Fabrication and development of High Temperature Shape Memory Alloys

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Abstract

In the present day, the operating temperature of Ti-Ni shape memory alloys in practical applications are limited at relatively low temperature of 100 °C. For this reason, Ti-Ni shape memory alloys cannot be used in the industry where higher temperature range are required, for example, sensor in nuclear reactor, sensor control fuel injector and semiconductor inspector, etc. This research aims to fabricate shape memory alloys which can be used in high temperature range in order to extend the applications. Zirconium (Zr) was selected to be the third element to add in Ti-Ni alloy for increasing transformation temperature. The effect of Zr – content on mechanical properties and transformation behavior of Ti-Ni-Zr alloys were investigated. Ti-Ni-Zr alloys with Zr – content of 20 – 30 at. % ($Ti_{51.5-X}Ni_{48.5}Zr_X$ with X = 20-30 at. %) were prepared by induction furnace under Ar atmosphere. Transformation temperatures were detected by differential scanning calorimeter (DSC). Oxidation tests under 800°C were carried out in order to evaluated the oxidation resistance. In order to investigate the effect from cold work hardening, the alloys were cold-rolled to thin plate with reduction ratio of 5 %. Mechanical properties were evaluated by universal tensile testing. From the results, it is seen that transformation temperatures of $Ti_{51.5-X}Ni_{48.5}Zr_X$ increases from 397 - 452°C with increasing Zr – content from 20 to 25 at. %. Oxidation resistance of each specimen was clearly enhanced with increasing Zr – content. Micro – hardness and yield strength increases from 434 to 521 Hv and 300 to 383 MPa with increasing Zr – content from 20 to 30 at.%, respectively. On the other hand, percentage of elongation decreases from 8.35 to 2.16 % with increasing Zr – content from 20 to 30 at.%.

Keywords: High Temperature Shape Memory Alloys (HTSMA), Shape memory effect, Superelastic, Transformation temperature, Oxidation resistance

1. Introduction

Shape memory alloys (SMAs), TiNi alloys are an extraordinary group of materials that been attracting much attention in recent years because of their unique combination of excellent shape memory characteristics and sufficient strength and ductility. In some of practical applications, in which the requirement on high temperature transformation feature is to be met, the TiNi alloys are limited by allowing temperatures not higher than 373 K, at which the thermoelastic martensitic transformation occurs. At present, there is a strong need to develop high temperature SMAs to be applied to aircraft, automobile engines, heating and air-conditioning, and many other industries.

Ternary TiNi-*X* high – temperature SMAs with *X* being precious metals Pd, Pt, and Au, also have been developed [4-7]. However, the high cost of precious metals limits the practical application of these alloys. For this reason, other TiNi-*X* high – temperatures SMAs need to be investigated. Among them, TiNiZr SMAs are the most prospective one.

Meisner and Sivokha [2] reported that $(Ti,Zr_2)Ni_7$, $(Ti,Zr)_7Ni_{10}$ and NiZr phases can be observed in Ni-rich $Ti_{50-X}Ni_{50}Zr_X$ alloys with Zr content in the range of 30-50 at.% at room temperature. Three phase, (Ti,Zr)Ni, $(Ti,Zr)_2Ni$, and λ_1, are observed at room temperature in Ti-rich $Ti_{53-X}Ni_{47}Zr_X$ alloys with the Zr content in the range of 5-20 at.% [8]. Here, the λ_1 phases is a TiNiZr ternary solid solution and the (Ti,Zr)Ni phase can exhibit B2 ↔ B19' martensitic transformation with an M_s temperature in range of 60 – 260°C [8]. Mulder et al. [9] reported that decrease in transformation temperatures in the thermally cycled $Ti_{31.5}Ni_{48.5}Zr_{20}$ alloy is affected by the $(Ti,Zr)_2Ni$ precipitates. The aim of this study is to fabricate Ti-Ni-Zr shape memory alloys and investigate the effect of Zr-content on transformation behavior and mechanical properties.

2. Experimental

The conventional vacuum arc melting with tungsten electrode technique was employed to prepare $Ti_{51.5-X}Ni_{48.5}Zr_X$ (*X* = 20-30 at.%) alloys. Titanium (purity, 99.97%), nickel (purity, 99.9%) and zirconium (purity, 99.9%) totally about 120 g were melted and re-melt at least six times in argon atmosphere. A pure titanium button was used as a getter during the arc melting. Weight loss during melting was negligibly small. The as-melted ingots were homogenized at 900°C for 1 hr and then quenched in ice - water. The ingots were cut into several plates with EDM wire cut machine and then cold-rolled at room temperature to 5% reductions in thickness. After cold rolling, specimens were prepared for a DSC measurement, hardness test, tensile testing and oxidation test. Transformation temperatures were detected by differential scanning calorimeter (DSC). The running temperature range was from 25°C to 600°C with a heating/cooling rate of 10°C min^{-1}. Specimens for the hardness test were first mechanically polished and then subjected to measurement in a Vickers micro hardness tester with a 500 g load at room temperature. For each specimen, the average hardness value was taken from at least nine test readings. Tensile test was conducted in air with at a strain rate of $5X10^{-4}\cdot S^{-1}$. Specimens of 5X5X1.5 mm for oxidation testing were carefully cut from EDM Wire Cut machine, the cut specimens were polished on emery paper up to 1000 grit, then cleaned with ultrasonic machine in an acetone solution and weighted before test. A Du Pont Thermal Analysis System 9000 equipped with a TGA 51 thermogravimetric analyzer was used to run TGA analysis. The specimen was held in a platinum basket and surrounded by dry air flowing at a rate of 60 cm^3/min. Testing temperature was 800°C. Each sample was heated from room temperature to the testing temperature at rate of 100°C/min and then kept isothermally at that temperature for 20 min to 6 hr.

