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ORIGINAL REPORT



# Achieving Elinvar effect over a wide temperature range in an additively manufactured titanium alloy

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## ABSTRACT

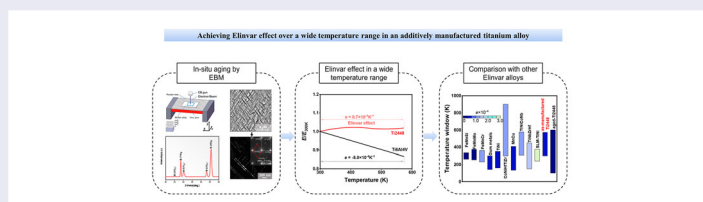
Temperature-insensitive elastic modulus known as Elinvar effect is typically achievable in metastable titanium alloys only through thermomechanical processing. Here reports that a directly additively manufactured TiNb-based alloy exhibits Elinvar effect over a wide temperature range of 273 K. This is attributed to its  $\alpha'' + \beta$  dual-phase microstructure wherein both the elastic modulus and transition strain of the  $\alpha''$  phase increase monotonically with increasing temperature. The  $\alpha''$  phase was obtained by setting a base-plate temperature of 723 K to act as in-situ aging. This provides a new way to optimize mechanical and functional properties simultaneously by utilizing thermal fields of additive manufacturing.

## ARTICLE HISTORY

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## KEYWORDS

Additive manufacturing; electron beam melting; TiNb-based alloy; Elinvar effect



## 1. Introduction

Materials with a temperature-insensitive elastic modulus, known as Elinvar effect, are indispensable in high-precision instrumentation [1,2]. This novel property can be achieved by compensating the inherent phonon vibrations and the consequent elastic softening via several reversible mechanisms [3–11]. For example, Elinvar effect can be achieved by spin-state transition in ferromagnetic Fe-based alloys via composition optimization [12–15], or by strain-glass transition in shape memory alloys via severe plastic deformation [16–23]. Recently, a novel mechanism has been pioneered in a metastable  $\beta$ -type titanium alloy with a composition of Ti–24Nb–4Zr–8Sn in weight percent (abbreviated as Ti2448), which enables the continuous tailoring of the temperature coefficient of elastic modulus ( $e$ ), from negative, to zero (exhibiting the Elinvar effect), and further to positive values [24–26]. This is realized through aging

treatments within the  $\alpha + \beta$  two-phase field to produce a  $\alpha'' + \beta$  dual-phase microstructure, wherein thermally induced modulus softening of  $\beta$  phase can be balanced by the modulus hardening of  $\alpha''$  phase [24–26]. As a result, a continuously tunable  $e$  can be realized by controlling over the volume fraction and transition strain of the  $\alpha''$  phase through tailored aging treatments [26].

Electron beam melting (EBM) is an advanced additive manufacturing (AM) technique, which melted metals layer-by-layer using a high energy electron beam under a vacuum environment [27,28]. During electron beam melting process, in-situ aging treatment can be realized through the synergistic thermal fields resulting from the preheating of both the base plate and powder bed [29]. This allows for the regulation of the microstructure of as-manufactured alloys for achieving excellent properties such as high strength and good ductility [30,31]. However, directly achieving Elinvar effect by AM is

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seldomly reported [10]. This is mainly attributed to the complex post treatments required to tailor the temperature coefficient of elastic modulus ( $e$ ) in these previously reported Elinvar alloys [22,23]. By contrast, drawing inspiration from the tunable  $e$  by a single-step aging treatment [25,26], it is appealing to explore the Elinvar effect directly by in-situ aging inherent from the EBM process. A novel strategy will be explored in this study, that is, utilizing both manufacturing and thermal fields to achieve Elinvar effect while maintaining good mechanical properties in as-manufactured alloy.

Here reports Elinvar effect across a wide temperature range of 273 K in an as-manufactured Ti2448 alloy by in-situ aging to produce a  $\alpha'' + \beta$  dual-phase microstructure. This was achieved directly by setting an initial base plate temperature of about 723 K during the EBM process, which is much lower than about 1000 K typically used to manufacture Ti-6Al-4 V alloy but higher than about 673 K used to manufacture single  $\beta$  phase Ti2448 alloy (Supplemental materials) [32–34]. The Elinvar effect is explained associated with the Nb-lean  $\alpha''$  phase, whose elastic modulus and transition strain increase with increasing temperature. Our results provide insights for achieving Elinvar effect directly by AM.

## 2. Materials and methods

An ingot of Ti2448 alloy, with a diameter of 380 mm, was fabricated through vacuum arc melting using a Ti–Sn master alloy, along with pure Ti, Nb, and Zr as raw materials. The ingot was hot-forged at 1123 K into round bars of 55 mm diameter. EBM powders with an average diameter of 73.6  $\mu\text{m}$  were produced using the electrode induction-melting inert gas atomization method with the hot-forged bars.

