Effect of heat treatment on morphology evolution of Ti$_2$Ni phase in Ti-Ni-Al-Zr alloy

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Abstract. The Ti6Al2Zr alloy with 15 wt.% Ni addition was prepared and then heat treated in the research. The microstructure of the alloy and evolution of Ti$_2$Ni precipitate were investigated. The microstructure observations demonstrate that the Ni addition could promote the formation of eutectoid and eutectic structures in Ti-Al-Zr alloy. In the eutectoid structure, the ultrafine Ti$_2$Ni fiber precipitates in the $\alpha$-Ti matrix, but in the eutectic structure, the fine $\alpha$-Ti phases precipitate in the Ti$_2$Ni matrix. The heat treatment could change the morphology of Ti$_2$Ni precipitates by thinning, fragmenting, merging and spherizing. In the alloy heat treated at and below 1073K, the coarsening of $\alpha$-Ti precipitates in eutectic structure and Ti$_2$Ni precipitates in eutectoid structure is the mainly characteristic. In the alloy heat treated above 1073K, the phase transformation of $\alpha$ to $\beta$ phase is the main characteristic, which changes the morphology and amount of Ti$_2$Ni phase by the solid solution of Ni. The phase transformation temperature of Ti-Ni-Al-Zr alloy is between 1073-1123K, which is increased compared with that of the Ti-Ni binary phase diagram.

1. Introduction
Titanium (Ti) has been extensively investigated and applied in medical, sports and aircraft industries because of its good corrosion resistance and mechanical properties [1]. In fact, the strength of the Ti is relative low. In order to increase its strength, alloying elements have been introduced and many Ti based alloys have been designed [2-3]. The Ti-Al-Zr based alloy is a typical one with $\alpha$ phase and high strength [4]. Once, it is considered as one promising candidate to used as tube in reactor field. However, the high processing cost and poor formability handicap its application. Moreover, the high internal stress in titanium alloy generated by hot working always needs further heat treatment [5]. On the other side, the processing and heat treatment would exert great influence on microstructure, phase and precipitate. The recent researches exhibit that the performance of the alloy could be strongly affected by the microstructure and precipitate [6-8]. Then the titanium alloy needs a processing with less internal stress. The previous research exhibited that the semi-solid processing might be a promising technique for titanium alloy processing by involving liquid phase, which could improve the formability and decrease the internal stress [9-11]. Moreover, the investigations on the semi-solid processing of Al and Ni based alloys shows that the semi-solid state could lower the deformation resistance [12,13]. Therefore, it can be believable that the semi-solid processing could be helpful to the processing of Ti alloy. However, the former study exhibits the semi-solid processing has obvious difference between titanium alloy and conventional materia[14]. It requires that the alloy should have a big difference between solid temperature and liquid temperature. In fact, the liquid temperature and solid temperature of Ti-Al-Zr alloy differ little. Therefore, the Ni has been added in the alloy to lower its melting point. While, it is disappointed that the addition of Ni would promote the precipitation of stiff Ti$_2$Ni phase which is harmful to the formability. Then the further study on the
precipitation behavior of Ti$_2$Ni phase in the Ni doped Ti-Al-Zr alloy should be carried. Therefore, the Ti6Al2Zr alloy with 15% (wt.%) Ni is prepared and heat treated in the present study. Its microstructure have been investigated to reveal the evolution of Ti$_2$Ni precipitate.

2. Experimental procedure

The alloy with chemical composition of Ti-15Ni-6Al-2Zr (wt%, Ti-Ni-Al-Zr for short) was fabricated by arc-melting under vacuum condition and the metals of Ni (99.9%), Zr (99.8%), Al (99.9%) and Ti (99.9%) were used. To obtain the alloy with heterogeneous composition, the prepared alloy button was remelted for four times. The observation and heat treatment specimens (8 mm×8 mm×10 mm) were cut from the as fabricated alloy. Then the heat treatments between 973K and 1173K with 50K interval were performed on the specimens for 30 minutes in vacuum heat treatment furnace and followed air quenching. The metallographic samples were fabricated by mechanical polishing and then chemical etching by a solution of 25% hydrochloric acid and H$_2$O. The X-ray diffraction (XRD) analysis was performed on the Rigaku D/max 2400 x-ray diffractometer with Cu Ka radiation to identify constituent phases. The S-3400 scanning electron microscopy (SEM) with Energy Dispersive Spectrometer (EDS) was applied for microstructure characterization. The slices for transmission electron microscope (TEM) observation were cut from alloy with thickness about 0.5 mm. Then the specimen was polished to 30 μm and shaped into φ3 mm in size followed by ion milling to perforation. TEM observation and analysis were performed on the JEOL-2100.

