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Tensile Properties of Ti-Nb-Ge Biomedical Shape Memory Alloys

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Tensile properties and shape memory behavior of Ti alloys containing non-toxic Nb and Ge were investigated for biomedical applications. These alloying elements were chosen to remove a risk of Ni-hypersensitivity in conventional Ti-Ni shape memory alloys (SMAs). The Ti-Nb-Ge alloys with various compositions were fabricated by Ar arc melting followed by homogenization at 1273K for 7.2ks. They were then cold-rolled to a reduction of 95% in thickness. Some pieces of rolled sheets were again solution-treated at 1273K for 1.8ks and then water-quenched. Both cold-rolled and solution treated alloys were examined by shape-recovery tests in bending, tensile tests and dynamic mechanical analysis (DMA). Some of the alloys tested show good shape memory effect and/or superelasticity. The ultimate tensile strength (UTS) and fracture strain of the solution-treated alloys are in the ranges of approximately 500-600MPa and 10-40%, respectively, and their Young's modulus values are around 50GPa at human-body temperature. It is concluded that the Ti-Nb-Ge SMAs developed here are hopeful for biomedical applications.

Keywords: shape memory alloys, Ti alloys, Ti-Nb-Ge, tensile properties, DMA, superelasticity

1. INTRODUCTION

A shape memory alloy (SMA) is an important functional material for biomedical implant applications. Such biomedical SMAs should exhibit good corrosion resistance and biocompatibility as well as shape memory effect (SME) and/or superelasticity (SE). Currently, the well-known practical SMAs, namely Ti-Ni SMAs, are exclusively applied in biomedical filed; however, a risk of Ni-induced hypersensitivity has been pointed out. Therefore, from the viewpoint of biocompatibility, toxic element free, or rather, "Ni-free" biomedical SMAs are better and actually required to replace Ti-Ni SMAs so as to pursue absolute safety. Hence our group has made a systematic study to develop new Ni-free SMAs composed of Ti and non-toxic elements [1-7]. However, information available about such Ti-base SMAs is still insufficient at present. In this study, non-toxic Nb and Ge was chosen as alloying elements in Ti and the room-temperature tensile properties as well as the shape memory behavior of Ti-Nb-Ge alloys were systematically investigated.

2. EXPERIMENTAL PROCEDURE

Ti-Nb-Ge alloys containing less than 50mol%Nb and 20mol%Ge were systematically prepared using high purity elemental materials (>99.99% for Ti and Ge; >99.9% for Nb). The details of chemical compositions will be reported in near future. Before alloying, sponge Ti and granular Nb were melted by arc melting in Ar-1%H_2 using a non-consumable W electrode to eliminate impurities. Then, the arc-melted Ti and Nb above, and Ge were mixed with the total weight being 20g for each ingot and alloyed by the same arc melting method. Each button ingot was melted six times for homogenization. Since the weight change after the melting was small, no chemical analysis was carried out. The arc-melted buttons, encapsulated in evacuated quartz tubes, were homogenized at 1273K for 7.2ks, and then quenched into water. The buttons were then cold-rolled up to 95% reduction to obtain sheets of thickness 0.4mm.

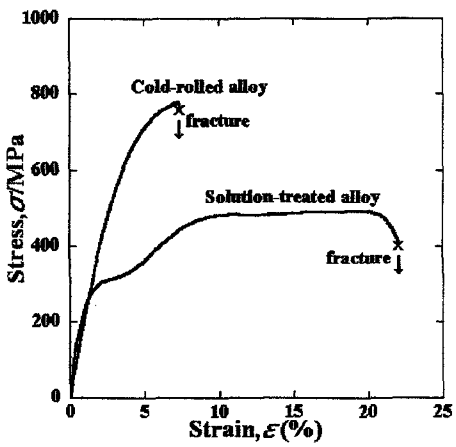

Figure 1 Tensile stress-strain curves of solution-treated alloy and cold-rolled alloy at room temperature.

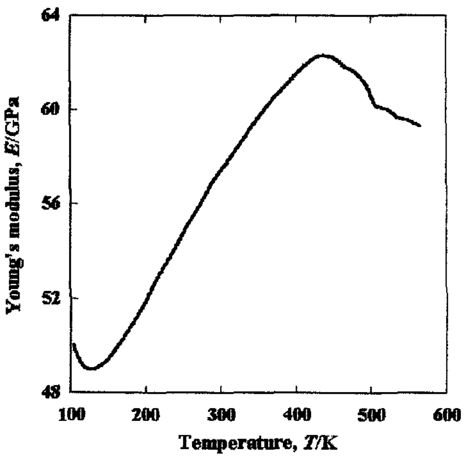

Figure 3 Young's modulus as a function of temperature in solution-treated alloy during cooling.

