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Effect of Re Addition on Martensitic Transformation Behavior of Ni-Al Alloys

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The martensitic transformation behavior and shape memory properties were investigated in Ni-(32-37)at%Al-(0-2)at%Re alloys by differential scanning calorimetry(DSC), transmission electron microscopy (TEM) and thermal cycling tests under various stresses. The transformation temperature increases linearly with decreasing Al content from 37at% to 35.4at%. For Ni-(34-35.2)at%Al ribbons, the Ni_5Al_3 phase formed during heating at 10K/min disturbed the reverse martensitic transformation above 540K. The addition of Re raised the formation temperature of Ni_5Al_3 phase by about 150K, so the stable martensitic transformation and shape memory effect were obtained between 500-600K in Ni-34Al-2Re ternary alloy.

Key Words : Ni-Al, Shape Memory Alloy, Martensitic Tranformation, Rapid Solidification

1. INTRODUCTION

High temperature shape memory materials have attracted much interest in recent years because of their potential applications for high temperature devices. Conventional Ti-Ni binary alloys are limited due to the martensitic transformation start (*Ms*) temperature below 350K. Several candidates for high temperature shape memory alloys have been investigated [1, 2]. The addition of platinum, palladium, gold in replacement of Ni in Ti-Ni alloys can raise the *Ms* temperature more than 800K. Besides, 20% addition of zirconium and hafnium increase the *Ms* temperature to about 550K. However, the TiNi-based alloys have an intrinsic problem for high temperature applications because the titanium is quite active in air at elevated temperatures. Not only high transformation temperature, but also high critical stress for slip or creep, stable microstructure and oxidation resistance are required for stable shape memory effect at high temperatures.

Ni-rich Ni-Al alloys are considered as prospective shape memory materials for high temperature applications due to high martensitic transformation temperatures and good oxidation resistance. The martensitic transformation behavior of Ni-Al alloys has been investigated extensively in the last decades. The B2 parent phase transforms to the $L1_0$ and/or 14M thermoelastic martensite on fast cooling. The martensitic transformation temperature of the Ni-Al alloy increases linearly with increasing Ni content, and can be as high as 1173K [2-5]. However, the instability of the martensitic phase and low ductility are major problems for engineering applications. It has been reported that the formation of the equilibrium Ni_5Al_3 in the martensite phase disturbs the reverse martensitic transformation and shape memory effect in Ni-Al alloys [6-13].

In this study, the martensitic transformation behavior was investigated in rapidly solidified Ni-(32-37)at%Al-(0-2)at%Re alloys by differential scanning calorimeter (DSC), transmission electron microscope (TEM) and thermal cycling test. The effect of Re addition on the martensitic transformation behavior and the shape memory property was discussed.

2. EXPERIMENTAL PROCEDURE

Master alloys of Ni-(32-37)at%Al-(0-2)at%Re were prepared by arc melting under an argon atmosphere. Hereafter, Ni-xat%Al-yat%Re is abbreviated to Ni-xAl-yRe. Ribbons were fabricated by the single roller melt-spinning technique with a surface velocity of 42m/s in an argon atmosphere. The fabricated melt-spun ribbons were of 25-35μm in thickness and 1mm in width. The martensitic transformation behavior of as-spun ribbons was investigated using DSC in the range from 173K to 873K at a heating and cooling rate of 10K/min. Thermal cycling tests were carried out under various constant stresses. Microstructure was observed by TEM operated at 1000kV voltage. The specimens for TEM were

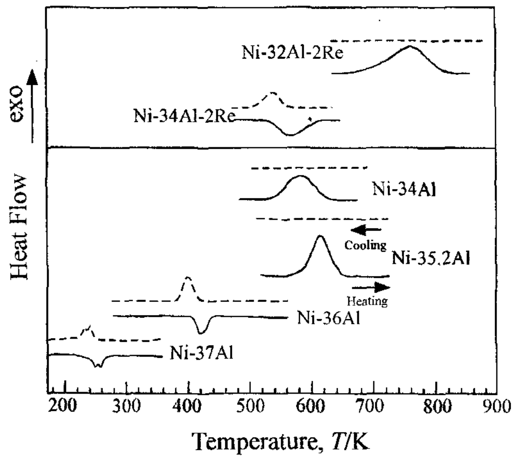

Fig. 1. DSC curves of Ni-Al and Ni-Al-Re as-spun ribbons.

prepared by electro-polishing using CH_3COOH-5%$HClO_4$ electrolyte.