3. Results and Discussion

Microstructure observations on the as fabricated Ti-Ni-Al-Zr alloy are exhibited in Fig.1. Obviously, the alloy mainly demonstrated the dendritic structure which comprises the eutectic structure and eutectoid structure, as exhibited in Fig.1 (a). The observation on the eutectic structure reveals that there are small precipitates in the eutectic structure, as exhibited in Fig.1 (b). The composition analysis by EDS reveals that it is rich of Ti. Then, it can be deduced that the precipitate should be α-Ti phase, which exhibits fine rod-like shape and has the average diameter of about 450 nm. In the eutectic structure, the Ti$_2$Ni becomes the matrix. The SEM image of eutectoid structure demonstrates the α-Ti matrix contains fine fiber phases, as exhibited in Fig.1 (c). Combining with composition analysis, the fiber phase should be Ti$_2$Ni phase with the average diameter of about 100 nm.

In order to confirm the precipitate phase in the as fabricated Ti-Ni-Al-Zr alloy, the XRD analysis has been carried out. The XRD pattern is shown in Fig.2. Based on the XRD analysis, one can find that the α-Ti phase is the main matrix and the Ti$_2$Ni is the main precipitate. It also reveal that the α-Ti phase prefers to grow along (101) crystal plane and the Ti$_2$Ni prefer to grow along the (511) crystal plane. What is interesting is that the α-Ti phase almost has the similar growth preference on other crystal plane.
The characterization on the as fabricated alloy by TEM is exhibited in Fig.3 (a). The result reveals that the eutectoid structure comprises ultrafine Ti$_2$Ni phase. The average width of the Ti$_2$Ni phase is about 50 nm but the $\alpha$-Ti has average width of 100 nm. According to the recent researches [15-18], the microstructure would be affected by the additional elements, especially the final solidification region. However, the EDS analysis on the eutectoid structure and eutectic structure reveals that the eutectic structure contains more Zr element. Then it can be deduced that the increased Ni and Zr concentration promotes the formation of the coarse microstructure in eutectic structure. The selected electron diffraction (SAD) analysis on the Ti$_2$Ni/$\alpha$-Ti eutectoid structure demonstrates that the $\alpha$-Ti and Ti$_2$Ni has an orientation relationship of $[231]_\alpha \parallel [741]_{Ti_2Ni}$ and $(0-13)_\alpha \parallel (1-35)_{Ti_2Ni}$, as exhibited in Fig.3 (b).

![Fig.3](image)

**Fig.3 (a) TEM image of ultrafine Ti$_2$Ni fiber phase, (b) SAD pattern of the Ti$_2$Ni/$\alpha$-Ti structure**

Microstructure of the Ti-Ni-Al-Zr alloy with different heat treatment is exhibited in Fig.4. Obviously, the heat treatment has generated great influence on precipitate morphology and microstructure. At relative low temperature, the coarsening of precipitates is the main feature, as exhibited in Fig.4 (a) and (b). When the heat treatment temperature increases further, the eutectic structure decreases and becomes fine, but it changes from the original semi-continuous state into the continuous state and separates the eutectoid into small cells, as exhibited in Fig.4 (c) and (d). Moreover, during the heat treatment the elevated temperature induces the rapid growth of $\alpha$-Ti and Ti$_2$Ni precipitates. And the coarsening rate increases with the temperature increasing. When the temperature increases to 1123K, the merging of Ti$_2$Ni in eutectoid structure leads to the forming of bulk black phase which prefers to form along the interface of eutectic and eutectoid structures. Based on the form research [19], the bulk black phase should be $\beta$-Ti phase which is the allotrope of the $\alpha$-Ti phase. Compared with the Ti$_2$Ni phase in eutectoid structure, the $\alpha$-Ti phases just coarsens a little. According to recent researches [20-23], the heat treatment would promote the element diffusion but the diffusion rate differs greatly. Therefore, it can be deduced that the Ti could diffuse along the eutectic and eutectoid structure interface rapidly. Then the growth of $\alpha$-Ti in eutectoid structure and degeneration of eutectic structure are so great. Certainly, the enrichment of Ni along the grain boundary also promotes the formation of continuous Ti$_2$Ni phase which connects with the original eutectoid structure and separates the eutectoid structure further. With the temperature of heat treatment increased to 1173K, there is only $\beta$-Ti phase in the original eutectoid structure but the eutectic structure become fine and semi-continuous again, as exhibited in Fig.4 (e). While in the alloy treated at 1223K, the eutectic structure disappears and the left is the Ti$_2$Ni particles with polygon and stick shapes, as exhibited in Fig.4 (f).
Fig. 4 Microstructure of the heat treated alloy with variation temperature for 30min and air quenching:
(a) 973K, (b) 1023K, (c) 1073K, (d) 1123K, (e) 1173K, (f) 1223K

