinetic effect of plastic deformation. However, in iron-base alloys, the temperature hysteresis is large, and the amount T_0 would be raised by elastic stress is small compared with $M_d - M_S$, and $A_S - A_d$.

(b) The Non-chemical Free Energy Change.

It has been mentioned earlier that the

martensite transformation does not start at T_0 when the driving force becomes positive. This supercooling ($T_0 - M_S$) is due to the non-chemical restraining forces. Therefore, for martensite to form the driving force must not only be greater than zero, but greater than some finite value, dependent on the alloy system.

When a martensite plate forms, an interface is formed between it and the parent phase. For a lenticular plate of radius 'r' and thickness 'd', where $r \gg d$, the energy of the interface is taken as⁵⁹:

$$\Delta G_S^{\gamma \rightarrow \alpha'} = 2\pi r^2 \sigma \text{ cal./particle ... (2)}$$

where σ is the specific interfacial free energy and $2\pi r^2$ is the surface area of the plate. Kurdjumov² has regarded the interface between austenite and martensite as coherent, and Fisher et al.⁵⁹ have calculated a value of 24 ergs/cm.² for σ , also using a coherent interface model. On the other hand, Frank²⁰ and Read et al.¹⁸ have proposed models of the interface consisting of dislocation arrays. Under these conditions, σ may be as high as 500 - 1000 ergs/cm.², which is of the same order as that of an ordinary inter-phase boundary. Knapp and Dehlinger⁶⁰, have calculated a value of 200 ergs/cm.² based on Frank's model of the interface of an iron-

carbon alloy.

The other principal non-chemical factor arises from the different specific volumes of austenite and martensite. Elastic strains are developed both in the plate and its surroundings, by the dilatational and shear components of the displacements. The dilatational contribution is neglected in comparison with the shear component, and the strain energy term is calculated by considering a sphere of radius 'r' surrounding the plate, then the elastic strain at any point is assumed to be proportional to $\frac{d}{r}$. The strain energy

$$E_v \propto \left(\frac{d}{r}\right)^2$$

A similar proportionality holds at every point of the sphere, and therefore the total strain energy is proportional to $\left(\frac{d}{r}\right)^2$ multiplied by the volume of the sphere. Therefore,

$$E = \Delta G_e = \left(\frac{3\theta}{4}\right) \cdot \left(\frac{d}{r}\right)^2 \cdot \left(\frac{4\pi r^3}{3}\right) = \theta \pi r d^2 \quad \dots (3)$$

where $\frac{3\theta}{4}$ is the constant of proportionality.

By assuming that the strain in the austenite is uniform throughout the sphere of radius r, a value of the strain energy constant θ may be evaluated⁵⁹:

$$\theta = \frac{\phi^2 G}{6}$$

where ϕ = martensite shear angle.

G = shear modulus.

By taking $\phi = 0.34$ (the Nishiyama¹⁴ relationship), a value of $\theta = 1.54 \times 10^{10}$ dynes/cm² was obtained by Fisher et al.⁵⁹ This is in good agreement with the value obtained by Knapp and Dehlinger⁶⁰ by another method of calculation.

There are other non-chemical factors associated with the formation of a martensite plate, such as the dilatation strain energy previously mentioned, and the energy required to produce the clicks that are sometimes heard during transformation. There is also an energy term resulting from any non-reversible plastic deformation of the matrix surrounding the growing embryo. In ferrous materials it seems that the accommodation strains are only relieved by slip in the austenite, but in some transformations the accommodation strains are elastic, and then the phenomenon of thermo-elastic martensite may be observed.

(iv) The Nucleation of Martensitic Transformations.

It is now known that the co-operative atomic movements producing martensite must originate from very small regions, or embryos, in the austenite. It is, however, the origin and form of these embryos and the mechanism by which they may grow into a complete plate of martensite, that is still in doubt.

(a) Classical Nucleation Theory applied to Martensitic Transformations.

Classical homogeneous nucleation theory was first applied to martensitic transformations by Kurdjumov^{2,28}, by Fisher, Holloman and Turnbull⁵⁹, and in a modified form by Fisher and Turnbull⁶¹ to include the effects of stresses.

A martensite nucleus is assumed to be lenticular in shape, and the total free energy change for the formation of such a particle is given by :

$$\Delta G^{\gamma \rightarrow \alpha'} = \Delta G_s^{\gamma \rightarrow \alpha'} + \Delta G_e^{\gamma \rightarrow \alpha'} + \text{chemical free energy change} \dots (4)$$

where $\Delta G_s^{\gamma \rightarrow \alpha'}$ is the free energy of the interface, and $\Delta G_e^{\gamma \rightarrow \alpha'}$ is the strain energy.

Therefore, from equations 2 and 3,

$$\Delta G^{\gamma \rightarrow \alpha'} = 2\pi r^2 \sigma + \pi r d^2 \theta + \pi r^2 \frac{d}{2} \Delta f^{\gamma \rightarrow \alpha'} \dots (5)$$

Where $\Delta f^{\gamma \rightarrow \alpha'}$ is the chemical free energy change per unit volume of martensite formed. Below T_0 , $\Delta f^{\gamma \rightarrow \alpha'}$ is negative, and σ and θ are always positive. By minimizing $\Delta G^{\gamma \rightarrow \alpha'}$ at constant volume, by differentiation, the energy of formation and the volume of a critical size nucleus are found to be :

$$\Delta G_* = \frac{8192\pi\theta^2\sigma^3}{27\Delta f^4} \quad \text{cal./particle} \quad \dots \dots \dots (6)$$

$$V_* = -\frac{32,768\pi\theta^2\sigma^3}{27\Delta f^5} \quad \text{cm}^3 \quad \dots \dots \dots (7)$$

ΔG_* is the energy barrier that must be mounted for embryos to reach a critical size and spontaneously grow.

The rate of nucleation $\dot{N}$, of martensite plates per cm^3 per sec. is given by :

$$\dot{N} = N \cdot \frac{kT}{h} \cdot e^{-\frac{(\Delta G_* + Q)}{kT}} \quad \dots\dots\dots (8)$$

where N = number of atoms/ cm^3

Q = activation energy for coherent growth

and $\frac{kT}{h}$ = lattice vibration frequency.

The activation energy term may be neglected, since it is assumed that the interface is sufficiently mobile to maintain an equilibrium distribution of embryos even down to very low temperatures.

Originally, Fisher et al. assumed that in interstitial alloys embryos will form preferentially in carbon free areas, in an otherwise structurally perfect matrix. The model visualises a small incoherent ferrite region in a carbon-free area in the austenite. Upon quenching, this ferrite region grows coherently to the boundaries of the region. Then this carbon-free ferrite acts as a nucleus for the growth of martensite of average carbon content at a temperature when the volume exceeds V_* . If the rate of thermal nucleation is negligible, the

available nuclei will grow rapidly, but transformation will then stop until V^* is decreased by further cooling. The athermal characteristics are thus explained.

The implication of the theory is that martensite nucleates only isothermally; equation 8 corresponds to typical C-curve behaviour. The theory has been applied by Fisher⁶² to the results of Cech and Holloman³⁰ for the isothermal transformation of an iron-nickel-manganese alloy and good agreement was obtained with the experimental observations.

However, to explain the athermal behaviour in iron-nickel alloys, Fisher⁶³ has identified M_s as the temperature at which $\dot{N} = 1 \text{ nucleus/cm}^3/\text{sec}$. At higher temperatures $\dot{N}$ is so small that isothermal nucleation is not observed, while at a lower temperature, $\dot{N}$ is so large that isothermal nucleation is not suppressed even on rapid cooling. Fisher's work predicts that below 31 atomic % nickel no transformation should be observed, at a minimum M_s of 120°K. But Kaufman and Cohen²⁷ have found that M_s temperatures in these alloys decrease continually to 50°K, and they say that no reasonable alteration of Fisher's thermodynamic values will explain the results. On the other hand, the occurrence of M_s points at such low temperatures is in accordance with the concept of heterogeneous nucleation at preferred sites.

Fisher, Holloman and Turnbull have modified their views on homogeneous and heterogeneous nucleation and now consider that embryos form around lattice imperfections, such as dislocations⁶¹. This is stated in a paper in which the classical nucleation theory is modified to include the influence of stress in the nucleation of martensite, by modifying the volume free energy change.

There is now a large amount of evidence that martensitic reactions are in fact heterogeneous, and nucleate at preferred sites, rather than at random. The most straightforward clues come from metallographic investigations. In β -brass⁶⁴, and other transformations which are easily reversible, the position and the sequence of the formation of the plates on cooling are repeated almost precisely on the next cooling cycle, after complete reversion to the high temperature phase. This observation certainly suggests nucleation at preferred sites. In the gold-cadmium system¹⁵, cooling a single crystal usually results in many plates, but if the single crystal is first well-annealed at a relatively high temperature in the austenitic phase, the nucleation is so changed, that only one interface may move across the specimen, producing a single crystal of

the martensite phase. Another interesting series of experiments confirming heterogeneous nucleation was performed by Cech and Turnbull⁶⁵. Tiny particles of an iron-nickel alloy were austenitized and quenched. It was found that transformation started at widely different temperatures, and some particles did not transform at all. It was concluded that some particles had fewer effective nucleation sites than others, and supercooled further, showing that nucleation was quite heterogeneous. Particles larger than 100 microns had M_s temperatures comparable with that of bulk specimens.

(b) Nucleation at Strain Centres.

As an alternative to the classical nucleation theory, Cohen, Machlin and Paranjpe⁴², proposed the reaction-path model. Since this model appears to be the forerunner of the more recent embryo theory⁷, it will not be very fully discussed. It is assumed that the transformation is nucleated at strain embryos and growth is by the propagation of a shear wave over a reaction path which describes the relative motions of atoms during the transformation.

Frank²⁰ has suggested that the austenite-martensite interface in the iron-carbon system having a $(225)_\gamma$ habit plane, may comprise a disloc-

ation array. In the model, close-packed planes of the two phases meet along close-packed rows. In converting the austenite (f.c.c.) into martensite (b.c.t.) a shear and a dilatation, plus a grid of screw dislocations lying parallel to the close-packed direction, one between every sixth plane, produces the correct final structure. The interface produces a highly mobile connection between the two phases, and the growth of a martensite plate takes place by the movement of the interface of dislocations into the austenite.

Using Frank's²⁰ model of the interface, Knapp and Dehlinger⁶⁰ regarded the embryo of martensite as a thin oblate spheroid surrounded by loops of dislocations, as shown in Fig. 4. These loops are assumed to consist mainly of screw dislocations, with short edge components joining the positive and negative screws. Growth of the embryo is achieved by the expansion of the loops into the austenite. Expansion in the $[225]_{\gamma}$ and $[1\bar{1}0]_{\gamma}$ directions is by the growth of existing loops, while growth in the $[55\bar{4}]_{\gamma}$ direction requires the generation of new loops. The chemical driving force $\Delta f^{\gamma \rightarrow \alpha'}$ supplies the energy required for the expansion. Knapp and Dehlinger⁶⁰ assume that an embryo will "trigger"

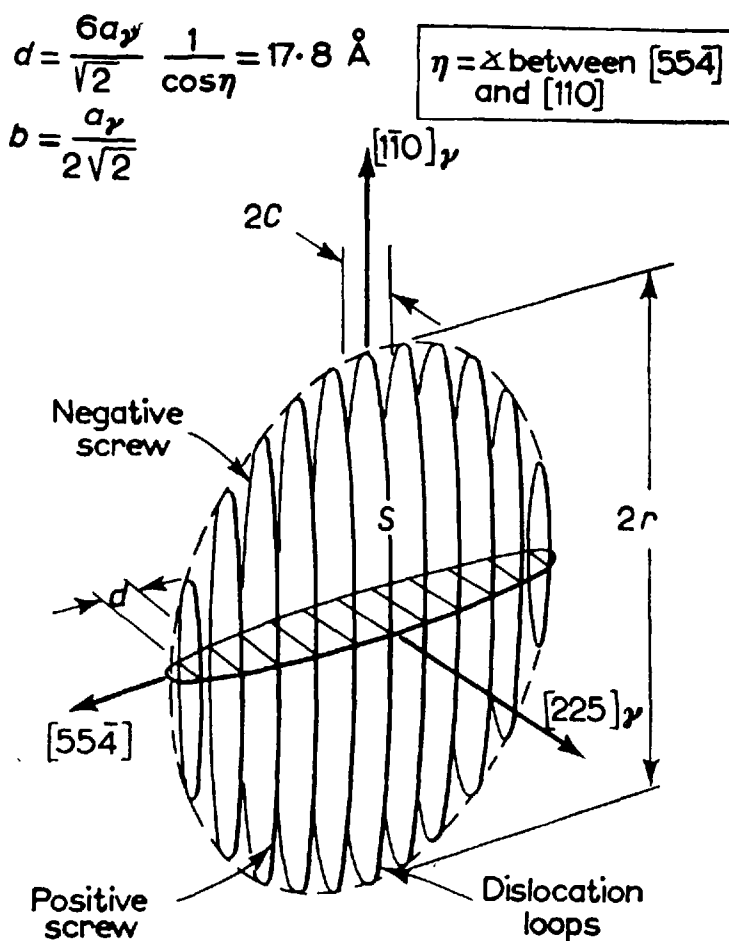


FIG.4. MODEL OF THE MARTENSITE EMBRYO.
(AFTER KNAPP AND DEHLINGER⁶⁰).

spontaneously into full sized plates as soon as the chemical driving force exceeds the restraining interfacial and strain energies. They are not therefore considering the nucleation process in which a free-energy barrier must be surmounted, but the conditions for propagating an existing embryo.

Using an expression for the restraining force similar to that obtained by Fisher⁵⁹, (equations 2 and 3), Knapp and Dehlinger⁶⁰ calculated the minimum value of the non-chemical free-energy difference between austenite and martensite per unit volume ($\Delta g_{\min.}$), with respect to a given thickness of martensite embryo. However, $\Delta g_{\min.}$ is more accurately minimized relative to a given volume of the embryo⁷, and a value is then found :

$$\Delta g_{\min.} = \frac{5}{2} \left(\frac{\sigma A}{r} \right)^{\frac{1}{2}} = \frac{5\sigma}{2c} \text{ cal/cm}^3$$

and $c = \left(\frac{\sigma r}{A} \right)^{\frac{1}{2}} \text{ cm.}$

Here, c is the half-thickness of the plate assumed to be an oblate spheroid and is equal to $d/2$ as used by Fisher⁵⁹; as a result the elastic constant $A = 40$.

Based on values of $\sigma = 200 \text{ ergs/cm}^2$ and $A = 500 \text{ cal/cm}^3$, Kaufman and Cohen⁷ have calculated $\Delta g_{\min.}$ as a function of embryo size as shown in Fig.5.

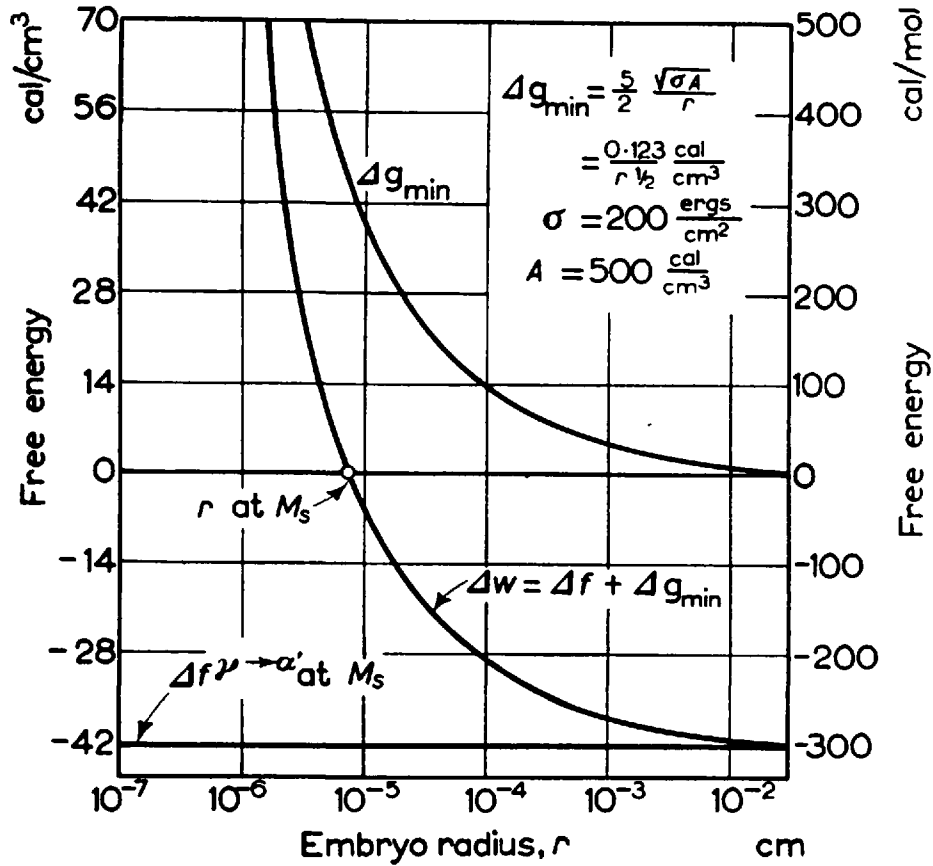


FIG.5. EFFECT OF EMBRYO SIZE ON THE RESTRAINING FORCE $\Delta g_{\min}$. AND THE NET DRIVING FORCE Δw . (AFTER KNAPP AND DEHLINGER⁶⁰).

The embryos that grow at the M_s temperature are presumably the largest ones available. $\Delta f^{\gamma \rightarrow \alpha'}$ (290 cal/mol.) the driving force at M_s is known for steels, and since $\Delta g_{\min.}$ must equal this, the size of the embryo may be calculated, giving a radius of 850 Å and a thickness of 70 Å. Smaller embryos are restrained because of larger $\Delta g_{\min.}$ values. As a given embryo cools, the chemical driving force becomes more negative, until it exceeds the value of $\Delta g_{\min.}$ of the embryo, and a net driving force results. This may be likened to a physical stress which acts on the dislocation interface, which is pushed outward into the austenite to generate martensite from the embryo.

The embryos are assumed to result from the interaction of certain pairs of edge-edge and edge-screw dislocations which generate regions geometrically similar to martensite. According to Knapp and Dehlinger⁶⁰, the embryos do not grow at temperatures above T_0 , because both the chemical, and strain and interfacial, energies favour the formation of austenite. But the embryos do not disappear, because the dislocations cannot be removed even by extensive annealing. Between T_0 and M_s the net driving force is still insufficient for propagation of the embryo, while below M_s the chemical driving

force exceeds $\Delta g_{\min}$. and the interface is moved into the austenite producing martensite.

However, Kaufman and Cohen⁷ picture the embryos as growing in size on cooling by the coalescing of dislocations into an interface, and they have calculated the decrease in strain energy associated with dislocations in an interface of the Frank type compared with those at random. The coalescence will depend upon the mobility of the dislocations, and it is suggested that there may be a temperature above T_0 at which the embryos will cease to grow and become "frozen-in". At the M_s a spectrum of embryos sizes is assumed to exist, the largest ones propagating first. As the temperature is lowered, smaller and smaller embryos become activated, and the predominantly athermal characteristics of the transformation are thus nicely explained. Kaufman and Cohen⁷ have shown that the model may also be used to explain the isothermal characteristics of the transformation.

The growth of a martensite plate is terminated at physical barriers, such as other plates, grain boundaries and inclusions. Some other mechanism must be operable, because, except in the case of thermoelastic martensite, the plates do not

thicken when 'r' is prevented from increasing. It has been suggested⁷ that growth may be halted by jamming of the dislocations in the interface, thus also preventing the reversible transformation. This method of stoppage may account for the observation that martensite plates often do not extend the whole way across a single crystal of austenite. Mechanical stabilization of the austenite may also be attributed to this mechanism.

This model of nucleation requires the existence of relatively large embryos in the austenite above M_s . The first experimental evidence of these has been obtained recently by Richman et al.⁶⁶ By means of transmission electron microscopy of thin films of iron-nickel alloys, they have reported the presence of 'plate-like' markings in the austenite which were interpreted as martensite embryos. The measured size of the largest plates agreed reasonably well with the calculated values. The micrographs also showed the distribution of embryos required by the theory. However, more experimental data are required before the theory is substantiated, and may be considered to rest on a firm foundation.

(c) Dislocation Generation Models of Nucleation.

A number of investigators⁶⁷⁻⁶⁹ have used the idea that there may be faults in the austenite .

bounded by imperfect dislocations, which have a structure similar to that of the martensitic phase. These faulted regions tend to grow as the temperature falls, generating a thin plate of martensite, and it is these that may be the original nuclei. To produce the final product, some method must be devised so that the process occurs on a regular sequence of parallel planes.

One possible mechanism is the dynamic multiplication of fast moving dislocations⁷⁰, which has been used by Christian in a theory of the f.c.c.—h.c.p. transformation in cobalt. An alternative proposal, which does not depend on the velocity of dislocations, is called the 'pole-mechanism'⁷¹. This is a generalization of the Frank-Read⁷² dislocation source, in which the rotating dislocation climbs on a helicoidal surface, thereby producing transformation (or slip) on successive planes. This mechanism has also been applied to the cobalt transformation⁶⁸.

In iron alloys, the most precise model is that due to Jaswon⁶⁹. Kurdjumov and Sachs¹³ first showed that the martensite structure may be generated from austenite by the sequence of two shears: (1) half the twinning shear along the elements

$\{111\}_\gamma$ $\langle 112 \rangle_\gamma$, having a Burgers vector $\frac{d}{3} \langle 112 \rangle_\gamma$, producing a b.c.t. structure (α') which is almost martensite.

(ii) a second shear along $\{112\}_\gamma$ $\langle 110 \rangle_\gamma$, producing the final structure, apart from small dimensional changes. Jaswon⁶⁹ pointed out that shear (i) may be accommodated by dislocations already present in the austenite. These dislocations of Burgers vector $\frac{d}{3} \langle 112 \rangle_\gamma$, arise from a further splitting of the Heidenreich and Shockley⁷³ partial dislocation into quarter dislocations. This dissociation :

$$2 \frac{d}{3} \langle 112 \rangle_\gamma = \frac{d}{3} \langle 112 \rangle_\gamma + \frac{d}{3} \langle 112 \rangle_\gamma$$

is energetically favourable, since it creates a low energy stacking fault of α' . At high temperatures this fault becomes very small, while on cooling the dislocations move apart, until below M_s , the stacking fault becomes unstable and rapidly propagates to form a thin plate of martensite.

(v) Effect of Stress on the Formation of Martensite.

It has now been established that internal or external elastic and plastic stresses applied above or within the temperature range of martensite formation have a marked effect on the kinetics of the transformation. This effect has a number of

practical applications in industry. For example, stainless (18:8) and Hadfield's manganese steel which are austenitic at room temperature, may be strengthened by cold work, which induces transformation.

An applied stress may affect the course of the transformation in two ways :

(a) It tends to promote the formation of a plate, by changing the rate of nuclei formation, or aiding nucleation, in the same way as the formation of a mechanical twin.

(b) Also, plastic deformation of the parent phase may decrease the rate of transformation by mechanical stabilization of the austenite.