3. RESULTS AND DISSCUSSION

3.1. Martensitic transformation behavior

Fig. 1 shows the DSC curves of Ni-(34-37)Al and Ni-(32-34)Al-2Re as-spun ribbons. Both forward and reverse martensitic transformation peaks were observed in the Ni-(36-37)Al and Ni-34Al-2Re as-spun ribbons. However, the DSC curves of the Ni-(34-35.2)Al and Ni-32Al-2Re as-spun ribbons exhibit an exothermic peak instead of an endothermic peak corresponding to the thermoelastic reverse martensitic transformation to the parent phase. It has been known that the exothermic peak is due to the formation of Ni_5Al_3 phase during heating [12, 13]. It is considered that the formation of Ni_5Al_3 in the martensite phase suppressed the reverse martensitic transformation. Fig. 2 shows the effect of Al content on the *Af* temperature and the start temperature(*Xs*) of the exothermic reaction in Ni-Al binary and Ni-Al-Re ternary alloys. It is clear that the *Af* increases linearly with decreasing Al content from 37at% to 35.4at% for the Ni-Al. The Al dependence of *Af* in the Ni-Al can be expressed by $Af(K) = 6359 - 165(at\%Al)$. The *Af*-Al line shifted toward the lower Al content side by adding Re. Re is considered to occupy the Ni site in the B2 NiAl structure [14]. Thus, the shift indicates that the addition of Re decreased the *Af*. The Al dependence of *Af* in the Ni-Al-Re alloy is similar to that of the Ni-Al alloy. It is also important to note that the addition of Re raised the exothermic peak by about 150K as shown in Fig 2. For the Ni-Al binary ribbons as shown in Fig. 1, an exothermic peak appeared above 540K upon heating at 10K/min, although the ribbons were of a martensite phase below the exothermic reaction. This indicates that the reverse martensitic transformation cannot be observed above 540K in the Ni-Al. Whereas, the reverse martensitic transformation occurred between 530K and 610K in the Ni-34Al-2Re as shown in Fig. 1. Since the addition of Re raised the *Xs* temperature by about 150K, the reverse martensitic transformation is expected to occur up to 700K in the Ni-Al-Re ternary alloy.

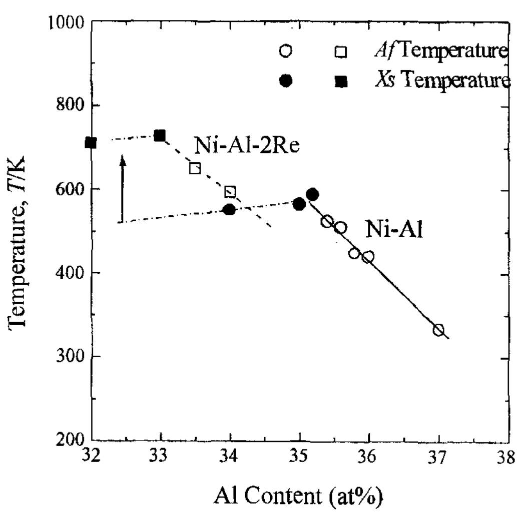

Fig. 2. Effect of Al content on Af and Xs temperatures for Ni-Al and Ni-Al-Re as-spun ribbons [13].

3.2. Shape memory property

Shape memory characteristics were evaluated by strain-temperature relationships measured during thermal cycling under constant stresses. Fig. 3 shows the

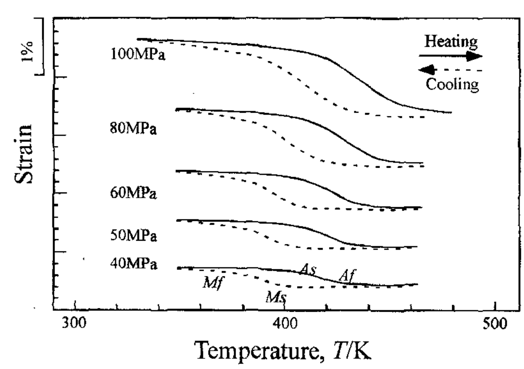

Fig. 3. Strain-temperature curves at constant stress for a Ni-36Al as-spun ribbon.

strain-temperature curves during thermal cycling between 323K and 473K under constant stresses for the Ni-36Al as-spun ribbon. The test was performed in such a way that the magnitude of the applied stress was increased stepwise in each thermal cycle, using a same specimen throughout the test. The solid and dashed lines indicate heating and cooling processes, respectively. It is clear that the transformation temperatures increased with increasing applied stress. This indicates that the martensitic transformation of the Ni-36Al satisfies the Clasius-Clapeyron relationship. According to this relationship, the martensitic transformation and the reverse martensitic transformation temperature under no applied stress can be determined. The *Ms* and *Af* were estimated as 383K and 425K, respectively. These are consistent with the results obtained by DSC. The recovered strain ε_A increased with increasing applied stress. A recovered strain of 1% was obtained at 100MPa.

