# The effect of athermal omega on the transformation behaviour of Ti-24Nb-4Zr-8Sn (wt%)

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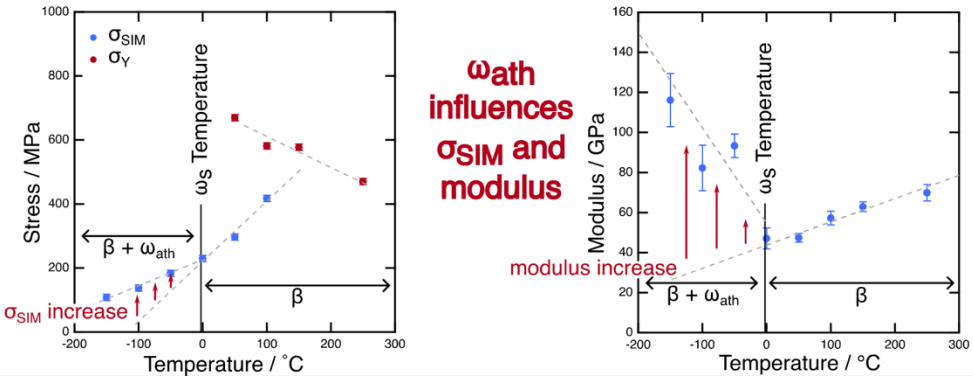
## Graphical Abstract




## Abstract

Ti-Nb based alloys are candidate materials for orthopaedic and orthodontic applications due to a low elastic modulus and superelastic properties. However, many of these alloys are also susceptible to a transformation to the hexagonal ω phase. When ω is formed isothermally it can stiffen and embrittle the alloy, however, there is a limited understanding of the role it plays when formed athermally on cooling, with many conflicting statements made within the literature. As such, this study assesses the role of athermally formed ω on the superelastic behaviour and elastic modulus of the exemplar superelastic alloy, Ti-24Nb-4Zr-8Sn. It was found that the ω phase raised the modulus and the stress required for superelastic behaviour. This highlights the need to design alloys resistant to both forms of the ω phase, for low modulus superelastic alloys to be produced.

Metastable β Ti alloys have received considerable attention for use as orthopaedic and orthodontic implant materials due to their excellent biocompatibility, intrinsic corrosion resistance, low elastic modulus and an ability to display superelastic properties [1–3]. The superelastic transformation from the bcc β phase to the orthorhombic α" martensite relies on suppressing the formation of the thermodynamically stable hcp α phase. This results in a β phase that is metastable at the testing temperature such that the alloy is susceptible to the shear transformation to the α" martensite [4,5]. However, this metastability means these materials are also vulnerable to the formation of the hexagonal ω phase, which can increase the material stiffness and influence the transformation behaviour [6,7].

The ω phase can exist in one of two forms, which are crystallographically identical but compositionally distinct, and can be distinguished based on their formation mechanism [8]. Isothermal ω ($\omega_{iso}$) typically forms at intermediate temperatures between ~ 100-500˚C depending on the alloy composition [9]. This form of ω relies on atomic rearrangement and results in a Ti rich precipitate within the β matrix [10]. It is commonly reported that $\omega_{iso}$ is highly detrimental to mechanical behaviour, embrittling and stiffening the alloy [6,10,11], and preventing a transformation to α" [12].

The other form of the ω phase, athermal ω ($\omega_{ath}$), forms without diffusion on cooling from elevated temperatures. This can occur by one of two mechanisms; either via the "frozen phonon" mechanism when cooling rapidly from the β phase field [13], or when cooling below a well-defined temperature, the ω start temperature ($\omega_s$) [14]. $\omega_{ath}$ is therefore present in many metastable β Ti alloys following solution heat treatment.

