

Development of Ni-Al High Temperature Shape Memory Alloys

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Ni-rich NiAl alloys are prospective shape memory materials for high temperature applications. In this study, the martensitic transformation behavior and shape memory property were investigated in rapid solidified(melt-spun) Ni-(34-37)at.%Al alloys by differential scanning calorimetry(DSC) and thermal cycling test under a constant stress. The as-spun ribbons were fully crystallized to B2 phase, L1₀ and 14M martensite phases according to the composition. The stability of the martensitic transformation was shown to be dependent on heating rate and Al content. For Ni-(35.4-37)at.%Al alloys, the stable martensitic transformation and shape memory effect were observed, and the martensitic transformation temperature increased with decreasing Al content. For Ni-(34-35.2)at.%Al alloys, an exothermic peak by the precipitation of Ni₅Al₃ was observed around 600K during heating at 10K/min. The precipitation of Ni₅Al₃ in L1₀ martensite interfered the reverse martensitic transformation. The exothermic peak could be suppressed and stable reverse martensitic transformation was obtained by rapid heating for Ni-(35-35.2)at.%Al alloys.

Key Words : Ni-Al, Shape Memory Alloy, Martensitic Transformation, 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. Ni-rich Ni-Al alloys are prospective shape memory materials for high temperature applications due to a high martensitic transformation temperature, high temperature strength and good oxidation resistance [1]. The martensitic transformation behavior of Ni-Al alloys has been investigated extensively in the last decades. The B2 parent phase transforms to L1₀ and/or 14M thermoelastic martensite on fast cooling. The martensitic temperature of Ni-Al alloys increases linearly with increasing Ni content, and can be as high as 900°C [2-5].

However, the unstable martensite phase and low ductility are major problems for engineering applications. Various attempts have been made to improve the ductility by rapid solidification [6-8] or addition of alloying elements [8-10]. In spite of significant improvement in ductility, degradation of martensitic transformation due to the unstable martensite phase is still key issue to be solved for the engineering shape memory alloys. The precipitation of the equilibrium Ni₅Al₃ disturbs the reverse martensitic transformation and shape memory effect [11-14]. Schryvers et al. [15] reported that Ni₅Al₃ precipitation could be delayed by prior precipitation of metastable Ni₂Al in the B2 phase by using slow quenching rates. But the conditions required for the formation and stability of either Ni₅Al₃ or Ni₂Al phase are still unclear. And Dunne and Zhu [11] suggested that the rapid up-quenching could suppressed the precipitation

of Ni₅Al₃. Although many studies on the precipitation of Ni₅Al₃ from B2 phase or martensite phase have been reported in the last 10 years, the mechanism of formation of the Ni₅Al₃ phase and its effect on the shape memory effect have not been fully understood yet.

In this study, the martensitic transformation behavior and shape memory property were investigated in rapid solidified(melt-spun) Ni-(34-37)at.%Al alloys by differential scanning calorimetry(DSC) and thermal cycling test under a constant stress.

2. EXPERIMENTAL PROCEDURE

Master alloys of Ni-(34-37)at.%Al were prepared by arc melting under an argon atmosphere. Ribbons were fabricated by the single roller melt-spinning technique with a surface velocity of 42m/s in an argon atmosphere. The resulting melt-spun ribbons were 25-35μm in thickness and 1mm in width. Martensitic transformation behavior of as-spun ribbons was investigated using differential scanning calorimetry in the range from 173K to 873K at heating and cooling rate of 10K/min. Another series of DSC measurement was performed at various heating rates of 10-95K/min to investigate the effect of heating rate on martensitic transformation behavior of Ni-(34-35.2)at.%Al. Constant stress tests during thermal cycles were conducted between 273K and 473K. Crystal structures of the ribbons were determined by X-ray diffractometry using Cu-Kα radiation.