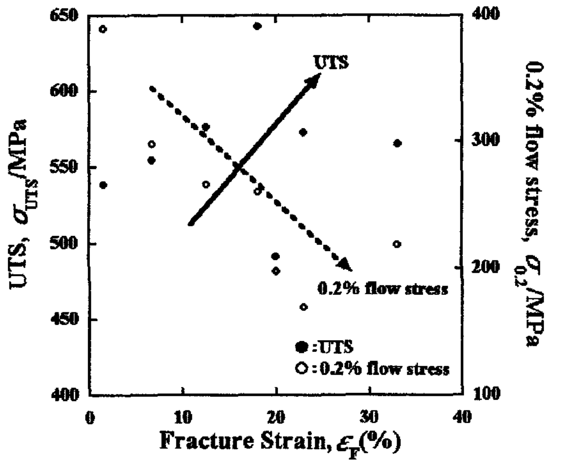

Figure 2 UTS and 0.2% flow stress as a function of fracture strain in solution-treated alloys.

Some of the rolled sheets were solution-treated at 1273K for 1.8ks.

Both cold-rolled and solution-treated alloy specimens were examined by shape recovery tests in bending and room-temperature tensile tests. In addition, dynamic mechanical analysis (DMA) was also made in the temperature range from 100K to 570K using NETZSCH DMA242C.

Bending tests revealing shape memory effect (SME) and superelasticity (SE) were carried out where specimens were deformed in a round shape at room temperature and then heated. Tensile tests were carried out at room temperature under the strain rate of less than 5×10^{-4}/s using Shimadzu Autograph AG500NI. The gauge length, width and thickness of the tensile specimens was 10mm, 1mm and 0.3-0.4mm, respectively. In order to evaluate SME and SE properties, cyclic loading-unloading tests with or without intermediate heating after unloading were performed. Young's modulus at temperatures ranging from 100K to 570K was measured by DMA (NETZSCH DMA242C) where the heating/cooling rate and the frequency were selected to be 5K/min and 5Hz, respectively.

3. RESULTS AND DISCUSSION

3.1 Mechanical Properties

Figure 1 shows examples of stress-strain (SS) curves obtained for solution-treated and cold-rolled alloys with the same chemical composition. With increasing strain (engineering strain), it is seen for the solution-treated alloy that (1) yielding occurs at 2% strain, (2) the work hardening after yielding becomes small below 5% strain, (3) second yielding and large work hardening occur over 5% strain and (4) small work hardening appears again after 10% strain. The initial part of the SS curve showing small work hardening between 2% and 5% strain is called the "stress plateau". It is known that the shape change at the plateau is mainly caused by the development of reorientation of martensite variants when the martensite phase is stable at the temperature, or of stress-induced martensitic transformation when the parent phase is stable. The strain to fracture is over 20% for

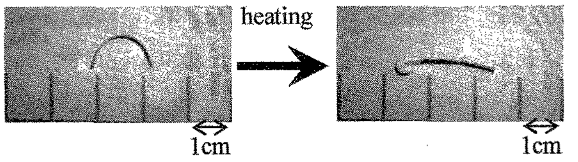

Figure 4 A bending test of solution-treated alloy. After deformation (left side), shape memory effect is observed by heating (right side).

the solution-treated alloy while it is less than 5% for the cold-rolled alloy. In common, it was seen that the fracture strain is larger in the solution-treated alloy than in the cold-rolled alloy. On the other hand, the ultimate tensile strength (UTS) reaches approximately 800MPa for the cold-rolled alloys. The UTS in solution-treated alloys is lower than in cold-rolled alloys.

Figure 2 shows the UTS and 0.2% flow stress (yield stress) as a function of fracture strain in solution-treated alloys. The UTS, 0.2% flow stress and fracture strain change in the ranges 490-640MPa, 170-390MPa and 9-37%, respectively. These values are enough for a biomedical shape memory alloy. It seems that UTS tends to increase with increasing fracture strain. However, 0.2% flow stress tends to decrease with increasing fracture strain.

In figure 3, Young's modulus measured by DMA is plotted as a function of temperature during cooling for a solution-treated alloy. Young's modulus is approximately 55GPa at around the human body temperature (~300K). This value is lower than that of most Ti-alloys (60-80GPa) and closer to that of the human bone (20GPa), suggesting that the Ti-Nb-Ge alloys are suitable for biomedical applications in terms of elastic modulus. Young's modulus of the alloy depends on temperature in a general manner due to the martensitic phase transformation [8]. Lower elastic modulus at the body temperature can be achieved by controlling phase transformation temperature.

