TiAu based shape memory alloys for high temperature applications

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Abstract. TiAu (equiatomic) exhibits phase transformation from B2 (ordered bcc) to thermoelastic orthorhombic B19 martensite at about 875K and thus TiAu is categorized as high temperature shape memory alloy. In this study, recent research and developments related to TiAu based high temperature shape memory alloys will be discussed in the Introduction part. Then some results of our research group related to strengthening of TiAu based high temperature shape memory alloys will be presented. Potential of TiAu based shape memory alloys for high temperature shape memory materials applications will also be discussed.

1. Introduction

Ti-50Au (atomic %) has B19 orthorhombic martensite at room temperature that transforms to detwinned martensite upon mechanical loading and B2 (ordered bcc) phase at around 875K upon heating. Upon cooling, B2 phase reverts back to B19 orthorhombic martensite phase at around 830K. Transformation from B19 ↔ B2 is thermoelastic in nature and Ti-50Au is categorized as high temperature shape memory alloy [1]. Melting point and phase transformation temperatures of Ti-50Au is ~100K higher than Ti-50Pd [2, 3]. Ti-50Ni also known as nitinol is famous shape memory alloy. However as phase transformation temperatures of Ti-50Ni are below 100K, so binary Ti-50Ni has room temperature engineering and biomedical shape memory and super-elastic applications [4].

Phase transformation temperatures of Ti-52.6Au, Ti-50Au, Ti-47.4Au, Ti-45Au and Ti-42.5Au (e.g. all compositions in atomic%) are reported by Donkersloot H C et al. in 1970 [5]. Donkersloot H C et al. showed that the phase transformation temperatures were decreased by decreasing Au content from 52.6at.% Au to 42.5% Au. X-ray diffraction data at room temperature (RT) showed only B19 martensite for Ti-52.6Au, Ti-50Au, Ti-47.4Au and Ti-45Au. However B19+Ti3Au two phase structure was identified for Ti-42.5Au [5]. Decrease in the austenite finish temperature ($A_f$) and the martensite finish temperature ($M_f$) with the decrease in Au content in TiAu from Ti-52.6Au to Ti-42.5Au is given in Figure 1 [5]. Decrease in the austenite transformation temperatures of TiAu per atomic percent decrease in Au content (e.g. $A_f$ and $A_s$=14K/Au) was found higher than decrease in the martensite transformation temperatures (e.g. $M_s$, $M_f$=8K/Au) from Ti-52.6Au to Ti-45Au.
Figure 1. Decrease in $A_f$ and $M_f$ with Au content of TiAu. Please see Ref. [5] for details.

Figure 2. Transformation hysteresis of Ti-50Au [9], Ti-50Pd [5], Ti-50Pt [11] and Hf-50Pd [10].
However, the decrease in the transformation temperatures from Ti-45Au to Ti-42.5Au was found at much higher rate ($\Delta T = 40K/Au$, $\Delta S = 58K/Au$, $M_s = 114K/Au$, $M_f = 136K/Au$) than decrease in transformation temperatures from Ti-52.6Au to Ti-45Au [5]. As from X-ray results, B19+Ti3Au two phase structure was analyzed for Ti-42.5Au compared to Ti-45Au that has only B19 martensite. It was analyzed from Figure 1 that there was abrupt decrease in $M_s$ and $M_f$ for Ti-42.5Au compared to Ti-45Au. This abrupt decrease in $M_s$ and $M_f$ is related to precipitation of Ti3Au for Ti-42.5Au compared to Ti-45Au that has only B19 martensitic phase at room temperature. This showed that the precipitation of Ti3Au phase in B19 martensite also affects the phase transformation temperatures [5]. Recently Hosoda-Inamura research group [6] showed that from geometrical point of view, Ti-53Au can exhibit 11% transformation strain comparable with Ti-50Ni shape memory alloy. Such high theoretical transformation strain and high transformation temperature (~875K) of Ti-50Au has attracted our research group interest to further explore this system for high temperature shape memory materials applications.

