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# Successive phase transformation in ferromagnetic shape memory alloy $Co_{37}Ni_{34}Al_{29}$ melt-spun ribbons*

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The martensitic transformation in $Co_{37}Ni_{34}Al_{29}$ ribbon is characterized in detail by means of in-situ thermostatic x-ray diffraction and magnetic measurements. The results show a structural transition from the body-centred cubic to martensite with a tetragonal structure during cooling. Comparison between the results of the diffraction intensity with the magnetic susceptibility measurements indicates that the martensitic transformation takes place in several different steps during cooling from 273 to 163 K. During heating from 313 to 873 K, the peak width becomes very wide and the intensity turns very low. The $\gamma$-phase (face-centred cubic structure) emerges and increases gradually with temperature increasing from 873 to 1073 K.

**Keywords:** ferromagnetic shape memory alloys, martensitic transformation, structure
**PACC:** 7520E, 0570F, 7550

## 1. Introduction

Ferromagnetic shape memory alloys (FSMAs) have attracted much attention due to their promising applications as functional materials. The martensitic transformation in FSMAs can be induced by changing temperature and stress or by applying a magnetic field in the hope that their applicabilities could be further improved. The magnetic and the transport properties of those materials, including Ni–Mn–Ga,[1−4] Ni–Fe–Ga,[5] Ni–Mn–Al,[6] Ni–Co–Ga,[7] and Fe–Co–Si[8,9] have been investigated in detail. In the Ni-Co-Al system, Oikawa *et al*[10] investigated the magnetism and the shape memory property of $\beta$-phase.[10] They found that this alloy system was characteristic of good ductility and a wide range of transition temperatures compared with other FSMAs. In the present paper, the structural transition behaviour of $Co_{37}Ni_{34}Al_{29}$ ribbon is studied by means of x-ray diffraction and ac magnetic susceptibility.

## 2. Method

The precursor ingot was prepared by melting pure metals (99.95%) in an induction furnace in an argon atmosphere. The ingot was melted in a quartz tube and rapidly cooled by spinning onto a copper wheel, spinning at a linear speed of about 25 m/s, subsequently. The prepared spun ribbons were generally 6 mm in width and 30 $\mu m$ in thickness. The x-ray diffraction patterns were measured by using a Philips X'pert MPD x-ray diffractometer with a non-ambient sample stage at temperatures ranging from 80 to 2273 K. The rate of temperature change is 10°C/min. The ac magnetic susceptibility was measured in a 77 Hz magnetic field of 5 Oe (1 Oe = 79.5775 A/m) and over a temperature range from 93 to 450 K.

## 3. Results and discussion

Figure 1(a) shows the x-ray diffraction pattern for the $Co_{37}Ni_{34}Al_{29}$ ribbon measured in cubic par-

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ent phase at 313 K. All intense peaks can be indexed to a body-centred cubic parent phase with calculated lattice parameter $a = 5.7138$ Å. When the temperature is lowered down to 163 K, martensite transformation occurs. Figure 1(b) shows the x-ray diffraction pattern for the $Co_{37}Ni_{34}Al_{29}$ ribbon measured in martensite phase at 163 K. The x-ray diffraction pattern of martensite is similar to that found in $Ni_2MnGa$ alloys at a lower temperature. For the stoichiometric $Ni_2MnGa$ alloy, the atomic parameters were suggested by Webster *et al.*[11] The same structure was assumed to be for the non-stoichiometric $Co_{37}Ni_{34}Al_{29}$ alloy in which the space group is Fmmm and the Wyckoff letter is Co: 8f, Ni: 4b, Ga: 4a. The Rietveld profile refinements were performed when the atom occupancy and space group were given according to the crystal data adopted above for the x-ray diffraction pattern of $Co_{37}Ni_{34}Al_{29}$ ribbon. The results of the Rietveld analysis show that the structure of the martensitic phase in $Co_{37}Ni_{34}Al_{29}$ ribbon is a tetragonal structure with lattice parameters $a = b = 5.411$ Å and $c = 6.392$ Å ($c/a = 1.18 > 1$).

