Phase stability and hardness of some ternary Ti–Zr based shape memory alloys

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The phase stability and hardness of Ti–30Zr–M (M = Nb, V, Cr, Mo, Fe, Ni and Al) shape memory alloys were investigated by structural observations, d-electron alloy design and microhardness tests. Optical microscopy and X-ray diffraction results show that Nb, V, Cr, Mo and Fe are all β-stability elements in Ti–30Zr–M alloys with the effect enhanced by the presence of Zr. The composition of the least stable β-phase alloy values of Nb, V, Cr, Mo and Fe in Ti–30Zr alloys are 12%, 9%, 5%, 3% and 2%, respectively, indicating an increasing sequence of the β-stability ability. Ni and Al show α-stability or moderate effects and the addition of Ni induces the appearance of (Ti, Zr)\textsubscript{2}Ni phase in Ti–30Zr–5/15Ni alloys. Based on the d-electron alloy design method, the bond order of Ti and alloying atoms (Bo) and the metal d-orbital energy level (Md) are calculated to build the Bo–Md diagram of Ti–30Zr–M alloys associated with the phase structure identification. The microhardness of Ti–30Zr alloy is increased by addition of a small amount of the alloying element, except for Nb. There is a drop of the microhardness of each Ti–30Zr–M alloys when β phase appears by the addition of more alloying elements.

Keywords: Ti–Zr shape memory alloy; microstructure; martensitic transformation; d-electron alloy design

1. Introduction

Shape memory alloys (SMAs) have been widely used in various applications, such as aerospace and biomedical fields due to their excellent shape memory effect and superelasticity [1,2]. In the last decade, some Ti-based solid solutions have attracted much attention as new SMAs because of their excellent properties of low density, high strength, low elastic modulus and good corrosion resistance. These SMAs, including Ti–Nb [3–5] and Ti–Mo [6,7] based alloys, generally exhibit a phase transformation between a martensite phase at low temperature and a β-phase (bcc) at high temperature. Three types of martensitic structures, i.e. α′-martensite (hexagonal), α′′-martensite (orthorhombic) and α′′′-martensite (orthorhombic), have been found showing the complexity of the phase stability of the Ti–Nb and Ti–Mo SMAs [7–9]. The transformation strain from β to orthorhombic α′′ is primarily accommodated by internal twinning and the shape memory effect is related with...
the reverse transformation from $\alpha''$ phase to $\beta$ phase [3,5,6]. The $\alpha''''$-martensite, with an orthorhombic structure, is a stress-induced martensite phase different from the commonly mentioned $\alpha''$-martensite [7]. Furthermore, some studies have shown the effectiveness of alloying elements, e.g. Zr, Nb, V, Al, Pd, Sn and Ag, on modifying the phase transformation characteristics and improving shape memory effect and superelasticity of Ti–Nb and Ti–Mo based alloys [6,7,10–12].

The $d$-electron alloy design method has been used to classify the effect of alloying elements on the phase stability of Ti alloys [13–16]. This method was developed based on molecular orbital calculations. Using the discrete variational Xα (DV-Xα) method, the electronic structures of bcc Ti containing alloying elements were calculated, and two parameters were obtained theoretically. One is the bond order (Bo) of Ti and alloying atom, which is a measure of the covalent bond. Another is the metal $d$-orbital energy level (Md), which correlates with electronegativity and the metallic radius of elements. Once the Bo and Md are calculated and the frontier of the phase region is crudely drawn, the composition of corresponding alloys can be simply determined. Furthermore, based on the corresponding experimental results of the phase composition of each alloy, one can confirm the phase boundary, e.g. separate $\alpha$-phase zone from $\beta$-phase zone, on the Bo–Md diagram, which is helpful for further investigations of phase stability and other properties.

Similar to Ti–Nb and Ti–Mo alloys, binary Ti–Zr alloys are also solid solutions with a phase transformation between $\alpha'$-martensite at low temperature and parent phase at high temperature, which has made them useful as good biomedical alloys [17,18]. Recently, the shape memory behavior has been found in binary Ti–Zr alloys and the Ti–30Zr alloy exhibited a maximum Shape Memory Effect (SME) of 1.4% and a martensitic transformation start temperature as high as 913 K, revealing it as a promising SMA for use in high-temperature applications, e.g. aerospace engines [19]. Moreover, the addition of 10%Nb into Ti–30Zr alloy can significantly decrease the martensitic transformation temperature, and improve the SME and workability [20]. In the present work, the phase stabilities and hardness of some ternary Ti–Zr based alloys were investigated based on the experimental observation and analysis of the Bo–Md diagram. The alloying elements V, Nb, Cr, Mo, Fe, Ni and Al were selected since they are the usual alloying elements added in Ti alloys [13–16].

