Microscopic Observation of the Thermoelastic α_2' Ni–Zn–Cu Martensite

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$Ni_{52-x}Zn_{48}Cu_x$ alloys undergo a martensitic transformation from the CsCl-type ordered cubic (β_2 phase) to the AuCuI-type ordered tetragonal (α_2' phase). The thermoelastic nature of the martensitic transformation in $Ni_{32}Zn_{48}Cu_{20}$ alloy was observed by an optical microscope. The microstructure of the α_2' $Ni_{34}Zn_{48}Cu_{18}$ martensite was investigated by transmission electron microscopy and found to be internal twinning on the $\{111\}\langle 11\bar{2}\rangle_{fct}$ system.

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I. Introduction

Ni-base β phase alloys such as Ni–Al and Ni–Zn undergo a martensitic transformation from the CsCl-type ordered cubic (β_2 phase) to the AuCuI-type ordered tetragonal (α_2' phase)(1)~(8). For example, in Ni–Al(4) and Ni–Zn(5) alloys, the surface relief has been found to appear due to a martensitic transformation by quenching. The microstructure of the thermoelastic α_2' Ni–Al martensite has been studied by several investigators(1)(2) and reported to be internal twinning on the $\{111\}\langle 11\bar{2}\rangle_{fct}$ system. However, in Ni–Zn alloy, the microstructure of the α_2' martensite has not been observed yet.

In the previous papers(6)~(8), the present authors have studied a phase relation of the ternary $Ni_{52-x}Zn_{48}Cu_x$ alloys and have shown that the martensitic transformation temperatures, M_s and A_s, decrease with increase in Cu content as shown in Fig. 1. In these studies, the structure of the α_2' Ni–Zn–Cu martensite was investigated only by X-ray analysis. On the other hand, in the martensite produced by the *bcc* to *fct* transformation, the $\{111\}\langle 11\bar{2}\rangle_{fct}$ twinning is expected to appear as a result of the lattice invariant shear(2)(3). Moreover, the shape memory effect has also been observed in the Ni–Zn–Cu alloys(8); this fact enables us to expect that the internal twins may exist and play an important role in the mechanical behaviour in this martensite. In this work, the microstructure and the thermoelastic nature of the α_2' Ni–Zn–Cu martensite are investigated by optical and electron microscopes.

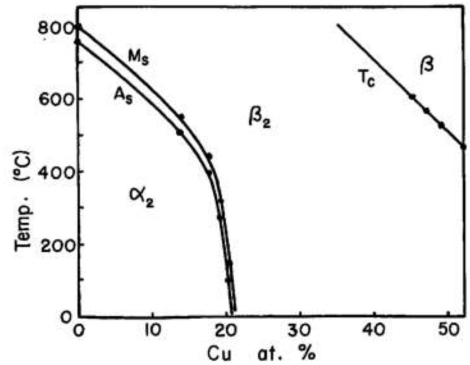

Fig. 1 Phase relation in $Ni_{52-x}Zn_{48}Cu_x$ alloys; β: disordered *bcc*, β_2: CsCl-type ordered cubic, α_2': AuCuI-type ordered tetragonal. T_c means the critical temperature of the order-disorder transition. M_s and A_s mean the starting temperature of the martensitic transformation upon heating and that upon cooling, respectively.

II. Experimental Method

$Ni_{34}Zn_{48}Cu_{18}$ and $Ni_{32}Zn_{48}Cu_{20}$ alloys were prepared by melting metals (99.5%Ni, 99.99%Cu and Zn) in an evacuated quartz tube. Alloys were annealed at 800°C for 60 hr and then quenched into water. A disc specimen, 4 mm in diameter and 0.3 mm in thickness, was cut from the alloy ingot, polished mechanically, and then quenched into water after annealing at 600°C for 15 hr. This disc specimen was at first polished by the jet polishing

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method using a 20% H_2SO_4 solution in methanol at a voltage of 35 V and then finally electropolished using a 40% H_3PO_4 solution in water at 3 V. The microstructure of the $Ni_{34}Zn_{48}Cu_{18}$ martensite was observed at room temperature using an electron microscope (JEM-120) operated at 120 kV. The surface relief of the $Ni_{32}Zn_{48}Cu_{20}$ alloy was observed with an optical microscope by varying the temperature in order to study the thermoelastic nature of the transformation.

