

Isothermal Omega Kinetics in Beta-Titanium Alloys

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Abstract

Small angle X-ray and neutron scattering (SAXS/SANS) provide a non-localised quantitative analysis of nanoscale ω precipitates in Ti-7Mo at.% and Gum metal, a Ti-Nb based alloy. The nucleation and coarsening kinetics are more rapid in the Ti-Nb alloy than the Ti-Mo alloy, presumably as Nb diffuses more rapidly than Mo in Ti. Therefore Mo-based β -Ti alloys are more stable during ω ageing than Nb-based β -Ti alloys. To the authors' knowledge, this represents the first publication quantifying ω size, volume fraction and element partitioning in Gum metal.

Key words: Titanium alloys, X-ray diffraction (XRD), Small Angle Scattering, Ageing, ω phase transformation.

Metastable β -Ti alloys are of significant current interest because of their low modulus for biomedical devices and potential for α'' superelasticity [1–4] or for high ductility through the production of work hardening by twinning-induced plasticity [5]. However, the almost fully retained β -microstructure that is obtained on quenching from above the β -transus is unstable, and subsequent low temperature ageing nucleates the embrittling isothermal ω phase [3]. This is particularly worrisome as ω phase appears to suppress twinning, the low modulus of the β , and α'' superelasticity [3]. There is evidence that in these alloys that the high pressure ω phase can be induced by cold work, presumably due to the hydrostatic stress fields around dislocations [6]. The ω phase is also known to be a precursor to stable nanoscale α precipitation that is desirable for high strength applications [7, 8], and the transformation process is an area of ongoing research [9].

To date, the study of ω nucleation and growth by small angle scattering has been very limited. In 1983, Lyon *et al.* applied small angle X-ray scattering (SAXS) to investigate spinodal decomposition in binary Ti-35Nb wt.% and the relationship between athermal ω and isothermal ω [10]. In 1991 Fratzl *et al.* characterised the coarsening rate of ω in Ti-20Mo at.% by SAXS and related the coarsening rate to Mo diffusion and elastic interactions between co-precipitates [11]. They subsequently incorporated the transition from ω to α precipitation [12]. More recently, Šmilauerová *et al.* performed the first *in-situ* SAXS measurements to reveal that the ω precipitates are weakly or-

dered along the $\langle 100 \rangle$ β direction, and deduced the particle growth rate and interparticle distance evolution for Ti-15Mo wt.% and Ti-6.8Mo-4.5Fe-1.5Al wt.% during thermal exposures [13–15]. These studies [11–15] were limited to small angle scattering, with little correlation to complementary experimental techniques such as TEM or atom-probe tomography (APT) measurements. Furthermore, the deconvolution of the SAXS data in order to quantify the precipitate volume fraction and element partitioning between precipitate and matrix was not attempted [11–15]. The current authors presented the first *in-situ* small angle neutron scattering (SANS) study of precipitate evolution in Gum metal at 400 °C, a Ti-Nb based alloy [6]. The precipitate evolution determined by SANS was correlated with a TEM study, however the authors did not succeed in deconvoluting precipitate volume fraction and element partitioning from the scattering data [6]. Subsequently the authors presented a multi-technique analysis of TEM, APT and *in-situ* SANS to quantify particle coarsening in Ti-5Al-5Mo-5V-3Cr wt.% (Ti-5553), which successfully deconvoluted ω precipitate volume fraction and element partitioning [7, 16].

In recent years the understanding of ω precipitation has developed by using TEM methods, in particular by high-angle annular dark-field (HAADF) imaging [9]. However TEM is not trivial as the ω precipitates are so small relative to the thickness of a TEM foil. The ω precipitates can be observed using APT, but this necessarily only studies small volumes and then, only where the compositional contrast with the matrix is relatively high [7, 9, 16–20]. Small angle scattering offers the possibility to study precipitation in a more robust fashion with better statistics, if volume fraction and composition of the precipitates formed can be deconvoluted from the data [7, 16].