Despite its prevalence, the effect of $\omega_{ath}$ on the mechanical behaviour of metastable β Ti alloys is poorly understood. Studies comparing the role of $\omega_{ath}$ and $\omega_{iso}$ have highlighted significant differences between their effect on mechanical behaviour [15]. However, within the literature this distinction sometimes unclear, with the negative implications of the two types often considered to be equal in magnitude. Possibly because of this,

many design criteria for low modulus structures highlight the importance of suppressing the $\omega_{ath}$ phase on cooling to achieve low stiffnesses [16,17] and better match the mechanical properties of bone. Furthermore, some of the lowest modulus alloys that have been produced contain elements such as Sn, which are thought to aid in the suppression of the ω phase [16,18,19]. Despite this, other studies have suggested that $\omega_{ath}$ has only a limited effect on the alloy stiffness [6].

The effect of $\omega_{ath}$ on the superelastic transformation to α″ is equally unclear. Some studies report that $\omega_{ath}$ competes with α″ on cooling with one forming to the exclusion of the other [9,20]. $\omega_{ath}$ has also been suggested to suppress the martensitic transformation during subsequent mechanical deformation [21]. In contrast, other reports suggest that $\omega_{ath}$ does not prevent a β to α″ transformation and instead α″ can consume the $\omega_{ath}$ phase as the α″ lath extends into the β grain [22,23]. Furthermore, studies on alloys containing $\omega_{ath}$ have demonstrated that both thermally and mechanically induced martensitic transformations are possible [14,24–26], and both α″ and $\omega_{ath}$ can form concomitantly on cooling [27].

However, the extent to which $\omega_{ath}$ may influence the β to α″ transformation remains unclear. For example, whilst it has been suggested that $\omega_{ath}$ does not prevent α″ formation, its presence may still influence the stress or temperature at which α″ can form [28]. In that study, the critical stress required to exhibit non-linear behaviour ($\sigma_{SIM}$) was measured and seen to decrease linearly as a function of temperature, consistent with the Clausius-Clapeyron relationship [29,30]:

$$\frac{d\sigma_{SIM}}{dT} = \frac{dS\,\rho}{d\varepsilon}$$

Where $d\sigma_{SIM}$ is the change in transformation stress with a change in temperature, $dT$. $dS$ is the entropy change between the β and martensite structures, $\rho$ is the density of the alloy and $d\varepsilon$ is the transformation strain between β and α″.

However, below a certain temperature, the trend changed and the stress required to transform to α″ increased. However, the presence of ω was assessed via laboratory-based diffraction techniques where the detection of ω necessitates its presence in larger volume fractions than may be expected in many Ti-Nb based alloys. Furthermore, other mechanisms such as detwinning of α″ would also be expected to result in an, albeit small, increase in the stress required for non-linear behaviour as temperature is reduced, with many of the compositions in the study reported to exhibit shape memory behaviour.

Despite this, studies on Ti-Nb based alloys with higher β phase stability also display similar trends in behaviour, for example, in the Ti-Nb-Ta system [31]. The temperature at which the deviation from the Clausius-Clapeyron relationship occurred was lower for alloys with a higher β phase stability. However, ω was reportedly present in TEM diffraction patterns at temperatures greater than those at which this change in gradient was observed, suggesting the cause of this response may be the result of a different underlying mechanism.

Other studies considering a systematic variation in alloy composition have also identified changes in the trend of $M_s$ temperature between alloys containing $\omega_{ath}$, and those without $\omega_{ath}$, similarly suggesting a deviation from the Clausius-Clapeyron relationship [32,33]. However, the presence of ω was again identified via laboratory-based techniques, necessitating larger volume fractions of ω. Furthermore, the variation in composition would also be expected to influence other aspects of the transformation, and therefore similarly be expected to influence the Clausius-Clapeyron relationship. Firstly, it may influence the heat treatment, and generation of residual stresses on cooling, both of which have been shown to be important parameters affecting the $M_s$ temperature [24,34]. Secondly, a change in composition would influence the entropy of transformation from the β to α″ phases, and has been shown in numerous studies to significantly influence the transformation strain from β to α″ [35–37].

