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Pseudoelastic Properties of Cold-Rolled TiNbAl and TiNbGa Shape Memory Alloys

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Ni-free titanium base shape memory alloys (SMAs) become significant as new candidates for biocompatible functional uses, and are expected to replace practical Ti-Ni SMAs with a possibility of Ni-hypersensitivity. In this study, two kinds of titanium base SMAs were investigated for the systems of Ti-Nb-Al and Ti-Nb-Ga in terms of mechanical properties. Especially, the effect of cold-rolling on pseudoelasticity and hardness was aimed in comparison with solution-treated alloys which exhibit superelasticity. The alloys were fabricated by Ar arc melting method and homogenized at 1273K, then cold-rolled up to 95% in thickness reduction. Vickers hardness measurements and tensile tests were carried out at room temperature. It was found the hardness values of cold-rolled alloys were HV222 and HV245, which were higher than those of solution-treated alloys (HV173 and HV200). It was also found that both the elongation and the fracture strength of TiNbGa were higher than those of TiNbAl, and that no or very small pseudoelasticity appeared for either cold-rolled alloy. However, small pseudoelastic shape recovery appeared and became larger with increasing the number of cyclic deformation even for cold-rolled alloys. It is concluded that the pseudoelasticity appeared for the cold-rolled alloys is not superelasticity and that the origin of the pseudoelasticity is due to the internal stress field formed by development and reconfiguration of dislocations during cyclic deformation.

Keywords: shape memory alloys, superelasticity, pseudoelasticity, Ti-Nb-Al, Ti-Nb-Ga, Vickers hardness

1. INTRODUCTION

Ti-Ni shape memory alloys (SMAs) are now widely and practically used for the biomedical applications such as stent and catheter. No biocompatible problems have been reported as far as we know. However, the elemental Ni exhibits so-called Ni-hypersensitivity, then, Ni-free SMAs composed of nontoxic elements should be developed in order to improve biocompatibility of SMAs. Hence our group has made a systematic work to develop new Ni-free SMAs based on titanium and other non-toxic elements [1-8]. In the previous report the superelasticity and effect of cyclic deformation on superelasticity were investigated for the solution-treated TiNbAl and TiNbGa alloys [8]. It was found that, with increasing the number of cycles, (1) the stress inducing martensitic transformation decreases and (2) the superelasticity becomes clear due to training effect. Then, the purpose of this paper is to clarify the pseudoelastic properties of cold-rolled TiNbAl and TiNbGa in comparison with the solution-treated alloys. The effect of cyclic deformation was mainly investigated.

2. EXPERIMENTAL PROCEDURE

Two kinds of titanium base SMAs, TiNbAl and TiNbGa, were prepared. The details of the chemical compositions and the fabrication process were described in Ref.[8]. The arc-melted ingots were homogenized at 1273K for 7.2ks in vacuum, and then cold-rolled to be 95% reduction in thickness. The final thickness of cold-rolled sheets was around 0.4mm. Mechanical and shape memory properties of the cold-rolled specimens were evaluated using Vickers hardness tests and tensile tests at room temperature (RT). Specimens for the mechanical tests were cut from the sheets and damaged surface was removed by polishing. Vickers hardness tests were performed using Akashi HM-103 under the load of 500g and loading time of 15s. At least 7 readings were carried out for each alloy and averaged excluding the highest and lowest values. Cyclic loading and unloading tensile tests were conducted under the stain rate of 5×10^{-4}/s using Shimadzu Autograph AG-100kNI. At the cyclic loading-unloading tests, the applied strain increased constantly by 2% per cycle with increasing the number of cycles, *i.e.*, a specimen was loaded to 2%, unloaded, loaded to 4%, unloaded, loaded to 6%, unloaded, and so on. The cyclic loading-unloading tests were done up to failure. The gauge size of specimens was 10mm in length, 1mm in width and 0.4mm in thickness.

3. RESULTS AND DISCUSSION

3.1 Vickers hardness

Vickers hardness of alloys after cold rolling is shown in Figure 1. Data for the solution-treated alloys were added. The hardness was HV173 for solution-treated TiNbAl, HV200 for cold-rolled TiNbAl, HV222 for solution-treated TiNbGa and HV245 for cold-rolled TiNbGa. HV values of TiNbGa are higher than those of TiNbAl alloys. By comparing the solution-treated and cold-rolled specimens, it is clear that HV values are raised by cold rolling due to work hardening. However, the increment of hardness is not so large. The values of hardness increases were ΔHV20-30 even though the cold-rolled specimens were severely deformed over 95% reduction in thickness.