At the M_s temperature, the specimen transforms spontaneously with no applied stress. Scheil⁷⁴ first predicted that as the temperature is raised, successively higher stresses would be required to induce transformation, until eventually the specimen deforms without transforming. He suggested that transformation and slip are alternative ways of plastically straining the lattice. The upper limit at which transformation may be induced by stress has been termed the M_d temperature, and according to Scheil⁷⁴, deformation by transformation would occur

spontaneously without stress at M_S , and more readily than slip at any temperature between M_d and M_S . The theory therefore implied that the parent lattice becomes mechanically unstable at the transformation temperature, and that the elastic limit would increase from zero at M_S to a maximum at M_d . This particular idea has not been substantiated, although most of Scheil's⁷⁴ proposals have since been confirmed by experiment. McReynolds⁷⁵ found that there is no effect on the shear modulus when iron-nickel alloys are cooled through the M_S point. The yield stress was found to increase markedly with decreasing temperature at M_d , and to reach a maximum just above M_S . As the temperature is decreased from just above M_S to just below, the yield stress changed discontinuously from a maximum to a very low value. McReynolds⁷⁵ found that plastic deformation by compression above M_S caused immediate transformation, the amount depending on the degree of straining and the temperature of application. He observed an M_d temperature about 75°C above M_S above which transformation could not be induced by compression. McReynolds⁷⁵ also found that plastic deformation at any temperature from below the M_S to above the M_d point, mechanically stabilizes the remaining austenite so that the beginning of subsequent trans-

formation on cooling is depressed.

The effects of plastic deformation on the course of transformation have also been studied extensively by Russian workers, in ferrous alloys and steels containing nickel, chromium and manganese 76-82. It was found that transformation was induced by the deformation but the subsequent course of transformation on further cooling depended on the degree of straining and the composition of the alloy. Prior deformation was found to influence the transformation in the alloys investigated in one of two ways, as follows :

- (i) Alloys in which the formation of martensite is stimulated by small strains and retarded by large deformations.
- (ii) Alloys in which the transformation is always retarded by prior deformation.

It has been suggested¹⁹ that the stimulation of transformation may result from nucleation at stacking faults in the austenite introduced by the deformation. In the alloys which showed evidence of stacking faults induced by deformation, transformation was stimulated by small amounts of deformation, while those in which the formation of martensite was retarded showed little indication of faulting⁸³.

It had originally been supposed that slip lines, deformation bands, etc., would provide barriers for the growth of martensite plates. However, a number of workers have observed that slip lines do not appear to inhibit growth of a plate⁷⁹.

Another interesting series of experiments has been made on lithium⁸⁴. The normal M_s for the cooling transformation is 70°K and cold-working the body-centred cubic lithium produced face-centred lithium at 90°K with clicking noises. But cold working at 110°K stabilized the high temperature form to such an extent that no transformation could be found on subsequent cooling to 4°K.

Although spontaneous deformation of austenite during the growth of a plate may, in its initial stages, activate the growth of suitably orientated nuclei, it has also been suggested that at any temperature the martensite plates already formed autocatalytically stabilize the austenite against further transformation⁶⁹. This accounts for the fact that most transformations only occur on further cooling as the driving force is increased. In support of this idea is the observation of the plastic deformation of austenite round a martensite plate in an iron-nickel alloy⁸⁵. Direct evidence of the spontaneous deformation of austenite has recently been

obtained by Kelly¹⁹ using transmission electron microscopy. High dislocation densities were observed surrounding martensite plates formed in a quenched iron-nickel-carbon steel.

Recently, Porter and Rosenthal⁸⁶ working on a eutectoid carbon steel, found that at the transformation temperature the specimen yielded to a very low applied stress.* The threshold stress for increased extension during transformation was found to be approximately 1000 p.s.i. while no increase in M_S was observed until a stress of approximately 30,000 p.s.i. was applied in tension. It appeared that a small amount of martensite was induced by the stress above the normal M_S , and when the normal M_S was reached transformation was found to begin and proceed just as if no stress were present. An explanation was advanced to explain the low value of the threshold stress. It was suggested that the 'triggering off' of embryos of martensite supplied the energy to drive dislocations through the austenite, producing pile-ups at the grain boundaries. The threshold stress then represents the

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* This phenomenon of "transformation plasticity" has been known for a number of years. It was observed by Sauveur⁸⁷ in 1924 in the allotropic change in pure iron.

increase of stress required to release these sources thereby producing the slip observed.

Porter and Rosenthal⁸⁶ were unable to detect any preferred orientation of the plates formed under the applied stress, but Chang and Read¹⁵ have reported an increased deformation in gold-cadmium alloys as a result of preferred orientation of martensite plates induced by applied stress.

When a martensite plate is formed, work is done by an externally applied stress in producing the total shape deformation. Le Chatelier's principle, which in effect states that the mode of transformation is such that the applied stress does the maximum amount of work, has been applied to molybdenum-titanium alloys⁸⁸. Stress was applied, and the distribution of martensite plates showed a preferred orientation parallel with the plane of maximum shear stress in agreement with Le Chatelier's principle.

If the M_s is assumed to be characterized by a critical value of the driving force, as shown previously, the effect of a given stress may be calculated quantitatively. This has been done by Patel and Cohen⁵⁸. The stress is resolved into components parallel to the shear and dilatational displacements of the transformation. These strains

have been measured for various systems, and the mechanical work done by the stress may be calculated. This energy term is then added algebraically to the chemical free energy (or driving force), to find the alteration in M_s temperature. Good agreement with experimentally observed values was obtained for an iron-carbon-nickel alloy and for iron-nickel alloys with M_s temperatures below room temperature. It was found that applied uniaxial tension raised M_s as shown in Fig. 6, and uniaxial compression also raised M_s but to a lesser degree, while hydrostatic compression lowered M_s . This treatment recognises both the shear and dilatational strains of the transformation, and from the observation that tensile stress raises M_s more than the equivalent compressive stress shows that the normal component is significant, since the resolved shear stress in these two cases is equal. It has also been observed in a bending experiment, that more martensite formed in the elongated section, than in the zone subjected to compression^{82,89}.

An essentially similar calculation has also been made by Crussard⁹⁰. The influence of stress is expressed in the generalized form of the Clapeyron equation :

$$\Delta M_s = \frac{WT_1}{L}$$

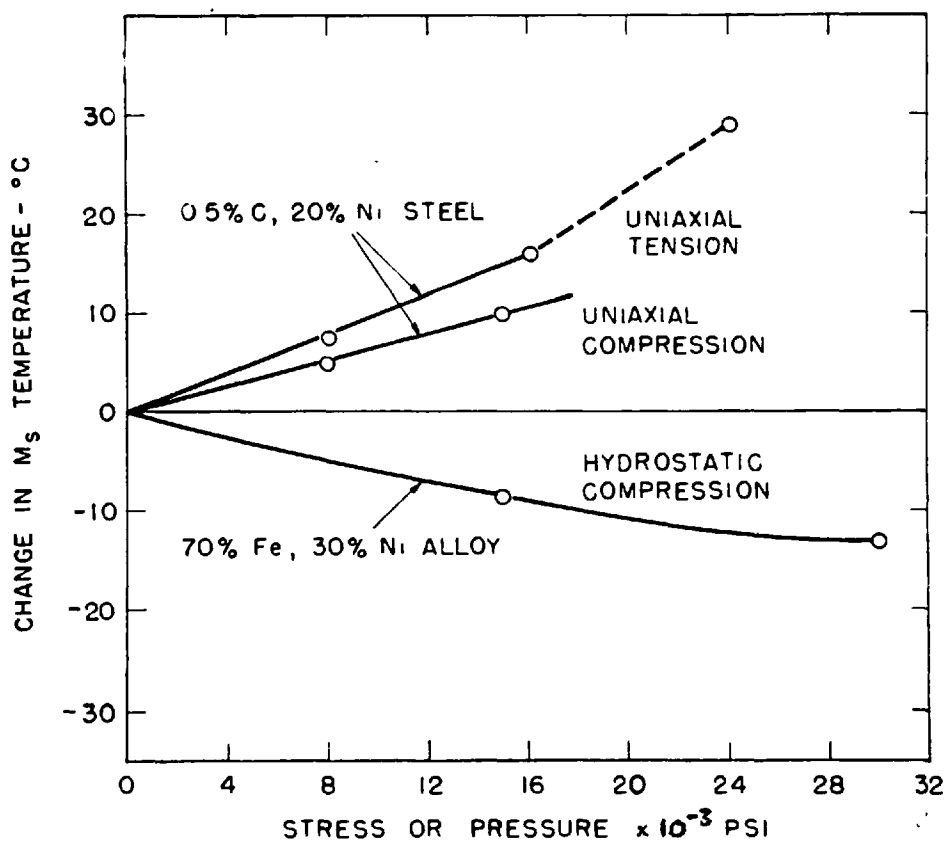


FIG. 6. CHANGE IN M_s TEMPERATURE AS A FUNCTION OF LOADING CONDITION. (AFTER PATEL AND COHEN⁵⁸).

where L = latent heat of transformation at temperature T_p

and W is termed the energy of interaction.

This energy is calculated for a uniaxial tension of 1 Kg./mm^2 (1420 p.s.i.) or 10^8 dynes / sq.cm. giving

$$W = 10^8 V \cdot \cos \theta \cdot (\epsilon \cdot \cos \theta + \gamma \cdot \sin \theta)$$

where V = volume transforming.

θ = angle between direction of tension and normal of the plate.

ϵ = dilatation.

γ = shear strain.

For a polycrystalline material, one martensite plate will have a favourable orientation and the algebraic maximum of W is calculated. ΔM_s is then found to be of the order of $+1.5^\circ\text{C}$ for 1 kg./mm^2 (or $1.05^\circ\text{C}/1000 \text{ p.s.i.}$), which is in good agreement with Patel and Cohen's results.⁵⁸

Fisher and Turnbull⁶¹ have postulated that stress influences the nucleation of martensite by modifying the volume free energy change. In general, shear transformations can occur in one direction only, and consequently a tensile or compressive component, σ_n , normal to the habit plane of the nucleus will either help or oppose the normal austenite to martensite volume change. The volume

free energy can then be considered to be modified, as energy is expended in pushing against the stress, by $(-\sigma_n \cdot \Delta v)$, where Δv is the volume expansion per unit volume of the transformation, and σ_n being negative for compression.

The shear component, τ_m , of the stress in the direction of the plate will also aid transformation, and may be shown to modify the volume free energy change by $-\frac{4}{3}\tau_m \cdot \phi$. This term is also negative because it aids transformation. Equation 5 may now be written as follows :

$$\Delta G^{\gamma \rightarrow \alpha'} = 2\pi r^2 \sigma_s + \pi r d^2 \theta + \pi r^2 \frac{d}{2} (\Delta F^{\gamma \rightarrow \alpha'} - \sigma_n \cdot \Delta v - \frac{4}{3}\tau_m \cdot \phi)$$

where σ_s = specific interfacial free energy.

θ = strain energy constant.

ϕ = martensite shear angle.

This equation was then used to calculate the influence of stress upon the transformation, and the results were shown to agree satisfactorily with the experimental determination of Kulin, Averbach and Cohen⁸⁹. However, Kaufman and Cohen do not consider the calculation to be a valid one⁷.

The M_s temperature is necessarily below the thermodynamic equilibrium temperature T_0 , in the absence of stress. Transformation, however, in

indium-thallium¹⁶ alloys, has been observed under stress above this equilibrium temperature, providing the work done by the applied stress exceeds the increase in volume free energy. Fig.7 shows the increase in the start of transformation for the heating and cooling reactions as a result of applied tensile stress. T_0 is assumed to lie midway between the heating and cooling curves. The change of T_0 is a thermodynamic effect, but, as mentioned previously, stress is not required to measure the equilibrium temperature T_0 because the hysteresis gap is small. Complete isothermal transformation could be induced in either direction by the application of stress. Similar curves have also been obtained for the gold-cadmium system.

Another interesting phenomenon is that of thermoelastic martensite observed by Reynolds and Bever⁹¹ in quenched β -brass. Many of the plates which formed as a result of compression at room temperature, disappeared on removal of the stress, and others grew smaller. On stressing again, plates formed in the same positions as before. This stress-induced martensite therefore seems to be in reversible equilibrium with the matrix, and may be compared with thermoelastic martensite. The effect of lowering or raising the temperature was found

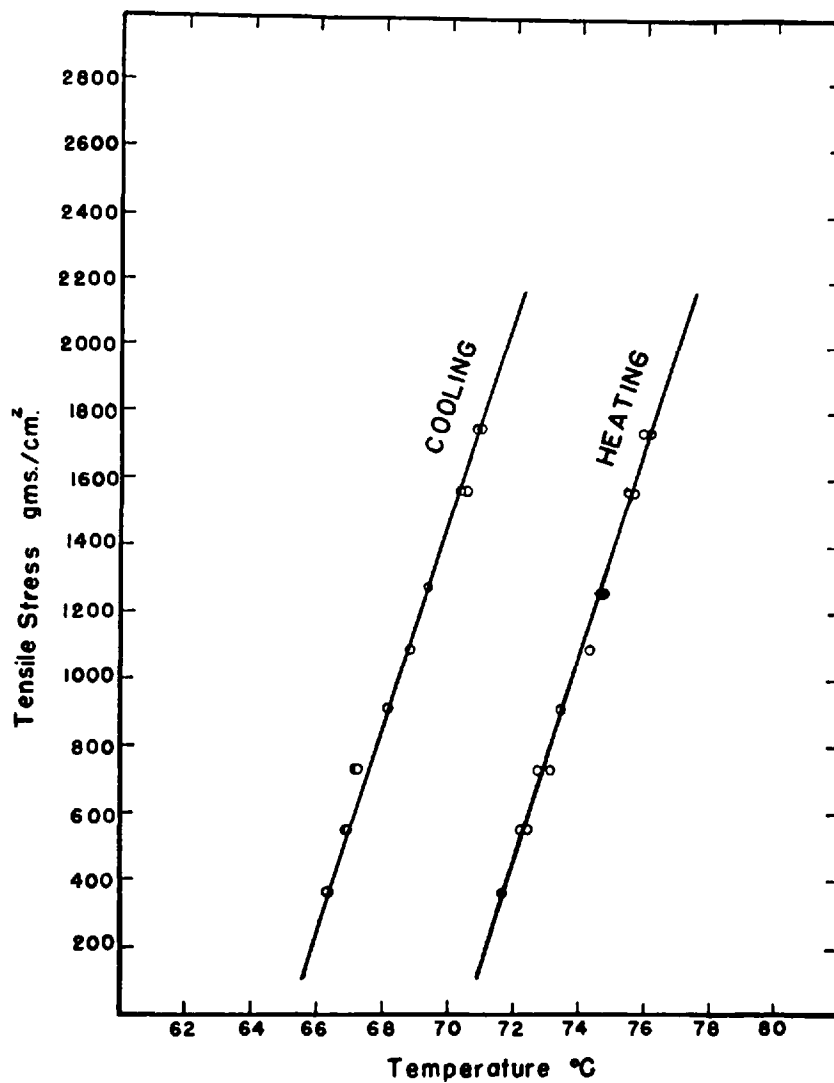


FIG.7. EFFECT OF TENSILE LOADING ON TRANSFORMATION TEMPERATURE FOR BOTH HEATING AND COOLING. COMPOSITION OF SPECIMEN : In — 20.7% Th. (AFTER BURKART AND READ¹⁶).

to be equivalent to applying or removing the stress. The stress-induced elastic martensite has only been seen in alloys having a high elastic limit.

(vi) The Effect of Austenitizing Conditions on the Formation of Martensite.

There has been little work done on the influence of various austenitizing treatments on the M_s temperature, and the formation of martensite. In general, the M_s temperature was thought to be only dependent on the composition of the austenite. For steels there are a number of formulae^{92,93} for calculating the M_s temperature taking into account only the alloying elements and not variation in austenitizing temperature. However, it has now been established that the M_s temperature is affected by the austenitizing temperature, and the present work has also shown that variation in austenitizing conditions affects the formation of martensite.

Earlier investigations on the variation of the M_s temperature as a function of grain size of the austenite, and of austenitizing temperature, resulted in differing and contradictory results. The principal masking influence was the gradual dissolution of stable carbides as the temperature and time of austenitizing increased. There are

two opposing effects :

(a) The M_s may be depressed since the alloy content of the austenite is increased as the carbide particles progressively dissolve.

(b) The M_s may be raised as the austenite becomes more homogeneous, thereby making nucleation more difficult. ⁵⁹

A number of investigators have reported ✓ that grain size has no significant effect on M_s ^{41,44}, while according to a few authors a larger grain size may even reduce the M_s temperature⁹⁴. However, it has now been clearly shown that increasing the grain size of the parent austenite increases the M_s point^{74,75,82,94-97}. In a detailed study, Meyerson and Rosenberg⁹⁴ found that in a 0.5 percent carbon, 0.8 percent manganese steel, the M_s temperature was raised from 302°C to 325°C by increasing the austenite grain size from ASTM 8 to ASTM 2. This variation was obtained by austenitizing at 820°C and 1200°C. They also found that the slope of the transformation curve (that is, the percentage of martensite formed per °C decrease in temperature) in an appreciable temperature range below M_s , decreased as the grain size increased. Vero and Szikszai⁹⁶ in a recent investigation of various low

alloy steels have found, by a dilatometric method, that doubling the grain size of the austenite raised the M_s by 12 - 13°C. Fisher et al.⁵⁹ have predicted an increase of M_s with increasing grain size. Since the growth of each martensite plate ceases at grain boundaries, each plate is restricted to a single austenite grain. The amount of transformation is the product of the number of nuclei and the size of each transformed region, and since the number of nuclei is independent of grain size, the measured M_s will be higher for larger grains. Although this explanation does predict the observed effects, the calculated values do not fit the experimental facts.

The influence of austenitizing time does not appear to have been the subject of much work, but it is probable that it affects the formation of martensite only by controlling the grain size and degree of solution of carbides, and hence the homogeneity of the austenite.

3. EXPERIMENTAL TECHNIQUES.

(i) Introduction.

Many different methods have been used to follow the course of decomposition of a parent phase to a martensitic product. These techniques may be broadly subdivided into discontinuous methods, and continuous methods that depend upon the measurement of some physical property.

(a) Discontinuous.

In this group, probably the most widely used method, at least in ferrous alloys, is that due to Greninger and Troiano⁹⁸ which is called the 'quench-temper' technique. The specimen, after an appropriate austenitizing treatment, is quenched to the desired temperature at which it is required to measure the percentage transformation. It is then up-quenched to temper the martensite formed, and after a suitable period is requenched to below M_f . The tempering 'darkens' the martensite initially formed, and the percentage transformation may then be found by quantitative metallography. In many cases, direct metallography has been used to observe transformation, particularly in those systems where the reaction occurs close to room temperature.¹⁵ X-ray diffraction has been used by a number of

investigators to determine the percentage of retained austenite.⁹⁹

(b) Continuous Techniques.

These methods are all based on the change of some physical property with transformation. There is usually an appreciable volume change associated with the transformation, and dilatometry has been successfully used to follow the progress of transformation in a number of alloys⁹⁶. In ferrous alloys, there is nearly always a change in the magnetic properties of a specimen during transformation and methods based on this change have been used^{48,97}. The magnetometric techniques have been extensively employed by Russian workers⁷⁷⁻⁸² in their investigations on highly-alloyed steels and iron-base alloys. The most sensitive methods available are those based on a change of electrical resistivity during transformation¹⁰⁰. In steels, the resistivity of the martensite is much less than that of austenite, and this property may be used to obtain a continuous recording of the course of transformation.

There are a number of advantages of using a continuous recording technique :

- (i) Precisely measured data may be obtained at every stage of the reaction.

- (ii) Only one specimen is required to obtain a complete record of percentage transformation against temperature, and the method is therefore less time-consuming.
- (iii) No visual estimate of the percentage transformation is necessary.

Although the continuous methods have great advantages, the changes in a physical property must be correlated with specific changes in the microstructure. Variations of a physical property can only give a relative measure of the amount of austenite decomposed unless two absolute values of percentage decomposition, together with the two corresponding values of the physical property are known. These two fixed points are usually taken as 0 percent (i.e. austenite) and 100 percent transformation (fully martensitic). Metallographic examination gives a positive identification of the constituents present, and is the generally accepted standard by which the other methods are judged¹⁰⁰.

In the present investigation the main results were obtained by the simultaneous measurement of the temperature and electrical resistivity of a wire specimen during continuous cooling. Metallography and X-ray diffraction studies were also made

to confirm and supplement the resistance measurements.

(ii) Choice of the Specimen Material.

The material used for the major part of the investigation was 0.010 in. diam. wire of En 23 steel. A few experiments were also made on a eutectoid plain carbon steel. The compositions of these steels are given in Table I.

TABLE I

Steel.	Chemical Composition, Weight Percent							
	C	Si	Mn	S	P	Ni	Cr	Mo
En 23	0.33	0.23	0.57	0.007	0.005	3.26	0.85	0.09
Plain Carbon	0.80	0.25	0.52	0.009	0.022	0.04	0.02	

The En 23 steel was chosen for a variety of reasons. A low alloy steel was used since the investigation was part of an overall project on the weldability of low alloy steels. The transformation characteristics⁹³ of En 23 are such that decomposition of the austenite in the intermediate range, particularly to bainite, may be easily avoided. A convenient cooling rate could then be used consistent with obtaining a fully martensitic structure.

The specimens were used in the form of 0.010 in. diam. wires, so that, for the required

stress values, the loads applied to the specimen would not be too large to accommodate in the vacuum chamber.

(iii) Apparatus for Transformation Measurements.

In order to obtain the required data, an apparatus had to be developed capable of simultaneously recording the temperature and electrical resistance of the specimen during continuous cooling, and also having the means to apply (or remove) a tensile stress to the specimen at any temperature. The system that was designed and assembled is based on an adaptation of that described by Colner and Zmeskal¹⁰¹.

The wire specimen is mounted vertically in a vacuum chamber, at the base of which is a moveable platform to facilitate the application of the load. The wire is austenitized by passing an alternating current through it. After austenitizing the alternating current is replaced by a small direct current, and the specimen cools in vacuum or in an inert atmosphere. During cooling a continuous record is obtained of the temperature and resistance of the specimen on a high-speed duplex recorder.

(iv) Details of the Apparatus.

(a) The Specimen Assembly.

The vacuum chamber containing the specimen was a brass cylinder 6 inches in diameter and 2 feet long, mounted vertically. An Edwards (Model 102) oil diffusion pump and a rotary backing pump (Model ISC30A) were used to evacuate the chamber. The system also contained suitable valves so that the cylinder could be isolated from the pumps. A needle valve was incorporated so that argon could be fed into the system when required. Measurement of the pressure was made on an Edwards Thermal (Pirani type) vacuum gauge (Model 7-2B).

