Enhanced phase stability of a BCC structure system high-entropy alloys by decreasing elastic distortion energy

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Abstract. Lightweight BCC high-entropy alloys exhibit outstanding specific strength. However, these alloys usually have poor phase stability, causing brittle precipitates. These precipitates would worsen the plasticity. In order to improve the alloy performance, it is important to improve its phase stability. In this paper, the phase stability of two kinds of BCC high-entropy alloys at 400℃, 500℃ and 600℃ is investigated. The contributions of mixing enthalpy and elastic distortion energy to their phase stability are discussed. Besides mixing enthalpy, elastic distortion energy also plays a significant role in phase stability. Our results prove that decreasing elastic distortion energy is an effective way to improve phase stability of typical BCC HEAs.

1. Introduction

High-entropy alloys (HEAs) have attracted significant attention due to their outstanding mechanical properties[1-4]. Al-Nb-Ti-V-Zr system is a recently reported body centered cubic (BCC) structured HEA combining low density and excellent strength[5], showing a potential as novel structural materials[6-8]. However, the phase stability of Al-Nb-Ti-V-Zr system is poor. The poor phase stability means brittle precipitations, such as Laves phase and Zr-Al phase, formed in center of the ingots in casting process. They are harmful to plasticity. Besides, the forming of Zr-Al precipitations will reduce the content of Zr in solid solution, leading to a decrease in the strength of alloys[9, 10]. The phase stability of Al-Nb-Ti-V-Zr system still needs to be improved.

In traditional alloys, mixing enthalpy (ΔH_{mix}) determines the phase formation. A negative ΔH_{mix} leads to the formation of intermetallic compounds, and a positive ΔH_{mix} leads to separation or segregation of different elements in alloy. When the ΔH_{mix} is close to zero, the disordered solid solution is stable. HEAs also obey the above rules. Besides ΔH_{mix}, the elastic distortion energy (ΔE_{els}) caused by difference in atomic sizes also play an important role in the phase stability of solid solutions in HEAs[11]. However, the contribution of ΔE_{els} in the phase stability of Al-Nb-Ti-V-Zr system HEAs is rarely studied.

In this paper, two kinds of alloys, Al_{0.3}NbTi_{3.6}V_{0.8}Zr_{1.2} and Al_{0.3}NbTi_{2}V_{0.8}Zr_{1.2}, with similar ΔH_{mix} and different ΔE_{els} are prepared. The phase stability, precipitation process and composite of second phase are investigated. The correlation about the phase stability and the ΔH_{mix} and ΔE_{els} is discussed.
2. Material and method

The present alloys with a nominal composition of \( \text{Al}_{0.3}\text{NbTi}_{3.6}\text{V}_{0.8}\text{Zr}_{1.2} \) (titled Ti3.6) and \( \text{Al}_{0.3}\text{NbTi}_{2}\text{V}_{0.8}\text{Zr}_{1.2} \) (titled Ti2) were prepared by induction melting under a high-purity argon atmosphere in a graphite crucible. Raw elements had purities better than 99.9 wt.%. The as-cast alloys were homogenized at 1100°C for 2h followed by water quenching. The as-homogenized alloys were deformed at room temperature by cold-rolling up to 70% reduction in thickness and subsequently annealed at 900°C for 1h for recrystallize. Annealed Ti3.6 were aged at 400°C, 500°C and 600°C for 2h, 4h and 6h. Annealed Ti2 were aged at 400°C, 500°C and 600°C for 20min, 40min and 60min. The aging time depends on the kinetics of precipitation. To prevent the oxidation, the alloys were sealed in a quartz tube filled with high-purity argon during heat treatment.