2. Experiment procedure and calculations of $\text{Bo}$ and $\text{Md}$

Ti–30Zr–$x$Nb ($x = 6, 8, 10, 12, 14$ and $16$), Ti–30Zr–$x$V ($x = 3, 5, 7, 9, 11$ and $13$), Ti–30Zr–$x$Cr ($x = 1, 2, 3$ and $5$), Ti–30Zr–$x$Mo ($x = 1, 3$ and $5$), Ti–30Zr–$x$Fe ($x = 1, 2$ and $3$), Ti–30Zr–$x$Ni ($x = 5$ and $15$) and Ti–30Zr–$x$Al ($x = 3, 6$ and $9$) alloys (in mol. %) were prepared using sponge Ti (purity 99.98%), sponge Zr (purity 99.98%) and other high-purity alloying elements. The alloy ingots about 30 g in weight were arc-melted under an Ar atmosphere four times and then were encapsulated within a vacuum quartz tube, followed by solution treatment at 1123 K for 2 h to ensure homogenization. After solution treatment the ingots were quenched into water by breaking the quartz tubes. Specimens with 10 mm $\times$ 10 mm $\times$ 2 mm dimensions were cut using an electro-discharge machine. The sample surface was treated by mechanical polishing. For optical microscopy the specimens were then etched using a solution of HF, HNO$_3$ and H$_2$O (1:4:8 in volume). In order to identify the phase components, X-ray diffraction (XRD) was conducted using Ni-filtered Cu Kα radiation with the scanning rate of 4°/min. The micro-Vickers hardness of each phase was measured with a HXZ-1000 microhardness tester. Indentation was obtained by
applying 300 g load for 10 s. An average of least six indentations was taken as the value of microhardness.

\( \overline{B_0} \) and \( \overline{M_0} \) are averages, which weighted with the atomic fraction of each alloying element, as shown in Equations (1) and (2), respectively:

\[
\overline{B_0} = \sum_{i=1}^{n} x_i (B_0)_i,
\]

\[
\overline{M_0} = \sum_{i=1}^{n} x_i (M_0)_i
\]

where \( x_i \) is the atomic fraction of element \( i \), \( (B_0)_i \) and \( (M_0)_i \) are \( B_0 \) and \( M_0 \) values of element \( i \), respectively.

For a certain element \( i \) in Ti alloy, the \( (B_0)_i \) and \( (M_0)_i \) are specific values, e.g. 3.099 and 2.424 for Nb, respectively, which can be found in [13]. Therefore, the corresponding \( B_0 \) and \( M_0 \) of the alloy with a given composition can be calculated based on Equations (1) and (2).

3. Results and discussions

Optical micrographs of Ti–30Ni–\( x \)Nb (\( x = 6, 8, 10 \) and 12) alloys are shown in Figure 1. It can be seen from Figure 1a that the Ti–30Zr–6Nb alloy exhibits some lamellar substructures in the grains, and the similar morphology are also appears in 8Nb and 10Nb alloys. This is the typical morphology of martensite twins shown in Ti–Zr binary alloys [17]. Figure 2 shows the XRD patterns of Ti–30Ni–\( x \)Nb (\( x = 6, 8, 10, 12 \)) alloys. The Ti–30Zr–6/8Nb alloys can be indexed as an hcp structure of \( \alpha' \)-martensite as that in Ti–30Zr alloy, whereas an orthorhombic structure of \( \alpha'' \)-martensite appears in the Ti–30Zr–10Nb alloy. For Ti–30Ni–12/14/16Nb alloys, however, no \( \alpha'' \)-martensite can be seen and only single \( \beta \) phase is detected by XRD, as shown in Figure 2, which is very similar to the result in [10]. Thus it can be concluded that Nb is a \( \beta \)-stability element in Ti–30Zr alloy and could suppress the appearance of martensite. The composition of the least stable \( \beta \) phase alloy (\( \beta_c \), defined as the alloy containing the least amount of the \( \beta \)-stability elements to get a \( \beta \) single phase [10]) of Nb in Ti–Zr alloy is 12 at. \%. It was demonstrated that the least composition for Nb keeping \( \beta \) phase stable at room temperature in Ti–Nb alloy is 25.5\% [5]. Therefore, Zr actually takes effect as a \( \beta \)-stability element rather than a neutral one in Ti–30Zr–\( x \)Nb alloy because of the reduced \( \beta_c \) value of Nb. More details of the phase stability of Ti–Nb alloy affected by Zr can be seen in the study presented by Abdel-Hady et al. [10].