The specimen, approximately 16 cms. long, was mounted vertically from the centre of the top plate of the chamber. A schematic diagram of the details of the assembly is given in Fig. 8. Although by loading a wire specimen in this manner, uniaxial stressing is virtually assured, a universal mounting was incorporated so that the wire was suspended vertically. Two pin-vices were used to grip the specimen, as shown in the diagram. The use of these vices facilitated the mounting and removal of specimens. No slipping was experienced, and a good electrical contact was made. The lower pin-vice was

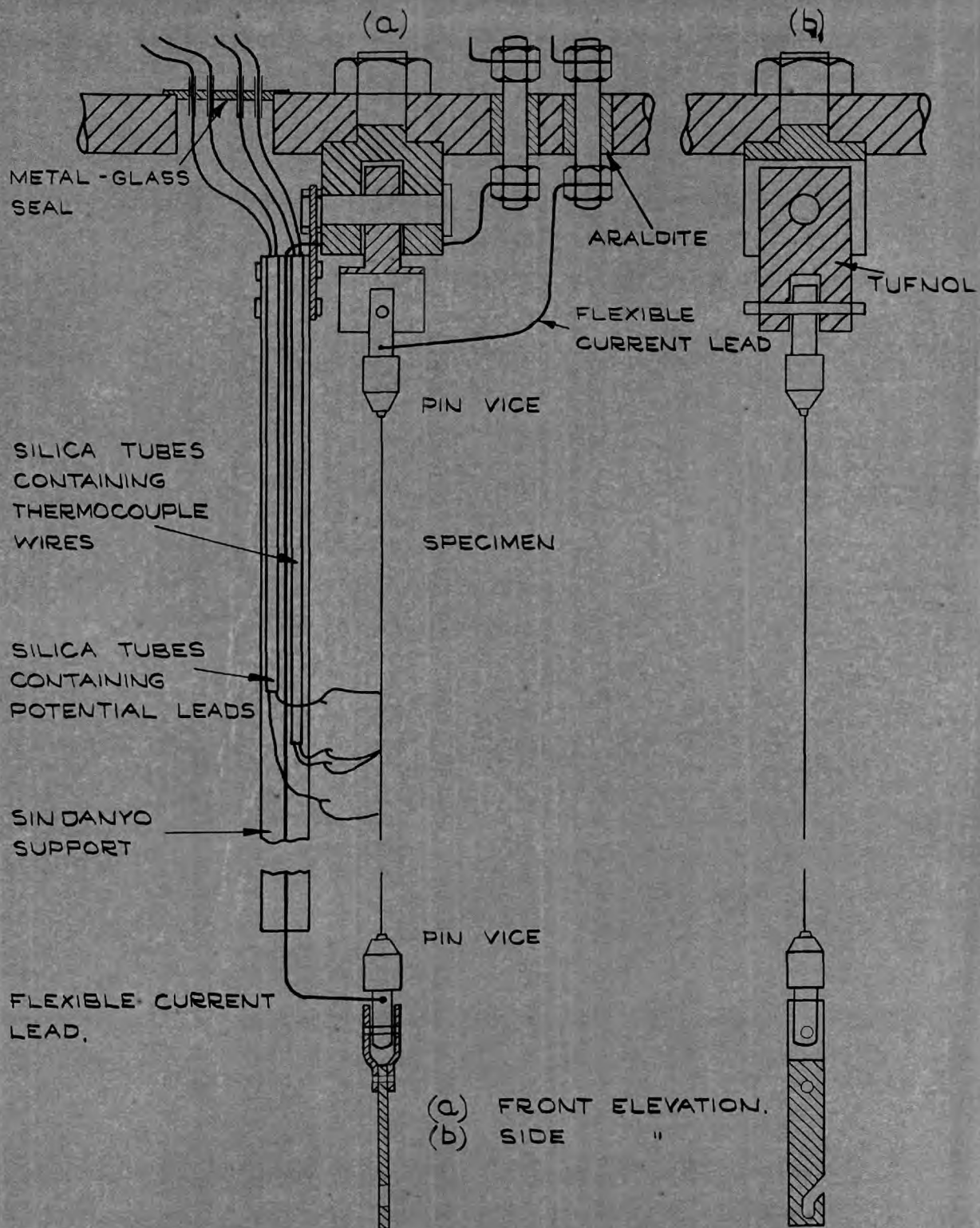


FIG. 8. THE SPECIMEN ASSEMBLY.

connected to the loading device, which will be discussed later. At the side of the specimen, a 'sindanyo' support carried the silica tubes containing the thermocouple wires and potential leads, and the current lead attached to the lower end of the specimen.

The temperature of the specimen was measured using a chromel-alumel thermocouple. 0.0124 in. diam. (30 s.w.g.) wires were introduced to the chamber, and these passed through a twin-bore silica tube fixed to the support. The final contact to the specimen was made with 0.002 in. diam. wires of the same composition, respectively, which were welded to the centre of the specimen. The wires were attached to the specimen (by a condenser-discharge method described later) at right angles to the vertical axis so that any current passing through the specimen would not interfere with the thermocouple reading. These very fine wires were used to minimize heat conduction from the specimen. If the temperature of the specimen was not uniform along the gauge length, spurious resistance effects were observed. It is shown later than good evidence was obtained to show that the temperature did remain substantially constant during treatment.

For the potential leads, pure iron wire was used, this being carried in another twin bore silica tube. The final length to the specimen also consisted of 0.002 in. diam. wires, which were welded to the specimen by the same method, at a distance of 2.5 cms. apart, equidistant about the thermocouple. In each case, the fine wires were attached to the thicker ones by the condenser-discharge technique. Besides minimizing heat flow, the fine wires allowed free vertical movement of the specimen resulting from the application of stress.

The thermocouple wires and the potential leads were introduced to the vacuum chamber through an Ediswan (Type 3294) metal-glass seal containing 0.040 in. diam. tubes. The seal was soldered to the top plate of the cylinder and the wires passed through the small metal tubes. Final sealing was made with a sealing compound, Apiezon 'Q'.

The current leads were also introduced through the top plate. Two brass rods having terminals at the ends, were mounted in 'araldite' as shown in the diagram, thus making vacuum-tight electrically-insulated connections. The current leads were attached to the pin vices by soldering. Flexible leads were used to ensure free vertical movement of the specimen.

(b) The Loading Device.

To apply a tensile stress to the specimen a dead weight load was used. In designing the apparatus, this load could be contained either inside or outside the vacuum chamber. If the load had been located on the outside of the cylinder, a Wilson seal or bellows would have been required. Some stress or friction component would be inherent in the seal, which would be large compared with the total stress applied to the specimen, particularly at low stress values, and would therefore require accurate calibration. For this reason it was decided to contain the load in the vacuum chamber.

A system was designed so that the load in the cylinder could be applied from the outside. A diagram of the device is given in Fig.9. Essentially it consists of a platform supported on a $\frac{1}{4}$ in. diam. rod passing through an Edwards seal, in the base-plate of the cylinder. This platform supporting the load could be raised or lowered by turning the hand-wheel and hence the threaded spindle. Two grub screws were fitted at the lower end of the rod, as shown in the diagram, to keep it in the spindle, for, when lowering the platform, small loads were insufficient to overcome the resistance of the seal.

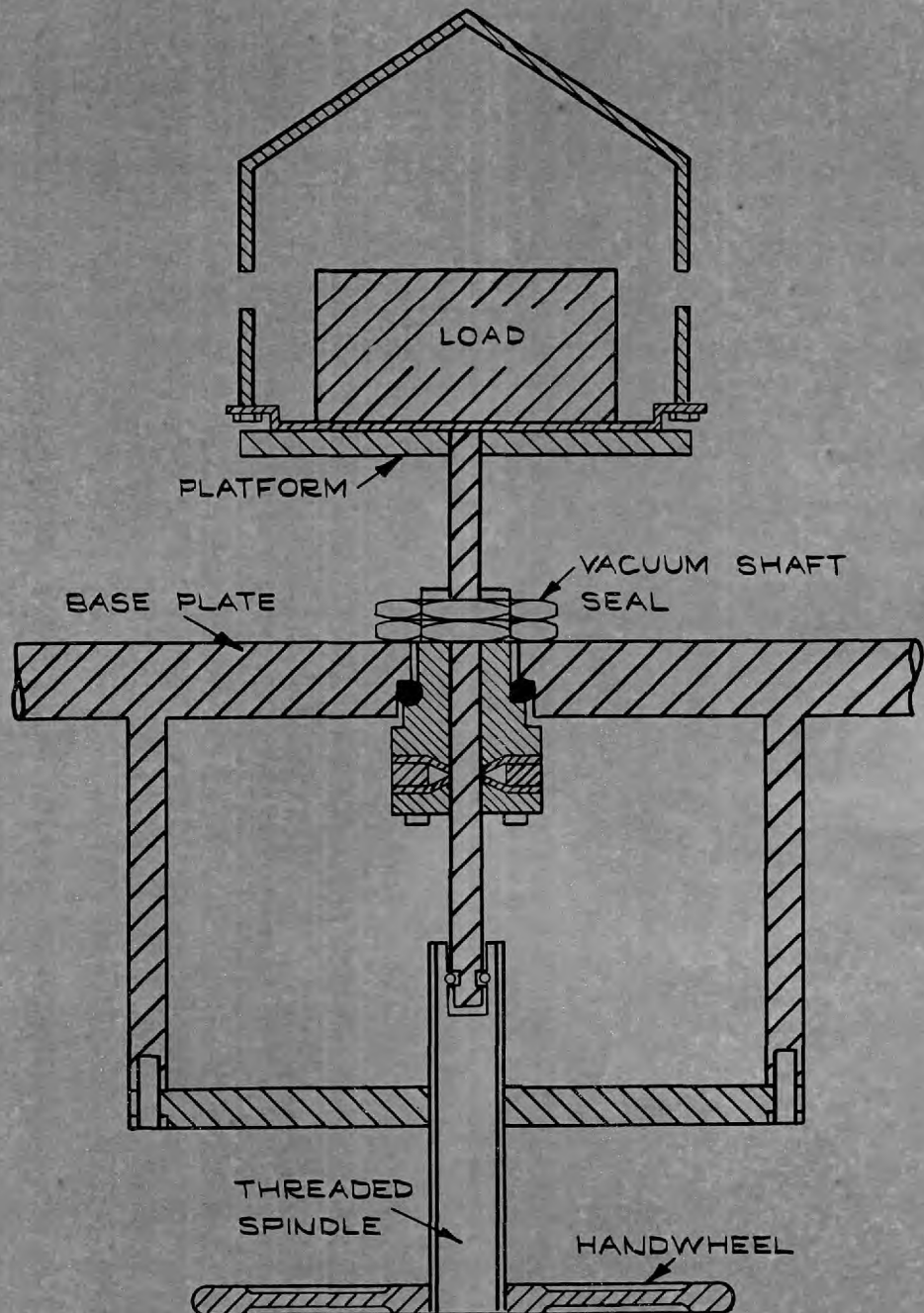


FIG. 9. THE LOADING DEVICE

The load, resting on the pan, hung from the specimen by the hook, as shown in Fig. 8. During austenitizing the load was supported on the platform, and then on cooling could be applied at the required temperature by turning the handwheel, and thus lowering the platform. At the lower end of the vacuum chamber a window was incorporated to observe the application and removal of stress.

(v) The Circuit Diagram.

The circuit diagram of the apparatus (shown in Fig.10) may be conveniently divided into three parts as follows :

- (a) The alternating current austenitizing circuit.
- (b) The direct current circuit.
- (c) The measuring circuits.

(a) The Austenitizing Circuit.

To austenitize the specimen a low-voltage high amperage current was passed through it. The current was controlled by a 500-watt variac on the input of an isolating transformer. This circuit was connected to the specimen by closing the DPDT (double-pole double-throw) switch as shown in Fig.10. The austenitizing temperature could be controlled to better than $\pm 5^{\circ}\text{C}$ by means of the variac. This value does not give the absolute limits of the

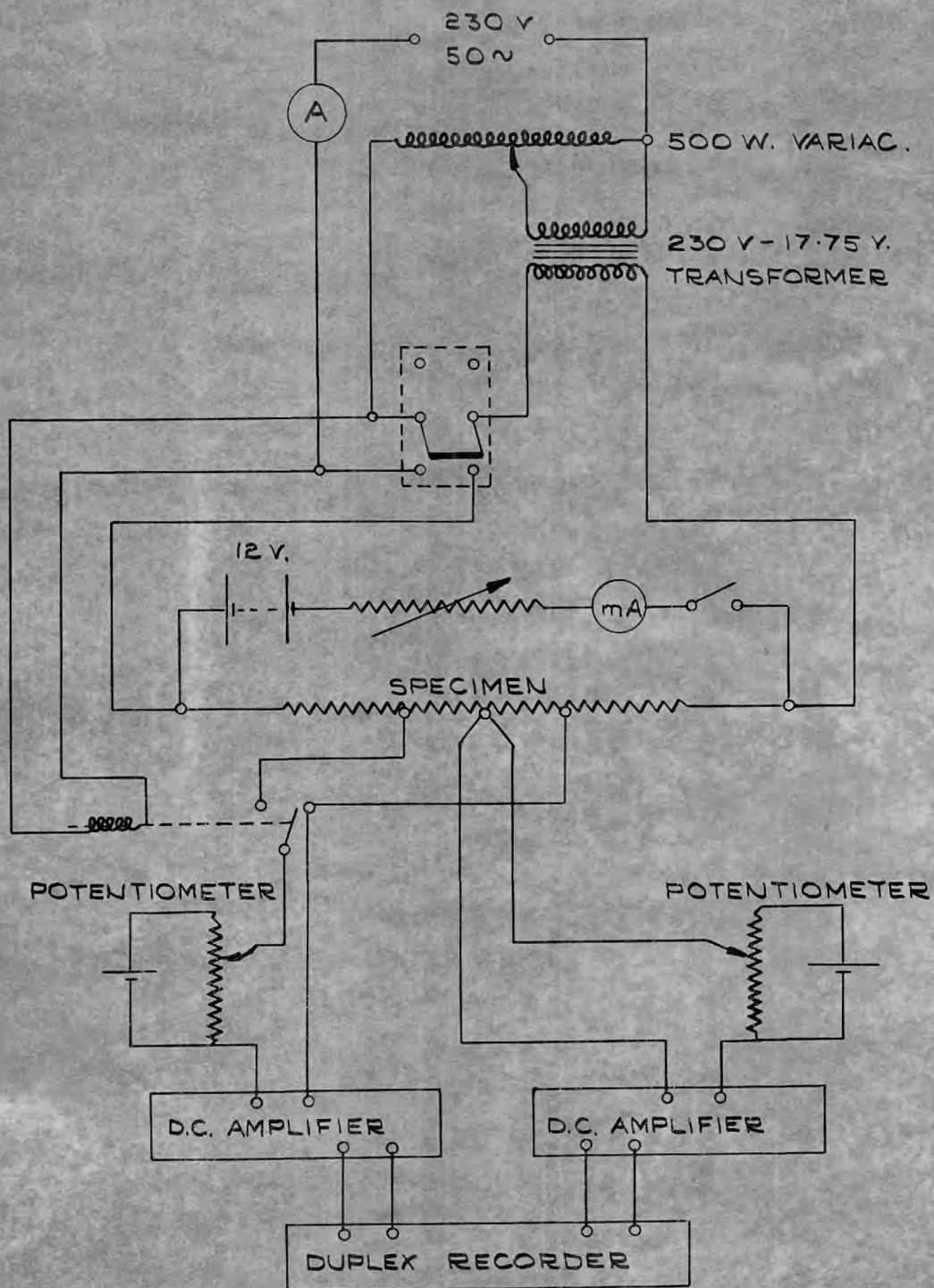


FIG. 10. THE CIRCUIT DIAGRAM.

austenitizing temperature, but it is considered to be not much in error, as described in the section on the calibration of the thermocouple (p.91) The results are however essentially comparative.

(b) The Direct Current Circuit.

The direct current circuit was powered by two 6-volt accumulators and included in addition to the resistance of the specimen a variable resistance. A milliammeter and switch then completed the circuit. The variable resistance fulfils a dual purpose. Firstly, it must be large compared with the total resistance of the specimen, so that any changes of resistance of the specimen do not significantly affect the total resistance of the circuit. The direct current passing through the specimen then remains substantially unaltered. Secondly, the relatively high resistance of this circuit enables the switch to be closed while the specimen is being austenitized, without the milliammeter being damaged.

The constant direct current passing through the specimen during cooling produces a voltage drop across the potential leads, and this then gives a measure of the resistance of the specimen.

(c) The Measuring Circuits.

These two circuits comprised the temperature measuring and the resistance measuring circuits.

The temperature measuring circuit incorporated the thermocouple, the output of which was fed (through a cold-junction at 0°C) to a d.c. amplifier and thence to one channel of the recorder. In the thermocouple circuit, a potentiometer was used to supply a back e.m.f. to oppose the thermocouple potential, so that a more sensitive scale on the recorder could be used. Most of the temperature readings were taken using a full-scale deflexion on the chart of 2 mv. or approximately 50°C. Some measurements were made using a full-scale deflexion of 0.5 mv. or 12°C.

No switch was incorporated in this circuit. The temperature could then be measured continuously during heating, austenitizing and cooling.

While cooling, the millivoltage drop across the potential leads was fed to another d.c. amplifier, and then to the other channel of the recorder. Thus a record of the resistance change of the specimen was obtained. In this circuit, also, a potentiometer was used to supply a back e.m.f., and most of the readings were taken using a full-scale

deflexion of 5 mv.

During austenitizing this circuit could not be closed directly with the amplifier, since the alternating current interfered with the amplifier. But, also, when the amplifier was in operation, it could not be used under open-circuit input conditions. To overcome this difficulty, a relay was connected in the potential measuring circuit, as shown in the diagram, Fig.10. While austenitizing the relay coil was energised and the amplifier terminals shorted, while on cooling the circuit was complete. Consequently, the resistance readings could only be obtained on cooling, when the alternating supply was switched off.

Details of the recording apparatus are given in the Appendix.

(vi) The Prevention of Decarburization.

Early in the investigation it was found that decarburization of the specimen during austenitizing was an extremely troublesome problem. The martensite transformation is very sensitive to the carbon content in steels, and any decarburization is manifested by an increase in the M_s temperature. Therefore, the prevention of decarburization is of the utmost importance.

It was found that the tendency of a specimen to decarburize was greater in an inert atmosphere such as argon than in a vacuum of 10^{-4} mm. of mercury. This is, however, without taking elaborate precautions to dry the argon and remove the last traces of oxygen. Most of the experiments were made on a specimen cooling freely in vacuum since it was found that the cooling rate was sufficiently high to obtain a fully martensitic structure. A slight tendency to decarburize was observed when austenitizing in vacuum, especially for the high temperature treatments. To combat the remaining tendency, the specimens were plated with a thin layer of nickel approximately 0.002 in. thick before testing. Prior to plating, the specimens were straightened and polished with 600 silicon-carbide paper. The layer of nickel surrounding a specimen with a tempered martensitic structure, may be seen in the photomicrograph in Fig.11.

The specimen was plated in a bath containing electrolyte of the following composition :

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	100 gms.
NH_4Cl .	12.5 gms.
H_3BO_3 .	12.5 gms.
Distilled water made up to 1 litre.	

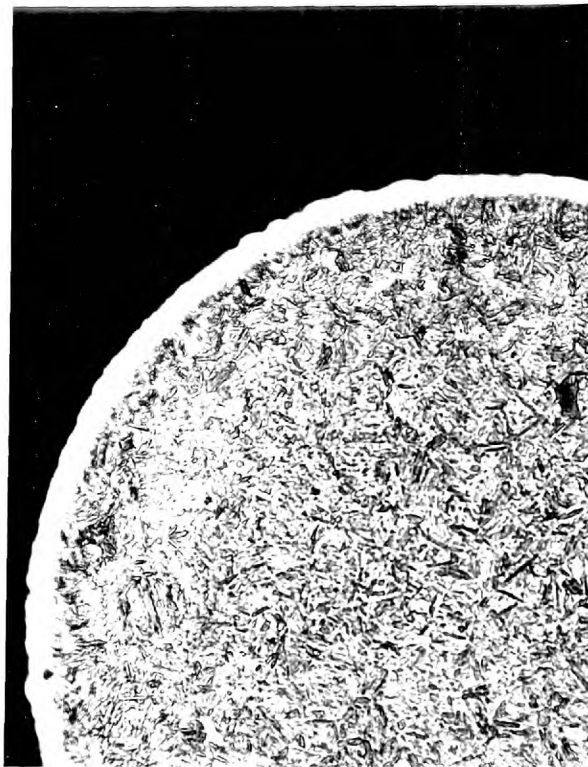


FIG. 11. PHOTOMICROGRAPH SHOWING THE
NICKEL PLATING ROUND A SPECIMEN. X500.

With the specimen as the cathode and a pure nickel sheet as the anode, the wire was plated for 4 minutes at a current of 50 ma. By plating the specimen and keeping the austenitizing time to a minimum, decarburization was effectively prevented. For several repeated cycles of austenitizing at 850°C and quenching the M_s temperature was reproducible to $\pm 1^\circ\text{C}.$, but some evidence of decarburization was found with prolonged use, or after a high temperature treatment. This is discussed further in a later section.

(vii) Operation of the Apparatus.

The sequence of operations for a typical run may be described as follows :

1. A nickel-plated specimen was mounted in the pin-vices and the thermocouple and potential leads attached. The required load was placed on the pan in the cylinder. The whole assembly was then placed in the chamber, by replacing the top-plate.
2. The system was then pumped down to approximately 10^{-4} mm. mercury. After connecting the respective leads in the top plate, the amplifiers were switched on. The direct current circuit switch was closed and the variable resistance adjusted until a suitable potential reading was obtained.

3. The DPDT switch was closed and the specimen austenitized at the required temperature.

4. Towards the end of the heat treatment, the system was isolated from the pumps, which were switched off, since the amplifiers were extremely sensitive to vibration. The recorder was then switched on, and the DPDT switch opened, and the specimen was then cooled. The potentiometers were operated to obtain the required trace on the recorder.

5. The stress could be applied or removed at the required temperature to $\pm 2^{\circ}\text{C}$. below M_s , or to $\pm 5^{\circ}\text{C}$. above M_s , where the cooling rate is more rapid.

6. After reaching room temperature, the specimen was heated in stages to approximately 200°C to determine the temperature-resistance relation of a fully martensitic structure. A continuous curve could not be obtained since resistance readings could not be made during heating.

7. The specimen could now be subjected to another cycle of austenitizing and cooling, or removed for examination.

(viii) The Welding of the 0.002 in. diam. Wires.

The potential and thermocouple wires were welded to the specimen using a condenser-discharge

technique, which has been previously used for this purpose¹⁰¹. The weld is made by the heat produced by the electric current discharged when a condenser is shorted. The circuit diagram of the condenser-discharge apparatus is shown in Fig.12.