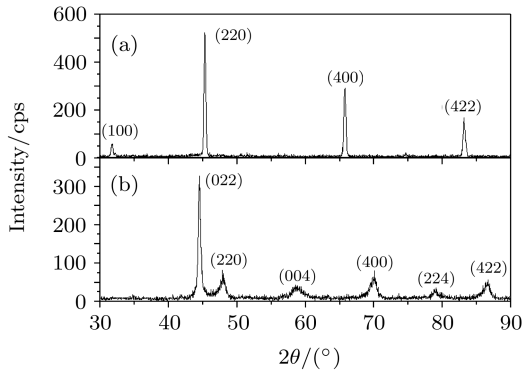



**Fig.1.** x-ray diffraction pattern for $Co_{37}Ni_{34}Al_{29}$ ribbon measured at 313 K (a) and 163 K (b).

Figure 2(a) shows the x-ray diffraction patterns of the $Co_{37}Ni_{34}Al_{29}$ ribbon measured at several different temperatures during cooling. Only one (220) peak of cubic parent phase at 45° can be found at a temperature of 298 K, which means that there exists a pure parent phase state in the sample. When the sample is cooled down to 243 K, an addition peak, the $(022)_M$ peak of martensite, appears at a lower angle and its intensity increases gradually with temperature decreasing. However, the diffraction intensity of the (220) peak of the parent phase decreases gradually with temperature decreasing, and disappears completely at 163 K. This means that the fraction of martensite increases gradually during cooling.

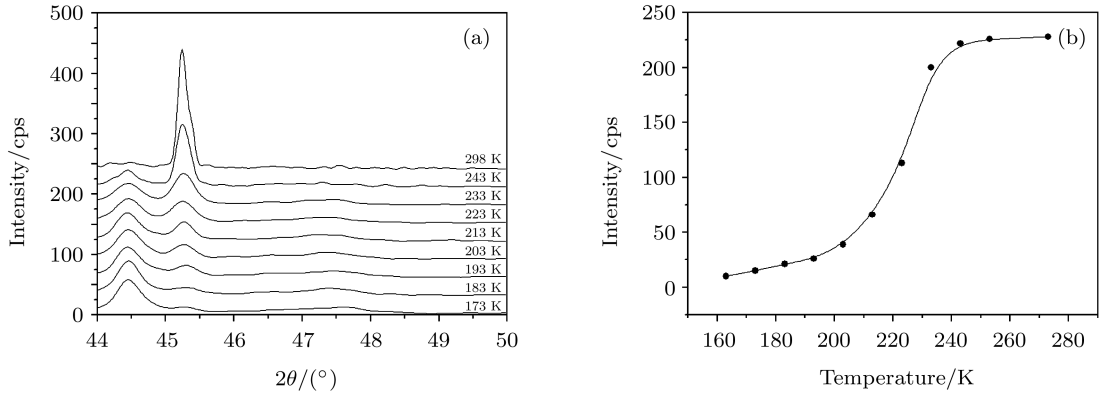



**Fig.2.** x-ray diffraction patterns for the $Co_{37}Ni_{34}Al_{29}$ ribbon measured at several different temperatures during cooling (a) and diffraction intensity for (220) peak of cubic phase as a function of temperature (b).

The diffraction intensity for the (220) peak of the cubic phase as a function of temperature is shown in Fig.2(b). One can see clearly that the curve of the diffraction intensity for the (220) peak of the cubic phase can be roughly divided into three parts during cooling. In a temperature range from about 253 to 233 K, the diffraction intensity decreases slowly, which means that the fraction of the martensite increases slowly in this temperature range, in a temperature range from 233 to 203 K, the diffraction intensity increases rapidly and then slowly below 203 K, which indicates that the fraction of the martensite in-

creases mainly within the temperature range from 253 to 233 K during cooling.

The reverse martensitic transformation occurs during heating from 163 to 313 K and the x-ray diffraction pattern recovers its original shape completely. This means that the $Co_{37}Ni_{34}Al_{29}$ ribbon exhibits a two-way shape memory effect.

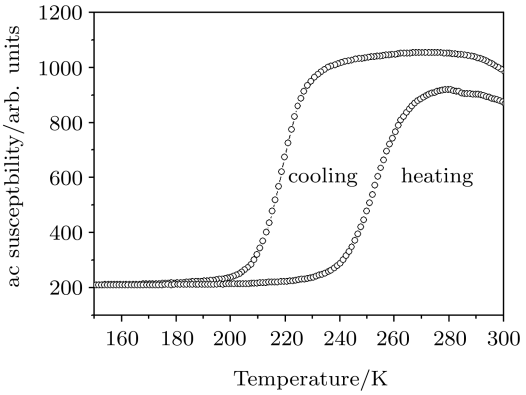



**Fig.3.** Temperature dependences of ac magnetic susceptibility for $Co_{37}Ni_{34}Al_{29}$ ribbons during cooling and heating separately.

Figure 3 shows the ac susceptibility as a function of temperature for the $Co_{37}Ni_{34}Al_{29}$ ribbon. Since the magnetic ordering strictly follows the crystal lattice deformation, the structural transition can be revealed by the ac susceptibility curve. It is found that the signal of ac susceptibility decreases sharply from 233 to 203 K during cooling. This means that the structure transition takes place mainly in this temperature region. In the temperature region from 253 to 233 K and from 203 to 183 K, the signal of ac susceptibility decreases slowly, which implies that the structure transition also occurs in these two temperature ranges. This result accords with the structure transition process determined by the x-ray diffraction intensity analysis in this work.