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The scattering contrast of different elements between neutron and X-ray scattering offers a means to deconvolute these microstructural parameters, particularly in binary alloys where a closed form solution can be obtained. This work applies a combination of room temperature SAXS/SANS, SAS modelling, and laboratory X-ray diffraction (XRD), to offer insight into the precipitation processes in the bulk of two metastable β -Ti alloys, binary Ti-13Mo wt.% (Ti-7Mo at.%) and Gum metal [1] Ti-33Nb-3Zr-2Ta-0.3O wt.% (Ti-21Nb-2Zr-1Ta-1O at.%). The Ti-Mo binary alloy was selected as a model system to demonstrate the merits of a SAXS/SANS combination analysis applied to metastable β -Ti alloys, and the technique was then applied to quantify microstructural parameters of the well known Ti-Nb based alloy Gum metal, for the first time. The methodology deconvolutes the precipitate volume fraction and element partitioning between precipitate and matrix, quantifies the precipitation kinetics of both alloys, and the differences between the Ti-Nb and Ti-Mo alloy systems are rationalised.

The compositions of the alloys studied were measured by inductively coupled plasma optical emission spectrometry ICP-OES and LECO analyses and are presented in Table 1. The alloys were obtained by the following processing routes: i) Ti-7Mo at. % was prepared by arc melting in an argon filled environment. The alloy was homogenised at 1000 °C for 2 h, cold-rolled to a thickness of ~ 1.5 mm, a reduction of $\sim 90\%$, solution treated at 1000 °C for 30 min and water-quenched. The material was encapsulated in an argon atmosphere for all heat treatments; ii) the Gum metal ingot was prepared from pure elements by plasma arc melting at the University of Birmingham, then homogenized at 1000 °C for 4 h and hot-rolled to plate at Timet (Henderson, NV). Following hot-rolling, it was cold-rolled to 3 mm sheet. The final heat treatment steps were: (i) Ti-7Mo + 300 °C/1 h; (ii) Ti-7Mo + 300 °C/4 h; (iii) Gum metal + 300 °C/4 h; (iv) Gum metal + 300 °C/8 h; with air cooling.

Room temperature pin-hole SANS was performed on 1 – 2 mm thick square samples of each heat treatment at the High-flux Advanced Neutron Application Reactor (HANARO) multi-purpose research reactor 18m SANS instrument, South Korea. The procedure is similar to previously described SANS measurements [6, 7], with a mechanical velocity selector defining the incident neutron wavelength $\lambda = 4.82$ Å and 9.57 Å for high $\mathbf{Q}$ and low $\mathbf{Q}$ vectors respectively with a 10% spread. The SANS raw data was corrected for transmissions, backgrounds, dark current background in the detector and detector efficiency variation, and reduced to absolute scattering probabilities $\partial\Sigma(Q)/\partial\Omega$ using a standard glassy carbon sample [22].

XRD was performed on the SANS samples following SANS experimentation, using a Rigaku Ultima IV with Cu-K α X-ray radiation at 40kV and 20mA. Data were collected over a range of 20 - 100° 2θ , and phase identification was performed using CrystalDiffract software.

SAXS samples were prepared from the SANS samples,

Table 1: Bulk compositions of the β -Ti alloys were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) and LECO analyses. The key element compositions are given in wt.%, and converted to at.% assuming the bulk is bcc β structure. The neutron and X-ray scattering lengths (ρ_N and ρ_X respectively) of each element are also given. Key parameters for treating small angle scattering in Gum metal as equivalent to that from a Ti-Nb binary system are highlighted in red, to aid the explanation provided in the text.