3. Result and discussion

3.1 Transformation behavior of $Ti_{51.5-X}Ni_{48.5}Zr_X$ (X = 20, 25, 30 at. %).

Figure 1 shows the experimental results of DSC measurement after solution treatment of $Ti_{51.5-X}Ni_{48.5}Zr_X$ alloys with X = 20, 25 and 30 in both forward and reverse transformations. The peaks appearing in Fig. 1 are identified as being associated with the martensitic transformation of B2 $\leftrightarrow$ B19' [1]. On the other hand, the peaks of forward and reverse transformations cannot be confirmed in $Ti_{21.5}Ni_{48.5}Zr_{30}$. It must be noted that, DSC test was conducted in the limited running temperature range from 25°C to 600°C. However, TiNiZr has a potential to show the both of peaks at temperature more than 600°C. Here M_s and M_f indicate the martensitic start temperature and finishing temperature, respectively, A_s and A_f refer to the reverse martensitic start and finish temperature, respectively. The transformation temperature versus Zr content in Fig. 1 are plotted in Fig.2, it is seen that the transformation temperature of $Ti_{51.5-X}Ni_{48.5}Zr_X$ alloys increases from 397 – 452 °C with increasing Zr – content from 20 to 25 at.%.

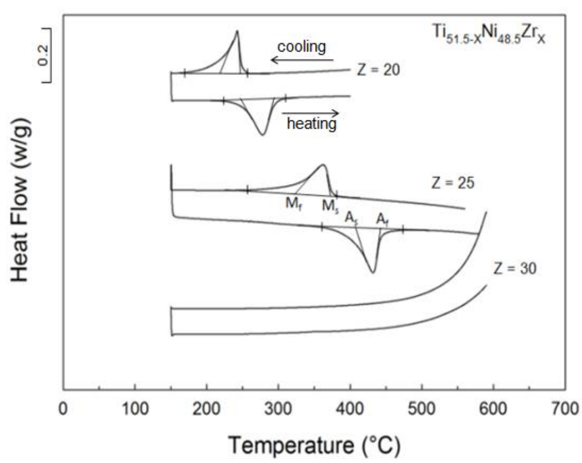

Fig.1. DSC curve of $Ti_{51.5-X}Ni_{48.5}Zr_X$ alloys (X = 20, 25, 30 at. %).

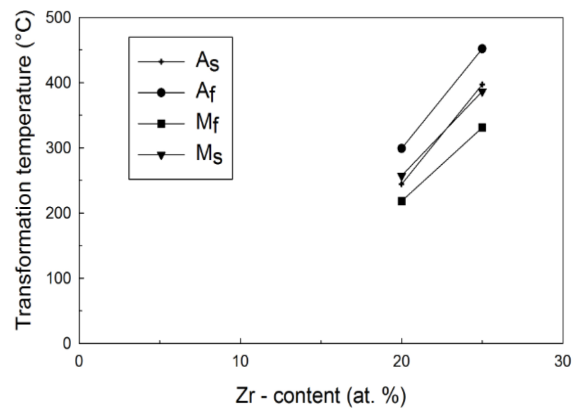

Fig.2. Effect of Zr content additions on the A_s, A_f, M_s and M_f temperature for $Ti_{51.5-X}Ni_{48.5}Zr_X$ alloys (X = 20, 25, 30 at. %)

3.2 Strengthening effect of cold rolling of $Ti_{51.5-X}Ni_{48.5}Zr_X$ alloys.

Figure 3 shows the effect of Zr content on hardness of $Ti_{51.5-X}Ni_{48.5}Zr_X$ alloys (X = 20, 25, 30 at. %) at various percent of cold rolling. Hardness increases from 434 to 521 Hv with increasing Zr – content from 20 to 30 at.%. It can be understood that, increasing the percent of cold rolling causes an increase in the volume fraction of residual martensite [3] and also introduce dislocations, which results in an increase in hardness and yield strength of these alloys.