The phase compositions of the alloy were investigated by high energy X-ray diffraction (HEXRD) technology and an X-ray with a wavelength of 0.01173nm at beamline 11-ID-C, Advanced Photon Source, Argon National Laboratory. The microstructures of the annealed alloys and aged alloys were observed by optical microscope (OM) and Hitachi Regulus 8230 scanning electron microscopy (SEM). The microstructure and compositions of structural constituents in annealed alloys and aged alloys were observed and measured through FEI Talos F200X transmission electron microscopy (TEM) equipped by super energy dispersive spectroscopy (EDS).

3. Results

Figure 1 shows the optical microscope images of annealed Ti3.6 and Ti2 and HEXRD results of annealed and aged Ti3.6 and Ti2. The compositions of annealed Ti3.6 and Ti2 are listed in Table 1. The optical microscope images show that the annealed Ti3.6 and Ti2 are mainly composed of equiaxed crystals. As shown in the HEXRD patterns, the annealed Ti3.6 and Ti2 both have a single-phase bcc structure. Regarding Ti3.6, no second phase is observed with the extension of aging time at any temperatures. Regarding Ti2, after aging at 600°C for 20 min, C14 Laves phases are observed in the matrix. After aging at 400°C for 60min and at 500°C for 60min, no second phase is observed. At the temperature of 600°C, the longer the aging time, the more Laves phases are induced. These results suggest that Ti3.6 is more stable than Ti2.

![Figure 1](image.png)

Figure 1. Optical microscope images of annealed Ti3.6 (a) and Ti2 (b), and HEXRD pattern of annealed and aged Ti3.6 (c) and Ti2 (d).

Table 1. Chemical compositions of structural constituents in annealed Ti3.6, annealed Ti2 and Ti2 aged at 600°C for 60min.

| Element          | Al(at. %) | Nb(at. %) | Ti(at. %) | V(at. %) | Zr(at. %) |
|------------------|-----------|-----------|-----------|----------|-----------|
| Laves (aged Ti2)| 11.7±0.2  | 14.2±0.2  | 11.6±0.3  | 29.6±0.2 | 32.8±0.1  |
| Matrix (aged Ti2)| 5.6±0.2   | 22.1±0.2  | 38.8±0.3  | 12.8±0.2 | 20.7±0.3  |
Ti₂ (annealed)  5.7±0.1  19.7±0.2  34.9±0.2  14.7±0.3  25.0±0.3  
Ti₁.₆ (annealed)  4.3±0.1  13.6±0.2  54.4±0.2  10.6±0.1  17.1±0.3

Figure 2 shows the microstructure of aged Ti₂ with different aging process. Laves phases are observed in all processes except 400°C-20min, 400°C-40min and 500°C-20min. The absent diffraction peaks of Laves phases in corresponding HEXRD patterns may be associated with the small sizes of Laves phases. Laves phases distribute inside grains and on grain boundaries. The amount of Laves phases distributed on grain boundaries is larger than that distributed inside grains (figure 2-a2 and figure 2-a3). Given these results, Laves phases have a tendency to form on grain boundaries, which is consistent with other literature reports[12].

Figure 2. Optical microscope images of aged Ti2 with different aging process: (a1) 600°C for 20min, (a2) 600°C for 40min, (a3) 600°C for 60min, (b1) 500°C for 20min, (b2) 500°C for 40min, (b3) 500°C for 60min, (c1) 400°C for 20min, (c2) 400°C for 40min, (c3) 400°C for 60min. The insert of (a3) shows the precipitates on grain boundaries.

Figure 3 shows the intra-grain microstructure of Ti₂ aged at 600°C for 60min. Spherical Laves precipitates are observed in bcc matrix. The diameter of precipitates is ~450nm. The element mappings show that the spherical precipitates are rich in Zr, V and Al and poor in Nb and Ti. The chemical compositions of precipitates and matrix are listed in Table 1. Given the above result, the precipitates in Ti₂ are a typical Zr-V-Al type phase.
Figure 3. The brightfield image of Ti$_2$ aged at 600°C for 60min (a) shows spherical precipitates in bcc matrix. The selected area electron diffraction (SAED) image shows a C14 structured precipitate (c) and a bcc structured matrix (b). The HADDF-STEM image and element maps (d) shows that the precipitates are rich in Zr, V and Al.

