



# The clarification of $\alpha''$ phase precipitate from $\beta$ phase in Ti-15Mn alloy by mismatch theory



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## ABSTRACT

The precipitation and growth of  $\alpha''$  phase from  $\beta$  phase in Ti-15Mn alloy after solid solution process was experimentally investigated. After heat treatment, the Ti-15Mn alloy consisted of  $\alpha''$  and  $\beta$  phases. The  $\alpha''$  and  $\beta$  phases were analyzed by X-ray diffraction, transmission electron microscopy and Fourier transforms. The results show a coherent relationship between  $\alpha''$  phase and  $\beta$ -Ti matrix, which is  $(200)_{\alpha''} // (110)_{\beta}$  and  $(020)_{\alpha''} // (1\bar{1}0)_{\beta}$ . Through calculating one-dimensional and two-dimensional mismatch, it comes to a conclusion that the two-dimensional mismatch of  $\alpha''$  phase and  $\beta$ -Ti matrix is 1.73%. It means that the  $\alpha''$  phase can efficiently precipitate from  $\beta$ -Ti matrix. Furthermore, it grows along the resultant vectors direction which determined by one-dimensional mismatch energy.

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## 1. Introduction

Titanium and its alloys have been widely used in medical devices including dental and orthopedic implants due to their high corrosion resistance, good strength, low young's-modulus [1–4]. There are  $\alpha$ -Ti (hcp) and  $\beta$ -Ti (bcc) two isomers in Ti alloys. Quenching of the  $\beta$  phase from elevated temperatures can result in the formation of two metastable martensitic structures,  $\alpha'$  (hexagonal) and  $\alpha''$  (orthorhombic) [5]. The  $\alpha'$  phase can be obtained in Ti alloys containing less  $\beta$ -stabilizer element, whereas Ti alloys obtained  $\alpha''$  orthorhombic martensite with more  $\beta$ -stabilizer element. During the last decades,  $\beta$ -Ti alloys have become most popular biological materials. Manganese is a strong candidate as an alloying element for new high-strength  $\beta$ -type titanium alloys [6]. At the beginning of the titanium alloy study, Ti-Mn alloy can be used in airplane bodies [7]. Among the developed Ti-Mn alloys, they have particularly gained attentions due to their additional functions of hydrogen storage property and low-cost biological materials [8]. Their mechanical properties can be modulated and tailored by heat treatment [9,10]. Additionally, it has been reported that the young's-modulus of Ti-Mn alloys can be easily influenced by heat treatment procedure and manufacturing

processes [11]. Manganese (Mn) is a highly available, low-cost,  $\beta$ -stabilizer element that can be alloyed with Ti. Furthermore, studies have reported that Mn plays a key role in osteogenesis and bone resorption mechanisms, as well as other essential mechanisms for regular body functions [8]. Therefore, it is strongly suggested that the microstructure of Ti-Mn alloys plays a key role in giving rise to their mechanical and functional properties.

The martensite transformation of  $\alpha''$  phase in titanium alloy is athermal transformation. The  $\alpha''$  phase and the orientation between  $\alpha''$  and  $\beta$  phase had been reported previously [5,7,12–14]. However the process of  $\alpha''$  phase growth wasn't be investigated yet. In this work,  $\alpha''$  phase precipitated and growth from the  $\beta$ -Ti matrix in Ti-15Mn alloy after solid solution process was firstly studied. The  $\alpha''$  phase was analyzed by HRTEM and XRD. The mismatch of  $\alpha''$  precipitates and  $\beta$ -Ti matrix was calculated by one-dimensional and two-dimensional mismatch theory. The obtained results will give some new insights of microstructure evolution of  $\alpha''$  phase in Ti-15Mn alloys.

## 2. Material and methods

The Ti-15Mn alloy (at. %) in this experiment was prepared by arc melting, the heat treatment was processed by solid solution at 1173 K for 14.4 ks (water quench) in Ar atmosphere to prevent oxidation. After that, the specimens were milled by precision ion polishing system (PIPS). The bright field and high resolution

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transmission electron microscopy (HRTEM) images were recorded by JEM-2100 transmission electron microscopy (TEM). X-ray diffraction measurements were performed with a Bruker-axs XRD (D8-A25) diffractometer using CuK $\alpha$  radiation.