3. RESULTS AND DISCUSSION

3.1. Martensitic transformation of as-spun ribbons

Fig. 1 shows the X-ray diffraction patterns obtained from as-spun ribbons at room temperature. The as-spun ribbons were completely crystallized during the solidification. All the peaks were identified as B2 parent phase in Ni-37Al as-spun ribbon. The diffraction profiles from Ni-36Al and Ni-35Al as-spun ribbons exhibit L1₀ martensite structure. Peaks corresponding to 14M martensite structure were also observed in Ni-36Al as-spun ribbons. These results indicate that the Ms

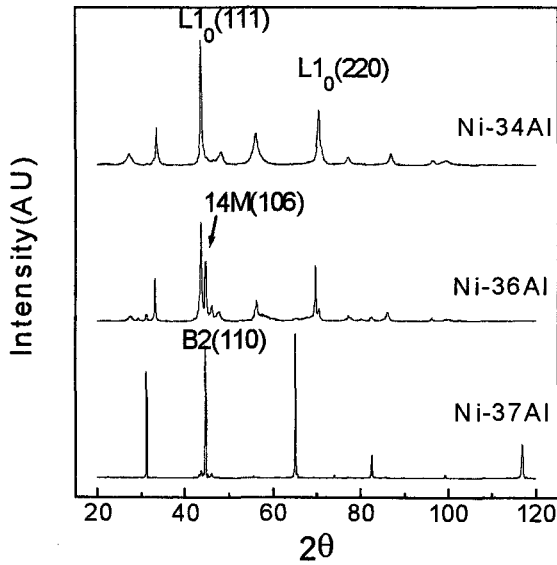


Fig. 1 X-ray diffraction profiles of as-spun ribbons at room temperature.

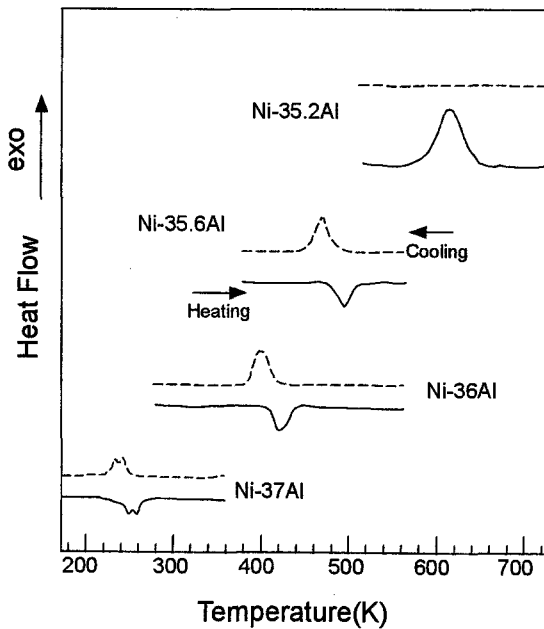


Fig. 2 Effect of composition on the DSC curves of as-spun ribbons

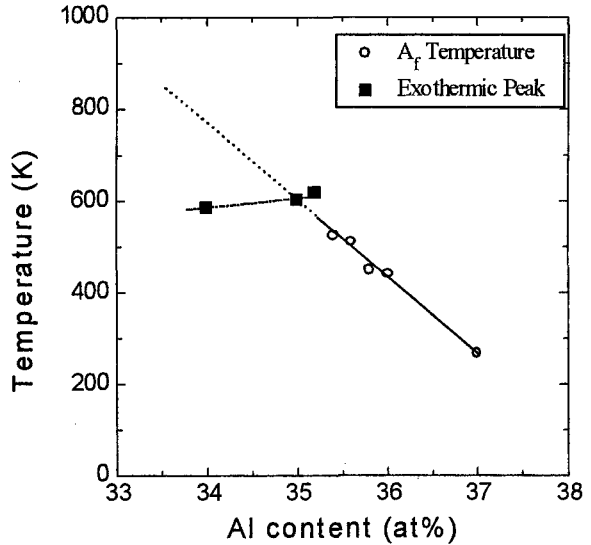


Fig. 3 Effect of Al content on Af temperature measured by DSC.

temperature in Ni-37Al is lower than room temperature, while the Ms temperatures are higher than room temperature in Ni-36Al and Ni-35Al.