The sequence of operation in welding the various leads to the specimen, is as follows :-

1. The specimen wire is connected to the negative lead of the discharge apparatus by means of a small spring clip. The positive lead is connected to a pair of finely pointed tweezers which are used to grip the 0.002 in. diam. wires.
2. The condensers are charged to the appropriate voltage through the power pack. The charge required depends primarily on the gauge, but also on the nature of the wire being welded. For this application it was found that condensers of 120 microfarad capacity charged to 30 volts d.c. when discharged produced a good weld. The charge on the condensers could be varied by changing the output voltage of the transformer.
3. The DPDT switch in the unit is thrown and the 0.002 in. diam. wire is touched with the specimen wire. On contact the condenser discharges and the heat generated is usually sufficient to cause fusion

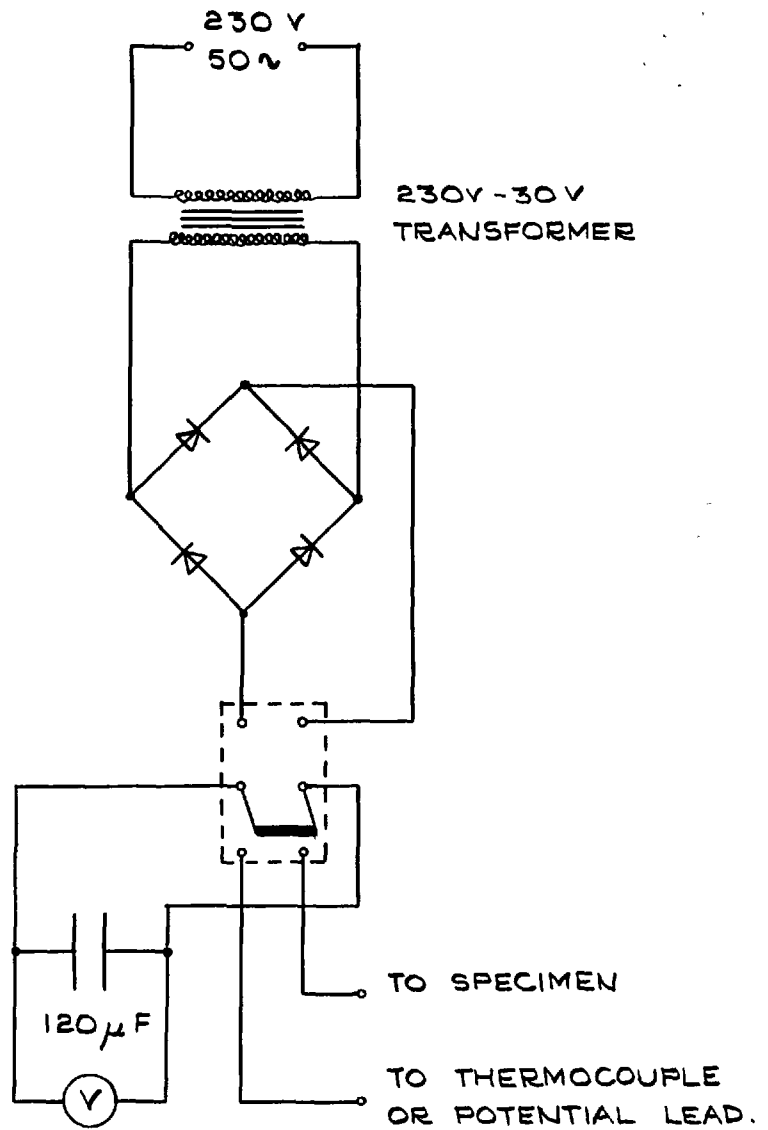


FIG. 12. CIRCUIT DIAGRAM OF THE WELDING APPARATUS.

between the wires. If the condensers are overcharged, then the end of the lead is vapourised on contact, and if undercharged, no welding takes place.

The fine wires were connected to the thicker wires leading from the chamber by the same method. A photomicrograph of the welded junction of a potential lead with the specimen is shown in Fig.13.

(ix) Metallographic Examination.

The specimens for metallographic examination were mounted in araldite, a cold-setting compound, either horizontally to produce a longitudinal section, or vertically to view the cross-section. Rough polishing was done on silicon carbide papers. The mount was then polished on a diamantine wheel followed by a diamond wheel (0 - 2 microns), with final polishing by hand with silvo on a selvyt cloth.

The specimens were etched for various times in 2 percent nital or Vilella's martensitic reagent, having the following composition :

Picric acid	1 gm.
HCl	5 ml.
Ethyl alcohol	100 ml.

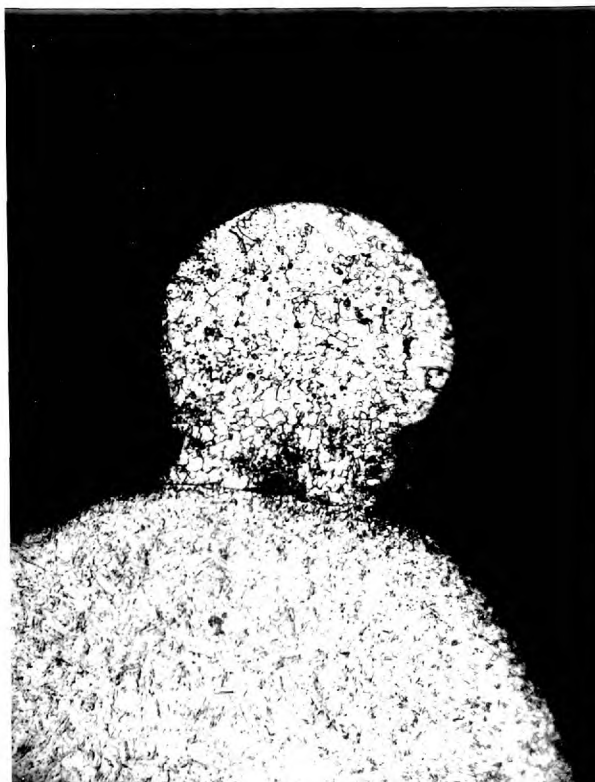


FIG. 13. PHOTOMICROGRAPH SHOWING THE WELDED
JUNCTION BETWEEN A 0.002 in. diam.
POTENTIAL LEAD AND THE SPECIMEN. X400.

(x) X-ray Diffraction Examination.

Only a few specimens were studied by X-ray diffraction. Powder patterns were obtained of the wire specimens in the stressed and unstressed conditions, using MoK_α radiation with an iron filter at 35 KV. in a Unicam camera.

4. EXPERIMENTAL RESULTS.

(i) Introduction.

The results of the investigation may be divided into three sections giving the various effects on the formation of martensite :

- (a) The effect of austenitizing conditions.
- (b) The effect of uniaxial tensile stress applied below the M_s temperature.
- (c) The effect of tensile stress applied above M_s .

The results of the various austenitizing treatments are reported first since this work was necessary to determine suitable standard austenitizing conditions for the investigation on the effect of applied stress on the martensite transformation.

Most of the results were obtained by electrical resistance measurements, and were confirmed and supplemented by metallographic studies and by X-ray diffraction.

In steels, austenite (face-centred cubic) transforms completely * to martensite (body-centred

.....

* Small amounts of austenite are frequently retained in low- and medium-alloy steels at room temperature, and even when the carbon content is not high the martensite reaction does not always proceed to completion at room temperature. An exponential equation has been proposed⁹⁹ describing the course of transformation in steels that does not predict an M_f point. The present results indicate that a small amount of austenite is retained in En 23 at room temperature.

tetragonal) at a low temperature if the cooling rate is sufficiently high to suppress any intermediate transformation to pearlite or bainite. Martensite has a lower specific resistivity than austenite at any temperature, so that as a specimen transforms to martensite its resistance decreases, and it is this property that has been used to follow the course of transformation.

As previously described, the temperature, and potential drop across a gauge length of 2.5 cm. of specimen, were measured continuously on a duplex recorder during cooling. Since the potential measuring circuit had a large external resistance in series with the specimen, the current remained substantially constant during a transformation cycle. The measured potential drop is directly proportional to the resistance of the specimen, and since

$$R = \frac{\rho l}{a}$$

where ρ = specific resistivity

l = gauge length

a = cross-section area,

the resistivity is directly proportional to the resistance, and hence to the measured potential drop.

Since the required results could be obtained by comparative resistance measurements it was not

thought necessary to determine the absolute resistivity. The effect of the thin coating of nickel plate was not taken into account in the calculations. The temperature - resistivity relation of pure nickel¹⁰² is very nearly linear over the temperature range of interest, from room temperature to 300°C, and therefore would not affect the results. The potential reading was taken as a measure of resistance in calculating the progress of the transformation.

In Fig.14, a typical section of the recorder chart is reproduced showing the traces of the temperature and resistance of a specimen freely cooled in vacuum. It will be noticed that in addition to a decrease in resistance accompanying transformation, there is a heat evolution associated with the formation of martensite, manifested by a decrease in cooling rate. The resistance is now plotted against temperature to calculate the percentage of martensite formed at any temperature (Fig.15). The two straight lines represent the resistance of completely austenitic and completely martensitic structures respectively, and the connecting curve is the resistance of the mixture of the two phases as transformation proceeds. The resistance of the fully martensitic structure was only measured up to 180°C, since above this temperature

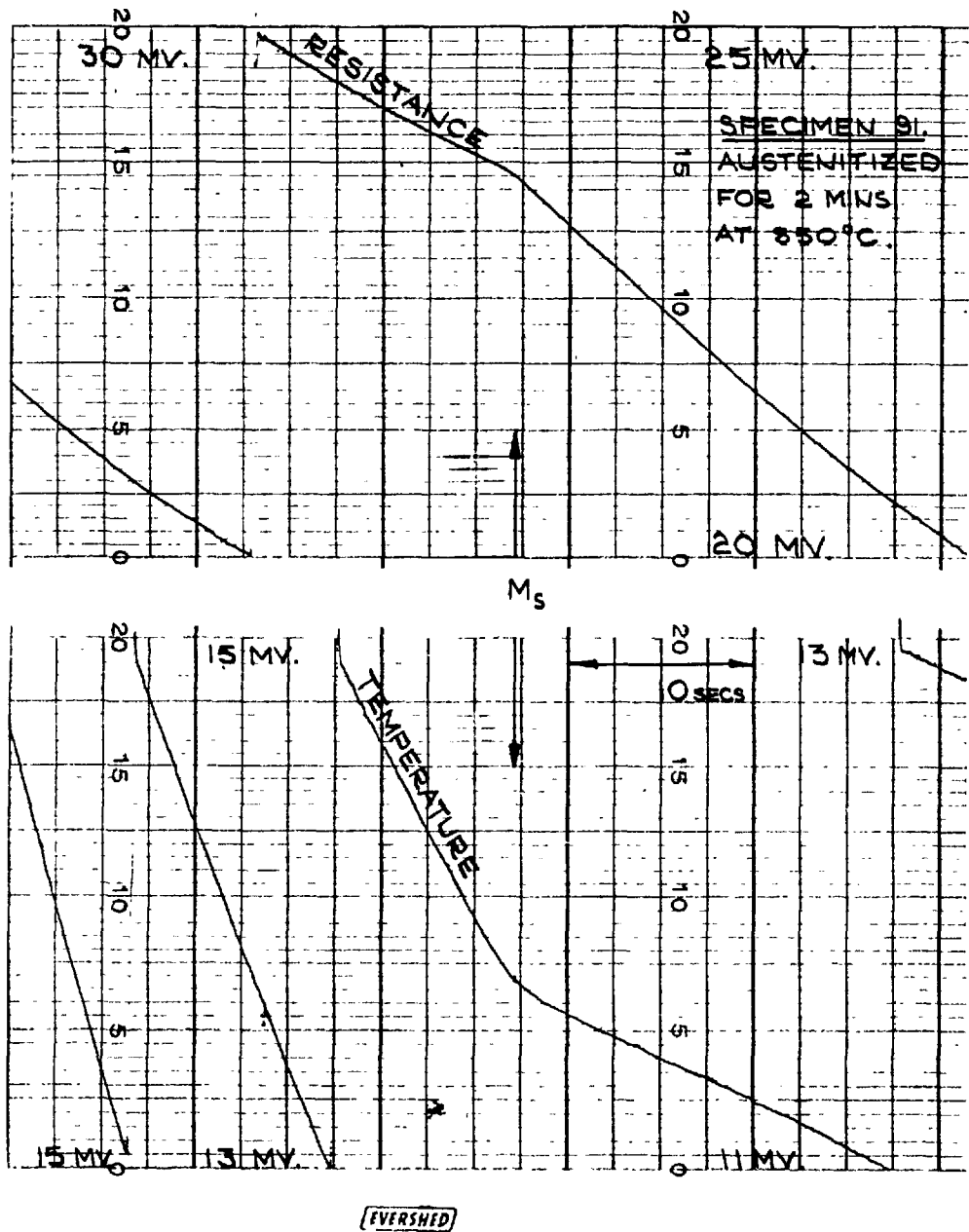


FIG. 14. REPRODUCTION OF A SECTION OF THE CHART SHOWING CHANGES IN THE RESISTANCE & TEMPERATURE CURVES AT M_s .

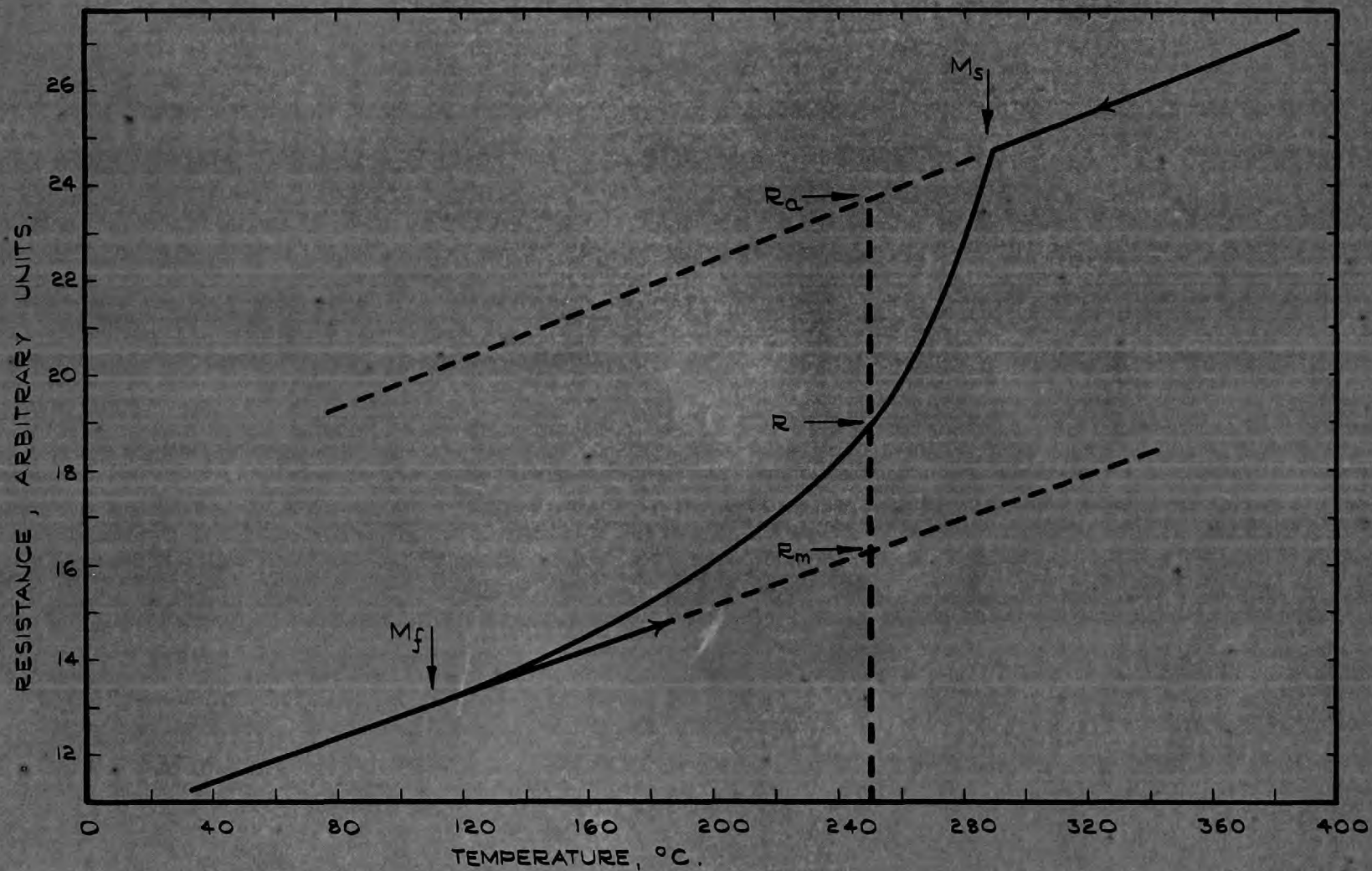


FIG. 15. TYPICAL TEMPERATURE - RESISTANCE CURVE.

tempering occurred rapidly and a true resistance reading would not be obtained. The curve was then extrapolated as shown by the dotted line in Fig.15.

The resistance measurements were converted to percentage transformation using the approximation that the percentage of the total resistance difference between austenite and the completely martensitic structure at a given temperature is equal to the volume per cent of martensite present. This assumption has been verified metallographically and used by a number of workers⁹⁷. By assuming that the resistance of the retained austenite may be found by extrapolating the resistance curve of pure austenite below M_s , the percentage transformation is obtained by simple proportion (Fig.15) as follows :

$$\% \text{ martensite} = \frac{R_a - R}{R_a - R_m} \times 100 \%$$

where R = specimen resistance at the required temperature,

R_a = resistance of retained austenite.

R_m = resistance of a completely martensitic structure.

It was found that after complete transformation to martensite the resistance of the specimen was decreased by approximately 30 %. Throughout

the transformation range the resistance could be measured to within 1 part in 350, and the temperature to within $\frac{1}{2}^{\circ}\text{C}$. The apparatus was therefore capable of detecting changes of less than 0.3 % transformation. The absolute accuracy is not, however, quite so good, particularly in the later stages of transformation, for the amount of retained austenite was not known to any great degree of accuracy. It was not therefore possible to measure M_f very accurately. The M_f was taken to be the temperature at which transformation virtually ceased, that is, the point where the temperature - resistance relation of the specimen on cooling coincided with the curve of a fully martensitic structure (Fig.15). The retained austenite was not taken into account in calculating the progress of transformation. A complete transformation curve for a specimen austenitized at 850°C is given in Fig.16. The M_f temperature occurred at approximately 110° - 120°C .

In the En 23 steel investigated the transformation started at a well-defined temperature indicated by a sharp break in the resistance curve (Fig.14). If the temperature of the specimen was not uniform along the gauge length, the start of transformation as given by the temperature and resistance differed and the temperature - resistance

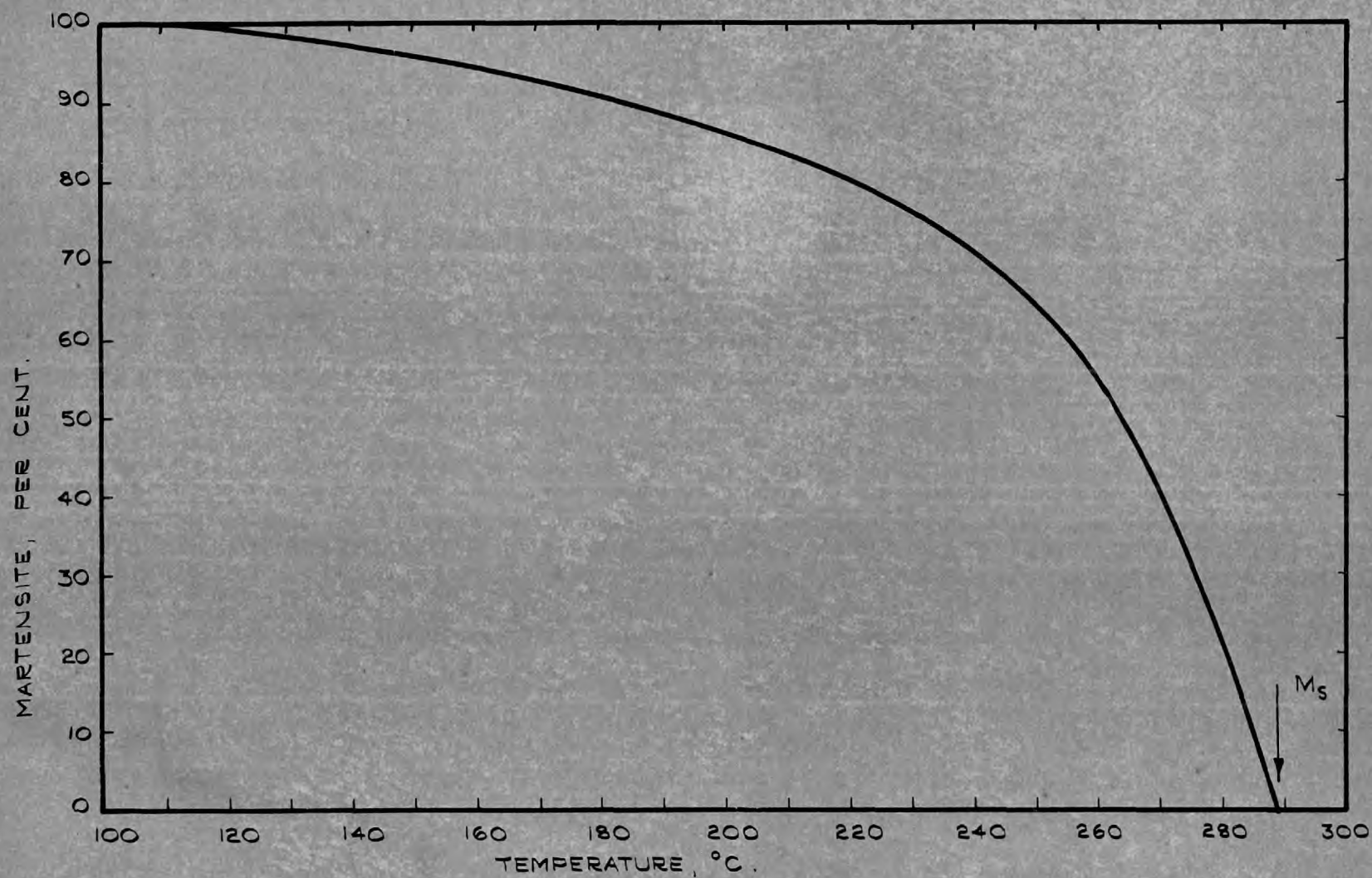


FIG. 16. CURVE SHOWING NORMAL PROGRESS OF TRANSFORMATION.

curve was then rounded in the vicinity of the M_s temperature. Any curve therefore that did not have a sharp discontinuity was discarded.

Calibration of the Thermocouple.

Although the results are essentially comparative, it was decided to calibrate the thermocouple and recording apparatus. This was carried out by measuring the temperature of the Curie point in pure iron. A 0.010 in. diam. wire of pure iron was mounted in the usual way. At the Curie temperature there is a small, but nevertheless well defined change in electrical resistance. A thermal change also occurs, but the Curie temperature is independent of the heating or cooling rate. The typical temperature-resistance curve as determined on cooling (Fig.17) shows the inflexion point at the Curie temperature. The results of a number of determinations gave a value of $763 \pm 5^\circ\text{C}$. This is in good agreement with the accepted value of 768°C for the Curie point¹⁰². Therefore the calibration data does indicate that in the transformation range the temperature measurement is at least accurate to $\pm 5^\circ\text{C}$. Since the results are essentially comparative this accuracy is sufficient, for good reproducibility was obtained, as discussed later.