3.3 Tensile behavior of $Ti_{51.5-X}Ni_{48.5}Zr_X$ alloys.

Figure 4 shows the effect of Zr content on yield strength and % elongation for $Ti_{51.5-X}Ni_{48.5}Zr_X$ alloys (X = 20, 25, 30 at. %) with various percent of cold rolling. It is clearly seen that the yield strength increases from 434 to 521 Hv with increasing Zr – content from 20 to 30 at.%. Moreover, yield strength also increases with increasing percent of cold rolling. On the other hand, percentage of elongation decreases from 8.35 to 2.16 % with increasing Zr – content from 20 to 30 at.%, and percentage of elongation decreased with increasing the percent of cold rolling.

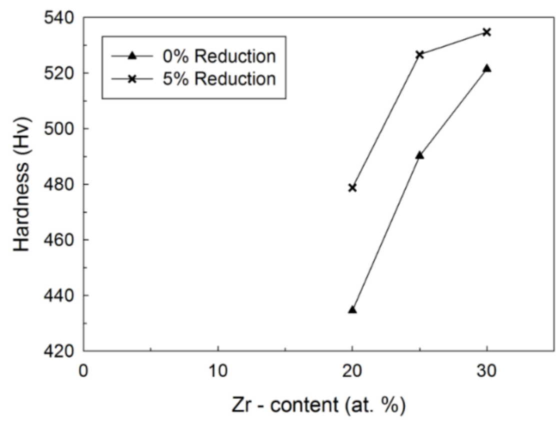

Fig.3. Effect of Zr content on hardness of $Ti_{51.5-x}Ni_{48.5}Zr_x$ alloys (X = 20, 25, 30 at. %) at various percent of cold rolling

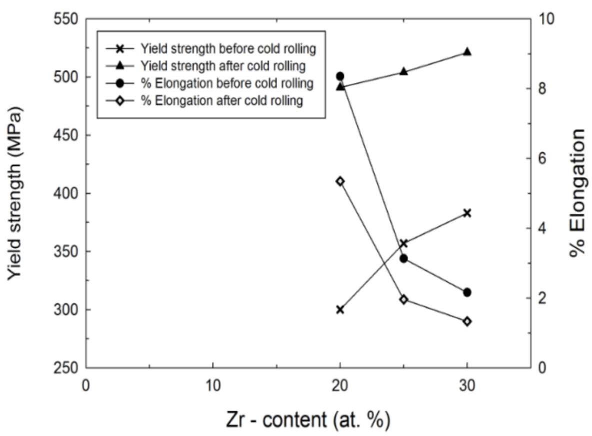

Fig.4. Effect of Zr content on yield strength and % elongation of $Ti_{51.5-x}Ni_{48.5}Zr_x$ alloys (X = 20, 25, 30 at. %) with various of percent of cold rolling

3.4 Mass gain after the oxidation resistance test.

Figure 5 shows the typical weight gain per unit surface area versus the exposure times in dry-air at 800°C. The weight gain increases rapidly at the first 120 minutes and slightly increases in the last period. The weight gain of each specimen clearly decreases with increasing Zr – content. Since it is know that Ti is easily oxidized than Zr. [10] Therefore, on the basic of the results of Fig. 5, a TiNiZr SMA alloy with more Zr – content shows better oxidation resistance.

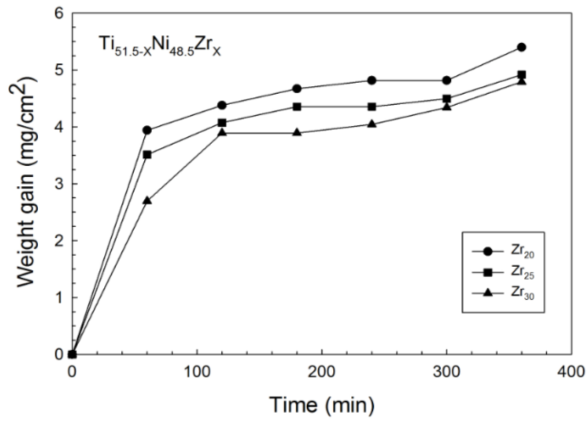

Fig.5. Weight gain vs. time plot from oxidation test of $Ti_{51.5-x}Ni_{48.5}Zr_x$ alloys (X = 20, 25, 30 at. %) at 800°C for 0-360 min. in dry air environment.

4. Conclusion

1. Transformation temperature of $Ti_{51.5-x}Ni_{48.5}Zr_x$ alloys (X = 20, 25, 30 at. %) increases from 397 - 452°C with increasing Zr – content from 20 to 25 at. %.

2. Oxidation resistance of each specimen was clearly enhanced with increasing Zr – content.

3. Micro – hardness and yield strength increases from 434 to 521 Hv and 300 to 383 MPa with increasing Zr – content from 20 to 30 at.%, respectively. On the other hand, percentage of elongation decreases from 8.35 to 2.16 % with increasing Zr – content from 20 to 30 at.%.

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