Understanding the role of $\omega_{ath}$ on the transformation behaviour is challenging as $\omega_{ath}$ in most superelastic materials is typically a nanoscale phase present in relatively low volume fractions within the microstructure [38,39]. This necessitates employing high energy diffraction techniques to study alloys containing the ω phase. Such techniques have the resolution to detect even small volume fractions of $\omega_{ath}$ within a sample and can facilitate an *in situ* assessment of the transformation behaviour [14,27,40].

This study therefore uses a combination of *in situ* and *ex situ* techniques to understand the effect of $\omega_{ath}$ on the mechanical behaviour of an exemplar commercial Ti-Nb based alloy, Ti2448 (Ti-24Nb-4Zr-8Sn, wt%), with a low susceptibility to the ω phase. This is achieved by investigating the mechanical response of the alloy across

a range of temperatures (from -150˚C to 250˚C), at some of which the $\omega_{ath}$ phase is present. Samples of a 2 mm thick commercially supplied plate of Ti2448 were rolled to 0.5 mm final thickness. Flat rectilinear dog-bone tensile samples with ~0.5 x 0.5 $mm^2$ gauge cross-section, and 14 mm gauge length were prepared by wire electro discharge machining (EDM) and then sealed in evacuated quartz ampoules with Ta foil as a getter for oxygen. Samples were then inserted into a pre-heated box furnace and solution heat treated at 900˚C for 5 min. The furnace temperature was calibrated to ± 1 °C with the use of an N-type thermocouple. Samples were subsequently quenched into ice water with the ampoule remaining intact.

*In situ* synchrotron X-ray diffraction (sXRD) data were acquired at the I12 beamline at Diamond Light Source in transmission Debye-Scherrer geometry. The X-ray energy (~ 80 keV) was calibrated with a NIST $CeO_2$ standard sample at multiple sample-to-detector distances. Diffraction data were acquired from tensile samples secured in negative impression grips in a Linkam TST350 using a 1 s exposure and a Pilatus 2D CdTe detector. Samples were heated or cooled within the test frame under an inert $N_2$ atmosphere at 25˚C $min^{-1}$, and then loaded at a cross-head displacement rate of 4 µm $s^{-1}$.

The $\omega_s$ temperature was determined by fitting a unique $\omega$ phase reflection with a gaussian in WaveMetrics Igor Pro 9 and monitoring the peak area as a function of temperature. $\omega_s$ was then taken as the temperature above which the $\omega$ phase reflection could no longer be discerned from the background. The critical stress required to form $\alpha''$ ($\sigma_{SIM}$) was determined from the *in situ* data by using the same methodology to fit an $\alpha''$ peak and identifying the stress at which the peak became discernible from the baseline. The errors in $\sigma_{SIM}$ were determined by considering the stress resolution of the diffraction data.

*Ex situ* digital image correlation (DIC) data were acquired using the same test frame and testing parameters. A 10 µm speckle pattern was applied to the gauge of each specimen using an Iwata CM-B airbrush. Images were acquired at a rate of 2 $s^{-1}$ during deformation using an LaVision Imager E-lite camera, with an exposure time of 1100 µs. These images were then analysed using DaVis software to obtain an average strain over the sample for each frame.

The modulus of each sample was determined by fitting a linear function to the initial portion of the stress-strain curve. *In situ* $\sigma_{SIM}$ values were considered in each case, to ensure that the modulus was only measured during the linear-elastic regime. $\sigma_{SIM}$ and $\sigma_Y$ were determined from the *ex situ* data by offsetting the linear fit and considering an intersection of this line with the data. The linear offsets used were 0.05 % strain for $\sigma_{SIM}$ and 0.2 % for $\sigma_Y$, with the latter consistent with proof stress calculations in ASTM E8 [41]. Errors in these measurements were obtained by considering the errors in the measurement of cross sectional area of each sample. Separate linear trend lines were fit to the data above and below $\omega_s$, by weighting each datapoint by its associated error bar.