Nomenclature		wt.%	at.%	$\rho_N \times 10^{-5}$ Å [21]	$\rho_X \times 10^{-4}$ Å
Ti-7Mo	Ti	86.63	92.7	-3.4	6.2
	Mo	13.3	7.1	6.7	11.2
	O	0.07	0.2	5.8	2.3
Gum metal	Ti	62.0	75.7	-3.4	6.2
	Nb	32.7	20.6	7.1	11.6
	Zr	3.1	2.0	7.2	11.3
	Ta	1.9	0.6	6.9	20.6
	O	0.3	1.1	5.8	2.3

by grinding to a thickness $t < 100\mu\text{m}$. The SAXS instrument at Hokkaido University along with methodology have been previously described [3]. Two sample-to-detector distances were used (1360 mm and 360 mm), probing a Q-region of about $0.2 - 10 \text{ nm}^{-1}$, all within vacuum at room temperature. Reduction to absolute scattering probabilities $\partial\Sigma(Q)/\partial\Omega$ was performed in a similar manner to SANS, using a glassy carbon sample as standard [22] and data processing with the Nika software package [23].

Room temperature XRD patterns of each alloy heat treatment are presented in Figure 1 a) and c). The α'' and ω peaks of Ti-7Mo at.% were identified from the lattice parameters of Blackburn [24] and of Jamieson [25] respectively. The peak locations of bcc β phase are easily identified. Given the extent of overlapping peaks of the metastable and stable phases in these alloys, phase identification can be difficult. On quenching Ti-7Mo at.% (Figure 1a, 0 h heat treatment), the β phase is retained, and both athermal ω and martensitic α'' phase transformations have occurred. Extensive isothermal ω precipitation occurs on ageing, observed as the relative increase in intensity of the ω (110), (111), (002) and (112) peaks. 300 °C is above the martensite start temperature [26], therefore it would re-precipitate as a diffusionless process on re-cooling back to room-temperature after each heat-treatment (and be observed in the room-temperature diffraction pattern). The lower intensity of the α'' peaks following the aging heat-treatments relative to the initial quenched diffraction pattern may be associated with the precipitation of isothermal ω limiting the precipitation of the α'' phase [3]. As α'' precipitation is a diffusionless process, there is no compositional contrast between α'' precipitates and matrix. Therefore the presence of α'' does not contribute to a small angle scattering pattern and does not complicate the data analysis. There is also no indication of α formation from laboratory-XRD. The laboratory-XRD results are in agreement to the synchrotron-XRD results of Joris [27] on the same alloy at room-temperature in (i) a quenched condition and (ii) a 300 °C/16 h heat-treated condition. The initial quenched microstructure is composed of athermal ω