Cuboid block samples with a size of  $60 \times 10 \times 10 \text{ mm}^3$  were manufactured in a vacuum environment using a commercial Arcam A1 EBM machine. The beam speed was set at 1400 mm/s, beam current at 7 mA, and focus offset at 10. The manufacturing process commenced with a layer thickness of 70  $\mu\text{m}$ . To ensure uniformity, the hatch pattern was rotated by 90° between adjacent layers to homogenize temperature fields and alleviate residual stress (Figure 1(a)). The samples have a relative density of  $99.02 \pm 0.11\%$  measured by the Archimedes method [35]. The composition of both the powders and the samples after printing was analyzed according to the standard ASTM E2371-21a (Table 1). The decrease in Sn content after printing compared to the initial powders is attributed to the vaporization of Sn from the upper part of the melting pool due to the high energy density of the electron beam. Figure 1(b) shows the temperature profile of the as-manufactured alloy during EBM [36,37].

**Table 1.** Chemical composition of powder and printed samples (wt.%).

|                 | Ti   | Nb    | Zr    | Sn    | O    |
|-----------------|------|-------|-------|-------|------|
| Powders         | Bal. | 23.8% | 3.98% | 8.06% | 0.07 |
| Printed samples | Bal. | 23.8% | 4.00% | 7.96% | 0.09 |

After final solidification, the temperature oscillates significantly due to the melting of adjacent lines and layers. A near-constant building temperature is achieved after 10–20 layers, with this oscillation period lasting about 10 min. Subsequently, the temperature stabilizes to the base plate temperature, and the alloy undergoes in-situ aging. The preheating temperature of the base plate was set at 723 K in this study according to our previous investigations that the temperature coefficients of elastic modulus of Ti2448 alloy can be tuned continuously by aging treatment at 723 K [26].

The sample real image is shown in Figure 1(c). Samples were sliced parallel to the X-Y plane from center of the as-manufactured alloy (Figure 1(a)). Scanning electron microscopy (SEM) observation was conducted using a FEI Apreo microscope (Thermo Fisher, USA). Thickness and volume fraction of  $\alpha''$  phase were determined quantitatively using an image processing software ImageJ [38–40]. Transmission electron microscopy (TEM) analyses were performed with a FEI Tecnai F30 (Thermo Fisher, USA), equipped with a high-angle annular dark field (HAADF) detector. X-ray diffraction (XRD) with Bruker D8A (Bruker, German) spectra were measured under a slow scanning speed of 1 degree per minute with a wavelength of 0.15406 nm at 173, 298, and 573 K, respectively [41]. Tensile properties were measured using samples with a diameter of 3 mm and a gauge length of 20 mm by an Instron E10000 (Instron, USA) testing apparatus under a strain rate of  $2.5 \times 10^{-4} \text{ s}^{-1}$  at room temperature. The tensile strain was measured by a contact extensometer (Instron 2620-601). Storage modulus was measured between 300 and 573 K using a TA Q800 (TA, USA) dynamic mechanical analysis (DMA) under a double cantilever mode at a fixed strain of  $1 \times 10^{-4}$  with a frequency of 1 Hz and a heating rate of 3 K/min. Dynamic Young's modulus was measured by a resonance method using JE-RT apparatus (Nihon, Japan) at room temperature using samples with a size of  $58 \times 8 \times 1 \text{ mm}^3$ . Differential scanning calorimetry (DSC) was conducted using a TA Q20 (TA, USA) calorimeter with a cooling/heating rate of 10 K/min.

## 3. Results and discussion

XRD spectrum at room temperature (Figure 1(d)) reveals that the as-manufactured alloy has a dual-phase