4. Discussion
When the aging temperature is the same (for example 600°C), Ti$_{3.6}$ retains a single-phase structure after 6h, whereas Laves precipitations form in Ti$_2$ after 20min, proving that Ti$_{3.6}$ is more stable than Ti$_2$. According to the study of Yang et al.[11], $\Delta H_{mix}$ and $\Delta E_{els}$ are two mainly factors affecting the phase stability of HEA precipitates. Negative or positive $\Delta H_{mix}$ and too large $\Delta E_{els}$ are not conducive to the stability of the solid solutions. In next part, the source of the difference in phase stability of the two kinds of alloys will be discussed from $\Delta H_{mix}$ and $\Delta E_{els}$.

4.1. Mixing enthalpy
A regular solution model is employed to determine the $\Delta H_{mix}$ of the present alloys. The $\Delta H_{mix}$ can be calculated by the following equation:

$$\Delta H_{mix} = \sum_{i=1}^{\Omega_{ij}} c_i c_j (1)$$

where $c_i$ and $c_j$ is respectively the atomic percentage of $i$-th and $j$-th elements, and $\Omega_{ij}$ is the regular solution interaction parameter between above two elements. $\Omega_{ij}$ can be determined by the following equation:

$$\Omega_{ij} = 4 \Delta H_{AB}^{mix} (2)$$

where $\Delta H_{AB}^{mix}$ is the mixing enthalpy of binary alloy AB. A and B respectively stand for $i$-th element and $j$-th element. The value of $\Delta H_{AB}^{mix}$ in this paper comes from Ref.[13].

Calculated $\Delta H_{mix}$ of annealed Ti$_{3.6}$ and Ti$_2$ and matrix of aged Ti$_2$ is shown in figure 4. Since the negative $\Delta H_{mix}$ between Al and other elements, three phases all have negative $\Delta H_{mix}$. The $\Delta H_{mix}$ of annealed Ti$_{3.6}$ and Ti$_2$ is -4.7 kJ/mol and -6.0 kJ/mol, respectively. After the forming of Laves phases, the $\Delta H_{mix}$ of matrix in Ti$_2$ increases from -6.0 kJ/mol to -5.5 kJ/mol. Zhang et al.[14] proposed that the $\Delta H_{mix}$ of HEAs’ solid solutions are in range of -15kJ/mol to 5kJ/mol. Since the $\Delta H_{mix}$ of Ti$_{3.6}$ and Ti$_2$ are in this range, the difference between $\Delta H_{mix}$ of Ti$_{3.6}$ and Ti$_2$ is not the main reason for the differences in phase stability.

4.2. Elastic distortion energy
A calculation method reported by A.B. Melnick and V.K. Soolshenko[15] is employed to calculate the $\Delta E_{els}$ of the alloy systems in this paper. The equation is as follow:
\[ \Delta E_{\text{els}} = \sum_{i=1}^{n} c_i B_i \left( \frac{V_i(T_m) - V(T)}{2V(T)} \right)^2 \]  

where \( c_i \), \( B_i \), \( V_i(T) \) and \( T_m \) is the atomic percentage, bulk modulus, atomic volume and melting temperature of \( i \)-th element; \( V(T) \) and \( T_m \) is the average atomic volume and effective melting temperature of the alloy. \( V_i(T) \), \( V(T) \) and \( T_m \) are determined by following equations:

\[ V_i(T) = V_0 \left( 1 + \alpha_i (T - T_0) \right)^3 \]  

\[ V(T) = \sum_{i=1}^{n} c_i B_i \]  

\[ T_m = \sum_{i=1}^{n} c_i T_m^i \]

where \( V_0 \) and \( \alpha_i \) is atomic volumes and linear expansion coefficient of \( i \)-th element, and \( T_0 = 273 \text{K} \). The value of the constants of elements in Al-Nb-Ti-V-Zr system comes from Table [16] and Ref. [17].