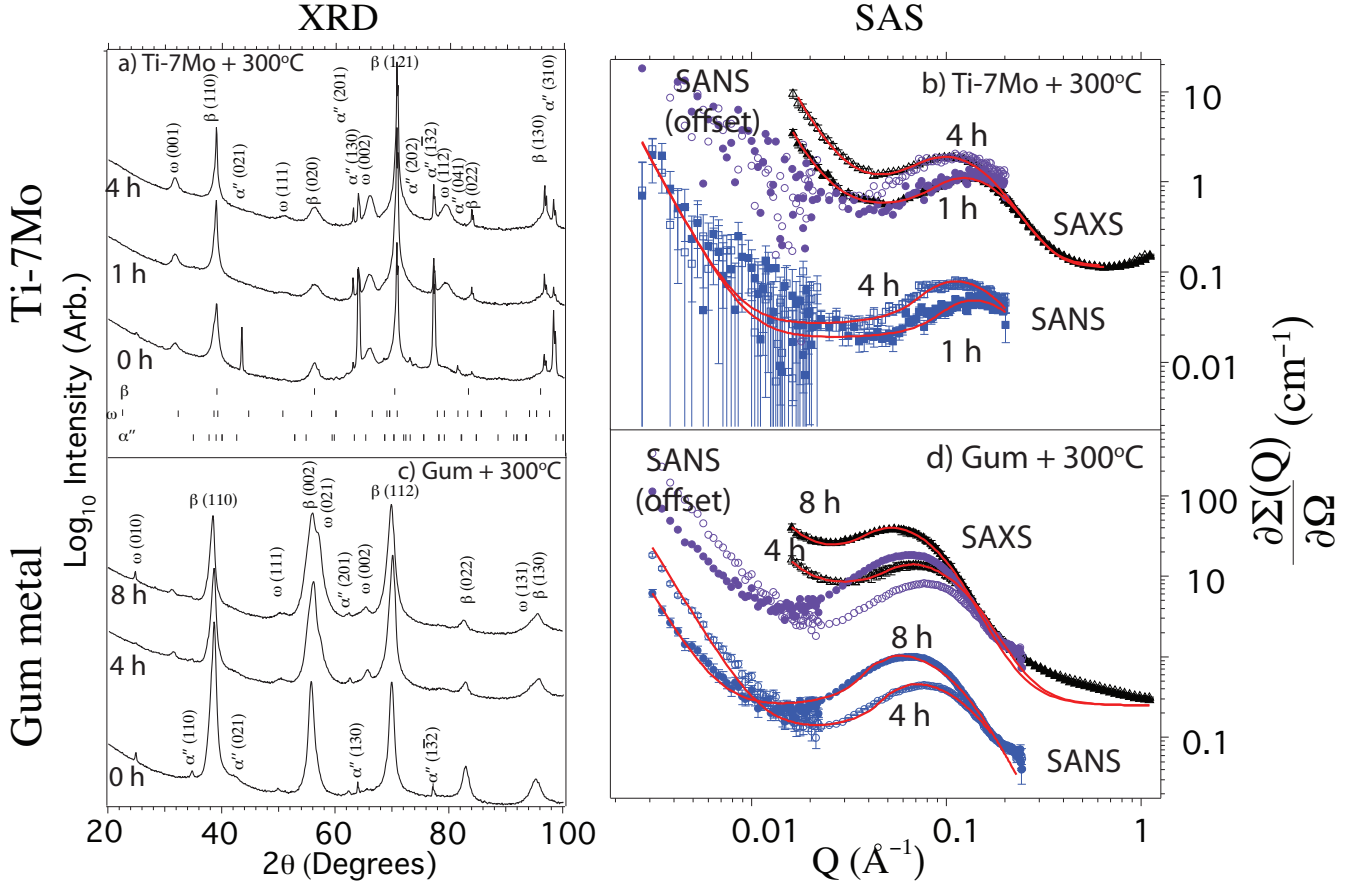


Figure 1: Room temperature laboratory XRD profiles for a) Ti-7Mo at.% and c) Gum metal in the initial and 300 °C aged conditions. b), d) Corresponding SAXS and SANS curves with model fits. b) and d) show the higher intensity SAXS curves, lower intensity SANS curves, model fits to both the SAXS and SANS data, and also the SANS curves scaled (offset) to a higher intensity by a calculated ratio of X-ray/neutron scattering length density contrasts between the scattering precipitate and matrix phases.

and α'' , and the heat-treatment precipitates isothermal ω α'' is observed in both XRD patterns as the measurements are below the martensite start temperature, phases other than isothermal ω and the martensite are not observed.

The α'' and ω diffraction peaks of Gum metal (Figure 1c) were identified from the lattice parameters of Talling [28] and Jamieson [25] respectively. It appears that at room temperature ω is initially present in the cold-rolled (0h) material, observed at the (111) and (002) reflections. α'' is present, deduced from the reflections labelled as (021) and (132). Further ω precipitation occurs during ageing, identified by the appearance of the (001) and (131) peaks and more intense (002) and (111) reflections. Similarly to the Ti-7Mo at.% diffraction patterns described above, 300 °C is expected to be above the martensite start temperature of this alloy [29]. Following the thermal hold the α'' reprecipitates on cooling by a diffusionless process, and again does not contribute to SAXS patterns. The intensity of the α'' peaks are lower following aging, as previously mentioned for Ti-7Mo at.%. There is no indication of α formation from XRD.