### 3. Results and discussion

Fig. 1(a) shows the bright field image of Ti-15Mn alloy and its XRD curve. In bright field image, the crisscross-like structure precipitating in the matrix was observed. The XRD pattern shown two phases in the figure:  $\beta$  phase and  $\alpha''$  phase. In Fig. 1 (b), three different electron diffraction patterns by Fourier transform were marked. Area I is  $\beta$ -phase. Both Area II and Area III are  $\alpha''$  phase. Fig. 1(c) is the results by Fourier transformation of Red square shown in Fig. 1(b). The three patterns in Fig. 1(c) belong to two kinds of structures which represent  $\beta$ -phase and  $\alpha''$  phase, respectively. The reason is that Ti-15Mn alloy contains mess of beta-stabilizer element Mn, leading  $\beta$ -phase directly transformed to orthorhombic  $\alpha''$  phase rather than hexagonal martensite  $\alpha'$ . As shown in the Fig. 1(c), two sets of  $\alpha''$  phase patterns just present at 90°. The  $\alpha''$  phase belongs to orthorhombic crystal system, in which its lattice constants are:  $a = 4.824\text{\AA}$ ,  $b = 4.63\text{\AA}$ ,  $c = 3.15\text{\AA}$ , ( $\alpha = \beta = \gamma = 90^\circ$ ) [12–14]. By analyzing the diffraction patterns in Fig. 1(c), it is found that  $\alpha''$  precipitates and  $\beta$  phase satisfy a coherency relationship of  $(200)_{\alpha''} // (110)_{\beta}$  and  $(020)_{\alpha''} // (1\bar{1}0)_{\beta}$ . The direction of  $[110]_{\beta-Ti}$  and  $[1\bar{1}0]_{\beta-Ti}$  represent at 90°. Fig. 1(d) indicates a noise-eliminated iFFT image. Through analyzing it, there

are three areas in the image: Area I belongs to  $(001)_{\beta-Ti}$ , while Area II and III both represent  $(001)_{\alpha''}$ . However, the difference between Area II and Area III, it can be concluded that the relationship in Area II  $(200)_{\alpha''} // (110)_{\beta}$ , and  $(020)_{\alpha''} // (1\bar{1}0)_{\beta}$  in Area II. Fig. 2(a) is  $(001)$  crystal plane in  $\beta$ -phase. Fig. 2(b) and (c) exhibit the crystal direction relationships of  $[1\bar{1}0]_{\beta} // [010]_{\alpha''}$  and  $[110]_{\beta} // [100]_{\alpha''}$ , respectively. In the right upper corner, the white and blue circles represent the atoms of  $\beta$ -phase and  $\alpha''$  phase, respectively. The interplanar distance of  $\beta$ -phase is  $d[110]_{\beta} = d[1\bar{1}0]_{\beta} = 4.675\text{\AA}$ . By reason of the  $\alpha''$  phase belongs to orthorhombic crystal system, its lattice constant are  $a \neq b \neq c$ . The interplanar distance of orthorhombic  $\alpha''$  phase emerges:  $d[010]_{\alpha''} = 4.63\text{\AA}$  while  $d[100]_{\alpha''} = 4.82\text{\AA}$ . The interplanar distance  $d[100]_{\alpha''}$  ( $4.82\text{\AA}$ ) is larger than  $d[110]_{\beta}$  ( $4.675\text{\AA}$ ). At the process of crystal arrangement, two different interplanar distances  $d_1$  and  $d_2$  are shown in Fig. 2(b and c). The  $d_1$  indicates the short parallel crystal plane distance between  $\alpha''$  and  $\beta$  phase, and  $d_2$  indicates the long distance next to the  $d_1$ . Due to the different lattice constants between  $\alpha''$  and  $\beta$ -Ti, the  $d_1$  is shorter than  $d_2$ , which produces a phenomenon that adjacent crystal planes distributed close and far interlaced, as shown in the Fig. 2(b) and (c). Therefore, the atoms need to transfer a long distance during the formation of  $\alpha''$  phase. It means that the atoms will face a greater resistance and produce greater mismatch energy.