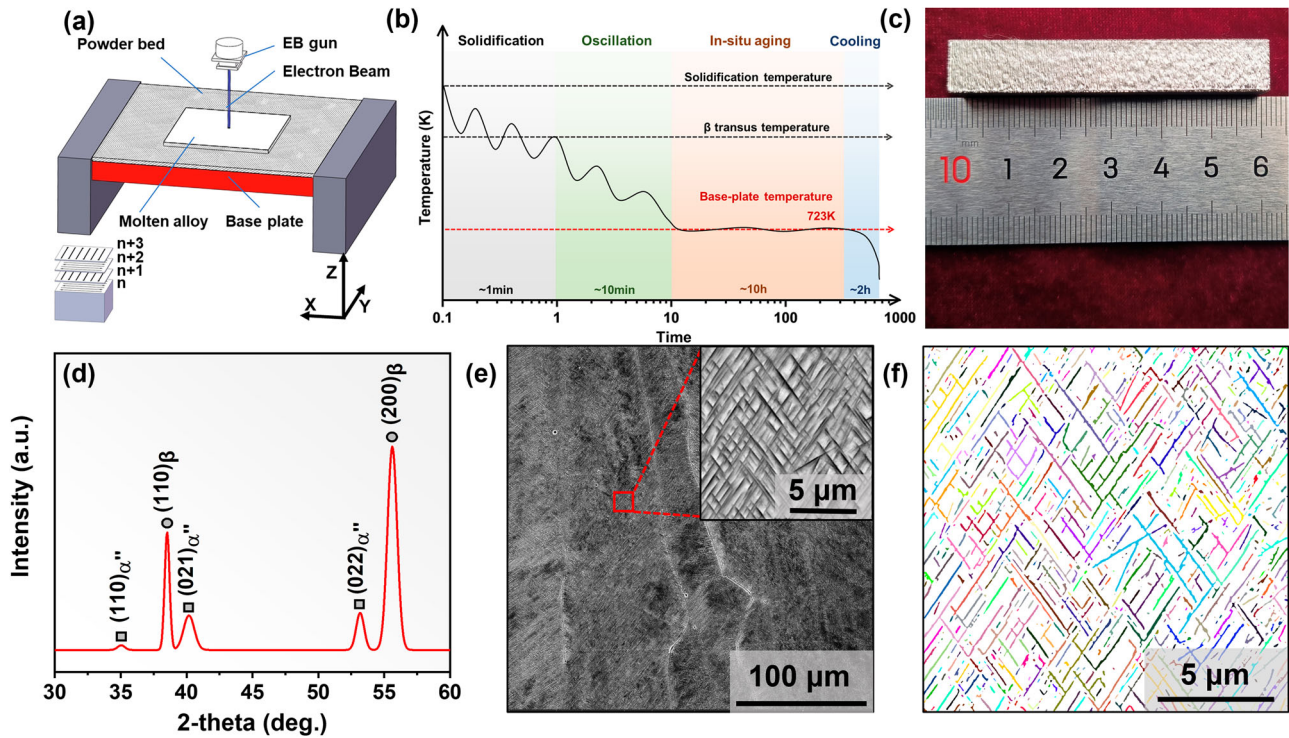


**Figure 1.** Dual-phase microstructure induced by in-situ aging treatment of EBM in Ti2448 alloy. (a) Schematic illustration of scanning strategies. (b) Schematic of the temperature evolution during EBM. (c) Real image of as-manufactured Ti2448 alloy. (d) XRD profile and (e) SEM microstructures of the as-manufactured alloy. (f) Processed image of the inset in (e) for quantitative analyses.

microstructure consisting of orthorhombic (orth)  $\alpha''$  phase and bcc  $\beta$  matrix phase with a strong  $\langle 100 \rangle$  orientation texture. SEM observations (Figure 1(e)) show a typical column-like grains along the building direction, which is attributed to the well-known strong thermal gradients generated by AM [42–46]. The enlarged section inserted in Figure 1(c) together with its processed image (Figure 1(f)) shows a densely distributed  $\alpha''$  phase with a plate-like morphology. Quantitative analysis in Figure 1(d) reveals that the  $\alpha''$  phase has a volume fraction of about 31 vol.%, which is close to that of the aged alloy ( $\sim 33$  vol.%) in previous studies that exhibits Elinvar effect [26].

In agreement with XRD and SEM analyses, the bright-field TEM image (Figure 2(a)) and dark-field TEM image of the as-manufactured alloy (Figure 2(b)) further reveal a  $\alpha'' + \beta$  dual-phase microstructure, wherein the plate-like  $\alpha''$  phase has a thickness of about 27 nm. Selected area electron diffraction (SAED) pattern (Figure 2(b)) shows an intersection angle  $\theta$  between the two (110) diagonals to be  $\sim 63^\circ$ , which further confirms the formation of orthorhombic symmetry  $\alpha''$  phase in the as-manufactured alloy [47,48]. The HAADF image (Figure 2(c)) shows that the dual-phase microstructure displays microscopic fluctuations in composition. Specifically, energy-dispersive X-ray spectrometry (EDS) line scan (Figure 2(d)) shows that the  $\alpha''$  phase is lean in Nb

whereas the  $\beta$  matrix phase is lean in Ti. High-resolution observation along the  $[100]$  direction (Figure 2(e)) and the corresponding inverse fast Fourier transform (IFFT) show the  $\alpha'' + \beta$  dual-phase microstructure with coherent/semi-congruent interfaces. These features agree with previous studies that this Nb-lean  $\alpha''$  phase is produced by a diffusional-displacive mechanism [47,49]. Because the temperature coefficient of elastic modulus ( $e$ ) can be tailored by the volume fraction of the  $\alpha''$  phase and its crystal parameters [25], it is feasible to achieve the Elinvar effect in the as-manufactured alloy without post treatments.