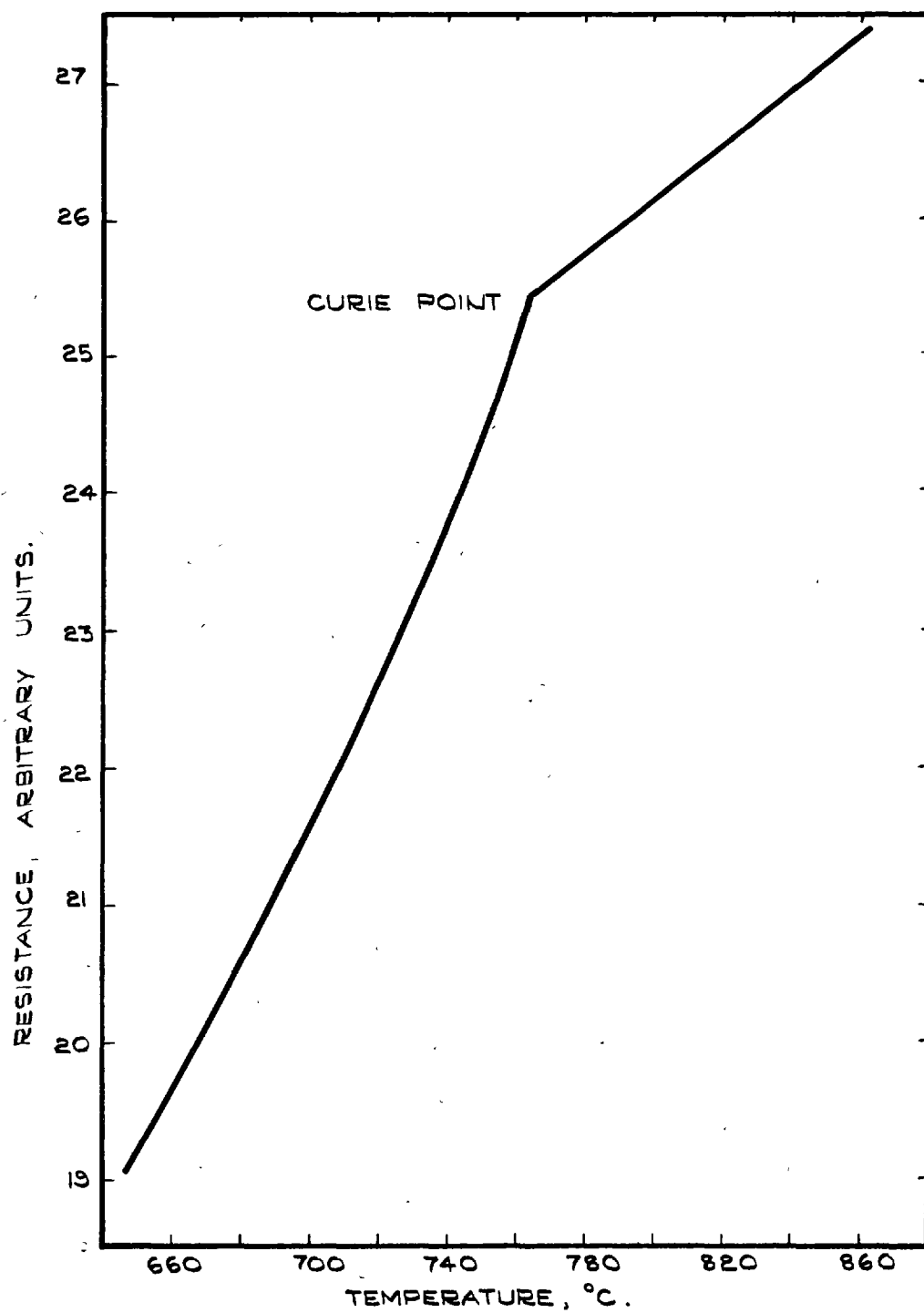


FIG. 17. TEMPERATURE - RESISTANCE CURVE OF PURE IRON.

(ii) The Effect of Austenitizing Conditions on the Formation of Martensite.

The investigation of the effect of various austenitizing treatments on the martensite transformation was made for two purposes which may be stated as follows :

- (a) To select a suitable standard austenitizing treatment for the study of the effect of stress on the formation of martensite.
- (b) To determine the effect of various austenitizing conditions on the M_s temperature and the progress of transformation.

The 'as-received' structure of the wire consisted of carbide particles in a ferrite matrix. For a high heating rate of 100°C./sec. the A_c transformation was observed to occur between 710°C and 750°C , which is the approximate temperature range observed for larger specimens heated more slowly.⁹³ On reheating at the same rate from a martensitic structure, the A_c transformation occurred at $690^\circ\text{C} - 700^\circ\text{C}$, the transformation being completed in a short temperature range. The M_s temperature after the first treatment was $2 - 3^\circ\text{C}$ higher than those observed on subsequent cycles.

It has also been reported in the literature

that the initial product has a marked effect on the homogeneity of the austenite, and hence upon subsequent transformation. Therefore, to assist in obtaining homogeneous austenite, the specimens were initially brought to the martensitic condition, and to avoid tempering were rapidly heated at 100°C per second.

Initially experiments were made to determine the effect of austenitizing time on the formation of martensite. These were carried out mainly at 850°C, which is in the usual heat treatment range. For the En 23 steel it was found that M_s remained constant for times longer than 15 seconds at 850°C. For decreasing times, the M_s temperature was depressed, being lowered about 25°C after austenitizing for approximately 2 seconds above the A_c transformation.

Some experiments were also carried out using the eutectoid carbon steel. For this steel, the specimen had to be quenched in an atmosphere of argon to attain a cooling rate sufficient to prevent the formation of intermediate products. When a specimen was rapidly heated from a martensite structure, it was found that all austenitizing treatments resulted in martensite after quenching. However, if a specimen in the pearlitic condition was heated rapidly, austenitized for short times, and then

quenched, the formation of pearlite was always observed. In the latter case, if the austenitizing time was increased to more than approximately 5 seconds, no pearlite was formed on subsequent cooling. It may thus be assumed that inhomogeneities in the austenite causing the nucleation of pearlite, are dissolved after 2 minutes in the austenite region.

From the above results, it was decided to adopt 2 minutes as the standard austenitizing time, at a temperature of 850°C. Although it was not possible to be certain that this treatment produced completely homogeneous austenite, the conditions gave reproducible results, and no detectable effect on transformation was observed for longer times. Under these conditions the M_s was reproducible within $\pm 3^\circ\text{C}$ (except for the first cycle) from specimen to specimen, and within $\pm 1^\circ\text{C}$ for several repeated cycles of austenitizing and cooling on the same specimen, although the M_s did tend to rise by 1° or 2°C after about 6 cycles.

To determine the effect of austenitizing temperature on the course of transformation, specimens were austenitized at various temperatures between 750°C and 1250°C at intervals of 50°C. In all cases, a time of 2 minutes was used, except at

1150°C, 1200°C and 1250°C, when the holding time was 1 minute.

The results showed that as the austenitizing temperature was increased, the M_s temperature also increased. After a high temperature treatment, at say 1200°C, the M_s on a subsequent run, at say 850°C, had risen several degrees, but was still well below the M_s characteristic of the high temperature. The M_s points associated with the high temperatures have not therefore been as accurately determined as those for the lower temperature treatments.

Figure 18 shows the relation between austenitizing temperature and the onset of the martensite transformation in the En 23 steel. The M_s was found to vary as shown, rising from 275°C when austenitized at 750°C, to 310°C when austenitized at 1250°C. The curve has not been calculated by mathematically analysing the points, but by drawing through the observed average values.

It was found that the higher is the austenitizing temperature, the smaller is the initial slope of the transformation curve. This initial slope, or the percentage of martensite formed per °C decrease in temperature, changed markedly, from approximately 3.5 percent per °C after austenitizing

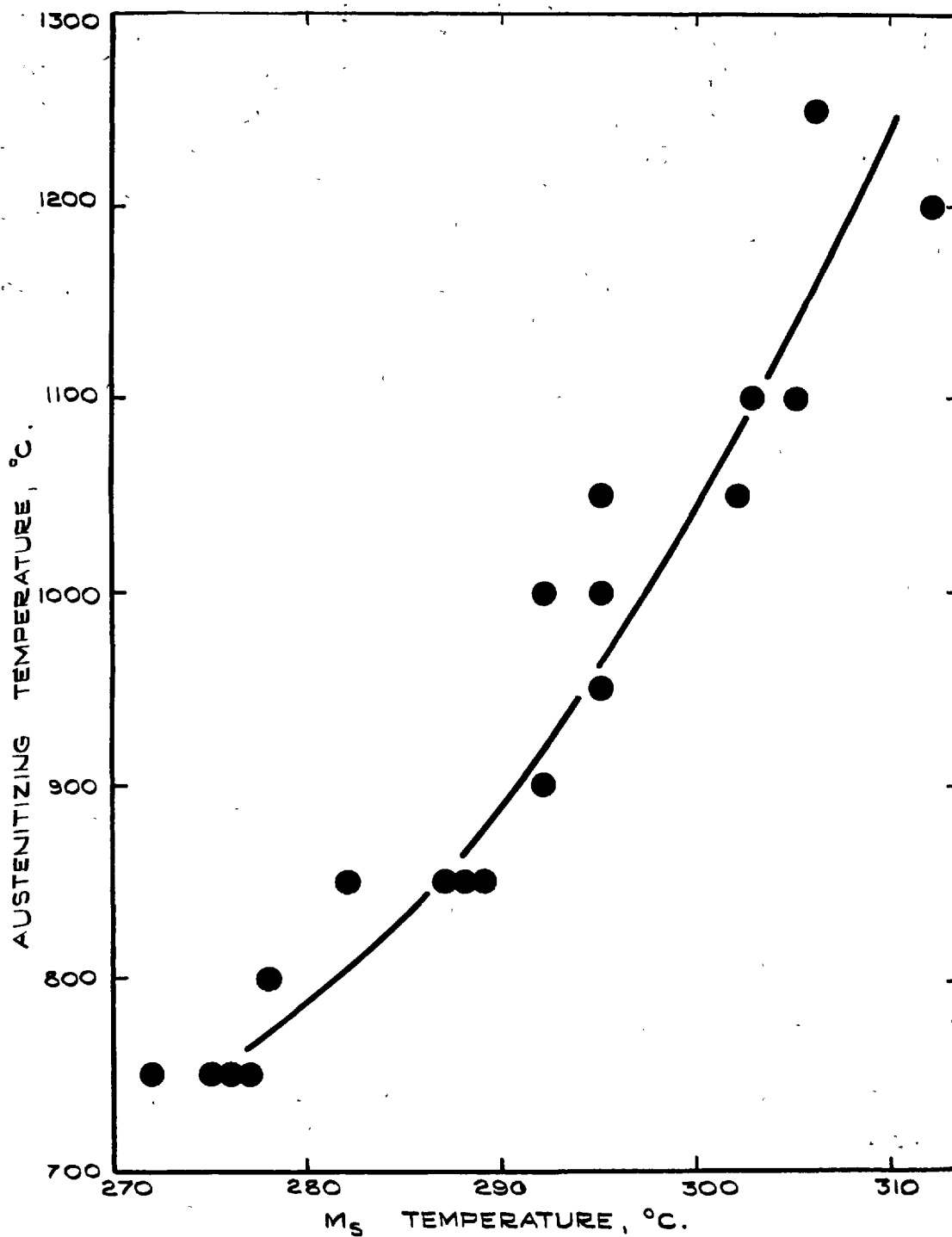


FIG. 18. EFFECT OF AUSTENITIZING TEMPERATURE ON THE M_s TEMPERATURE.

at 750°C, to 0.8 percent per °C after a treatment at 1250°C. These results are summarised in Fig.19.

For specimens austenitized at the lower temperatures, (that is, less than 850°C) the initial slope of the transformation curve is greatest, and the slope continuously decreases with falling temperature. However, with increasing austenitizing temperature, the maximum ³⁶⁻³⁸rate does not occur at M_s , but some 20°C lower. This effect becomes more marked the higher the austenitizing temperature. Fig.20 shows the initial part of three typical transformation curves for specimens austenitized at 800°C, 950°C and 1200°C, respectively. A few double heat treatments experiments were also made. After a double austenitizing treatment, of for example, 2 minutes at 1050°C followed by 2 minutes at 800°C, the M_s temperature and the shape of the transformation curve were always found to be characteristic of the high temperature treatment.

As mentioned previously, it is difficult to measure the M_f temperature with any great degree of accuracy since the last few percent of austenite transform very sluggishly. It does appear in the present steel that some austenite is retained at room temperature. No retained austenite could be

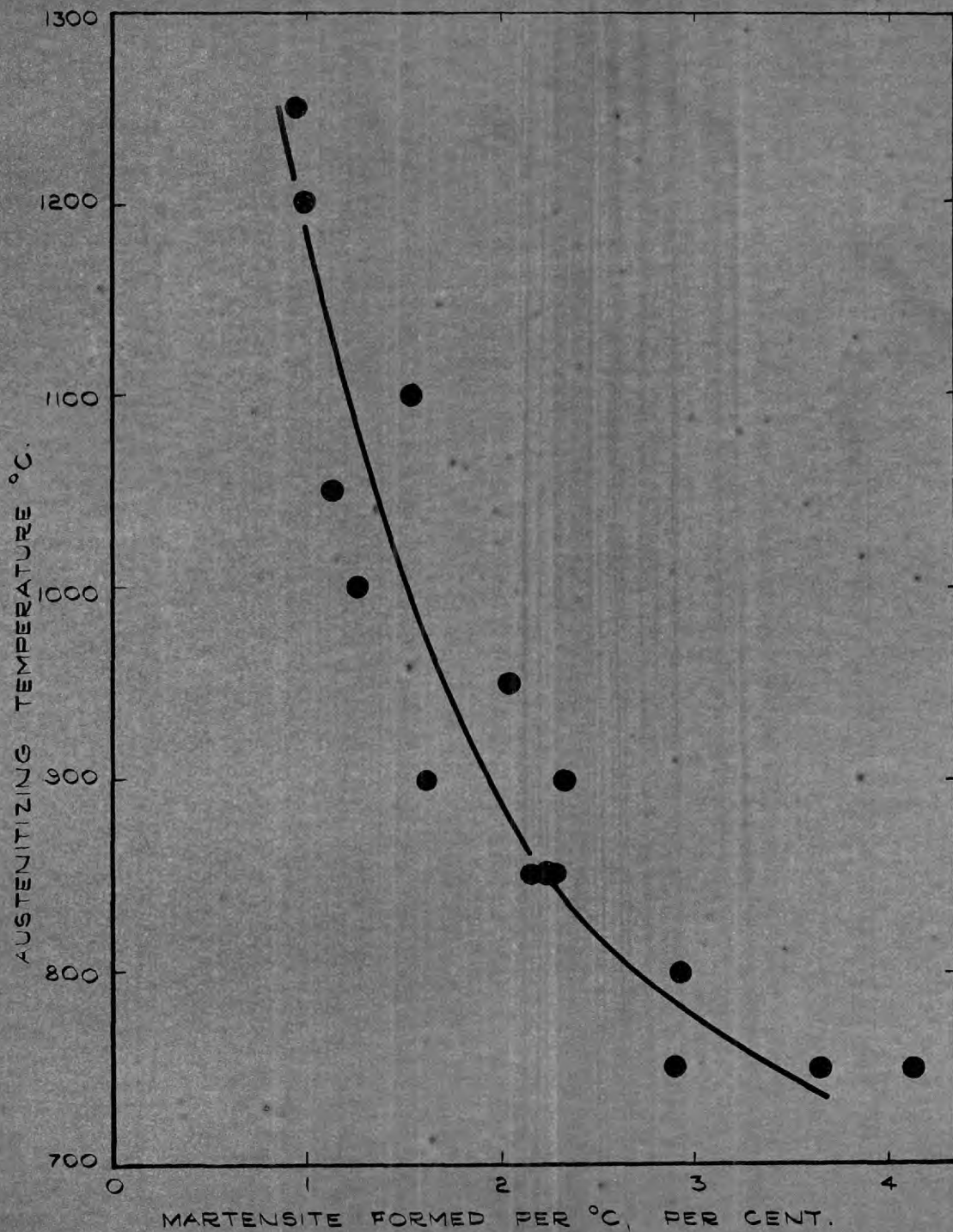


FIG. 19. EFFECT OF AUSTENITIZING TEMPERATURE ON THE PERCENTAGE OF MARTENSITE FORMED PER °C. DECREASE IN TEMPERATURE.

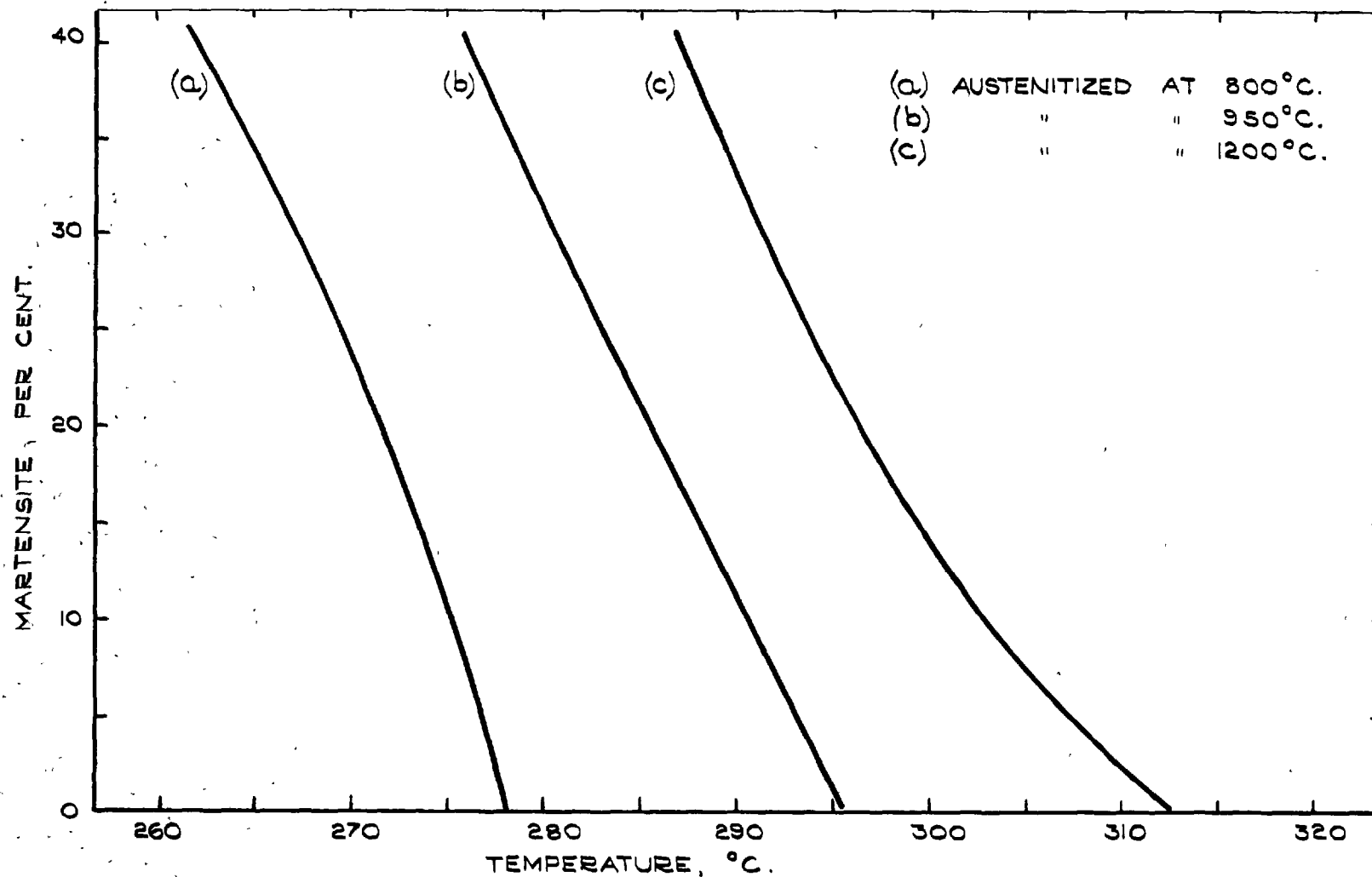


FIG. 20. EFFECT OF AUSTENITIZING TEMPERATURE ON THE INITIAL PROGRESS OF TRANSFORMATION.

detected by metallography, but in the X-ray diffraction photographs the face-centred cubic lines characteristic of austenite were always seen though very faintly. The various austenitizing conditions did not appear to have any marked effect on the M_f temperature, as measured by the resistance readings. Although the amount of martensite at any particular temperature below M_s was greater for a high austenitizing treatment, the later stages of transformation were more sluggish. An M_f temperature of approximately $110^\circ - 120^\circ\text{C}$ was observed for all the austenitizing treatments investigated. The complete transformation curves are given in Fig.21 for specimens austenitized at 800°C , 950°C and 1200°C respectively.

Some metallographic studies were made of specimens austenitized at different temperatures. The plates of martensite that formed in a small temperature range below M_s , were examined by the Greninger-Troiano technique. The specimen was cooled to 8°C below M_s , and then rapidly heated to 500°C and tempered for 10 seconds, followed by quenching to room temperature. This tempering temperature is in the 'bay' of the TTT diagram and was used to minimize the tendency for bainite formation. It is known that the incubation period of the bainite transform-

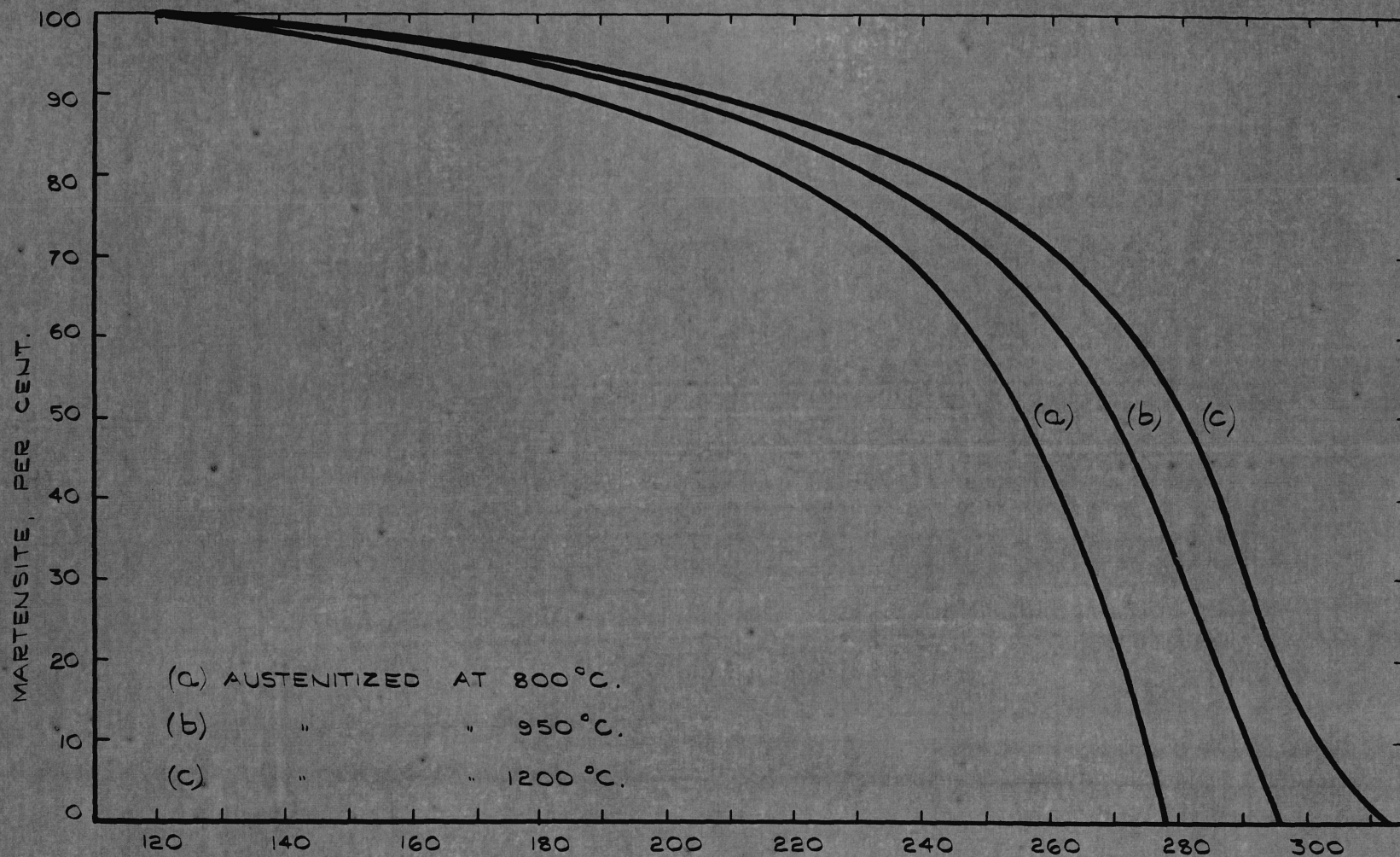


FIG. 21. EFFECT OF AUSTENITIZING TEMPERATURE ON THE PROGRESS OF TRANSFORMATION.

ation is reduced in the presence of martensite, and the tempering time was therefore also kept to a minimum.