Although Donkersloot H C et al. showed the potential of Ti-50Au for high temperature applications in 1970 [5], however even uptill now, there is not much literature available related to Ti-50Au. One reason may be the high cost of Au. However for high temperature shape memory materials applications, functionality of materials is more important than cost. Compare to Ti-50Pd and Ti-50Pt high temperature shape memory alloys, cost of Au is comparable with that of Pd and Pt metals. One advantage of Ti-50Au is small temperature hysteresis compared to Ti-50Pd and Ti-50Pt as shown in Figure 2. Small temperature hysteresis is required for shape memory alloys as large temperature hysteresis results plastic deformation [1]. Hosoda-Inamura research group [7] also showed the effects of ternary additions on martensitic transformation temperatures of Ti-50Au and co-related the decrease in $M_s$ with e/a ratio, valence electron number ($N_v$), Mendeleev number ($N_m$) and lattice parameters of martensite phase. Wu S K and Wayman C M [8] showed the martensitic transformation in Ti-50Au and Ti-40Au-10Ni (atomic%) alloys. Both Ti-50Au and Ti-40Au-10Ni has orthorhomic B19 martensite (2H) and both compositions exhibit one way shape memory effect, not two way shape memory effect.

Recently Declaireieux C et al. discussed the potential of Ti-50Au as high temperature shape memory alloy [9] as Ti-50Au exhibit stable phase transformation temperatures during thermal cycling, showing thermal stability. Authors of Ref. [9] also showed that Ti-50Au exhibits partial shape memory effect (e.g. 78%) and has potential as high temperature shape memory alloy due to small temperature hysteresis and stability of transformation temperatures during thermal cycles. For comparison, transformation temperature hysteresis of Ti-50Au [9], Hf-50Pd [10], Ti-50Pd [5] and Ti-50Pt [11] is given in Figure 2. It is clear from Figure 2 that Ti-50Au exhibits small temperature hysteresis compared to Ti-50Pd, Ti-50Pd and Hf-50Pd intermetallic alloys. Small temperature hysteresis is beneficial for good shape memory properties [1]. Vermaut P et al. [10] showed that although Ti-50Au exhibits ~950MPa strength at RT and ~600MPa at 50K below $M_s$ in B19 martensite phase. However strength of Ti-50Au drastically decreases when it transforms from B19 martensite to B2 phase (~120MPa). So this is an important research challenge to improve the high temperature strength of Ti-50Au in B2 phase region. It is expected that by increasing the strength of Ti-50Au in B19 and B2 phase, its shape memory properties will also improve due to increase in critical stress for slip deformation. So we tried to improve the high temperature strength of Ti-50Au by partial substitution of Ti whose atomic radii is 0.147nm with Zr whose atomic radii is 0.158nm and size misfit parameter [19] between Ti and Zr is 0.075.

In our previous studies, we found that Zr is an effective element to improve the high temperature strength and shape memory properties of Ti-50Pt [13-14] and Ti-50Pd [15-16] alloys. Both Ti and Zr belongs to same group IV of periodic table, same crystal structure (hcp; α) at room temperature that transforms to β (bcc) phase at 1155K. Melting point of Zr (2130K) is 187K higher than Ti (1943K). Ti-Zr phase diagram shows that both Ti and Zr have complete solubility in solid (α, β) as well as in liquid phase [17]. Au-50Zr intermetallic compound also exists in Au-Zr phase diagram [18]. So due to
these properties, we were expecting that partial substitution of Ti with Zr can improve the room temperature to high temperature strength of Ti-50Au in B19 as well as in B2 phase region.