DMA measurement reveals that the Nb-lean  $\alpha''$  phase results in remarkable Elinvar effect in the as-manufactured alloy over a wide temperature range. As illustrated in Figure 3(a), the normalized storage modulus ( $E/E_{300K}$ ) of the as-manufactured alloy remains almost unchanged from 300 to 573 K, in sharp contrast to the conventional thermally induced modulus softening of Ti–6Al–4V alloy [50]. To quantitatively evaluate the Elinvar effect, the  $e$  was calculated from the measured normalized modulus-temperature curve as:

$$e = \frac{\Delta E}{\Delta T} \times \frac{1}{E_{300K}} \quad (1)$$

where  $E_{300K}$  is the modulus at 300 K and  $\Delta E$  is the modulus change in the corresponding temperature interval

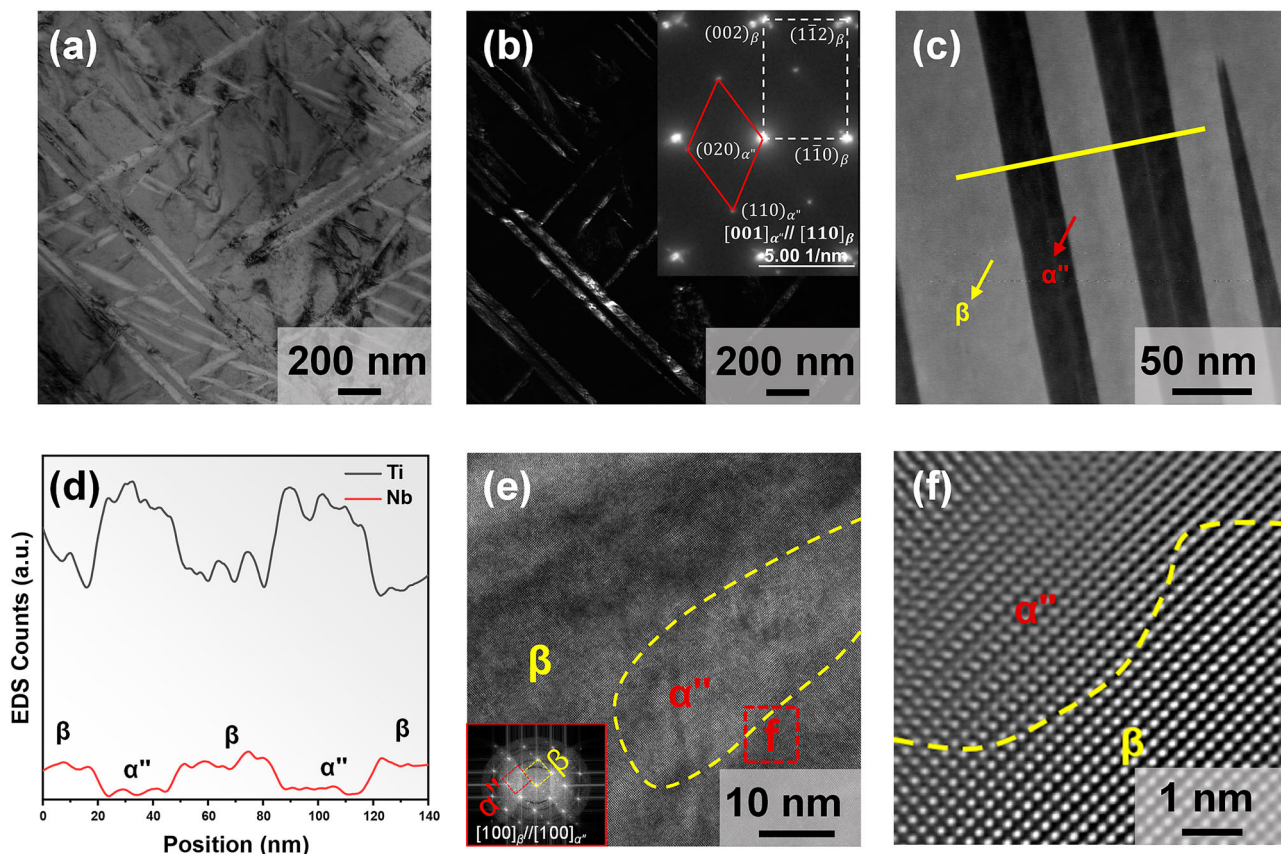


**Figure 2.** Plate-like Nb-modulated  $\beta + \alpha''$  dual-phase microstructure. TEM microstructures of the as-manufactured alloy. (a) bright-field and (b) dark-field TEM images (b) images of  $\beta + \alpha''$  dual-phase microstructure together with SAED patterns along  $[110]$  zone axis of  $\beta$  phase inserted in (b). EDS scanning across the plate-like  $\alpha''$  phase noted by yellow line in (c) and the corresponding Ti and Nb distributions (d). High resolution TEM microstructure of  $\beta/\alpha''$  interface (e) with FFT image along  $[100]$  zone axis of  $\beta$  phase inserted in (e) and its IFFT image (f) along  $[100]$  zone axis of  $\beta$  phase.