However orthorhombic  $\alpha''$  phase is different with bcc  $\beta$ -Ti. The two-dimensional mismatch formula (below) which is put forward by Bramfitt [15]. The advantage of two-dimensional mismatch

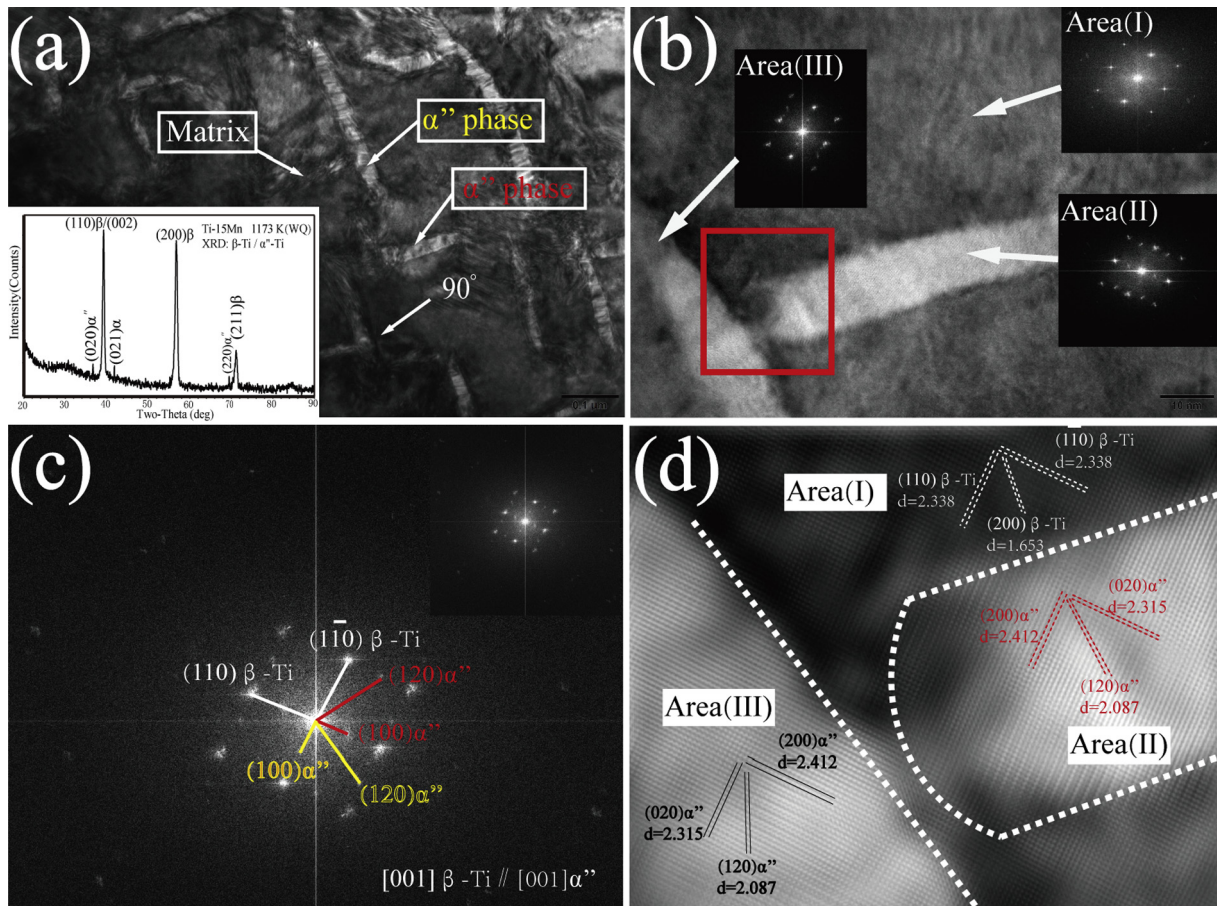


Fig. 1. The TEM images of Ti-15Mn alloy, (a) Bright field image of Ti-15Mn alloy and its XRD curve in the lower left corner; (b) HRTEM of crisscross-like precipitates area; (c) Fourier transform image of red square shown in (b); (d) Inverse Fourier transform image of red square shown in (b). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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