The XRD patterns of Ti–30Zr–\( x \)V (\( x = 3, 5, 7, 9, 11 \) and 13) alloys are shown in Figure 3. It can be seen that the Ti–30Zr–3/5V alloys are composed of \( \alpha' \)-martensite, whereas only single \( \beta \) phase exists in Ti–30Zr–9/11/13V alloys. This result indicates that V is also a \( \beta \)-stability element in Ti–30Zr alloy and the \( \beta_c \) value is detected as 9\%. It is noted that the \( \beta \) phase at high temperatures can be retained by quenching when the V content is higher than 15.2 at. \% in Ti–V alloys [21]. Therefore, it can be concluded that Zr also shows \( \beta \)-stability effect in Ti–30Zr–\( x \)V alloys as it does in Ti–30Zr–\( x \)Nb alloys.

Figure 4 shows the XRD patterns of Ti–30Zr–\( x \)Cr (\( x = 1, 2, 3 \) and 5) and Ti–30Zr–\( x \)Mo (\( x = 1, 3 \) and 5) alloys. It can be seen from Figure 4a that the \( \alpha' \)-martensite is found
Figure 1. Optical micrograph of (a) Ti–30Zr–6Nb, (b) Ti–30Zr–8Nb, (c) Ti–30Zr–10Nb and (d) Ti–30Zr–12Nb alloys.

Figure 2. XRD patterns of Ti–30Zr–xNb (x = 6, 8, 10, 12, 14 and 16) alloys.

It is to be the dominant phase in Ti–30Zr–1/2/3Cr alloys and the β single phase is retained in Ti–30Zr–5Cr. These results are consistent with a study of Ti–10Zr–xCr (in wt. %) alloys, in which Cr showed remarkable effect of suppressing the appearance of α′-martensite at room
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Figure 3. XRD patterns of Ti–30Zr–xV (x = 3, 5, 7, 9, 11 and 13) alloys.

temperature and raising the β-stability [22]. The XRD results of Ti–30Zr–xMo alloys obviously indicate the β-stability effect of Mo with the βc value of 3%, as shown in Figure 4b. For the binary Ti–Mo alloys, it was found that the β phase was stabilized when the Mo content reached 4.7% [8]. This suggests that the β-stability effect of Mo in Ti alloys can be enhanced by Zr.

The XRD result for Ti–30Zr–xFe as shown in Figure 5. It can be seen that Fe displays a very strong β-stability effect in Ti–30Zr alloys since its βc value is as low as 2%. This can be understood because Fe not only shows the strongest β-stability effect in other Ti alloys, but also can suppress the martensitic transformation temperature of TiNi SMAs from above room temperature to near liquid nitrogen temperature [23].

The above results indicate that Nb, V, Cr, Mo and Fe are all β-stability elements reducing the transformation temperature between martensite and β phase in Ti–30Zr alloy. The reason is that these five alloying elements are all in bcc structure at room temperature, the same as the β phase of Ti–Zr alloys. Furthermore, the βc values of Nb, V, Cr, Mo and Fe in Ti–30Zr alloys are 12%, 9%, 5%, 3% and 2%, respectively, indicating an increasing sequence of the β-stability ability. This phenomenon should be correlated to the Pauling’s electronegativity of the alloying elements, which are 1.6, 1.63, 1.66, 2.16 and 1.83 for Nb, V, Cr, Mo and Fe, respectively. It seems that a larger Pauling’s electronegativity is a benefit to the β-stability ability and the exception of Fe may be due to the strong 3d electron configuration. On the other hand, it should be emphasized that the β-stability effect of these alloying elements on Ti are enhanced by the existence of Zr.