$\Delta T$ . To ensure validity, three samples were tested from 300 to 573 K, and an averaged  $e$  of about  $0.7 \times 10^{-4} \text{ K}^{-1}$  was obtained (Figure 3(a)), which satisfies the common definition of Elinvar effect that an absolute value of  $e$  should be less than  $1 \times 10^{-4} \text{ K}^{-1}$  [11]. In this scenario, our results confirm that Elinvar effect can be obtained in a broad temperature range of 300–573 K by electron beam melting without post treatments. In addition to the remarkable Elinvar effect, the as-manufactured alloy has a yield strength of 710 MPa, a tensile strength of 850 MPa and an elongation of 19% (Figure 3(b)). Because it has a dynamic Young's modulus of 61 GPa at room temperature, this results in a high yield strength-to-modulus ratio (elastic strain) of about 1.2% and a tensile strength-to-modulus ratio of about 1.4%. Both values are higher than conventional alloys [51,52].

Our results pioneer the fabrication of Elinvar titanium alloys using AM techniques without post-processing. On the one hand, the as-manufactured Ti2448 alloy has a low  $e$  comparable with other Elinvar alloys fabricated by conventional processing techniques (Figure 3(c)), which

ensures its stable elastic properties under temperature fluctuations. On the other hand, despite a narrower functional temperature range than aged Ti2448 alloy and  $\text{Co}_{25}\text{Ni}_{25}(\text{HfTiZr})_{50}$  alloy [4,25], it has a wider temperature window than conventionally fabricated Elinvar alloys such as ferromagnetic FeNi-based alloys (about 100 K) and anti-ferromagnetic FeMn-based alloys (about 50 K) (Figure 3(c)) [4,9,10,12–14,16–19]. Moreover, a recent study has reported the achievement of Elinvar effect in a layered-structured NiTi alloy by selective laser melting (SLM), which results in a  $e$  of about  $3 \times 10^{-4} \text{ K}^{-1}$  within a temperature window of about 130 K [10]. Notably, our results demonstrate that the  $e$  is smaller by  $\sim 77\%$  while its temperature window is wider by  $\sim 210\%$  compared with that of the SLMed NiTi alloy (Figure 3(c)), suggesting the in-situ aging of EBM is advantageous to obtain Elinvar effect. Because the processing parameters can be freely adjusted to tailor the microstructure, both the Elinvar temperature range and  $e$  can be further optimized by carefully regulating the volume fraction of the  $\alpha''$  phase together with its crystal parameters by