3.2 Cyclic loading-unloading tests

Figures 2 shows stress-strain curves obtained for the cyclic loading-unloading tests. In these experiments, the specimens were firstly deformed up to 2% and unloaded. Then, the specimens were again loaded up to 4% (previous strain of 2% and additional constant strain

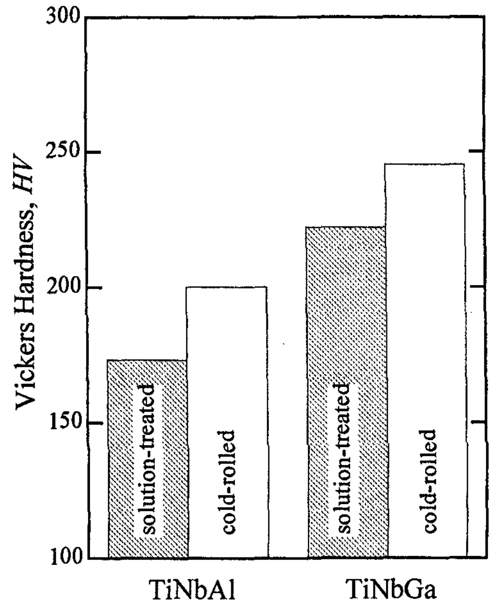

Figure 1 Vickers hardness of solution-treated and cold-rolled TiNbAl and TiNbGa.

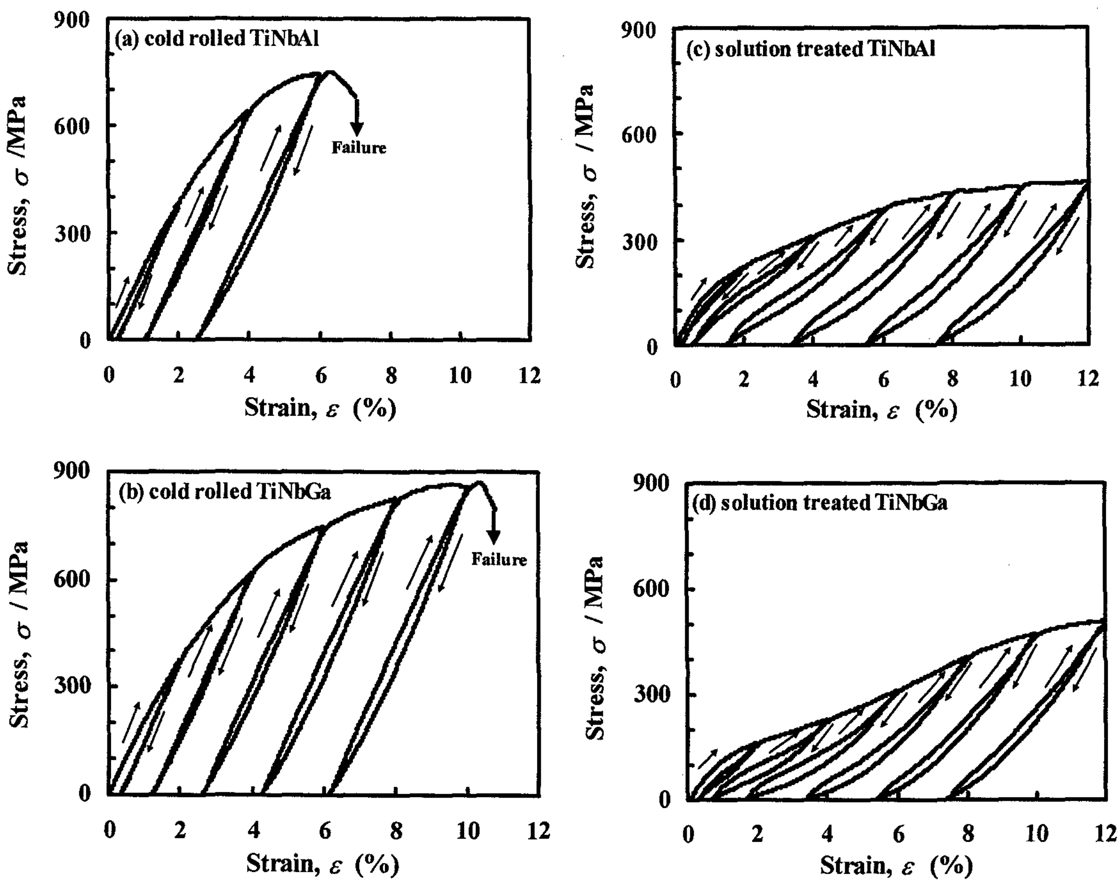

Figure 2 Stress-strain curves obtained by cyclic loading-unloading tests at RT: (a) cold-rolled TiNbAl, (b) cold-rolled TiNbGa, (c) solution-treated TiNbAl and (d) solution-treated TiNbGa. SS curves of (c) and (d) were redrawn from Ref.[8].

of 2%) strain and unloaded. Moreover, they were loaded again up to 6% (=4%+2%) and unloaded. The specimens were deformed up to 12% if they were not fractured. The data for the solution-treated alloys in Ref.[8] were added. It is clear that both cold-rolled TiNbAl and TiNbGa exhibit no superelasticity at the first deformation cycle. However, with repeating deformation, small pseudoelastic behavior appears. Such training effect is clearly seen in (c) and (d): the stabilization of pseudoelasticity for the solution-treated alloys is considered to be caused by the development and configuration of dislocations introduced during deformation. A mechanism of the training effect of the cold-rolled alloys will be discussed in the below section.