The presence of metastable isothermal orthorhombic phases in five alloys has recently been suggested: Ti-5Al-

5Mo-3Cr wt.% (Ti-5553) [30, 31], Ti-5Al-2Sn-2Zr-4Mo-4Cr wt.% (Ti-17) [31], Ti-5Al-5Mo-5V-1Fe-1Cr wt.% (VT22) [32], Ti-2Al-7Mo-5Fe wt.% (TIMETAL-LCB) [32], and Ti-19Nb-2Mo-4Zr-8Sn wt.% [33]. Aeby-Gautier *et al.* [31] tentatively suggest that such a phase may be related to a slight enrichment in oxygen, while Ivasishin *et al.* [32] suggested that it may be related to internal strains and that it decomposes on further aging. The current authors also identified an orthorhombic α'' phase that decomposes on aging in Ti-24Nb-4Zr-8Sn wt.% (Ti-2448). Associating the observed small angle scattering as the scattering arising from the isothermal ω phase alone is reasonable in this work (and in agreement with the literature [3, 6, 7]) as: (i) it is well known that isothermal ω precipitates form by diffusion and there is a compositional contrast between the isothermal ω precipitates and matrix [7, 16]; (ii) the peak positions of the α'' phases do not alter in 2θ with aging time, which would be one indication of a compositional change of the α'' phase related to the heat-treatment. It is reasonable to conclude that the α'' phase observed in the XRD profiles are formed by a diffusionless process as the alloy is cooled from the aging temperature, and thus has the same composition as the matrix and

would not be observed by SAXS; (iii) the literature does not suggest that isothermal orthorhombic phases form in the two alloys studied under the heat-treatment conditions employed; and finally (iv) in the alloys where isothermal orthorhombic phases do form, the literature does not suggest that these form with a compositional change required such that they would contribute significantly to a SAXS pattern.

The comparison of SAXS and SANS data is particularly useful for the analysis of element partitioning between phases during ageing [35]. The probability of small angle scattering from uniform monodisperse particles is

$$\frac{\partial \Sigma(Q)}{\partial \Omega} = NV^2(\Delta\rho)^2 P(Q) \quad (1)$$

where N is the number of particles per unit volume, V is the volume of one particle, and $P(Q)$ is the particle form factor or shape function. $\Delta\rho = \rho_{\text{ppt}} - \rho_{\text{matrix}}$ is the neutron or X-ray scattering length density difference between the particle and its matrix. The scattering length density of phase x is

$$\rho_x = (\rho_{\text{mass}} N_A / M_r) \sum n_i b_i \quad (2)$$

where ρ_{mass} is the phase mass density, N_A is Avogadro's number, M_r is the molecular weight of the phase, n_i is the atomic fraction of element i in the phase, and b_i is that element's associated neutron or X-ray scattering length. Analysis of Eqn. 1 illustrates that any difference in $\partial \Sigma(Q) / \partial \Omega$ between SAXS and SANS curves of identical samples is due to the difference in $\Delta\rho$ values produced from X-rays and neutrons, as the other parameters are material properties that are independent of analysis technique.

$$\frac{(\partial \Sigma(Q) / \partial \Omega)_{\text{SAXS}}}{(\partial \Sigma(Q) / \partial \Omega)_{\text{SANS}}} = \frac{(\Delta\rho)_{\text{SAXS}}^2}{(\Delta\rho)_{\text{SANS}}^2} \quad (3)$$

Unlike X-rays where scattering lengths are proportional to atomic number, neutron scattering lengths vary across the periodic table [21]. Referring to Eqn. 2, any difference in $\Delta\rho$ value between SANS and SAXS is due to the differences in the elements neutron and X-ray scattering lengths n_i , therefore element partitioning can be identified from the comparison of SANS and SAXS spectra.

APT has shown that: (i) Ti strongly partitions to the isothermal ω phase in binary Ti-10Mo at.% [18], Ti-5Al-5Mo-5V-3Cr-0.3Fe wt.% (Ti-5553) [7, 16], and Ti-24Nb-4Zr-8Sn wt.% (Ti-2448) [20]. The ω precipitate composition in these three alloys is $\sim 95\text{Ti}$ at.%, and depleted in all solute additions. Thus, it is assumed that the ω precipitates in Gum metal are also enriched in Ti and depleted in all solute additions. With this assumption based upon APT, and referring to the composition of Gum metal (Ti + Nb = 95 at.%) and the similar scattering lengths of the solute additions (Table 1), it is reasonable to treat the small angle scattering from the Gum metal as a Ti-Nb binary system with Ti rich precipitates.