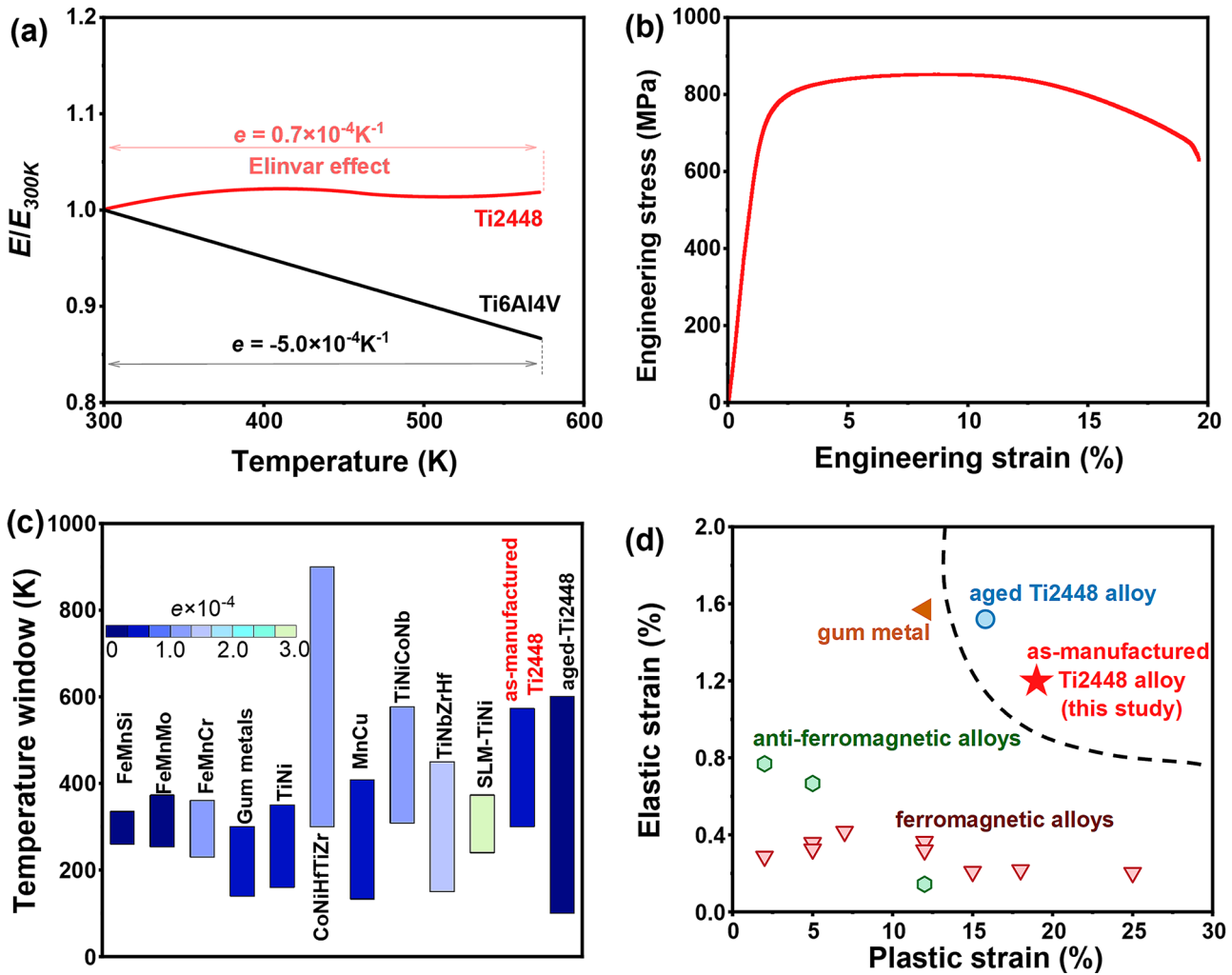


**Figure 3.** Integrated functional and structural properties in the as-manufactured Ti2448 alloy. (a) Normalized storage modulus,  $E/E_{300K}$ , of the as-manufactured Ti2448 alloy in comparison with that of a reference Ti-6Al-4V alloy. (b) Engineering tensile stress-strain curve of as-manufactured Ti2448 alloy. (c) Temperature range and  $e$  of the as-manufactured Ti2448 alloy in comparison with other Elinvar alloys. (d) the elastic strain with plastic strain of the as-manufactured Ti2448 alloy in comparison with other Elinvar alloys.

optimizing the processing parameters. In addition to the functionality, the as-manufactured alloy has also good mechanical properties, including high elastic strain (the yield strength-to-elastic modulus ratio) of 1.2% and good tensile elongation of  $\sim 19\%$  (Figure 3(d)). The combination of functional and mechanical properties makes the alloy highly desirable for advanced applications such as flexible skin of morphing aircraft [53,54].

Because the Elinvar effect is associated with the Nb-lean  $\alpha''$  phase in the as-manufactured alloy, its phase transition behavior was characterized across a wide temperature range in order to explain its origin. DSC measurements were conducted between 225 and 573 K for Ti2448 alloy (Figure 4(a)). The smooth DSC curves with neither endothermic nor exothermic peaks suggest that DSC is invalid for detecting reversible phase transitions in Ti2448 alloy [26]. Therefore, the temperature-induced crystal change of the  $\alpha''$  phase was investigated and

XRD measurements were conducted at 173, 298, and 573 K. These XRD profiles and the corresponding fitted curves in Figure 4(b) show that the diffraction angle of (022) peak of the  $\alpha''$  phase reduce as the temperature rises. That is, the  $\alpha''$  phase has larger transition strain at higher temperatures (Figure 4(c)) [25], indicating the  $\alpha''$  phase becomes gradually closer to hcp  $\alpha$  phase in the as-manufactured alloy.

Based on the XRD analysis, the Elinvar effect can be attributed to the crystal structure transition of the aging-induced Nb-lean  $\alpha''$  phase. As illustrated schematically in Figure 5, both the elastically stable  $\beta$  and  $\alpha$  phases exhibit a normal negative temperature coefficient of the elastic modulus ( $e$ ) due to thermally induced phonon vibrations (the blue and green lines in Figure 5). In contrast, the transitional orthorhombic  $\alpha''$  phase demonstrates an abnormal positive  $e$  (the red line in Figure 5). This phenomenon is reasonable because the modulus of