The XRD analysis is applied on the alloy with treatment of 1073K and 1173K to confirm the phase. The result of XRD analysis is exhibited on Fig. 5. It can be found that the heat treatment has changed the phase constituent obviously. In the alloy with treatment of 1073K/30min/air quenching, the α-Ti phase is still the main phase, but its diffraction peak becomes weak greatly compared with the as fabricated alloy, as exhibited in Fig. 5 (a). In addition, the diffraction peaks along 38.4° and 71° become strong. Though the β-Ti and Ti₂Ni phases both have the diffraction on this position, the limited Ni content indicates there would be formation of β-Ti phase. Due to the existence of Ni and Al, there is little deviation of the diffraction peak of β-Ti phase. In the alloy with treatment of 1173K/30min/air quenching, there is almost no α-Ti phase but Ti₂Ni and β-Ti become the main phases, as exhibited in Fig. 5 (b). Moreover, the β-Ti mainly prefers to grow along the (110) crystal plane. The small diffraction peak at 70.5° indicates the residual α-Ti phase in the matrix.

Fig. 5 (a) XRD pattern of the alloy treated by 1073K/30min/air quenching, (b) XRD pattern of the alloy treated by 1173K/30min/air quenching

According to the former research, the phase transformation in the Ti based alloy is mainly controlled by the composition and processing. In the present research, the Ni addition in the Ti-Al-Zr alloy promotes the formation of Ti₂Ni precipitation. However, the 15% Ni content change the alloy into the hypoeutectic region of the β-Ti/Ti₂Ni phase diagram and hypereutectoid region of the α-Ti/Ti₂Ni phase diagram, as shown in Fig. 6. Therefore, during the equilibrium crystallization there would be two reaction: L→β + Ti₂Ni and β→α + Ti₂Ni. The β-Ti phase would be the primary phase, but the α-Ti would be the stable matrix phase and Ti₂Ni phases would be the precipitation phase. At the end of the solidification, the consumption of Ti deviates the residual liquid to eutectic point and promotes the eutectic structure whose primary phase is Ti₂Ni. The heat treatments below 1073K just changes the morphology of the precipitate by coarsening but have no influence on the phase.
constituent. With the heat treatment temperature increasing to 1073K, there is the beginning of phase transformation since it is higher than the eutectoid temperature. However, the microstructure observation confirms that the transformation is little, which may be attributed to the existence of Al. With the temperature of heat treatment increased above 1123K, a lot of phase transformations from $\alpha$ to $\beta$ occur. With the phase transformation proceeding, the $\beta$-Ti phase becomes the matrix, which increase the solid solubility of Ni in matrix. Then one can see that the amount of Ti$_2$Ni phase decreases greatly. Moreover, based on the Ti-Ni phase diagram, it can be found that the solid solubility of $\beta$-Ti could increase obviously with the temperature increasing. So it would be understandable the alloy with treatment of 1173K/30min/air quenching has the minimum Ti$_2$Ni. In addition, the redissolution of Ti$_2$Ni by $\beta$-Ti phase transformation mainly take place in the eutectoid structure. The evolution of eutectic structure depends on the diffusion of Ni. Therefore, it experiences the thining, disconnecting and granulating.

Fig.6 A phase diagram of binary Ti-Ni alloys

4. Conclusions
1) The Ni addition in Ti-Al-Zr alloy promotes the formation of eutectoid and eutectic structures. In the eutectoid structure, the fine Ti$_2$Ni fiber precipitates in the $\alpha$-Ti matrix, but in the eutectic structure, the fine $\alpha$-Ti phases precipitate in the Ti$_2$Ni matrix.
2) The heat treatment could change the morphology of Ti$_2$Ni precipitates by thinning, fragmenting, merging and spherizing. In the alloy heat treated at and below 1073K, the coarsening of $\alpha$-Ti precipitates in eutectic structure and Ti$_2$Ni precipitates in eutectoid structure is the mainly feature. In the alloy heat treated above 1073K, the phase transformation of $\alpha$ to $\beta$ phase is the main characteristic, which changes the morphology and amount of Ti$_2$Ni phase by the solid solution of Ni.
3) The phase transformation temperature of Ti-Ni-Al-Zr alloy is between 1073K-1123K, which is increased compared with that of the Ti-Ni binary phase diagram. Such a phenomenon should be ascribe to the coexistence of Al and Ni in the alloy.

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