To assess the initial condition of each sample, sXRD patterns were acquired at the test temperature of each sample, shown in Figure 1. At all temperatures, strong reflections consistent with the $\beta$ phase were present. At the lower test temperatures, a broad reflection consistent with the $\omega$ phase was also present. None of the

samples contained any evidence of the α" martensite, suggesting the $M_s$ temperature is below -150˚C. The two peaks indicated by the asterisk, present in all patterns, are known artefacts relating to the EDM process.

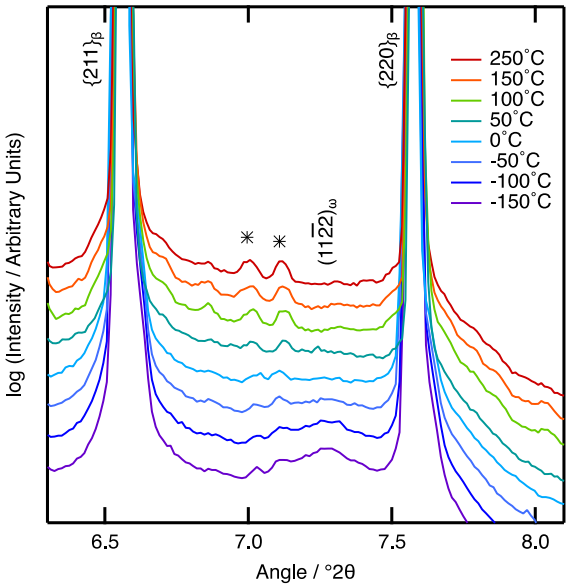



*Figure 1. sXRD diffraction patterns highlighting the phases present at the test temperature of each sample.*

To measure the $\omega_s$ temperature, the $(11\bar{2}2)_\omega$ reflection was monitored on cooling from 25 to -150˚C and the peak area taken as a proxy to volume fraction. The ω peak intensity was normalised to the value at -150˚C with these data given in Figure 2. The temperature at which the ω phase reflection could no longer be discerned from the baseline was taken as $\omega_s$, at ~ -2˚C. This demonstrated that samples tested at 0˚C and above contained solely the β phase, whereas samples tested at -50˚C and below, comprised a β + $\omega_{ath}$ structure.

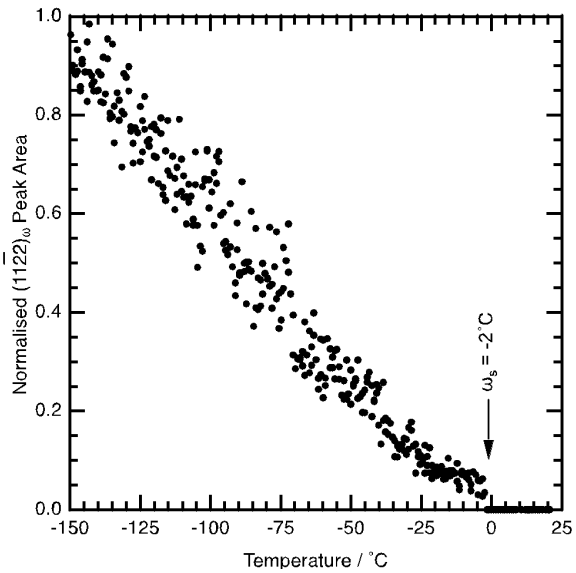



*Figure 2. Evolution of the $(11\bar{2}2)_\omega$ reflection on cooling the sample.*

The mechanical behaviour at each testing temperature was evaluated *ex situ* using DIC, with the corresponding σ-ε data shown in Figure 3. These tests were repeated *in situ* to provide information regarding the deformation processes occurring within the material. At temperatures of 250˚C and 150˚C, the sample initially deformed in a linear-elastic manner. Above ~ 400 and 600 MPa respectively, there was a significant deviation from linear behaviour, and a large accumulation of strain. There was no evidence of any transformation to α" within the diffraction data when tested at these temperatures, and hence, this deviation from linear behaviour corresponds to the onset of slip.