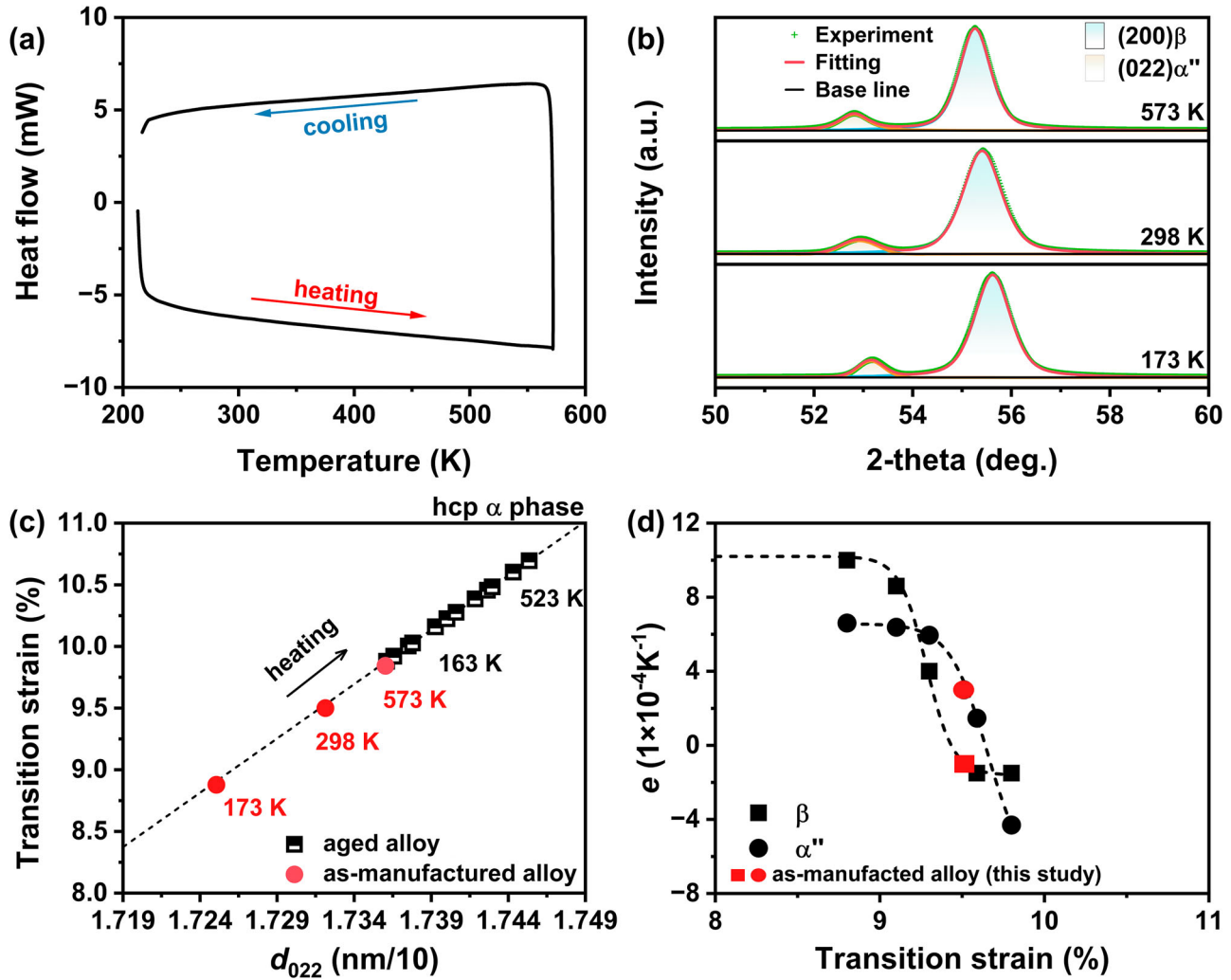


**Figure 4.** Continuous crystal change of  $\alpha''$  phase. (a) DSC curve of the as-manufactured sample. (b) Varied-temperature XRD profiles together with their fitting curves at 173, 298 and 573 K. (c) Temperature-dependent phase transition strain for both as-manufactured and aged alloys [25,26]. (d) The coefficients of both  $\beta$  and  $\alpha''$  phases as a function of the transition strain [25,26].

the orthorhombic  $\alpha''$  phase lies between the low modulus  $\beta$  phase and the high modulus  $\alpha$  phase. Furthermore, the XRD results show that the crystal structure of the Nb-lean  $\alpha''$  phase gradually shifts toward that of the high modulus  $\alpha$  phase as the temperature increases (Figure 4(c)). Consequently, the modulus of the  $\alpha''$  phase should increase with rising temperature, resulting in a positive  $e$ . This positive  $e$  of the  $\alpha''$  phase can offset the negative  $e$  of the  $\beta$  phase. By controlling the volume fraction and lattice parameters of the  $\alpha''$  phase, the  $e$  values for both phases can be tailored (Figure 4(d)) to achieve the desired Elinvar effect (the dark line in Figure 5).