3.2 Shape Memory Properties

Figure 4 shows a result of bending tests for the same alloy shown in Fig.1. It is clearly seen that the specimen possesses shape memory effect. The shape of

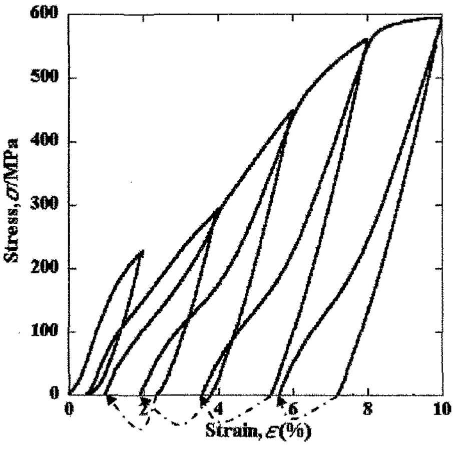

Figure 5 Cyclic loading-unloading tensile tests for solution treated alloy. Potted arrows indicate shape recovery by heating.

specimen is not completely recovered after heating. Such incomplete shape recovery is often seen in solution-treated or annealed SMAs because of dislocation slip. A shape memory treatment improving SME of the Ti-Nb-Ge alloys should be developed.

Figure 5 shows SS curves obtained through cyclic loading-unloading tensile deformation. The dotted allows indicate the shape recovery by heating. Few shape recovery strain was recognized after the first deformation. However, the shape recovery strain increased with increasing the order of cycles in deformation. The maximum shape recovery strain seen in Fig.5 exceeds 2.1% after the third cycle. The reasons why the shape recovery strain increases with increasing deformation strain are that: (1) at the first cycle, the plastic deformation strain by dislocation slip and growth takes place prior to martensitic transformation and then (2) deformation structure by dislocations is developed and the critical stress for slip increases due to the work hardening, therefore, (3) martensitic transformation occurs stably prior to dislocation slip in the deformed alloy. It is also seen in Fig.5 that the stress required for the reorientation of martensite variants (stress plateau) decreases with increasing cycles of deformation. This is due to the development of internal stress field caused by increasing dislocation density.

Figure 6 shows SS curves obtained through cyclic loading-unloading tensile deformation of the same alloy shown in Fig.3. Dotted arrows indicate the superelastic shape recovery by unloading only. Small shape recovery strain was recognized after the first deformation but the shape recovery strains increased with increasing the order of cycles in deformation. These phenomena are similarly to Fig.5. The stress for inducing martensitic transformation decreases by developing internal stress caused by dislocations. The maximum superelastic shape recovery strain seen in Fig.6 exceeds 1.9% after the third cycle. A bending test for this alloy shows small shape recovery by heating. Reverse martensitic transformation is not completely finished in the experimental conditions.

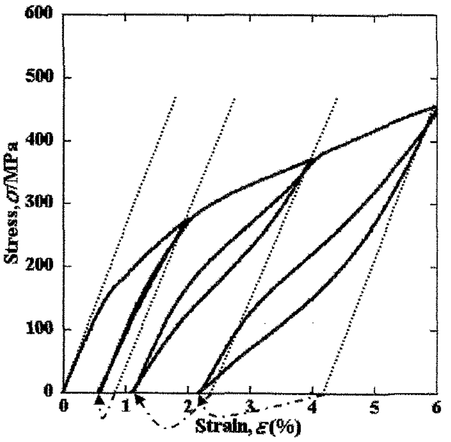

Figure 6 Cyclic loading-unloading for solution treated alloy. Potted arrows indicate superelastic shape recovery by unloading.

4. SUMMARY

In order to develop new Ni-free biomedical shape memory alloys replacing Ti-Ni, tensile properties and shape memory properties were investigated for Ti-Nb-Ge alloys. It was found that all alloys fabricated in this study exhibit superior ductility; and cold rolling can be performed more than 95% in reduction of thickness. UTS, 0.2% flow stress and tensile elongation of solution-treated alloys are ranged to be 490-640MPa, 170-390MPa and 9-37% respectively. Young's modulus is around 55GPa at the body temperature. Selected alloys indicate shape memory effect and superelasticity at room temperature. The shape recovery strain with heating and the superelastic shape recovery are improved by cyclic deformation. Martensitic transformation of the alloys must be closely related to the dislocation substructure developed during deformation.

ACKNOWLEDGEMENTS

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