The experimental results of DSC measurements for Ni-(35.2-37)Al as-spun ribbons are shown in Fig. 2. The DSC curves show both forward and reverse martensitic transformation peaks in Ni-(35.4-37)Al as-spun ribbons. The temperature hysteresis(A*-M*) was measured as about 25K. However, the DSC curve of Ni-35.2Al as-spun ribbon exhibits the exothermic peak instead of thermoelastic reverse martensitic transformation to parent phase at heating rate of 10K/min. The Af temperature is represented in Fig. 3 as a function of composition. It is clear that the Af temperature increases linearly with decreasing Al content from 37at.% to 35at.%. For Ni-(34-35.2)at.%Al ribbons, an exothermic peak was observed around 600K during heating at 10K/min although the ribbons were of martensite phase. It is considered that the microstructural change corresponding to the exothermic peak suppressed the reverse martensitic transformation. No exothermic peak was observed after the ribbon was transformed into B2 phase. Therefore, it is important to note that the exothermic reaction occurred only in the martensite phase.

3.2. Effect of composition and heating rate on reverse martensitic transformation

Fig. 4 shows the effect of heating rate and composition on the DSC curves of Ni-35.2Al, Ni-35Al and Ni-34Al as-spun ribbons. As stated above, the DSC curves exhibit similar behavior showing an exothermic peak upon heating when the heating rate is 10K/min. However, the DSC curves represent different behavior when the heating rate is 50K/min. In Ni-35.2Al ribbon, an endothermic peak was observed, indicating that only the

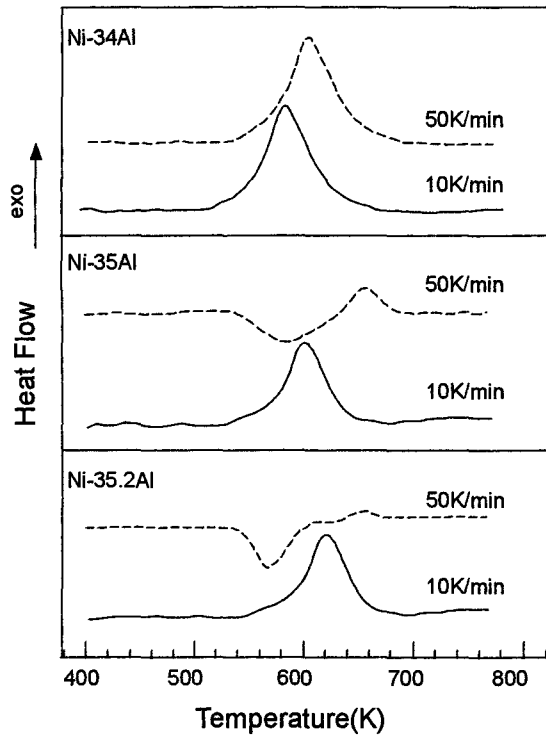


Fig. 4 Effect of heating rate on DSC curves of Ni-Al as-spun ribbons.