Because the Elinvar effect is controlled by the volume fraction and transition strain of the  $\alpha''$  phase, the  $e$  can be modeled by the rule-of-mixture modeling, represented by the equation:

$$e = (1 - V_{\alpha''}) \cdot e_{\beta} + V_{\alpha''} \cdot e_{\alpha''} \quad (2)$$

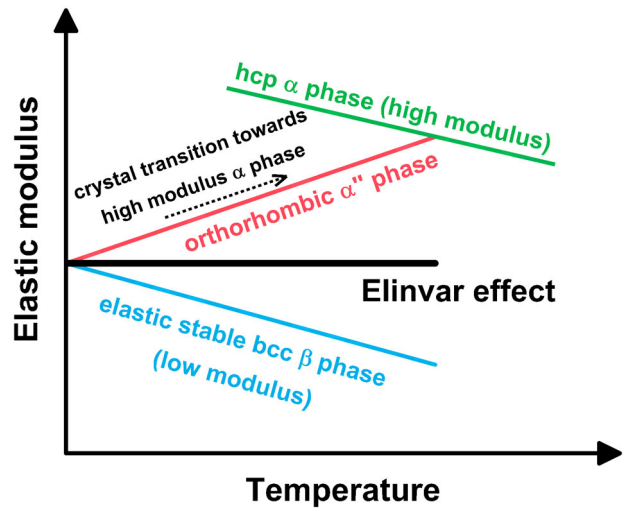


**Figure 5.** Illustration of the mechanism of Elinvar effect induced by inverse thermal effects on elastic modulus of  $\beta$  and  $\alpha''$  phases.

where  $e_{\alpha''}$  and  $e_{\beta}$  are the temperature coefficients of elastic modulus of  $\alpha''$  and  $\beta$  phases, respectively,  $V_{\alpha''}$  and  $V_{\beta}$  are their volume fractions, and  $e$  is the overall temperature coefficient of elastic modulus of the alloy, respectively. Previous studies demonstrate that both  $e_{\beta}$  and  $e_{\alpha''}$  are dependent on the transition strain of  $\beta$ - $\alpha''$ - $\alpha$  (Figure 4(d)), leading to the tunable  $e$  through aging at 723 K. Based on the transition strain of the as-manufactured alloy (Figure 4(b,c)), its  $e_{\alpha''}$  and  $e_{\beta}$  can be estimated from the sigmoidal relations in Figure 4(d) to be about  $3.0 \times 10^{-4} \text{ K}^{-1}$  and about  $-1.0 \times 10^{-4} \text{ K}^{-1}$ , respectively. Using these values with a volume fraction of  $\alpha''$  phase at  $\sim 31\%$ , the modeled  $e$  can be calculated to be about  $0.6 \times 10^{-4} \text{ K}^{-1}$ , which is close to the experimental result of  $0.7 \times 10^{-4} \text{ K}^{-1}$  [26].

Several points should be clarified with respect to the Elinvar effect between the aged and as-manufactured Ti2448 alloys. On the one hand, the transition strain of  $\alpha''$  phase in the as-manufactured alloy is smaller than that of the aged alloy at all temperatures (Figure 4(c)). Based on previous studies that the temperature dependence of the transition strain is governed by its initial value [25], it is reasonable that the smaller transition strain in the as-manufactured Ti2448 sample might lead to a slightly altered thermal response of elastic modulus of the  $\alpha''$  phase. Consequently, this would result in a larger  $e$  and a narrower temperature window for the as-manufactured sample as compared to that of the aged sample [26]. On the other hand, the  $\alpha''$ -to- $\alpha$  transition is reversible thermally but its atomic pathway is contrast with the well-known  $\beta$ - $\alpha''$  martensitic transformation mechanism. For example, the  $\alpha''$  martensite induced by deformation or quenching in Ti-based shape memory alloys transforms to  $\beta$  phase, whereas the aging-induced  $\alpha''$  phase in Ti2448 alloy evolve toward hcp  $\alpha$  phase upon heating [47,49]. Thus, the aging-induced  $\alpha''$  phase might provide a new opportunity to pioneer continuous and reversible phase transitions for further exploring novel functional properties over a wide temperature range [55–60].

## 4. Conclusions

In conclusion, we have achieved the Elinvar effect directly in an as-manufactured Ti–24Nb–4Zr–8Sn alloy by utilizing the inherent thermal fields of electron beam melting to act as in-situ aging treatment. The diffusion of Nb during in-situ aging is crucial for obtaining a Nb-modulated  $\alpha''$ + $\beta$  dual-phase microstructure. The resulting Nb-lean  $\alpha''$  phase not only compensates for the modulus variation of the Nb-rich  $\beta$  matrix phase but strengthens the alloy. This results in the Elinvar effect over a wide temperature range of  $\sim 273 \text{ K}$ , along with a high elastic

strain of  $\sim 1.2\%$  and good ductility of  $\sim 19\%$  in the as-manufactured alloy. Our findings provide insights into achieving integrated structural and functional properties in metallic materials through the strategic use of inherent thermal fields of additive manufacturing processes.

## Disclosure statement

No potential conflict of interest was reported by the author(s).

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## Data availability statement

Data available within the article or its supplementary materials.

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