2. Experimental Procedures

Ti-50Au-10Zr (atomic %) alloy ingot was prepared by Ar arc melting method using high purity (99.9%) metals. Then alloy ingot was sealed in a silica tube with small amount of Ar gas and solution-treated at 1273K for 10.8ks followed by ice-water quenching. Sputter etching (dry etching) was performed by glow discharge optical emission spectrometer (GD-OES) using 200Pa pressure, 20W power for 30s sputtering time in Ar and N₂ gas mixture. SEM analysis was conducted of sputter etched Ti-50Au-10Zr samples at an accelerating voltage of 20KV using JEOL JSM-7001F field emission SEM. Electron probe micro analysis (EPMA) was also conducted for composition analysis. For shape memory effect measurement, rectangular samples of 3mm × 3mm × 6mm dimensions were cut from the solution-treated alloy ingot using wheel cutting machine. These samples were then compressed for 5% applied strain at test temperature of 50K below the martensite finish (Mᶠ) temperature using Shimadzu AG–X compression test system. Sample’s dimensions were measured before compression test, after 5% applied strain and after heat-treatment above the austenite finish temperature. The recovery ratio due to the shape memory effect (RSME) was calculated using following equation:

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RSME \% = 100 \times (e_s - e_r) / e_s
\]

Where \(e_s\) is the strain after deformation and \(e_r\) is the residual strain after heat-treatment above the austenite finish temperature followed by air cooling. For high temperature mechanical testing, cyclic loading–unloading compression tests were conducted for 20% applied strain at room temperature, test temperature of 50K below the martensite finish temperature and 50K above the austenite finish temperature using Shimadzu AG–X compression test system. Thermo-mechanical analyzer (TMA) was used for phase transformation temperatures between room temperature (RT) to 1073K at a heating and cooling rate of 0.17K/s in air environment.

3. Results and Discussion

Room temperature SEM micrograph of solution-treated and sputter etched Ti-50Au-10Zr alloy is presented in Figure 3. It was analyzed from Figure 3 that Ti-50Au-10Zr intermetallic alloy has two phase structure; twinned oriented martensite (matrix) and second phase at grain boundary as well as inside the matrix. Electron probe micro analysis (EPMA) of Ti-50Au-10Zr is given in Table 1. From this EPMA composition analysis, it was analyzed that the composition of matrix was close to theoretical composition and second phase at grain boundary was analyzed as (Ti,Zr)₃Au type precipitates. Some Ti₃Au second phase was also analyzed inside the matrix. It is not clear either this (Ti,Zr)₃Au second phase was formed during liquid solid transformation or it was formed during solid solid transformation. Transformation temperatures of Ti-50Au (\(M_s=870K, M_f=859K, A_s=888K\) and \(A_f=897K\)) [9] were decreased by partial substitution of Ti with Zr in Ti-50Au-10Zr alloy (\(M_s=758K, M_f=741K, A_s=768K, A_f=784K\)). Decrease in transformation temperatures was ~12K/atomic% partial substitution of Ti with Zr in Ti-50Au alloy. This showed that the role of Zr addition in Ti-50Au is to stabilize the B2 phase structure.
Ti-50Au-10Zr specimens deformed successfully for 20% applied strain at room temperature, 50K below $M_f$ and 50K above $A_f$ in air environment. This showed that Ti-50Au-10Zr has good ductility. Stress for reorientation of martensite and maximum stress for 20% applied strain at room temperature, 50K below $M_f$ and 50K above $A_f$ of Ti-50Au [10] and Ti-50Au-10Zr are presented in Figure 4 and Figure 5 respectively. It was analyzed from Figure 4 that the stress for reorientation of martensite decreased with increasing temperature for Ti-50Au [10] and Ti-50Au-10Zr. Figure 4 also showed that

**Figure 3.** SEM micrograph of Ti-50Au-10Zr. Martensite and second phase at grain boundary was analyzed.

**Table 1.** EPMA composition analysis of matrix and second phase in Ti-50Au-10Zr.

| Matrix (atomic %) | Ti   | Zr   | Au   | Comment                        |
|-------------------|------|------|------|--------------------------------|
|                   | 39.7 | 10   | 50.3 | (Ti, Zr)$_{50}$Au$_{50}$        |

| Black phase at grain boundary (atomic %) | Ti | Zr | Au   | Comment   |
|------------------------------------------|---|----|------|-----------|
|                                          | 69| 3.3| 27.7 | (Ti, Zr)$_{1}$Au            |

Ti-50Au-10Zr specimens deformed successfully for 20% applied strain at room temperature, 50K below $M_f$ and 50K above $A_f$ in air environment. This showed that Ti-50Au-10Zr has good ductility.
Figure 4. Martensite reorientation stress in B19 and flow stress in B2 phase of Ti-50Au [10] and Ti-50Au-10Zr.