The scattering profile observed (Figure 1b and d) can arise from a core-shell-matrix structure [36]. Reasonable

fits to the data were obtained with a core-shell model [37] applied in IRENA software package [38]. However the precipitate volume fraction from this model were an order of magnitude lower than that observed in APT data [7, 18]. The fits were improved using a spherical particle small angle scattering model with hard sphere structure factor [39]. A structure factor accounts for interparticle scattering effects arising from reasonably high volume fractions, as is the case in these alloys [7, 18]. The full model accounts for (i) Porod scattering aQ^{-4} , (ii) a form factor of spheres, (iii) a hard sphere structure factor, and (iv) a flat background to account for incoherent scattering. The fitting parameters are: (i) precipitate volume fraction; (ii) precipitate radius; (iii) standard deviation using a log-normal distribution; (iv) scattering contrast; (v) the parameter a for Porod scattering; (vi) the structure factor hard sphere volume fraction; and (vii) hard sphere radius.

In this case of a binary alloy with hexagonal ω precipitates and bcc β matrix, the atomic packing factors are similar, so the scattering length density contrast $(\Delta\rho)^2$ is dependent only on the magnitude of $\Delta\text{Ti}_{\text{ppt - matrix}}$, irrespective of how this partitioning occurs.

The SAXS data was first fitted, Figure 1b and d. The value of $\Delta\text{Ti}_{\text{ppt - matrix}}$ was iteratively increased from zero, and ω volume fraction calculated for each iteration. As it is a two phase system, the lever rule was applied for each iteration: $\text{Ti}_{\text{error}} = \text{Ti}_{\text{bulk}} - [\text{Ti}_{\text{ppt}} V_f + \text{Ti}_{\text{matrix}} (1 - V_f)]$. This methodology allowed for the partitioning of Ti to be determined to within 1 at.%, Table 2, with a corresponding precipitate volume fraction. The same model was then used to fit the SANS data, constraining (i) the neutron scattering length density contrast as that arising from the Ti partitioning determined by SAXS, and (ii) the structure factor fitting parameters to be equal to those determined by SAXS. The particle radius, the standard deviation of the radius, Porod fitting parameter a , and background were unconstrained.

In all cases, the ω volume fraction determined by SANS is slightly lower than that from SAXS, so the volume fraction lies within the range of SAXS and SANS values, *e.g.* Ti-7Mo at.% 1 h age, $V_f = 34.5 \pm 5.5\%$. The parameters of note in Table 2 are: (i) the ω precipitate size is constant at ~ 2 nm mean diameter during the heat treatment of Ti-7Mo at.%, while the volume fraction increases by $\sim 6\%$, therefore there is an increase in number density; (ii) the Gum metal ω precipitate size coarsens, while the volume fraction only increases marginally. This indicates that after 4 h heat treatment, Ti-Mo is still in a nucleation regime, while Gum metal (Ti-Nb), has entered the coarsening regime. The faster kinetics of Ti-Nb are presumably due to the faster diffusion of Nb than Mo in Ti [40].

A sub-nanometer size distribution of particles exist in the Gum metal that has not been fitted at high Q , Figure 1d. Also, the extent of Ti partitioning between precipitate and matrix in Gum metal is large $\Delta\text{Ti}_{\text{ppt - matrix}} \sim 30\%$, and the precipitate volume fraction is high (Table 2). A significant depletion of Ti in the β phase is required for

Table 2: SAS Model Results from fitting of Ti-7Mo at.% and Gum metal data. As discussed in the main text, the Ti partitioning between precipitate and matrix $\Delta\text{Ti}_{(\text{ppt-matrix})}$ and precipitate volume fraction V_f are iteratively calculated from the lever rule. The bulk Ti composition from the lever rule is presented, along with that experimentally measured by ICP-OES and LECO analyses. The sphere mean radius ($\bar{R}$), standard deviation (std. dev.) of the radius, and Porod scattering parameter a are shown.