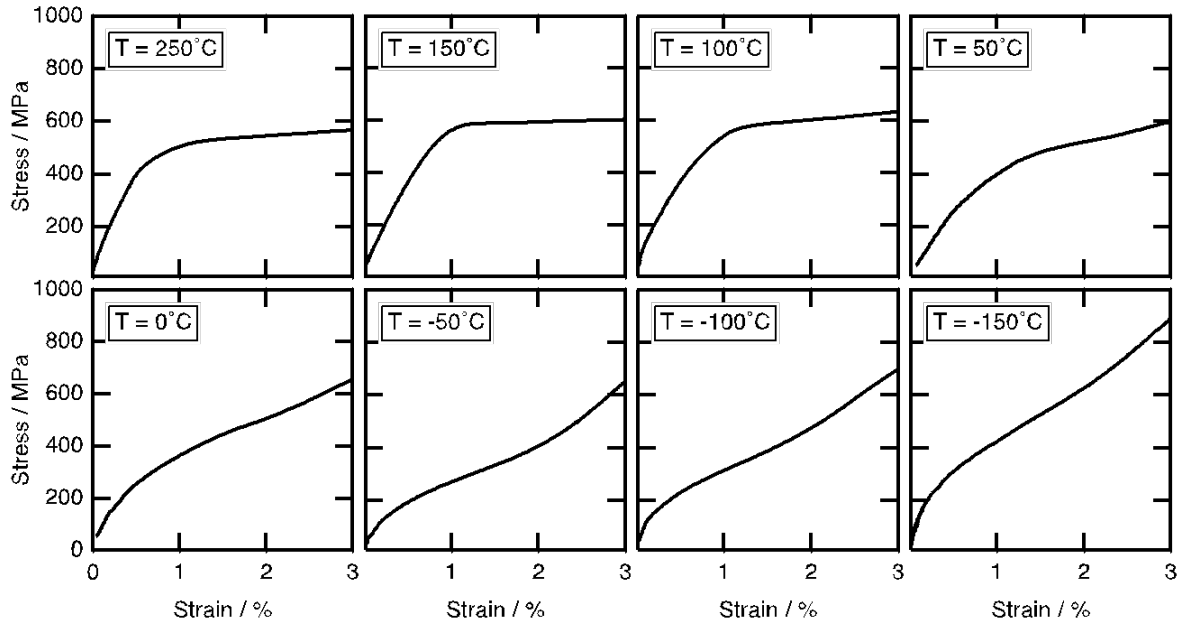



*Figure 3. Mechanical testing data of Ti2448 at different temperatures.*

At all other test temperatures, the samples initially deformed in a linear-elastic manner before some deviation from linear. This deviation coincided with the evolution of diffraction peaks corresponding to α", and hence is taken as $\sigma_{SIM}$. At higher stresses, there was a second decrease in gradient observed within the *ex situ* data consistent with slip.

The stresses at which these changes in gradient were observed are displayed graphically as a function of temperature in Figure 4. The $\sigma_{SIM}$ values from the *in situ* data were determined to be the stresses at which the first α" peak could be distinguished from the baseline. These data are also given in Figure 4.

The yield stress for the alloy was shown to decrease approximately linearly with an increase in test temperature, as expected. At test temperatures above $\omega_s$, the value of $\sigma_{SIM}$ increased linearly up to 100˚C, consistent with the Clausius-Clapeyron relationship. At higher test temperatures of 150˚C and 250˚C, there was no evidence of any stress induced transformation to α", in either the *in situ* or *ex situ* data. Due to the decrease in yield stress, and increase in $\sigma_{SIM}$ with temperature, this change in primary deformation mechanism can be readily understood. By extrapolating the gradient of $\sigma_{SIM}$ to higher temperatures, the value of $\sigma_{SIM}$ is estimated to exceed the yield stress at temperatures above ~150˚C. As such, the material will deform by conventional plastic flow above these temperatures with no formation of α".