Figure 6 shows the XRD patterns of Ti–30Zr–xAl (x = 3, 6 and 9) alloys. It can be seen that the Ti–30Zr–xAl (x = 3, 6 and 9) retains the single α′′-martensite structure independent of the Al content and thus Al performs as an α-stabilizer in Ti–30Zr alloy, the same as its normal effect in Ti or as a moderate element. However, Al showed very complicated effects on the phase stability of Ti–Nb based alloys [12].

The optical morphologies and XRD patterns of Ti–30Zr–xNi (x = 5, 10) alloys are shown in Figure 7. It can be seen from Figure 7a that the Ti–30Zr–5Ni alloy is composed of dual phases, in contrast with the single-phase structures of the abovementioned ternary Ti–Zr based alloys, and the volume ratio of the second phase increases with increasing
Ni content, as shown in Figure 7b. The XRD result in Figure 7c indicates that the dual phases can be confirmed as the $\alpha''$-martensite phase and the second phase as (Ti,Zr)$_2$Ni, which has already been found in Ni–Ti–Zr alloys [24]. This result suggests that Ni is also an $\alpha$-stabilizer or a moderate element and the solid solubility of Ni in Ti–Zr alloy is no more than 5%. The excess of Ni tends to form (Ti,Zr)$_2$Ni and thus restores the phase equilibrium.

Table 1 lists the calculated $\overline{Bo}$ and $\overline{Md}$ values, phase structures and microhardness of the Ti–30Zr–M alloys. It can be seen that the microhardness of Ti–30Zr alloy is increased by addition of a small amount of a third alloying element, except for Nb. Ti–30Zr–6Nb alloy shows a microhardness of 268.9 HV, which is approximate 13.2% lower than that of the Ti–Zr alloy. It is interesting to note that there is a drop of the microhardness of each Ti–Zr–M alloys when $\beta$ phase appears by the addition of more alloying elements,
e.g. the microhardness value decreases from 341.3 HV for $\alpha''$-Ti–30Zr–8Nb to 259.8 HV for $(\beta+\alpha')$-Ti–30Zr–10Nb. Similarly, the microhardness of the $\beta$ phase in Ti–Nb alloy was lower than that of $\alpha'$ or $\alpha''$ martensite phase [9]. Nb has been demonstrated to be effective in lowering the elastic modulus of Ti [9], and, on the other hand, a theoretical investigation indicated that maintaining the bcc structure in $\beta$-Ti results in the benefit of a low elastic modulus [25]. These results suggest that the addition of Nb and use of $\beta$ phase instead of $\alpha'/\alpha''$ phase are effective if Ti–Zr based alloys are promoted as a material with low elastic modulus. Furthermore, considering the good biocompatibility and the $\beta$-stability effect of Nb, Ti–Zr–Nb alloy is a good candidate as a SMA in biomedical applications. In addition, the solid solution strengthening effect is very pronounced when Ni or Al is added into Ti–30Zr alloy.
Based on the calculated Bo and Md values listed in Table 1, the Bo–Md diagram of Ti–30Zr–M alloys was plotted, as shown in Figure 8. It can be seen that each solid line represents the relationship between the Bo and Md of a certain alloying element in Ti–30Zr–M alloy. Each line radiates from the composition of Ti–30Zr with an arrow indicating the composition of Ti–30Zr–10M and extends towards the position where more alloying elements are added. Two dashed lines were drawn to show the frontier between the right-down $\alpha'$-phase zone and the left-up $\beta$-phase zone based on the phase structures of Ti–30Zr–M alloys shown in Table 1. Accordingly, we can classify the phase stability of alloying elements in Ti–30Zr alloy. Furthermore, once the Bo and Md values of an alloying element are calculated, its $\alpha$/$\beta$-stability effect on Ti–30Zr–xM can be identified without experimental investigation. For example, Mn may be a $\beta$-stability element because the corresponding Bo–Md line locates between those of Fe and Cr, whereas Si and Sn may be $\alpha$-stability or moderate elements due to the similar Bo–Md line trend to that of Al.