The calculation result of the \( \Delta E_{\text{els}} \) of annealed Ti3.6 and Ti2 and the matrix in aged Ti2 is shown in figure 4. The \( \Delta E_{\text{els}} \) of annealed Ti3.6 and Ti2 is 12.2 kJ/mol and 17.3 kJ/mol, respectively. The \( \Delta E_{\text{els}} \) of Ti2 is 5.1 kJ/mol higher than Ti3.6. After the forming of Laves phases, the \( \Delta E_{\text{els}} \) of matrix in Ti2 decreases from 17.3 kJ/mol to 14.6 kJ/mol.

The difference between Ti3.6 and Ti2 in \( \Delta H_{\text{mix}} \)s and \( \Delta E_{\text{els}} \)s is 1.3 kJ/mol and 5.1 kJ/mol, respectively. Comparing with \( \Delta H_{\text{mix}} \), the difference in \( \Delta E_{\text{els}} \)s is much higher. Besides, the \( \Delta H_{\text{mix}} \)s of Ti3.6 and Ti2 are in range of -15kJ/mol to 5kJ/mol, which is a proper range for stable solid solutions. The \( \Delta E_{\text{els}} \) occupies a significant proportion in the overall Gibbs free energy of solid solutions. A high \( \Delta E_{\text{els}} \) result in a high Gibbs free energy, leading poor phase stability of Ti2’s solid solution. The Laves phases obtained in Ti2 tends to form on grain boundaries. It is noted that the chemical compositions of Laves phase are Zr, V, and Al. The Zr element has the largest atomic size and the V and Al elements have the smaller atomic size among five elements in Ti2. Zr, V and Al elements prefer gathering at the grain boundaries to reduce the distortion of the lattice. After aging process, the \( \Delta E_{\text{els}} \) of matrix in Ti2 decreases 2.7 kJ/mol, whereas its \( \Delta H_{\text{mix}} \) increases 0.5 kJ/mol. The increase in \( \Delta H_{\text{mix}} \) is insignificant compared with the decrease in \( \Delta E_{\text{els}} \). These results suggest that the high \( \Delta E_{\text{els}} \) is a significant factor causing the poor phase stability of Ti2.

![Figure 4. Mixing enthalpy and elastic distortion energy of annealed Ti3.6, annealed Ti2 and the matrix in aged Ti2.](image)

**5. Conclusion**

In this paper, the phase stability of Ti3.6 and Ti2 was investigated. The influences of \( \Delta H_{\text{mix}} \) and \( \Delta E_{\text{els}} \) on phase stability were discussed. The conclusions are as follow:
$\text{Ti}_{3.6}$ is more stable than $\text{Ti}_2$. At the aging temperature of 400°C, 500°C and 600°C, $\text{Ti}_{3.6}$ stay single bcc phase after 6h, whereas Laves precipitates form in $\text{Ti}_2$ after 60 min, 40 min and 20 min, respectively. The C14 Laves phase obtained in $\text{Ti}_2$ is rich in Zr, V and Al. The $\Delta H_{\text{mix}}$s of $\text{Ti}_{3.6}$ and $\text{Ti}_2$ are similar, whereas the $\Delta E_{\text{els}}$ of $\text{Ti}_2$ is much higher than that of $\text{Ti}_{3.6}$. After the forming of Laves phases, the $\Delta E_{\text{els}}$ of the matrix in $\text{Ti}_2$ significantly decreases, indicating that $\Delta E_{\text{els}}$ is a significant factor affecting phase stability of Al-Nb-Ti-V-Zr system HEAs. Our work proved that reducing $\Delta E_{\text{els}}$ is an effective way to improve the phase stability of Al-Nb-Ti-V-Zr system HEAs.

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