Alloy	Method	HT time (h)	$\Delta\text{Ti}_{(\text{ppt-matrix})}$ at. %	$(\Delta\rho)^2 \times 10^{20} \text{ cm}^{-4}$	V_f %	Ti _{bulk} at. %	$\bar{R}$ nm	std. dev.	a
Ti-7Mo	SAXS	1	10.5 - 11.5	9.9 - 12.2	36 - 29	93.2 - 91.8 (92.7)	1.1 $\pm$ 0.1	0.34	1.99×10^{-8}
	SANS	1		0.40 - 0.46	40 - 35	93.3 - 92.5 (92.7)	1.0 $\pm$ 0.1	0.36	3.52×10^{-10}
Ti-7Mo	SAXS	4	10.5 - 11.5	9.9 - 12.2	43 - 35	94.0 - 92.5 (92.7)	1.2 $\pm$ 0.1	0.39	6.59×10^{-8}
	SANS	4		0.40 - 0.46	48 - 40	94.5 - 93.1 (92.7)	1.1 $\pm$ 0.1	0.38	3.43×10^{-10}
Gum	SAXS	4	30 - 31	59 - 64	22 - 20	76.6 - 75.2 (75.7)	2.1 $\pm$ 0.2	1.06	9.04×10^{-9}
	SANS	4		3.31 - 3.51	17 - 16	75.1 - 74.0 (75.7)	1.6 $\pm$ 0.2	0.45	5.97×10^{-10}
Gum	SAXS	8	31 - 32	64 - 69	23 - 22	76.1 - 75.8 (75.7)	2.8 $\pm$ 0.3	1.09	2.18×10^{-8}
	SANS	8		3.51 - 3.73	22 - 18	75.2 - 74.6 (75.7)	1.9 $\pm$ 0.2	0.46	1.30×10^{-10}

this to occur.

The SANS and SAXS data are fitted by the same model, with similar microstructural parameters determined. As mentioned in Eqn. 3, the SAXS/SANS intensity ratio is equal to the SAXS/SANS scattering length density contrast ratio, and is therefore a microstructural parameter. The ratio of $(\Delta\rho)_{\text{SAXS}}^2/(\Delta\rho)_{\text{SANS}}^2$ is calculated from Table 2 as ~ 24.75 for Gum metal, and ~ 18.25 for Ti-7Mo at.%. The SANS data is scaled by this ratio and replotted as the offset SANS data in Figure 1b and d. At high Q the curves overlay precisely. The difference between SAXS and offset SANS curves at low Q is attributed to the Porod fitting parameter a , Table 2. The low Q scattering arises from particles >200 nm, possibly corresponding to α'' based on the sharp XRD peaks (Figure 2a and c), a much larger size than the ω phase, and with different $\Delta\rho^2$ values.

In conclusion, (i) SAS quantifies precipitation in Ti-7Mo at.% and Gum metal, a Ti-Nb based alloy. (ii) In Ti-7Mo at.% the precipitate size is unchanged during heat treatment up to 4 h, while volume fraction increases, i.e. an increase in number density. (iii) Gum metal has entered a coarsening regime after 4 h heat treatment. Nb, compared to Mo, is a relatively fast diffuser in Ti [40]. Therefore, (iv) Mo-based β -Ti alloys will be more stable during ω ageing than Nb-based alloys. (v) To the authors' knowledge, this represents the first publication quantifying nanoscale precipitation in Gum metal, with $\sim 20\%$ ω volume fraction present after 4 - 8 h heat treatment at 300 °C.

Acknowledgements

The authors acknowledge support from the European Union Seventh Framework Programme under the Marie Curie grant agreement number 628643, the Japanese Society for the Promotion of Science (JSPS), The Great Britain Sasakawa Foundation, and EPSRC under grant EP/H0004882/01. This work made use of the J.B. Cohen X-ray Diffraction Facility at the Materials Research Center of Northwestern University supported by the National Science Foundation MRSEC program (DMR-1121262). The authors' thank Oliver Joris of Imperial College London and Timet for sample preparation, Shigeharu Ukai for the use of the Advanced High Temperature Laboratory at Hokkaido University, and HANARO for the SANS beam-time.

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