Figure 22 is a photomicrograph of a specimen subjected to the treatment described above after austenitizing at 750°C, while the structure in Fig.23 shows the plates formed after cooling to 8°C below M_s from an austenitizing temperature of 1200°C.

Although both these structures are those observed after cooling 8°C below M_s , the proportions of martensite formed are markedly different; the amount of transformation resulting from an austenitizing temperature of 1200°C is much less than that formed after treatment at 750°C, thus confirming the electrical resistance measurements. The size of the plates was not greatly different, but those plates forming after a high temperature treatment are slightly longer. No evidence of the position of the original grain boundaries was seen. A few fully martensitic tempered structures were examined after etching with Vilella's reagent. This agent has been used to determine the original austenite grain size of martensitic structures, but in the present investigation no definite indication of the original grains could be distinguished.



FIG. 22. THE MARTENSITE PLATES FORMED ON COOLING
8°C BELOW M_s , AFTER AUSTENITIZING AT 750°C.

X600



FIG. 23. THE MARTENSITE PLATES FORMED ON COOLING
8°C below M_s , AFTER AUSTENITIZING AT 1200°C.

X600

(iii) Effect of Tensile Stress Applied below M_s .

For all the experiments in this section, the austenitizing conditions were kept constant, namely 2 mins. at 850°C. In all cases, the specimen was heated to the austenite region at 100°C per second from a martensitic structure.

To determine the effect of applied stress on the formation of martensite in the normal transformation range, various loads were applied to the specimen at different temperatures below M_s . For the range of stresses investigated, that is, up to 55,000 p.s.i., application of the load did not usually produce any permanent extension of the specimen. However, plastic deformation of the specimen was noted in some instances, when stresses were applied in a small temperature range below M_s .

Figure 24 shows the shape of the temperature and resistance curves of a specimen with a stress of 50,200 p.s.i. applied at 5°C and 20°C below M_s , respectively. When this stress was applied at 5°C below M_s , a permanent extension of the specimen was noted (Fig.24b), while if the same stress was applied at 20°C below M_s only an elastic strain was observed (Fig.24a).

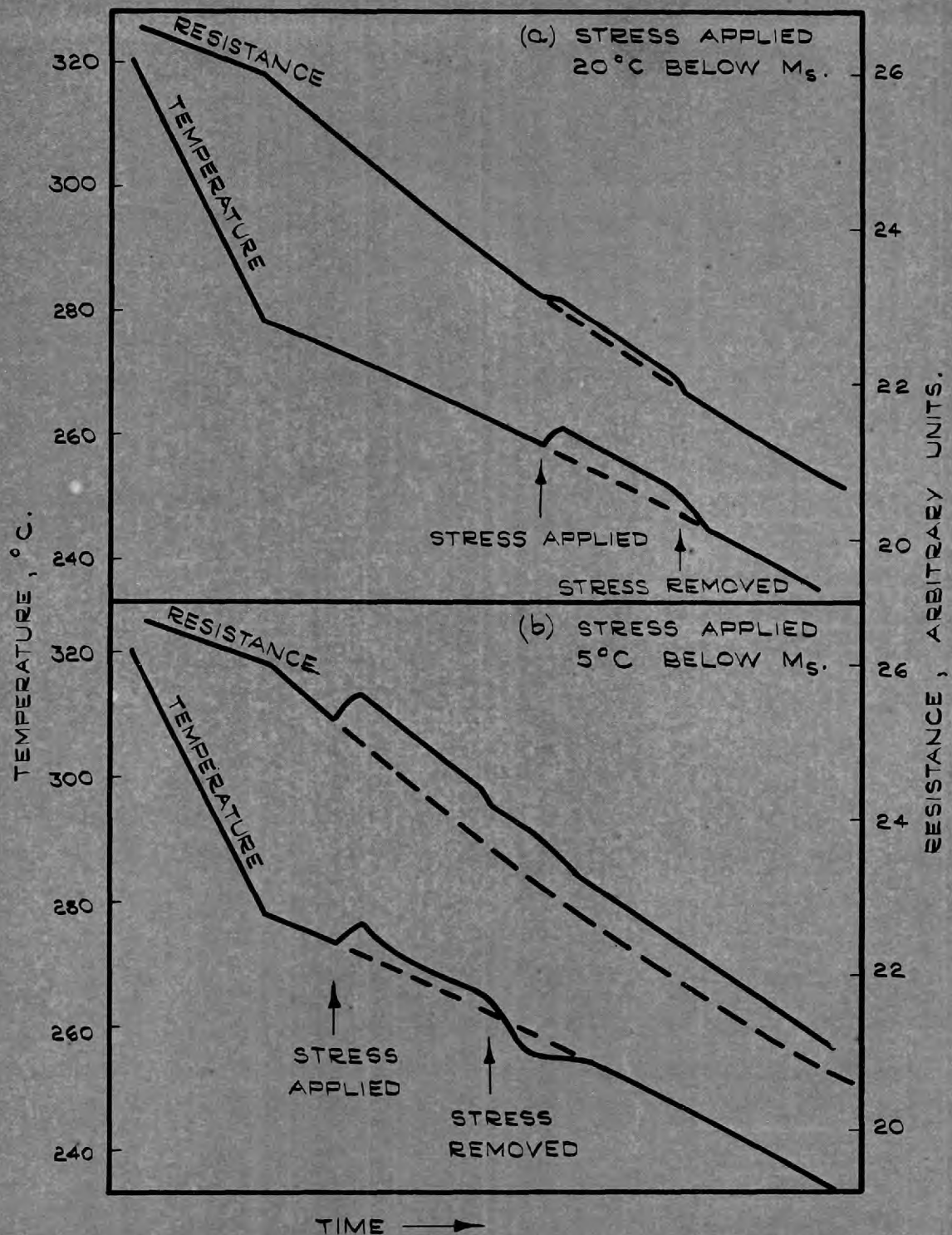


FIG. 24. THE EFFECT OF A TENSILE STRESS (APPROX. 50,000 p.s.i.) APPLIED BELOW M_s , ON THE TEMPERATURE & RESISTANCE CURVES.

For a stress that produced no deformation, the resistance of the specimen increased slightly at the temperature of application of the load, and then as the load was removed the resistance decreased by a small equivalent extent as shown in the diagram. This small increase is caused by the elastic extension of the specimen. Along the gauge length the length increases slightly while the cross-sectional area decreases slightly. Both these changes tend to increase the resistance of the specimen. Evidence that this is only an elastic extension is seen by the observation that no permanent increase of resistance was noted when the stress was removed.

Also, when the load was applied a rise in temperature was observed on the cooling curve. The rise was quite appreciable and amounted to 3° or 4°C for the larger stress values. After this initial increase, or recalescence, with the load fully applied to the specimen, the temperature curve followed a path parallel with a continuation of the cooling curve just before the load was applied. When the load was removed the cooling rate of the specimen increased markedly for a short period, and then followed a curve of the normal cooling rate.

When a load was applied to (or removed

from) a specimen with a stable structure, for example, pearlite or tempered martensite, the resistance curve showed the small increase (and decrease), but no discontinuity was observed in the cooling curve. For this reason the effects described above may be attributed to transformation behaviour. During transformation heat is evolved, and therefore the increase in temperature observed is associated with an increased amount of transformation, or burst, induced by the applied stress.

To calculate the progress of transformation the resistance must be plotted against temperature. In this case, the resistance values taken were those shown by the dotted line in Fig.24a, obtained by interpolation. These values were taken since this anomalous increase in resistance is a result of the applied load and not due to any transformation effect. The actual temperature values were plotted since the temperature of the specimen or its cooling rate is not substantially affected by these small dimensional changes. From the temperature-resistance relationship so plotted the course of transformation could be calculated. Fig.25 shows the course of transformation for a specimen with a stress of 50,200 p.s.i. applied at 20°C below M_s , and removed

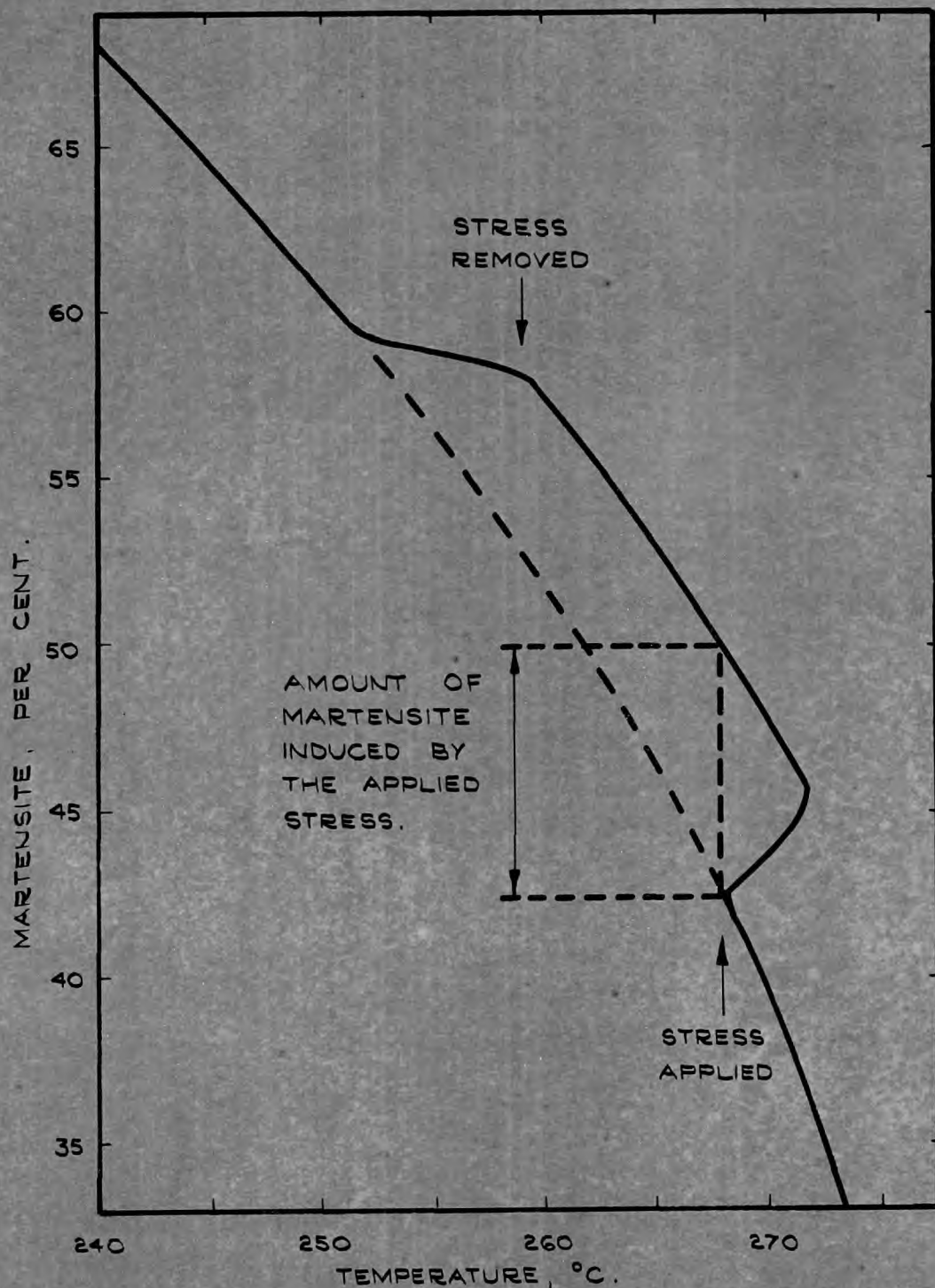


FIG. 25. EFFECT OF A TENSILE STRESS OF 50,200 p.s.i., APPLIED 20°C. BELOW M_s , ON THE PROGRESS OF TRANSFORMATION.

25°C below. The amount of transformation induced by the stress has been taken to be the increment of martensite formed at the temperature of application of the load. When the load was removed it may be seen that the slope of the transformation curve was reduced indicating little martensite was forming until a continuation of the normal transformation curve was reached, when transformation progressed as normally. The same shape of curve was obtained for all stress values producing no permanent deformation, and this high stress value was only used as a clear illustration of the observed effect.

If, however, the stress was sufficient to cause plastic deformation of the specimen, resulting in a permanent extension, the shape of the temperature and resistance curves was altered. This deformation was only observed for the larger stress values applied in a small temperature range below M_s . When the load was applied the increase in resistance was much larger, and when the load was removed, the resistance only decreased a small amount, equivalent to the elastic strain. The cooling curve also did not follow a similar path. The rise in temperature was observed as before, but then ^{the curve} fell a little, but not as far as the normal cooling curve. When the load was removed the cooling rate increased. The

rate approached that observed immediately above M_s , indicating that little or no transformation was occurring immediately after the load was removed. The cooling curve then passed below that of a specimen with no load applied. However, when transformation did take place the slope of the transformation curve was greater.

To calculate the progress of transformation the resistance curve was continued as indicated by the dotted line in Fig 24b. The results obtained when a stress caused plastic deformation are not as accurate as those when only elastic strain is observed, since the resistance could not be determined as precisely.

For a given load of 50,200 p.s.i. it was found that the amount of martensite formed in the burst depends on the temperature of application below M_s . Fig.26 gives the amount of martensite formed in the burst for a load of 50,200 p.s.i. as a function of the temperature below M_s at which the load was applied. The upper part of this curve, shown dotted, is the region in which the stress produced permanent extension of the specimen.

This curve reached a minimum value of approximately 0.5 percent martensite at the M_f

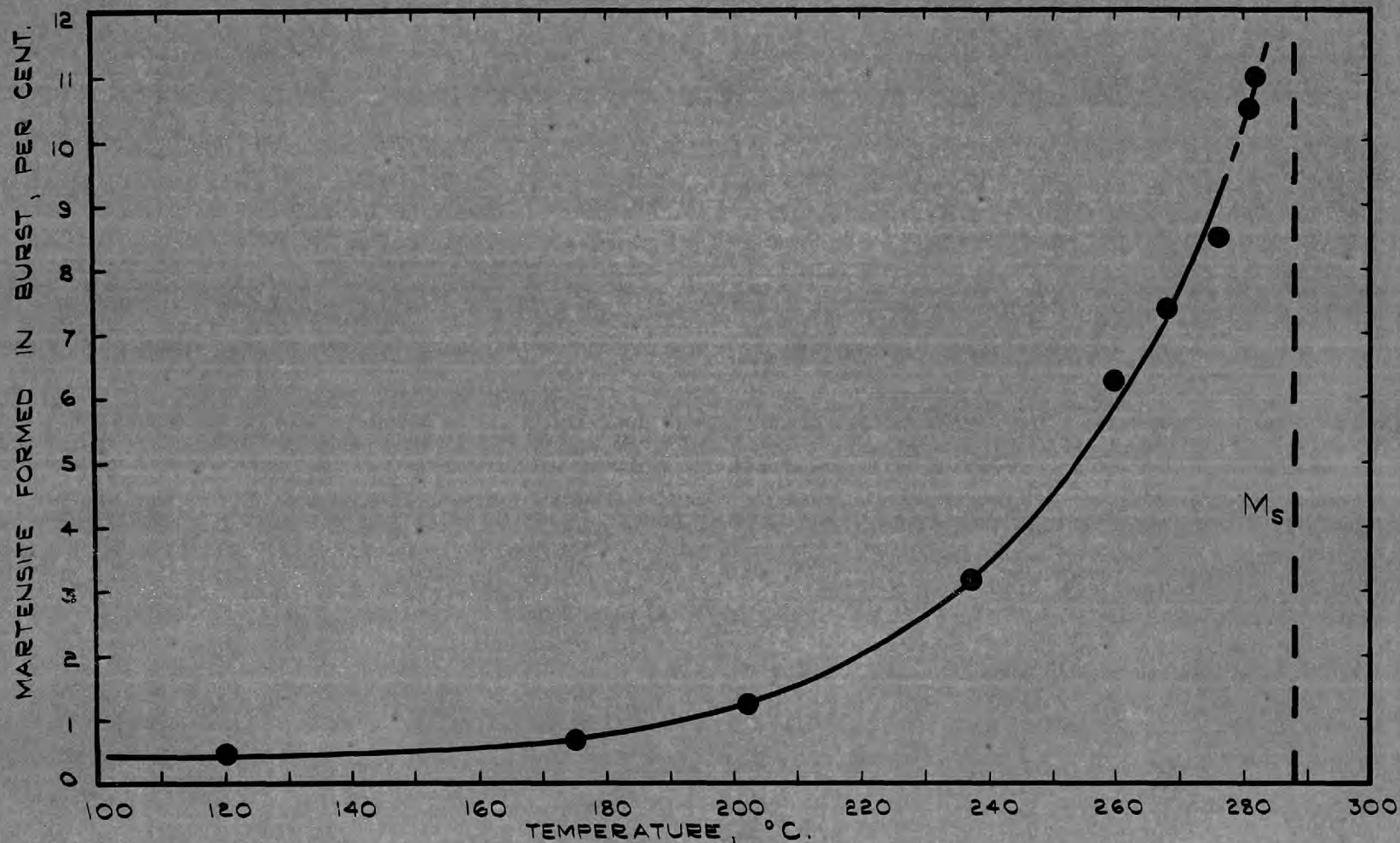


FIG. 26. VARIATION OF PERCENTAGE MARTENSITE FORMED IN BURST BY A TENSILE STRESS OF 50,200 p.s.i. APPLIED AT VARIOUS TEMPERATURES BELOW M_s .

temperature. But if the load was applied below the normal M_f then this same amount of martensite was formed. However, if the load was then removed and reapplied no transformation was observed. But if the load was applied and removed above M_f and then reapplied at a lower temperature additional transformation was noted.

For a given temperature of application of the stress, 12°C below M_s , the relation between the amount of martensite formed in the burst and the magnitude of the applied stress is given in Fig.27. For the low stress values very little increased transformation was observed, and the smallest stress for which an enhanced transformation was noted, was 3,700 p.s.i. The curve was extrapolated back to the origin as shown by the dotted line. The justification for this extrapolation is discussed later.

(iv) Effect of Tensile Stress Applied Above M_s .

To determine the effect of tensile stress applied above M_s , stresses up to 55,000 p.s.i. were applied at temperatures between M_s and approximately 600°C . The standard austenitizing conditions described previously were used for all experiments.

As described in the previous section, it

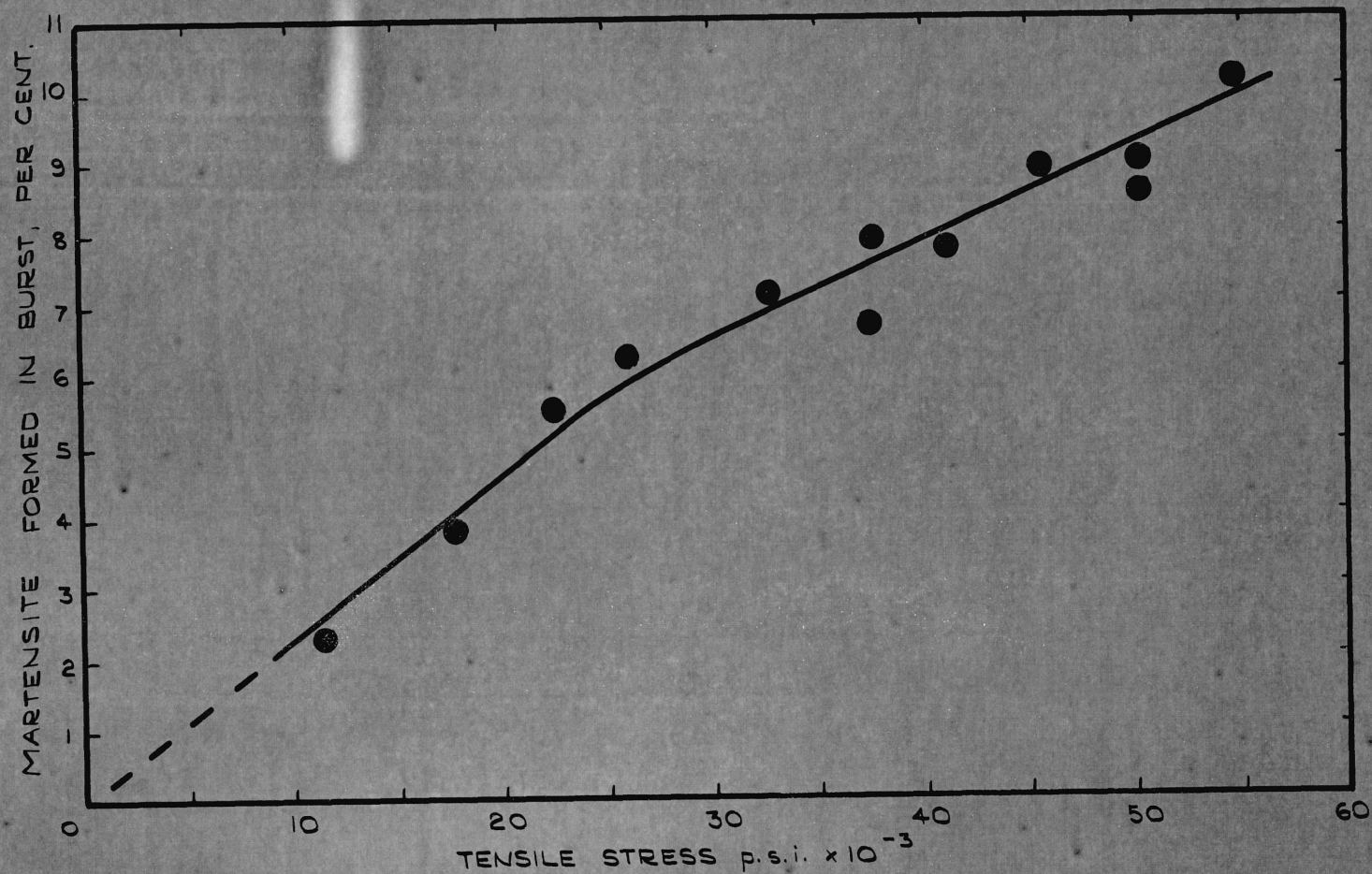


FIG. 27 EFFECT OF TENSILE STRESS, APPLIED AT 12°C. BELOW M_s , ON THE AMOUNT OF MARTENSITE FORMED IN THE BURST.

was possible to determine whether the specimen suffered any permanent extension from the shape of the resistance curve. It was found that a stress below the yield stress of the metastable austenite 86,104, that is one only causing elastic strain did not induce transformation to martensite. From the present experiments the yield stress of the austenite immediately above M_s , at approximately 300°C, was deduced to be about 25,000 p.s.i.