The reverse structural transformation from the martensite to the cubic phase occurs at 218 K with a temperature hysteresis of about 35 K during heating.

Figure 4(a) shows the x-ray diffraction patterns for the $Co_{37}Ni_{34}Al_{29}$ ribbon measured at several different temperatures during heating. One can find that the peak width becomes very wide and the intensity turns very low at 873 K. In order to describe the details of the structure transition, the full width at half maximum intensity (FWHM) of (422) as a function of temperature during heating is shown in Fig.4(b). It is clearly seen that there appears an ultimate value at about 873 K in the FWHM curve during heating. From 683 to 873 K, the FWHM increases with the temperature increasing. When the temperature goes up to 873 K, the FWHM decreases gradually with the temperature increasing. It is found that the $\gamma$-phase emerges and the fraction of $\gamma$-phase increases gradually in a temperature region from 873 to 1073 K, showing that the emergence of $\gamma$-phase is ascribed to the lattice distortion in the body-centred cubic phase.

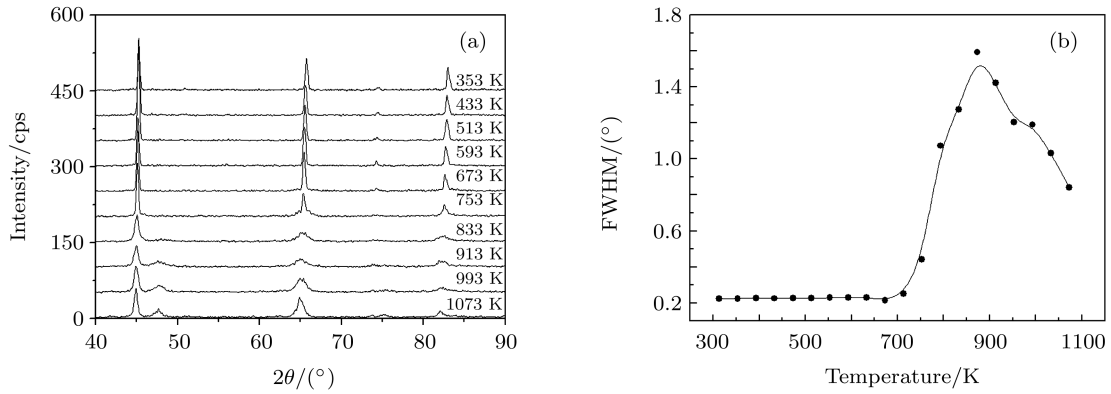



**Fig.4.** x-ray diffraction patterns for the $Co_{37}Ni_{34}Al_{29}$ ribbon measured at several different temperatures during heating (a) and the temperature dependence of FWHM for the (400) peak of the cubic phase in $Co_{37}Ni_{34}Al_{29}$ ribbon (b).

To evaluate the lattice distortions, the lattice strain is calculated from experimental results, defined as

$$\text{Latticestrain} = \frac{W_{\text{strain}}}{4\tan\theta}$$

where $\theta$ is peak position, $W_{\rm strain} = \sqrt{W_{\rm b}^2 - W_{\rm s}^2}$, with $W_{\rm b}$ being the broadened profile width and $W_{\rm s}$ the standard profile width. The lattice strain is calculated to be 1.077% at 873 K.

The increase in FWHM reveals an order–disorder transformation, which was found in Al–Ni–Co and Al–Cu–Co decagonal quasicrystals.[12,13] The strain is induced by the thermally activated random phason, and the peak broadening is caused by the random phason. The population of phason-like atomic flipping increases with temperature increasing. When the temperature reaches 873 K, the composition of the body-centred cubic phase varies because of the presence of $\gamma$-phase as a second phase in the Co–Ni–Al system. As the random phason is sensitive to composition, the peak broadening caused by random phason is mitigatory with the fraction of $\gamma$-phase increasing gradually.

# 4. Conclusions

The $Co_{37}Ni_{34}Al_{29}$ ribbon shows a structural transition from the body-centred cubic with indexed lattice parameter $a = 5.7138$ Å to martensite with a tetragonal structure with lattice parameters $a = b = 5.411$ Å and $c = 6.392$ Å. ($c/a > 1$) during cooling. During heating, the peak width becomes very wide and the intensity turns very low, then the $\gamma$-phase (face-centred cubic structure) emerges and the fraction of $\gamma$-phase increases gradually. The magnetic measurement results are consistent with the structure transition process determined by the x-ray diffraction.

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