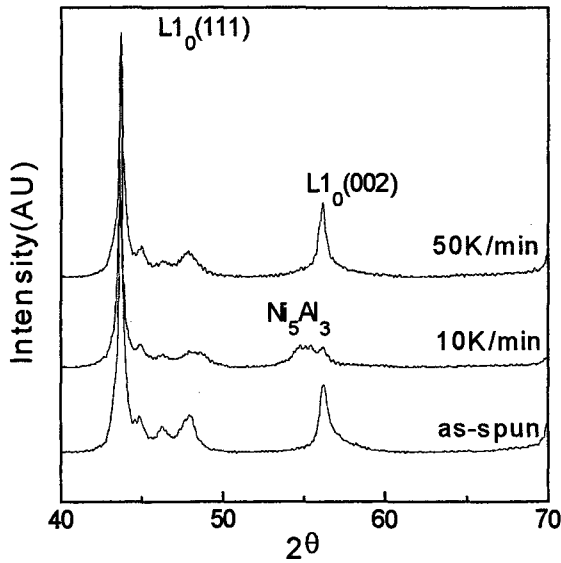


Fig. 5 Effect of heating rate on X-ray diffraction profiles of Ni-35.2Al as-spun ribbon.

reverse transformation from the martensite to B2 phase occurred. The XRD profiles of Ni-35.2Al ribbon before and after DSC measurements are compared in Fig. 5. Fig. 5 indicates that Ni-35.2Al as-spun ribbon consists of $L1_0$ martensite phase predominantly. The small amount of 14M martensite phase is also detected. Peaks corresponding to Ni_5Al_3 phase were observed in Ni-35.2Al ribbon after the DSC measurement at heating rate of 10K/min. However, there is no significant change

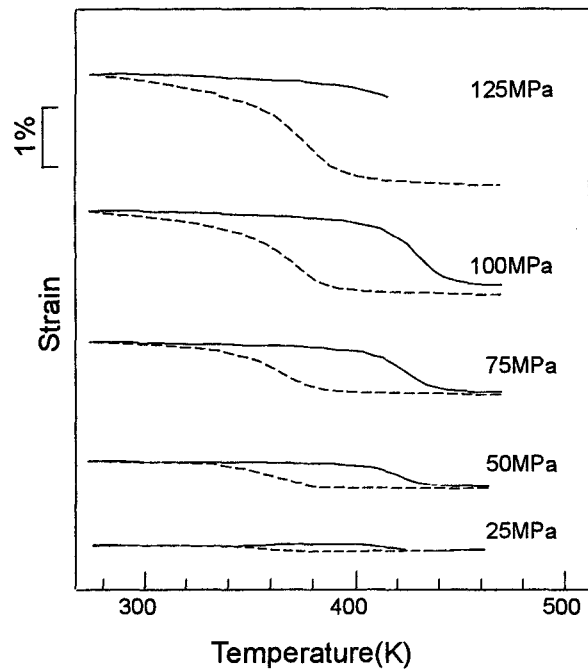


Fig. 6 Strain-temperature curves at constant stress for Ni-36Al as-spun ribbon.

in the specimen tested at heating rate of 50K/min. These results indicate that the exothermic peak is due to the precipitation of Ni_5Al_3 phase.

In Ni-34Al as-spun ribbon, the exothermic peak was observed at both heating rates of 10K/min and 50K/min. The exothermic peak upon heating at 50K/min shifted to a higher temperature compared to that of DSC curves obtained at 10K/min. This indicates that the precipitation of Ni_5Al_3 phase is diffusion-controlled process. Both endothermic and exothermic peaks were observed in Ni-35Al as-spun ribbon upon heating at 50K/min. The temperatures of the endothermic and exothermic peaks were measured as 585K and 660K, respectively. It should be noted that the exothermic peak temperature is decreasing slightly with decreasing Al content. This result confirms that the stability of the Ni_5Al_3 phase increases with decreasing Al content from Ni-35.2Al to Ni-34Al, as can be expected by the phase diagram [6].