If a stress producing an elastic strain was applied above M_s and the specimen was then cooled through M_s enhanced deformation of the specimen was observed at M_s and continued for a small temperature range below M_s . This increased extension was observed for stress values well below the yield stress of the austenite. Although no actual measurements of extension were made the effect was clearly observed from the shape of the resistance curve. Therefore on cooling the austenite was able to support relatively large loads above M_s , but at the start of transformation extensive yielding was observed. It was not possible to measure any definite increase of M_s as a result of elastic stress since the expected increase of 1 or 2°C is of the same order of magnitude as the reproduc-

ibility of M_s . But some trend was noticed, particularly for those stresses close to the yield stress of the austenite.

When a stress that produces plastic deformation of the austenite is applied above M_s transformation to martensite was induced. It was found that a small amount of martensite was formed as a result of the applied stress, only while the specimen was undergoing deformation. As the load was applied the resistance increased, and then with the load fully applied the specimen was able to support the increased load. While the resistance was increasing during the load application (i.e. during the extension) the cooling rate decreased indicating increased transformation. This observation was confirmed metallographically, as described below.

If the load was then removed from the specimen before the normal M_s was reached, a depression of the start of transformation was observed. This effect is shown in Fig.28. A load of 50,200 p.s.i. was applied at 305°C and then removed at 295°C. During the extension of the specimen a small amount of martensite was formed. Then on continued cooling no transformation occurred until a temperature of 286°C was reached. This corresponds to a

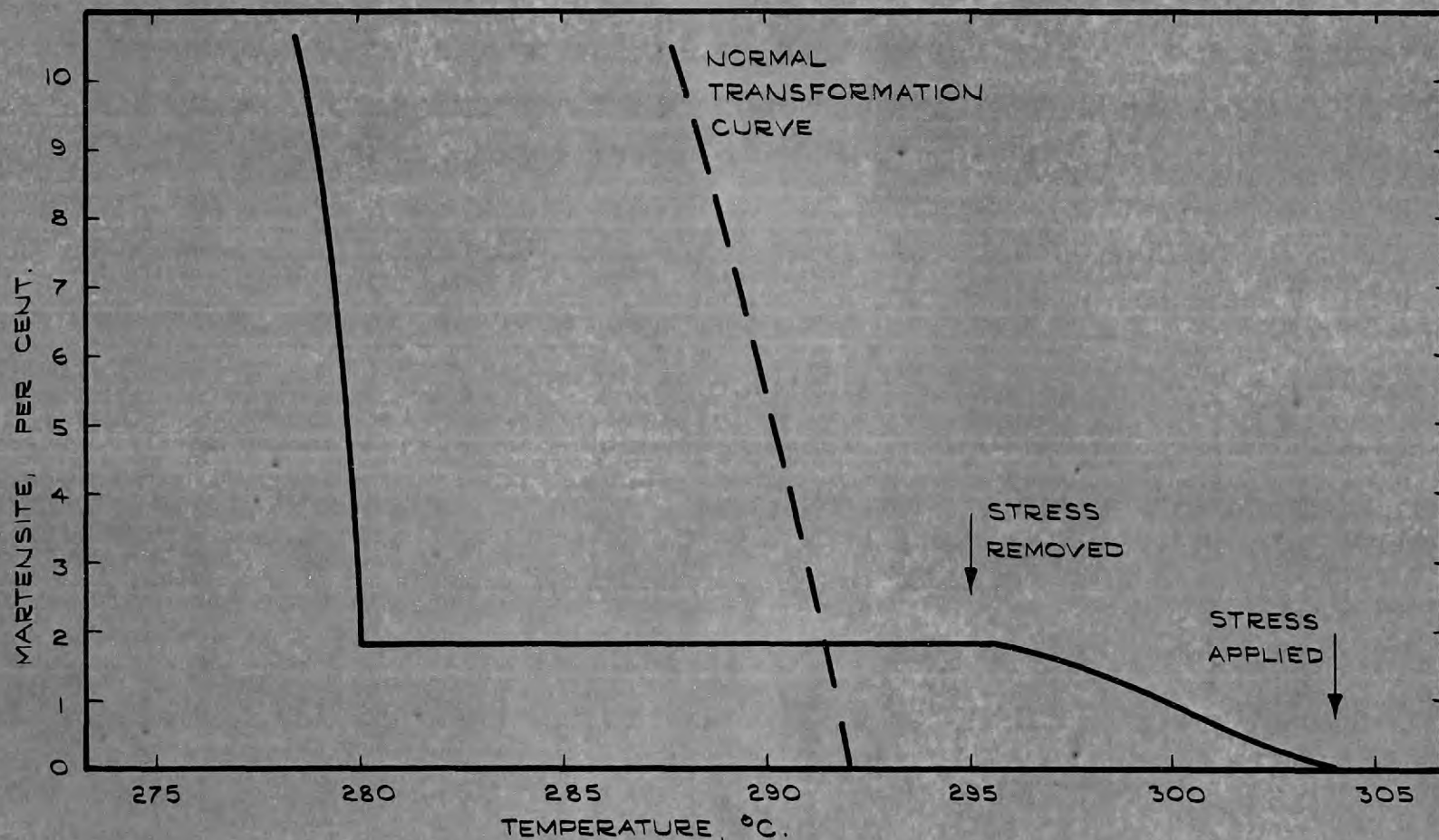


FIG. 28. EFFECT OF A TENSILE STRESS, APPLIED & REMOVED ABOVE THE NORMAL M_s , ON THE PROGRESS OF TRANSFORMATION.

lowering of M_s of about 12°C . However, when transformation did start the slope of the transformation curve was very steep, amounting to some 6 - 7 percent martensite per $^\circ\text{C}$ decrease in temperature, which is higher than the slope of the normal transformation curve.

But, if the same stress was applied at the same temperature, but not removed until below M_s , the progress of transformation was altered. In this case, the martensite was induced during deformation as before, and then no transformation was observed when the load was fully applied. But on continued cooling, transformation occurred just above the normal M_s temperature and the slope of the transformation curve was ~~similar to~~ ^{less than} the normal one. The load was then removed at ~~286~~²⁸ $^\circ\text{C}$ and little or no further transformation was observed while the temperature dropped 13°C . Then as before when transformation did take place the slope of the transformation curve was steep. Fig.29 shows the progress of transformation with a stress of 50,200 p.s.i. applied above M_s and removed below M_s .

Since transformation is induced only during deformation, the amount of martensite formed depends on the degree of strain or extension. The

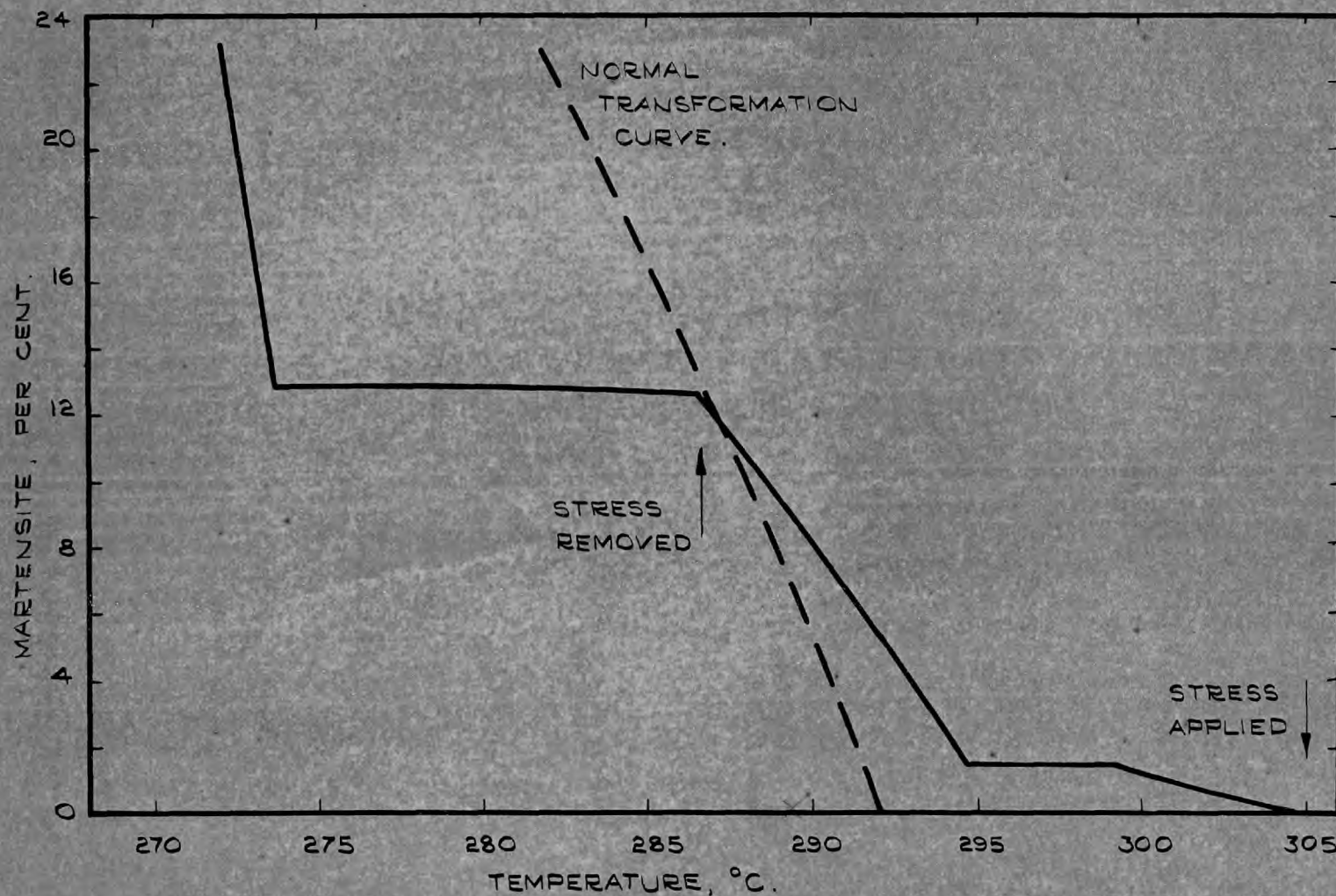


FIG. 29. EFFECT OF A TENSILE STRESS, APPLIED ABOVE & REMOVED BELOW THE NORMAL M_s , ON THE COURSE OF TRANSFORMATION

percent of martensite formed was found to increase as the applied stress increased when the temperature of application was constant. But for a given stress value the amount of martensite formed during deformation decreased as the temperature of application above M_s increased. As the temperature of application of the load increased the extension also increased slightly as the yield stress dropped. The highest temperature at which stress induced martensite was observed was approximately $70^\circ - 80^\circ\text{C}$ above M_s . This M_d temperature could not be determined with much accuracy because for the strains involved the amount of martensite formed was so small. With the present apparatus it was not possible to produce large strains, and in fact tensile strain is not usually used to measure M_d . Large deformations may be more easily accomplished by compression.

However, Fig.30 does show the approximate amount of martensite induced by a tensile stress of 50,200 p.s.i. applied at various temperatures above M_s . These points were mainly obtained from the shape of the cooling curve and it is emphasized that these values are not precise. But they do show the general trend.

If the load which deforms the austenite is removed above M_s the normal M_s temperature is depressed. This effect was observed when the load

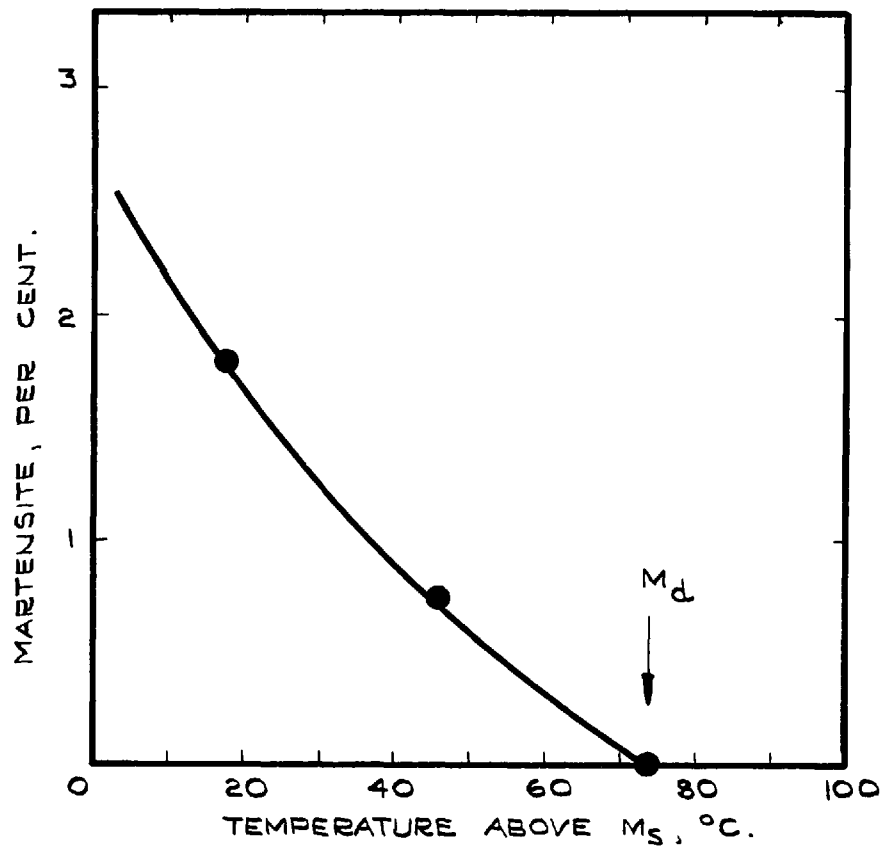


FIG. 30. AMOUNT OF MARTENSITE FORMED BY A TENSILE STRESS OF 50,200 p.s.i. APPLIED AT VARIOUS TEMPERATURE ABOVE M_s .

was applied at all temperatures between M_s and 600°C . That is, both in the range $M_s - M_d$, and above.

The martensite plates that are induced by the applied stress during deformation above M_s have been found to be much smaller than those that form just below the normal M_s . Fig.31 shows the martensite formed by applying a tensile stress of 50,200 p.s.i. 30°C above M_s and then tempering for 10 seconds at 500°C and quenching. The size of these plates may be compared with those formed below M_s viewed at the same magnification in the photomicrograph of Fig.32. It may be seen that the stress-induced plates are smaller by at least an order of magnitude.

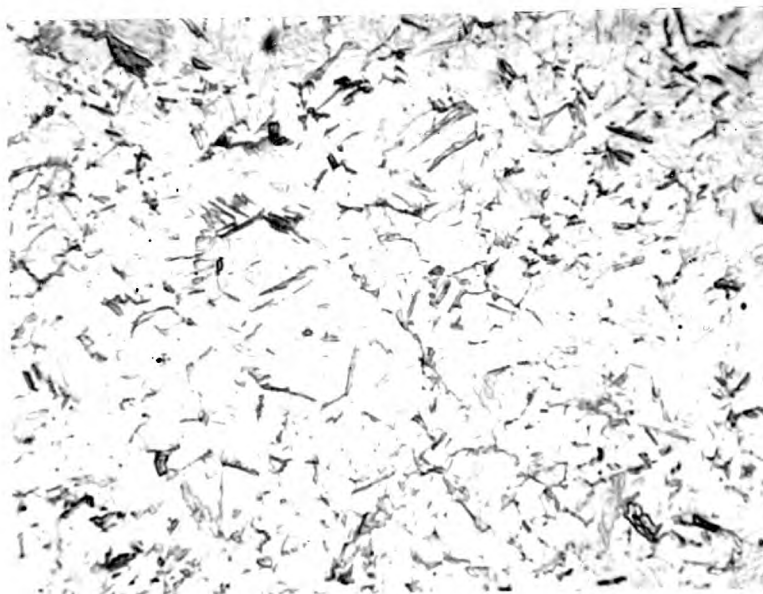


FIG. 31. THE MARTENSITE PLATES INDUCED BY A STRESS
OF 50,200 p.s.i. APPLIED 30°C ABOVE M_s . X1200

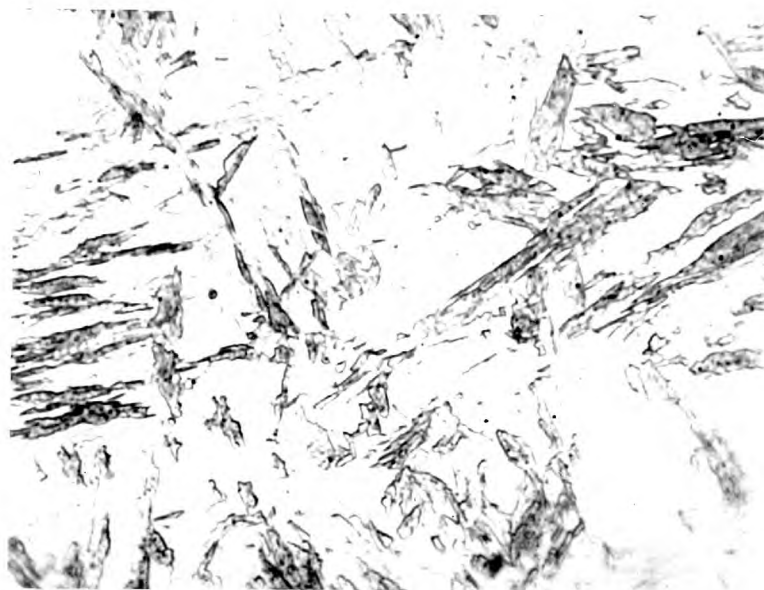


FIG. 32. PHOTOMICROGRAPH OF THE MARTENSITE PLATES
FORMED BELOW M_s . X1200.

5. DISCUSSION.

(i) The Effect of Austenitizing Conditions.

There now seems to be little doubt that increasing the austenitizing temperature raises the M_s temperature. It is not yet certain whether this effect may be attributed to the grain size "per se" or to the thermal history of the specimen. The present results have confirmed that increasing the austenitizing temperature increases M_s . Although no actual measurements of the austenite grain size were made it is safe to assume that the grain size will increase with higher austenitizing temperature. The extent of this increase was not known, but by comparison with the results of other workers on similar steels^{94,96}, it is quite probable that the austenite grain size doubles for each 100°C or so increase in austenitizing temperature.

Martensite plates are known to be halted at a grain boundary, or another plate, and it has also been observed that the growth of a plate may be halted inside the grain⁷. For example, in a single crystal the interface often does not extend completely across the crystal¹⁵. The present results appear to substantiate this observation, for the plates that form as a result of the high temperature are not markedly larger than those observed after a low

temperature treatment.

Another interesting observation is that the slope of the transformation curve in a small temperature range below M_s is substantially less when a high austenitizing treatment has been given (that is, less transformation occurs per °C decrease in temperature). For the lower austenitizing temperatures, 750°C - 850°C, the slope of the transformation curve is a maximum at M_s , and continuously decreases as transformation proceeds (Fig.20). At the high temperature treatments, however, the initial part of the curve has a low slope value, which increases with falling temperature. This curve is very similar to those obtained by Brook et al.¹⁰⁵ who observed that the initial portion of the transformation curve was rounded up to approximately 7 % martensite, and that this was followed by a linear portion up to 50 % transformation. These curves were obtained by the Greninger-Troiano⁹⁸ technique after austenitizing at 1200°C. Since this technique does not produce results as accurate as those obtained by electrical resistance measurements, the agreement with the present results is remarkably good.

Most of the theories of martensite transformation have a provision for predicting an increase of the M_s temperature with austenitizing temperature.

However, before the results are examined in the light of these theories, it is as well to look at the other possibilities, such as decarburization and the homogeneity of the austenite, which can affect the course of transformation in steels.

The M_s temperature is very dependent on the carbon content, increasing carbon lowering the M_s (Fig.1.) Therefore, removal of carbon by decarburization will tend to raise the M_s for a given austenitizing treatment. As described previously, the prevention of decarburization was a very troublesome problem. However, by taking suitable precautions decarburization was effectively eliminated, except for a slight tendency after several cycles, or a very high temperature treatment. These effects were extremely small, for the M_s temperature was only increased by 1 or 2°C after about 6 cycles of austenitizing at 850°C and cooling. At the higher temperature treatments this effect was more marked. When a specimen was austenitized under the standard conditions, after a high austenitizing temperature cycle, the M_s was found to have risen by a small amount, but the shape of the transformation curve remained unchanged. It is considered that any decarburization that did take place probably occurred

in the vicinity of the welded junction between the fine thermocouple and potential wires and the specimen, where the nickel plating was not completely continuous. Previous workers^{94,106} have not commented on this phenomenon, since for only one cycle of heating and cooling the small effect would not be observed, while in larger specimens the observation would be less noticeable. From the foregoing discussion it may then be said that decarburization of the specimen during austenitization has been effectively prevented.

Another effect which may change the course of transformation is the degree of solution of carbides in the austenite, that is, the homogeneity of the austenite. The 'as-received' structure of the wire consisted of carbide particles in a ferrite matrix. After an initial treatment at 850°C, an excellent reproducibility of M_s was found on repeated cycles of austenitizing and cooling. The M_s on the first cycle was slightly higher (2 - 3°C) than those observed on subsequent cycles, ~~thus confirming~~ ^{The results of} previous workers¹⁰³ ^{Suggest} ~~who found~~ that the initial structure and the rate of heating to austenite ^{might} affect subsequent transformation on cooling. It is possible that the initial structure affects subsequent transformation by altering the grain size of the austenite,

as well as the homogeneity. It is not certain whether the initial treatment does result in complete dissolution of the carbides, and therefore produce homogeneous martensite.

The results obtained on the eutectoid carbon steel also indicate that a time of 2 minutes at temperature was quite sufficient to produce homogeneous austenite, particularly by rapid heating from martensite. It was found that for all austenitizing times above approximately 5 seconds, after starting from a pearlitic structure, pearlite was not formed on subsequent cooling, and since pearlite is nucleated by carbides (or the associated carbon deficient regions), the achievement of homogeneous austenite is indicated.