Interestingly, at temperatures below $\omega_s$, the value of $\sigma_{SIM}$ also varied linearly, however at a shallower gradient. Previous studies on this alloy have shown that heating samples to elevated temperatures has resulted in increased values of $\sigma_{SIM}$ in subsequent room temperature mechanical tests [42]. Unfortunately, all samples tested above $\omega_s$ were heated to the test temperature, whereas all samples below $\omega_s$ were cooled to their test temperature. As such, it is unclear whether this change in gradient of $\sigma_{SIM}$ is a result of the ω transformation, or a function of heating the samples to elevated temperatures. Hence, an additional sample was first heated to 100˚C and then cooled and tested at 0˚C. If $\omega_{ath}$ were directly responsible for the change in gradient of $\sigma_{SIM}$, it would be expected that the value of $\sigma_{SIM}$ obtained would be unchanged with respect to the sample cooled directly to 0˚C. If, however, heating the sample was governing the change in response, it would be expected that the value of $\sigma_{SIM}$ would be elevated compared to the sample directly cooled to 0˚C. Here, the value of $\sigma_{SIM}$ for this test is also shown alongside the other data in Figure 4. $\sigma_{SIM}$ was shown to be the same (within error) of the value obtained without any prior heating step. This highlights that the change in gradient is related to the formation of $\omega_{ath}$.

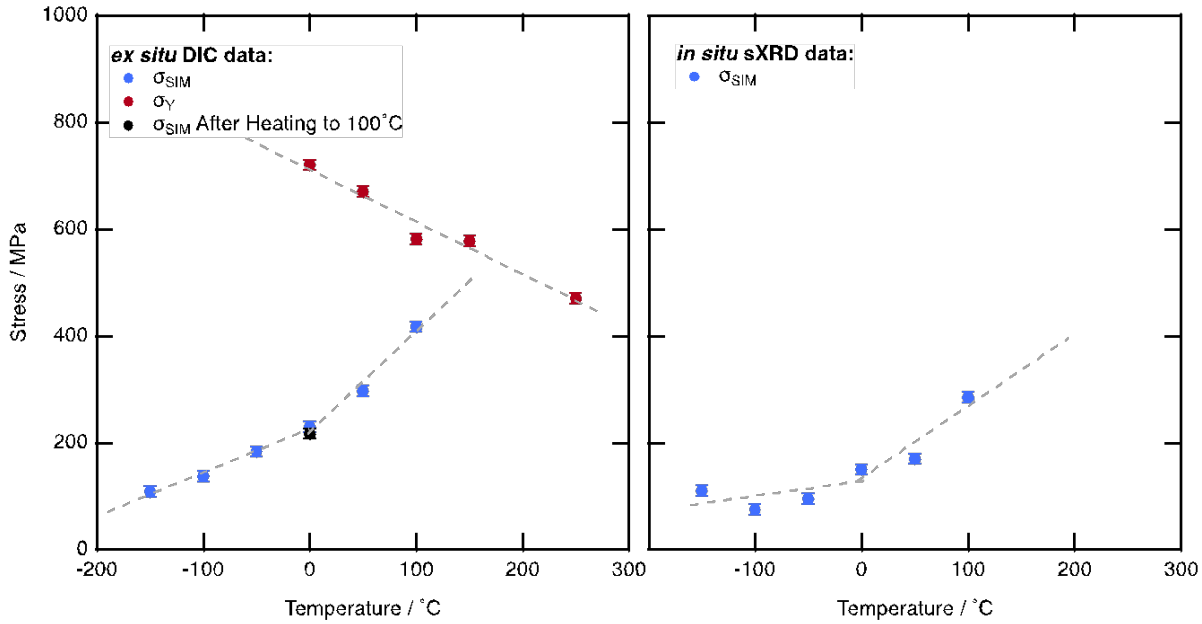



*Figure 4. In situ and ex situ values of $\sigma_{SIM}$ obtained at each test temperature. The ex situ data also contains measurements of the yield stress and the value of $\sigma_{SIM}$ at 0˚C following heating the sample to 100˚C.*