The forward or reverse martensitic transformation is diffusionless process, so the transformation temperature is not sensitive to heating rate or cooling rate. But the exothermic reaction temperature increased with increasing heating rate since the precipitation of Ni_5Al_3 is diffusion-controlled process, as mentioned above. When the heating rate is 10K/min, an only exothermic peak was obtained because the A_s temperature is higher than the start temperature(X_s) of the exothermic reaction in Ni-35.2Al, Ni-35Al and Ni-34Al as-spun ribbons. It is supposed that the X_s temperature increased up to above the A_s temperature in Ni-35Al and Ni-35.2Al as-spun ribbons. In Ni-35Al as-spun ribbon, the exothermic peak followed the endothermic peak. This indicates that the X_s

was between A_s and A_f in Ni-35Al as-spun ribbon upon heating at a rate of 50K/min. In the Ni-34Al, the A_f temperature is estimated as 755K using the extrapolation of the data in Fig. 3. No peak corresponding to the reverse martensitic transformation appeared because the A_s temperature is much higher than the X_s temperature in Ni-34Al as-spun ribbon. The above observations show that the exothermic reaction results from the precipitation of Ni_5Al_3 and it should be avoided to increase the temperature for showing shape memory effect. So further studies required to clarify the effect of addition of alloying elements and heat treatments on the stability of martensite phase.

3.3. Shape memory effect

Fig. 6 shows the strain-temperature curves during thermal cycling between 273K and 473K under constant stresses for a Ni-36Al 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 Ni-36Al obeys the Clausius-Clapeyron relationship. The recovered strain ϵ_A increased with increasing applied stress. A recovered strain of 1% was obtained at 100MPa. This results confirmed that Ni-Al ribbons represent shape memory effect.

4. SUMMARY

(1) The as-spun ribbons were fully crystallized to B2 phase for Ni-37at.%Al and martensite phase for Ni-(34-36) at.%Al.

(2) The transformation temperature increases linearly with decreasing Al content from 37at.% to 35.4at.%. For Ni-(34-35.2)at.%Al ribbons, an exothermic peak was observed around 600K during heating at 10K/min due to the precipitation of Ni_5Al_3 phase from martensite phase.

(3) The reversible shape change was observed during thermal cycling between 273K and 473K under constant stresses for a Ni-36Al ribbon.

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REFERENCES

- [1] D.B.Miracle, *Acta Metall. Mater.*, 41, 649 (1993)
- [2] Y.K.Au and C.M.Wayman, *Scripta Metall.*, 6, 1209 (1972)
- [3] K.Enami, S.Nenno and K.Shimizu, *Trans. JIM*, 14, 161 (1973)
- [4] J.L.Smialek and R.F.Hehemann, *Metall. Trans. A*, A4, 1571 (1973)
- [5] S.Chakraborty and C.M.Wayman, *Metall. Trans. A*, 7A, 569 (1976)
- [6] P.L.Potapov, P.Ochin, J.Pons and D.Schryvers, *Acta mater.*, 48, 3833 (2000)
- [7] N.F.Kennon, D.P.Dunne and J.H.Zhu, *J. de Phys. IV*, 1041 (1995)
- [8] E.P.George, C.T.Liu, J.A.Horton, C.J.Sparks, M.Kao, H.Kunsmann and T.King, *Mater. Char.*, 39, 665 (1997)
- [9] R.Kainuma, K.Ishida and T.Nishizawa, *Metall. Trans. A*, 23A, 1147 (1992)
- [10] K.Ishida, R.Kainuma, N.Ueno and T.Nishizawa, *Metall. Trans. A*, 22A, 441 (1991)
- [11] D.P.Dunne and J.H.Zhu, *Mater. Sci. Eng.*, A273-275, 690 (1999)
- [12] J.A.Wolska, J.H.Maas, G.B.Monster, W.Wei and J.Beyer, *J. de Phys. IV*, 1035 (1995)
- [13] P.L.Potapov, S.Y.Song, V.A.Udovenko and K.K.Jee, *J. de Phys. IV*, 245 (1997)
- [14] D.Schryvers and Y.Ma, *J. Alloy and Comp.*, 221, 227 (1995)
- [15] D.Schryvers, L.Toth, J. Van Humbeeck and J.Beyer, *J. de Phys. IV*, 1029 (1995)

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