The elongation and the ultimate tensile strength of the cold-rolled alloys estimated were 750MPa and 3% for TiNbAl and 870MPa and 7.6% for TiNbGa, respectively. TiNbGa shows better mechanical properties than TiNbAl under the experimental conditions.

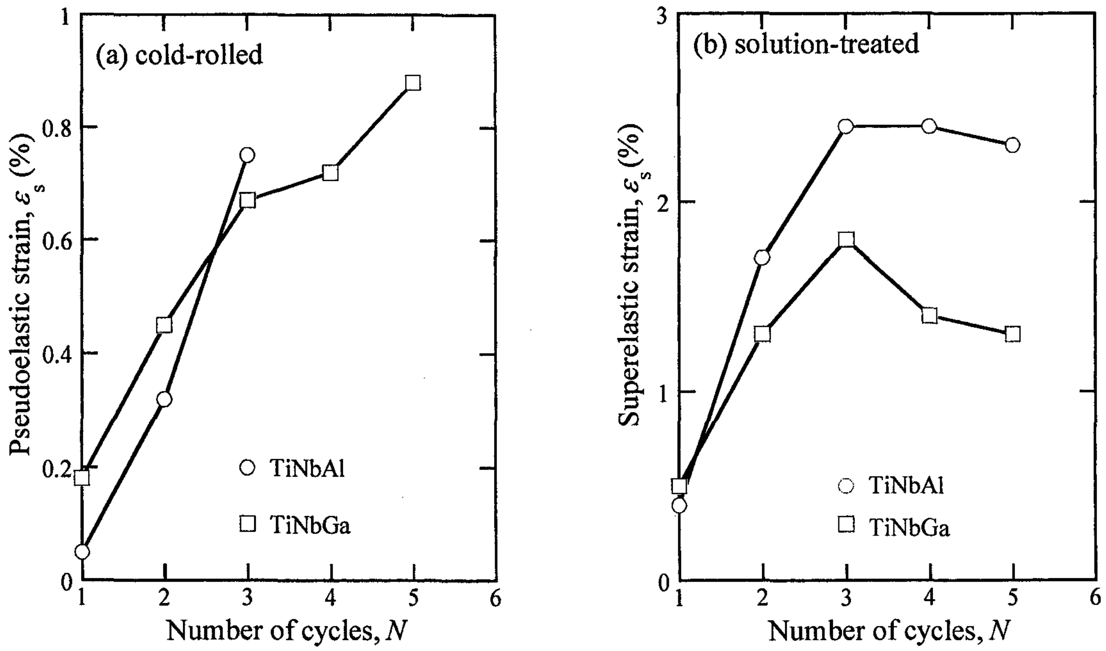

Figure 3 Pseudoelastic strain of TiNbAl and TiNbGa alloys as a function of number of loading-unloading cycles: (a) cold-rolled alloys (present work) and (b) solution treated alloys (previous work [8]).