Figure 5. Maximum stress for 20% strain of Ti-50Au [10] and Ti-50Au-10Zr.
Ti-50Au-10Zr exhibited lower stress for reorientation of martensite compared to Ti-50Au [10] at room temperature and at 50K below $M_f$. This result showed that stress for reorientation of martensite decreased by addition of Zr in Ti-50Au alloy. It was also analyzed from Figure 4 that Ti-50Au exhibits very low flow stress ($\sim 100$MPa) in B2 phase region, lower than stress required for martensite reorientation in B19 phase. From Figure 5, it was analyzed that Ti-50Au has very low strength in B2 phase region. Shape memory alloys having very low strength in B2 phase compared to their strength in martensitic phase are not suitable for shape memory materials applications as during mechanical loading, plastic deformation can easily introduce in such alloys in B2 phase region [1]. Figure 4 also showed that Ti-50Au-10Zr has high flow stress value in B2 phase region compared to Ti-50Au [10]. Comparing the stress values in B19 and B2 phase (Figure 4), flow stress value of Ti-50Au-10Zr in B2 phase was found higher than stress required for martensite reorientation in B19 phase region. This is an important research achievement by partial substitution of Ti with Zr in Ti-50Au alloy. Higher flow stress value in B2 phase region compared to stress required for martensite reorientation is beneficial for shape memory effect [1]. It was also analyzed from Figure 5 that the strength of Ti-50Au was improved by partial substitution of Ti with Zr in B19 martensite phase region as well as in B2 phase region.

Ti-50Au-10Zr exhibited 82% recovery ratio due to shape memory effect. Total recovery ratio (elastic recovery + recovery due to shape memory effect) after 5% applied strain for Ti-50Au-10Zr was 90% that was found higher that Ti-50Au that exhibits 78% total shape recovery ratio [9]. This result showed that partial substitution of Ti with Zr in Ti-50Au was found effective in improving the high temperature shape memory properties of Ti-50Au alloy. Still we could not achieve 100% recovery ratio due to shape memory effect and further research is in progress to enhance the shape memory properties of Ti-50Au alloy. Increase in the shape recovery ratio due to shape memory effect for Ti-50Au-10Zr as compared to Ti-50Au showed the increase in critical stress for slip deformation, decrease in residual strain and increase in recovered strain due to shape memory effect.

It should be noted that as martensite finish temperatures of Ti-50Au (859K) [9] and Ti-50Au-10Zr (741K) are well above the room temperature. So B2 phase upon cooling again transforms to twinned oriented martensite and at room temperature, there is single B19 martensite phase structure. As both Ti-50Au and Ti-50Au-10Zr exhibits partial shape memory effect, so some fraction of plastic deformation was introduced during shape memory testing.

4. Conclusions

Recent research and developments related to Ti-50Au high temperature shape memory alloys are discussed. Potential of Ti-50Au intermetallic alloy in terms of thermal stability, phase transformation temperatures, shape memory effect and temperature hysteresis is discussed in this paper. Some results of our research group to improve the strength and shape memory properties of Ti-50Au by partial substitution of Ti with Zr are presented. High temperature strength of Ti-50Au in B19 martensite as well as in B2 phase was improved by partial substitution of Ti with Zr. Partial substitution of Ti with Zr in Ti-50Au was also found effective in improving the high temperature shape memory properties. Transformation hysteresis ($A_f - M_f$) of Ti-50Au (38K) was slightly increased by partial substitution of Ti with Zr in Ti-50Au-10Zr (43K) alloy. Ti-50Au-10Zr has potential for high temperature shape memory materials applications.

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