By extrapolating the higher temperature gradient to temperatures where $\omega_{ath}$ is present, the effect of $\omega_{ath}$ can be readily rationalised. Hence, whilst $\omega_{ath}$ does not prevent the transformation to $\alpha''$, $\omega_{ath}$ is acting to increase the stress required to transform to $\alpha''$. The effect on transformation stress is significant given the very low volume fractions of $\omega_{ath}$ present in the sample.

The Young's modulus values of the sample at each test temperature are shown in Figure 5. There is a minimum in the modulus around $\omega_s$. Above and below this value the modulus of the alloy increases. This increase is most dramatic for the test performed below $\omega_s$, highlighting the significant stiffening effect caused by $\omega_{ath}$ as its volume fraction increases. It has been reported that the stiffening effect of $\omega_{ath}$ can be explained by the subsequent diffusion of oxygen into the phase [43], resulting in a precipitate that more resembles $\omega_{iso}$. However, in the present study, the stiffness is greater at colder temperatures, where diffusion is significantly more limited. For elevated temperatures, the increase in modulus is not particularly pronounced, but may be related to an increase in stability of the parent $\beta$ phase, and hence a lower susceptibility to shear transformations. Previously, an increase in $\beta$ phase stability has been shown to result in an increase in the modulus, both for Ti2448 and other alloys [16,44].

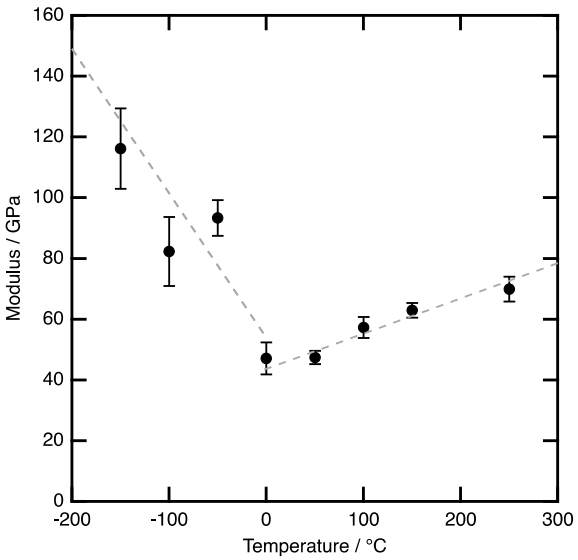



*Figure 5. Values of the modulus of each sample, tested at different temperatures.*

In summary, changes in mechanical behaviour of Ti2448 can be seen to directly correlate with the onset of $\omega_{ath}$ in this alloy. This includes both a significant stiffening of the alloy and an increase in the stress required to form $\alpha''$. Not only do these data rationalise some of the trends observed within the literature, but they also provide the first unambiguous experimental evidence, elucidating the role of small volume fractions of $\omega_{ath}$ on the mechanical response of Ti-Nb based alloys.

This observation has direct consequences for the development of new Ti-Nb biomedical alloys as it serves to highlight the critical need to avoid $\omega_{ath}$ formation, both to achieve low modulus structures, and to facilitate easy transformation to $\alpha''$.

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## Dataset DOI

The research data required to reproduce these findings are available from the University of Cambridge repository.

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## Credit

NL Church: Conceptualization; Methodology; Validation; Formal Analysis; Investigation; Writing – Original Draft; Visualisation. J.Y. Ang: Formal Analysis; Investigation. O.G. Reed: Methodology; Formal Analysis; Investigation. O.E. Gibson: Formal Analysis. NG Jones: Methodology; Investigation; Resources; Writing – Review & Editing; Supervision; Project Administration; Funding Acquisition.

## Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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