It is probable that the presence of carbides in the austenite tends to increase M_s , for nucleation of martensite occurs in carbon-depleted regions. As the austenitizing temperature is increased, carbide particles will dissolve more readily, and therefore these regions become smaller, and the total alloy content of the austenite increases thus causing the lowering of M_s .

However, in the present investigation no such depression was observed (except for the first cycle), and it may thus be concluded that homogeneous

austenite was produced under the conditions of austenitizing used.

Hence by eliminating the effects due to decarburization and the homogeneity of the austenite it has been established that the austenitizing temperature influences the nucleation pattern of martensite, which may be caused by the grain size or some other property which is a function of temperature.

Classical nucleation theory of Fisher, Hollomon and Turnbull⁵⁹ predicts an increase of M_s with increasing grain size. Grain boundaries act as barriers to the propagation of martensite plates, though it has been observed that a plate in a neighbouring grain may be nucleated by the stress field of one halted at the boundary. It is assumed that the number of nuclei per unit volume is not altered, so that when a plate is formed in a coarse-grained sample the volume percent transformed is larger than in a fine-grained material, if the plate grows to the grain boundary. The measured M_s is then higher. In the present investigation this explanation does not appear valid, because the martensite plates forming after different austenitizing treatments do not appear to differ greatly in size. This theory also does not predict the observed decrease in slope

of the transformation curve as the austenitizing temperature is increased; it would rather suggest an opposite effect.

All the recent work, both by practical and theoretical considerations, does suggest that nucleation occurs at some form of structural heterogeneity. Dislocations (which are strain sensitive) and associated stacking faults are the most likely defects. In Jaswon's⁶⁹ model of nucleation in iron-base alloys, the stacking fault of the intermediate α' structure is pictured as contracting as the temperature is raised since the α' structure is unstable relative to austenite. Then on quenching only the sources existing at the austenitizing temperature are available for transformation, and the M_s is depressed. Although this idea does not predict the experimentally observed M_s values, it may account for the low slope of the transformation curve. It may be suggested then that as the austenitizing temperature is increased, grain growth occurs and as the boundaries move they will act as a sink for the dislocations in the austenite. The mobility of dislocations also rises as the temperature rises and they will consequently tend to annihilate more easily. The density of dislocations will thereby be lowered, thus altering the nucleation pattern,

for there will be fewer effective sites. This would explain why a low initial slope of the transformation curve is observed after a high austenitizing treatment. Then as the temperature is lowered, the first formed plates effectively divide the austenite grains and the size is reduced, and the martensite that then forms will do so in a larger number of grains, and the slope of the transformation curve will increase. It is also probable that the stress field produced by the first plates aids nucleation for further transformation.

Another interesting observation was that after the high temperature treatments the cooling curve showed small kinks in the region immediately below M_s . These may be attributed to the growth of individual plates in the vicinity of the thermocouple. As a plate forms the heat of transformation will raise the temperature slightly (or retard the rate of cooling), producing a kink on the cooling curve. This effect was only observed during the first few degrees below M_s and only after high austenitizing temperatures. For low austenitizing temperatures, the plates that first form are smaller, and more transformation occurs per °C decrease in temperature, and although the integrated effect is to produce a greater thermal arrest, a smooth curve results.

Evidence that grain size "per se" is not the only factor that influences the martensite transformation is provided in experiments by Porter and Dienes⁹⁷. They found that the depression of M_s , caused by neutron irradiation of iron-nickel alloys, was markedly greater for coarse-grained specimens than fine-grained ones. It was suggested that the plates that formed in the coarse-grained material may be more sensitive to changes in the strength of the matrix. This would also suggest that the austenite in the coarse-grains contains less structural defects to impede transformation. These results therefore lend support to the idea expressed above.

There are similarities between the dislocation generation models of nucleation and those that envisage the embryo forming at strain centres or preferred sites. Both models use dislocations as the starting point and it is possible that the embryo as pictured by Kaufman and Cohen⁷ is a second stage in the nucleation process, which originates from dislocations and stacking faults. In fact, Knapp and Dehlinger⁶⁰ propose that the embryo forms by interaction of certain pairs of dislocations.

It is quite probable that the number of embryos resulting from a high temperature treatment would be less since the dislocation density may be

reduced. But each embryo may be larger since at a high temperature the dislocations are more mobile, and hence the coalescence of embryos would be favoured. Also the time on cooling would be slightly longer, tending to produce larger embryos. Since it is supposed that a spectrum of embryo sizes exists at M_s , the larger embryos propagating to martensite first, M_s would be raised in accordance with experiment. It is emphasized by Kaufman and Cohen⁷ that after transformation has begun the quantitative calculations on nucleation do not necessarily hold because of the catalytic effects of plates in nucleating others.

(ii) The Effect of Applied Tensile Stress.

The results have shown that both applied elastic and plastic tensile stresses influence the formation of martensite in En 23 steel, thus confirming the observations of investigators of other systems exhibiting martensitic transformations.

Evidence that the burst of transformation which occurs as the load is applied is a real effect is given in the experiment in which the stress was applied to a fully martensitic or pearlitic structure. No discontinuity in the temperature curve was observed. The marked recalescence that is observed as the load is applied during transformation in the

martensitic range results from the heat evolved by the additional transformation induced by the applied stress.

It was found that stresses of from 4,000 - 55,000 p.s.i. (the highest value investigated) applied below M_s induced transformation to martensite. The curve giving the amount of transformation induced by various stresses applied 12°C below M_s shows a change in slope at approximately 25,000 p.s.i. (Fig.27). This stress is approximately the yield stress of metastable austenite as determined by other workers^{86,104}. A good measure of this yield stress was also obtained from the load that the specimen could support without yielding above M_s . Fig.33 shows the yield stress of metastable austenite as a function of temperature. Since the martensite transformation is known to be strain sensitive, and although the minimum stress for which enhanced transformation was observed was approximately 4,000 p.s.i., it seems reasonable to suppose that all elastic strains will influence transformation, and hence the curve was extrapolated back to the origin.

These effects due to elastic strain would predict that an increase of M_s under applied stress should be observed. If the transformation curve (Fig.25) with the load applied was extrapolated back

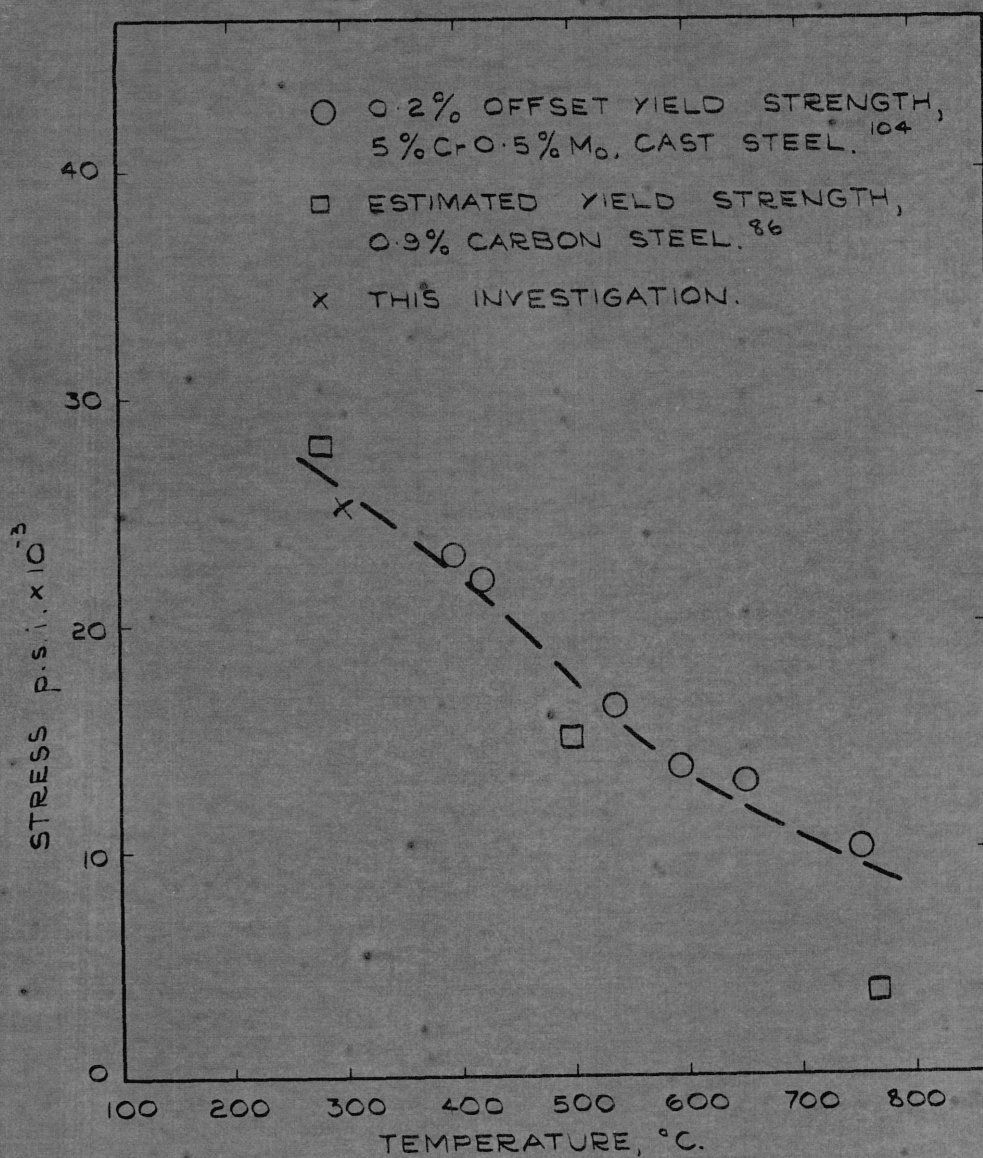


FIG. 33. THE YIELD STRENGTH OF METASTABLE AUSTENITE IN STEEL.

to the temperature axis, the intercept would give the increase in M_s , i.e. ΔM_s . It was not found possible, however, to measure this increase accurately. The load would necessarily have to be applied above the normal M_s , and for loads that are below the yield stress of the metastable austenite the increase is very small, only of the order of reproducibility of M_s , that is approximately 1 or 2°C, while for larger stresses, plastic deformation of the austenite occurs. This deformation induces transformation by another mechanism (which is discussed later), and also mechanical stabilization effects mask the influence of the elastic strains. However, an indication of a small increase in M_s due to applied elastic stress was observed.

Elastic strains have been found to influence martensitic transformations in many alloy systems but no quantitative work has been reported in the literature for plain carbon or low alloy steels. Patel and Cohen⁵⁸ have reported ΔM_s values of 1°C per 1000 p.s.i. for tensile stress in an iron-nickel-carbon alloy of high alloy content (Fig.6), while in the present work on En 23 steel a value of 1°C per 8,000 - 10,000 p.s.i. is indicated. It is not obvious why elastic stress should aid transformation to a greater extent in the highly alloyed steel.

The habit plane for this steel is $\{259\}_\gamma$ while in the low-alloy steel it is predominantly $\{225\}_\gamma$. The effect may then be partly attributable to the larger number of possible planes with the $\{259\}_\gamma$ habit, and therefore it is more likely that one plane will be more favourably orientated to the applied stress axis, thereby requiring a lower stress for propagation.

approximately

The behaviour of transformation induced by applied tensile stress (Fig.25), is consistent with the idea of a spectrum of embryo sizes 'frozen-in' from a high temperature⁷. As the stress below M_s is applied, the driving force for transformation is effectively increased, and embryos are activated that would not otherwise have propagated until a lower temperature was reached. When these embryos have been activated, the transformation curve follows an parallel path with the normal transformation curve. At each temperature embryos are activated at a slightly higher temperature than they would have if no applied stress were present. The magnitude of this temperature gap depends on the value of the stress. When the load is removed, the small increase in driving force is removed. The temperature must therefore be lowered until it is such that the remaining embryos become critical. Thus little or no transformation is observed for a small temperature

drop as the load is removed. The magnitude of this temperature drop depends on the value of the applied stress and on the temperature below M_s , that is, on the austenite available for transformation. It may then be stated that an elastic stress applied and removed in no way affects the course of subsequent transformation.

Evidence that some austenite is retained under normal conditions is provided by the stress measurements. A stress of 50,200 p.s.i. applied below the M_f temperature induces approximately 0.5% transformation, while if this stress is reapplied below M_f then no additional transformation is observed. Although this stress may not have been sufficient to transform all the retained austenite, it does suggest that only a very small percentage was retained. This conclusion was confirmed by X-ray measurements. Although the Debye-Scherrer lines characteristic of the face-centred cubic austenite were observed, they were extremely faint, indicating a very small percentage of retained austenite.

A stress below the yield stress of metastable austenite, that is, approximately 25,000 p.s.i. (Fig.33), applied above M_s does not induce transformation above the normal transformation temperature, except insofar that it raises the M_s by a small amount ΔM_s . The role of the elastic strain in raising M_s is a thermodynamic one. The total driving force for transformation is raised, and T_0 is then raised, as observed in the indium-thallium system (Fig.7). In the present case, however, the effect is very much smaller.

If the applied stress causes plastic deformation of the austenite the course of transformation is greatly changed. A stress that produces permanent deformation induces a small amount of martensite while the specimen is deforming. The influence of plastic deformation on the martensite transformation is a kinetic effect as distinct from the thermodynamic effect of elastic strain.

If the applied load was removed before the normal transformation temperature was reached, no transformation occurred until the temperature had fallen further (the amount depending on the degree of permanent deformation). When the reaction did start, however, the slope of the transformation curve was very steep, indicating a high percentage

of martensite forming per °C decrease in temperature. If the stress was kept applied, the normal M_s was raised slightly, and the slope of the transformation curve was lowered. Now when this load was removed below M_s little or no transformation occurred for an appreciable drop in temperature, and when transformation did recommence the slope of the transformation curve showed rapid transformation.

The plastic deformation influences nucleation either by introducing new nuclei, or by expanding the nuclei or faults that are already present. The shear stress required to initiate transformation increases as the temperature increases, until at M_d only slip occurs. It appears that within the temperature range $M_s - M_d$ martensite transformation constitutes a mode of stress relief which competes with slip, and in this respect is similar to deformation twinning. Jaswon⁶⁹ considers that it is probable that all three modes (martensite transformation, slip and twinning) originate from essentially similar kinds of source.

Cold work or deformation between M_s and M_d activates nucleation by expanding the proposed quarter-dislocations to produce martensite. It is not immediately obvious why the plates induced by plastic deformation are smaller than those that form

on normal cooling. However, it is not surprising since the conditions of formation are markedly different, and it may be that the propagation mechanism is halted by interacting dislocations on other slip systems.

The plastic deformation necessarily work-hardens the matrix and it is therefore not surprising that M_s is depressed on further cooling, for the critical shear stress of the austenite will have increased, thereby making the propagation of a plate more difficult. The driving force for transformation must then be greater and the temperature must be lower to activate sources, and M_s is accordingly depressed. However when transformation does occur the volume that transforms per °C is larger; the driving force required for a nucleus to reach critical size is larger than that required for propagation. This mechanical stabilization of the austenite is very similar to that observed due to thermal stabilization⁴⁸, and is analogous to the yield point phenomenon in mild steel²⁵, when dislocations are unpinned from their atmospheres.

When, however, the stress is not removed above M_s the main transformation occurs at a higher temperature, just above the M_s observed under normal

conditions. In this case the elastic component of the stress adds to the thermodynamic driving force to initiate transformation. The slope is not so great, but this is probably due to the retarding effect produced by the deformation. Although the relative effect of elastic strain is not known in this case, it is expected to exert the major influence. When the stress is removed no transformation occurs until the driving force without the additional elastic strain energy is sufficient to cause the nuclei to grow. Again when the specimen was mechanically stabilized the slope of the transformation curve was greater.

Another interesting observation is that of enhanced deformation or 'transformation plasticity' in a small temperature range below M_s . In the present work, this transformation plasticity has been observed for all stresses above approximately 10,000 p.s.i., while using a more accurate strain measuring device, Porter and Rosenthal⁸⁶ observed a 'threshold' stress for increased extension at 1,000 p.s.i. These values are significantly below the yield stress of the metastable austenite (Fig.33).

It has been suggested¹⁰⁷ that the most probable cause for this phenomenon is that applied

stress favours the formation of suitably orientated martensite plates. It has been found that elastic tensile stresses favour the formation of martensite plates; therefore during the early stages of transformation under an applied tensile stress, martensite plates which produce a deformation that relieves the applied stress, will be formed in preference to those of less favourable orientation, in accord with Le Chatelier's principle.

Increased deformation as a result of preferred orientation has been observed by Chang and Read¹⁵ in the gold-cadmium system. However, no evidence of preferred plates could be found by Porter and Rosenthal⁸⁶, and in the present case, no preferred orientation was detected.

Since the effect is only observed in a small temperature range below M_s the volume percentage of transformation of martensite plates with preferred orientations, would be small when compared with the fully transformed structure. Hence it is not surprising that the X-ray films did not show any evidence for preferred orientation.

However, metallographic examination of the first-formed plates by the Greninger-Troiano⁹⁸ technique should reveal plates with preferred

directions. However, no preferred orientation was observed; the structure consisted of a random distribution of plates.

Another mechanism to account for the increased plasticity has been suggested by Porter and Rosenthal⁸⁶. They assume that the transformation supplies energy to form dislocation pile-ups at grain boundaries, and that only a small additional stress is then required to activate slip in preferred directions. This explanation suffers from the disadvantage that it may be applied only to alloys of low stacking fault energy, in which such pile-ups occur¹⁰⁹.

This effect may be better explained in another way; a mechanism is proposed below. It seems more likely that the increased extension results from preferred slip in the austenite round a martensite plate. The deformation appears to be greater than that expected only from a consideration of preferred plates, especially as the phenomenon is observed only in a small temperature range below M_s where a small volume of transformation occurs. Internal twinning on a fine scale of a martensite plate, and also plastic deformation of the austenite surrounding a plate has been noted by transmission electron microscopy^{19,108}. The observed dislocation densities particularly near the tip of a plate may be as high as 10^{12} dislocat-

ions per sq. cm.¹⁹ As a plate grows, dislocations move through the austenite, and it is probable that only a small additional stress is required for slip to occur in a preferred direction by movement of dislocations in the slip system that is closest to the applied stress axis. Slip in the martensite plates would not occur preferentially because the critical shear stress for dislocation movement is much greater than in austenite, especially since the plates are internally twinned. The preferred slip in the austenite round a plate would then account for the enhanced extension.

The enhanced deformation is observed only in a short temperature range below M_s , because the martensite plates form a network in the austenite thereby strengthening it. As transformation proceeds the austenite becomes more deformed, and by interaction of dislocations, the movement of slip dislocations becomes very limited, and the increased extension is no longer observed.

A complete description of the cause of this deformation which is observed to accompany transformation under stress probably involves both the effects of preferred orientation and the mechanism proposed in this thesis, the relative proportions

depending on the alloy system investigated. In this case it appears that the latter mechanism is predominant.

(iii) Application to Hard-Zone Cracking.

A relation was established between the end-of-transformation temperature (M_f) of steels and their liability to cracking in the heat affected zone of welds. When transformation continues below a certain critical temperature with a given cooling rate then cracking is observed. The critical temperature varies with the diffusible hydrogen content of the weld metal and may be lowered $40^\circ - 50^\circ \text{C}$ from approximately 290°C by using low-hydrogen electrodes.

This investigation was undertaken primarily to determine the effect of stress on transformation and to elucidate the problem of the effect of restraint in the welded structure. The austenitizing conditions may also play a part in this connection. At different distances from the weld transformation will start at different temperatures because of the austenitizing conditions.

The results do tend to suggest that stress would not play a large part in promoting cracking, since generally stress does not lower transformation temperatures, and also the phenomenon of transformation plasticity would relieve stresses.

5. CONCLUSIONS.

It is considered that the results obtained and discussed in this thesis have materially contributed to the fundamental knowledge of the martensite transformation in steels, by providing new experimental data not hitherto reported, and by confirming the results of other workers on other materials. The results have a bearing in relation to the hard-zone cracking in welded steels, and their application to this phenomenon has been briefly discussed.

The findings of this investigation may be expressed as follows :

(a) Effect of Austenitizing Conditions.

- (i) The M_s temperature is raised as the austenitizing temperature is raised.
- (ii) The slope of the transformation curve decreases as the austenitizing temperature increases, that is, the percentage of martensite formed per $^{\circ}\text{C}$ decrease in temperature is lowered.

The results have been discussed in terms of the theories of the nucleation of martensite and a suggestion has been proposed to account for the observed effects based on nucleation at structural heterogeneities.

(b) Effect of Applied Tensile Stress.

- (i) Elastic stress applied below M_s causes a burst of transformation.
- (ii) Plastic deformation of the metastable austenite induces transformation to martensite in a limited temperature range above M_s .
- (iii) Plastic deformation above M_s mechanically stabilizes the austenite, thereby depressing M_s .
- (iv) After stabilization the slope of the transformation curve was high, that is transformation occurred at an accelerated rate.
- (v) During the early stages of transformation enhanced deformation occurs under a low applied stress.

These observations have been discussed in the light of current theories of martensitic transformations, and a suggested mechanism has been proposed to account for the enhanced deformation under applied stress, by preferred slip of the austenite adjacent to martensite plates.

ACKNOWLEDGEMENTS.

The author is grateful to Professor J. G. Ball for suggesting the problem, for his continued interest and encouragement and for providing the facilities for the investigation. He would especially like to express his gratitude to Dr. D.R.F. West for his advice and guidance throughout the project, and also to Dr. R.L.Bell, Dr. M.A.Jaswon and Professor T.A.Read for stimulating discussions.

The work was financed by the Ministry of Supply (latterly the War Office), and the author is indebted to them for the award of a maintenance grant during the tenure of which this investigation was carried out.

He would also like to thank Dr. J.S.White and the Mond Nickel Co. for the supply of the En 23 steel, and to Dr. H.H.Scholefield of the Telegraph Construction and Maintenance Co. Ltd. for wire drawing.

Thanks are also due to colleagues and the technical staff of the Metallurgy Department for their assistance.

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APPENDIX.Details of the Recording Apparatus.

The recording apparatus consisted of two d.c. Amplifiers and a Duplex Recorder, one channel being used for the electrical resistivity measurements and the other to obtain a continuous record of the temperature of the specimen.

(i) D.C. Amplifiers.

Two Tinsley d.c. Amplifiers (Type 6035) were used having input ranges of 0.5, 2, 5 and 40 millivolts, and 5, 10 and 25 millivolts, respectively, with an output current of 20 milliamps for full-scale deflexion. The response time of the amplifiers was about 0.15 seconds from zero to full scale.

(ii) Recorder.

The output from the amplifiers was fed to an Evershed and Vignoles High Response Duplex Pen Recorder. The chart was 7 ins. wide and 65 ft. long calibrated on two channels each $2\frac{1}{2}$ ins. wide. Chart speeds of $\frac{1}{2}$, 1, 3, 6 and 12 ins. per minute were obtainable, and it was possible to use these same speeds in inches per second by fitting a new clock in the recorder. The recorder had a full scale deflexion speed of 0.125 second.