Fig. 4 shows the strain-temperature curves obtained by thermal cycling tests for the Ni-36Al-0.5Re as-spun ribbon. A recovery strain of 0.8% was obtained at 80MPa.

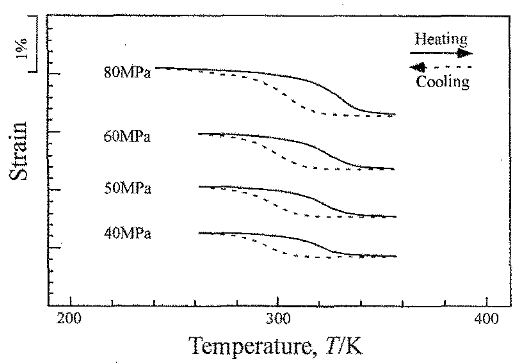

Fig. 4. Strain-temperature curves at constant stress for a Ni-36Al-0.5Re as-spun ribbon.

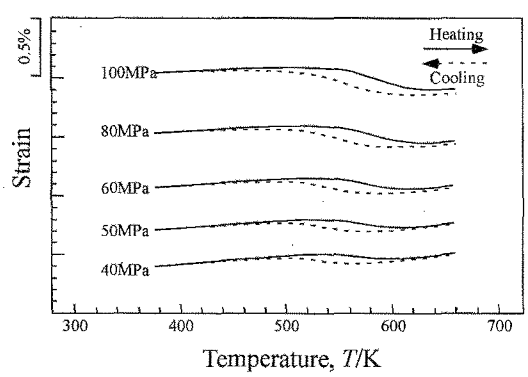

Fig. 5. Strain-temperature curves at constant stress for a Ni-34Al-2Re as-spun ribbon.

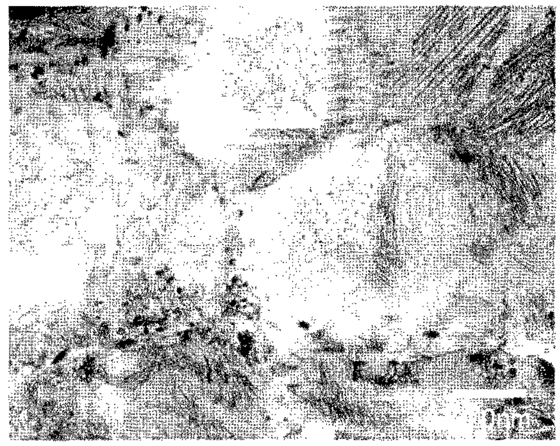

Fig. 6. TEM micrograph of a Ni-33Al-2Re as-spun ribbon.

The shape recovery strain of the Ni-36Al-0.5Re alloy is equivalent to that of the Ni-Al binary alloy.

Fig. 5 shows the strain-temperature curves obtained from Ni-34Al-2Re as-spun ribbon. The thermal cycling test was performed between 373K and 673K. The *Ms* and *Af* were estimated as 540K and 595K, respectively. This result confirmed that the Ni-Al-Re alloy represents the shape memory effect above 520K where the exothermic peak was observed in the Ni-Al binary alloy. However, the shape recovery strain decreased drastically in this specimen. The shape recovery strain of 0.2% was obtained at 80MPa.

Fig. 6 shows a TEM micrograph of the Ni-33Al-2Re as spun ribbon. The grain size was about 1μm. Precipitates were observed not only on grain boundaries but also in grains for the 2%Re added alloy. The size of precipitates in grains is 10-50nm. It is considered that the fine precipitates in the grains reduced the transformation strain in the 2% Re added alloy. The precipitates were identified as the Re by analyzing the electron diffraction patterns.

4. SUMMARY

(1) Transformation temperature increased linearly with decreasing Al content from 37at% to 35.4at%. For Ni-(34-35.2)at%Al, the formation of Ni_5Al_3 around 520K disturbed the reverse martensitic transformation.

(2) Addition of Re raised the temperature for the formation of Ni_5Al_3 by about 150K, so that the reverse martensitic transformation can be increased up to 700K.

(3) The reversible shape change was observed during thermal cycling tests under constant stresses for Ni-Al

and Ni-Al-Re as-spun ribbons. Addition of 2%Re decreased the recovery strain due to fine precipitates formed in grains and the lattice distortion.

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