4. Conclusion

This work investigated the phase stability and hardness of some ternary Ti–Zr based shape memory alloys. Nb, V, Cr, Mo and Fe are all $\beta$-stability elements in Ti–Zr based alloys and the composition of the least stable $\beta$-phase alloy values of them in Ti–30Zr alloys are 12%, 9%, 5%, 3% and 2%, respectively, indicating an increasing sequence of the $\beta$-stability
Table 1. $\beta$O, Md, phase structures and micro-hardness of Ti–30Zr–M (M = Nb, V, Mo, Cr, Fe, Ni and Al) alloys.

| Sample          | $x$ | $\beta$O (eV) | Md (eV) | Phases structures | HV    |
|-----------------|-----|---------------|---------|-------------------|-------|
| Ti–30Zr         | –   | 2.879         | 2.593   | $\alpha'$         | 309.7 |
| Ti–30Zr–6Nb     | 6   | 2.897         | 2.592   | $\alpha'$         | 268.9 |
|                 | 8   | 2.904         | 2.591   | $\alpha'$         | 341.3 |
|                 | 10  | 2.910         | 2.591   | $\beta+\alpha''$  | 259.8 |
|                 | 12  | (βc)          | 2.916   | $\beta$           | 226.9 |
| Ti–30Zr–8Nb     | 14  | 2.922         | 2.590   | $\beta$           | 272.9 |
|                 | 16  | 2.928         | 2.589   | $\beta$           | 365.5 |
| Ti–30Zr–3V      | 3   | 2.879         | 2.576   | $\alpha'$         | 347.9 |
|                 | 5   | 2.880         | 2.564   | $\alpha'$         | 328.2 |
|                 | 7   | 2.880         | 2.553   | $\beta+\alpha'$   | 305.0 |
|                 | 9 (βc) | 2.880     | 2.541   | $\beta$           | 281.5 |
| Ti–30Zr–5V      | 11  | 2.880         | 2.530   | $\beta$           | 334.6 |
|                 | 13  | 2.881         | 2.518   | $\beta$           | 327.4 |
| Ti–30Zr–1Cr     | 1   | 2.879         | 2.583   | $\alpha'$         | 417.1 |
|                 | 2   | 2.879         | 2.574   | $\alpha'$         | 435.5 |
|                 | 3 (βc) | 2.878     | 2.564   | $\beta+\alpha'$   | 373.3 |
| Ti–30Zr–3Cr     | 5   | 2.878         | 2.545   | $\beta$           | 364.4 |
| Ti–30Zr–1Mo     | 1   | 2.882         | 2.588   | $\alpha'$         | 336.2 |
|                 | 3 (βc) | 2.887     | 2.579   | $\beta$           | 309.9 |
| Ti–30Zr–5Mo     | 5   | 2.892         | 2.569   | $\beta$           | 239.6 |
| Ti–30Zr–1Fe     | 1   | 2.877         | 2.578   | $\alpha'$         | 439.4 |
|                 | 2 (βc) | 2.876     | 2.564   | $\beta$           | 368.4 |
| Ti–30Zr–3Fe     | 3   | 2.875         | 2.549   | $\beta$           | 394.6 |
| Ti–30Zr–5Ni     | 5   | 2.860         | 2.507   | $\alpha''/\alpha''$ | 393.1/431.2 |
|                 | 15  | 2.822         | 2.335   | $\alpha''/\alpha''$ | 522.6/411.2 |
| Ti–30Zr–3Al     | 3   | 2.868         | 2.586   | $\alpha'$         | 381.5 |
|                 | 6   | 2.857         | 2.578   | $\alpha'$         | 443.9 |
|                 | 9   | 2.846         | 2.571   | $\alpha'$         | 472.0 |

Figure 8. The $\beta$O–Md diagram of Ti–30Zr–xM (M = Nb, V, Mo, Cr, Fe, Ni and Al) alloys. The $\alpha'/\alpha''$ martensite and $\beta$ phases are identified by a black triangle and a black rectangle, respectively, whereas a black circle indicates the coexistence of both phases.
ability. Zr also exhibits $\beta$-stability effect in these alloys. Both of Ni and Al show pronounced solid solution strengthening effect and the addition of Ni induces the appearance of $(\text{Ti},\text{Zr})_2\text{Ni}$ phase in Ti–30Zr–5/15Ni alloys. The Bo–Md diagram shows the effectiveness of describing the phase structures of Ti–30Zr–M alloys and is helpful in investigating the alloying effect of other elements. Both the addition of a small amount of Nb and the use of $\beta$ phase are effective ways to decrease the microhardness of Ti–Zr based alloys. We expect that the Ti–Zr based alloys could be developed as shape memory alloys or low elastic modulus materials in aerospace and biomedical applications.

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