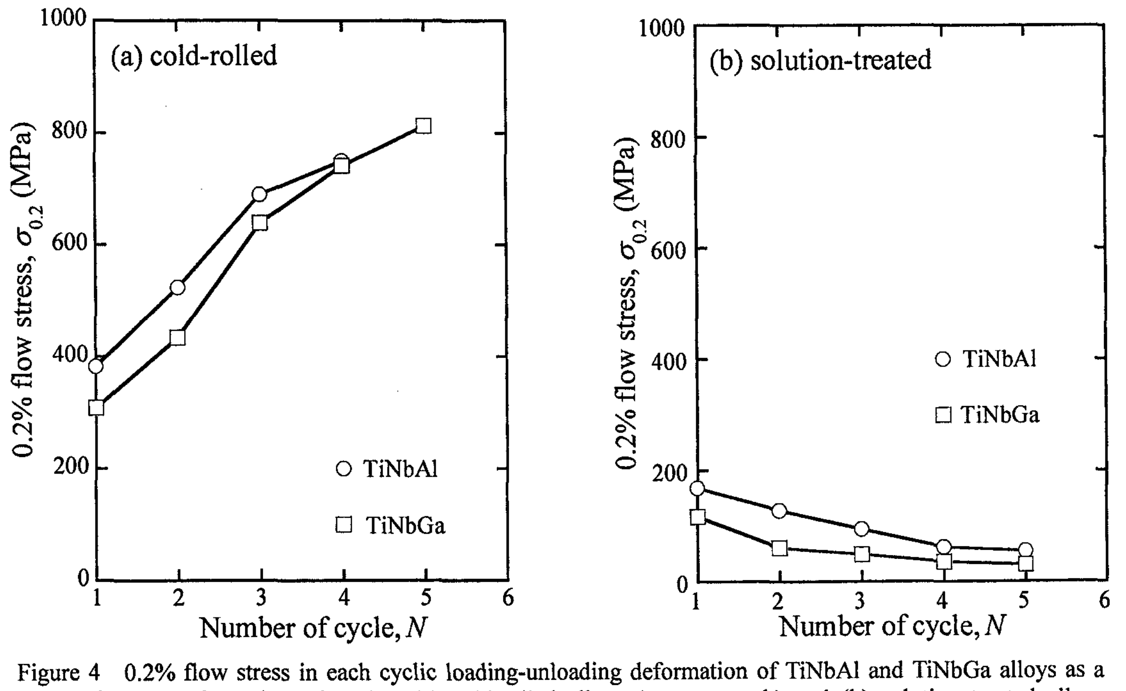

Figure 4 0.2% flow stress in each cyclic loading-unloading deformation of TiNbAl and TiNbGa alloys as a function of number of cycles: (a) cold-rolled alloys (present work) and (b) solution treated alloys (previous work [8]).

3.3 Pseudoelasticity

The cyclic loading-unloading deformation is clearly affects the pseudoelastic behavior of TiNbAl and TiNbGa cold-rolled alloys as well as solution treated alloys. However, a difference in the training effect is seen between cold-rolled and solution-treated alloys. Figure 3 shows the effect of cyclic deformation on pseudoelastic (superelastic) strain: (a) cold-rolled alloys and (b) solution-treated alloys [8]. The pseudoelastic stain of cold-rolled alloys in (a) monotonously increases with increasing the number of cyclic loading-unloading deformation. On the other hand, with increasing the number of cycles, the superelastic strain of solution-treated alloys in (b) increases, reaches the maximum values, and then keeps constant or slightly decreases. Therefore, the training effect of cold-rolled alloys is different from that of solution-treated alloys.

Figure 4 shows the effect of cyclic deformation on 0.2% flow stress of each cyclic deformation: (a) cold-rolled alloys and (b) solution-treated alloys [8]. The 0.2% flow stress of cold-rolled alloys in (a) monotonously increases with increasing the number of cycles. On the other hand, 0.2% flow stress of solution-treated alloys in (b) monotonously decreases with increasing the number of cycles. It was already mentioned that the superelasticity appeared for the solution-treated alloys becomes stable by the plastic deformation introduced during cyclic deformation. The stress for inducing martensitic transformation (σ_{SIMT}) of solution-treated alloys becomes lower with development of internal stress as shown in Fig.4 (b). This is due to the Clausius-Clapeyron relationship. However, the 0.2% flow stress shown in Fig.4 (a) increases with increasing the number of cycles, rather, with larger plastic deformation. The flow stress appeared for the cold-rolled alloys is not thought to be the stress for inducing martensitic transformation, but for the reorientation of martensite variants. It should be noted that these cold-rolled alloys were martensite phase (instead of parent phase) due to severe deformation. Then, the pseudoelastic behavior seen in the cold-rolled alloys was not superelasticity even though the solution-treated alloys exhibit superelasticity. The origin of the pseudoelastic behavior of the cold-rolled alloys is thought to be the reorientation of martensite variants due to the internal backstress field which is formed by development and reconfiguration of dislocations during cyclic deformation.

4. CONCLUSIONS

The effect of cyclic loading and unloading tensile deformation on pseudoelasticity was investigated for the cold-rolled TiNbAl and TiNbGa shape memory alloys which exhibit superelasticity after the solution treatment. It is found that both alloys possess higher hardness than the solution-treated alloys due to large cold deformation around 95% thickness reduction. No pseudoelastic behavior was observed after cold rolling. However, pseudoelastic behavior appears and becomes clear with increasing the number of cyclic loading-unloading deformation. Besides, with increasing the number of cyclic deformation, the 0.2% flow stress of each cycle increases in the cold-rolled alloys whilst it decreases in the solution-treated alloys. Then, the pseudoelasticity appeared for the cold-rolled alloys is not superelasticity, and the origin of the pseudoelasticity of cold-rolled alloys is probably reorientation of martensite variants due to the development and reconfiguration of dislocations during cyclic deformation.

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