III. Results and Discussion

The process of martensitic transformation in the $Ni_{32}Zn_{48}Cu_{20}\beta_2$ phase alloy was observed continuously by optical microscopy. The results are shown in Photo. 1(a)~(d). Surface relief, i.e. martensite plates, contracted gradually during heating above 80°C and almost disappeared at 125°C. When temperature was decreased, growth of the martensite plates was observed and the surface relief which was

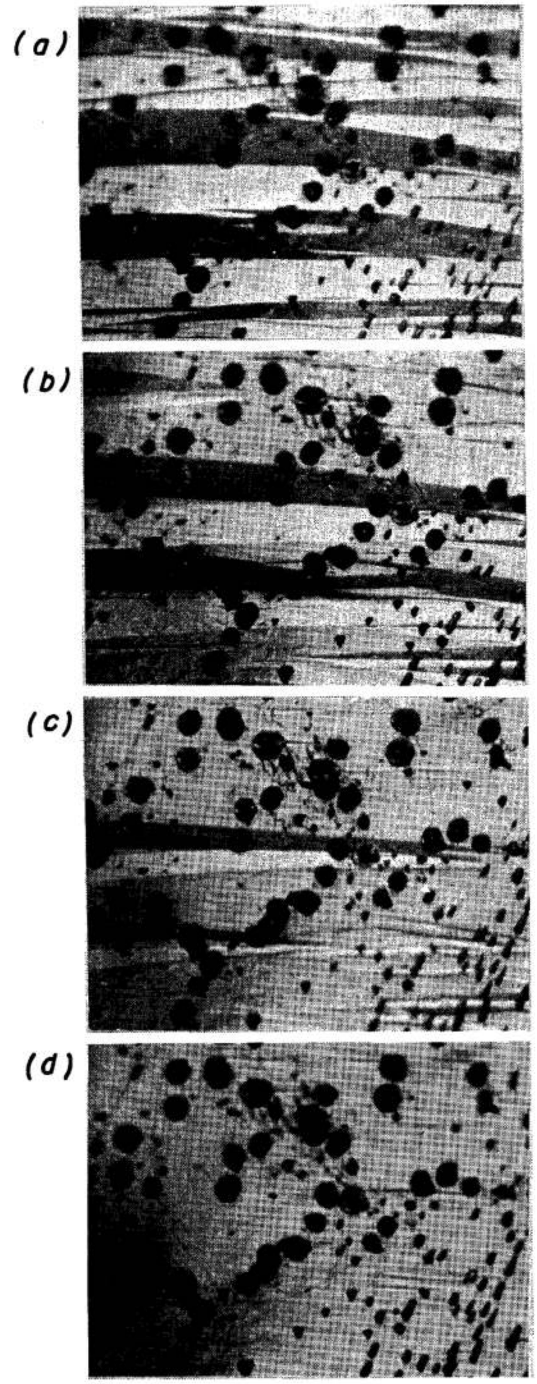

Photo. 1 Optical micrographs of the $Ni_{32}Zn_{48}Cu_{20}$ alloy as a function of temperature upon heating (×350): (a) 20°C, (b) 85°C, (c) 95°C and (d) 125°C.

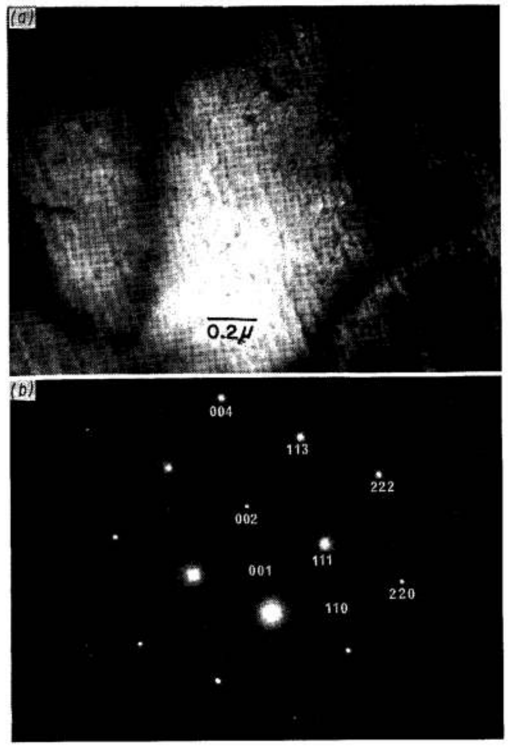

Photo. 2 Transmission electron micrograph of the $Ni_{34}Zn_{48}Cu_{18}$ martensite; (a) bright field image, and (b) diffraction pattern from (a) with the zone axis [1$\bar{1}$0].

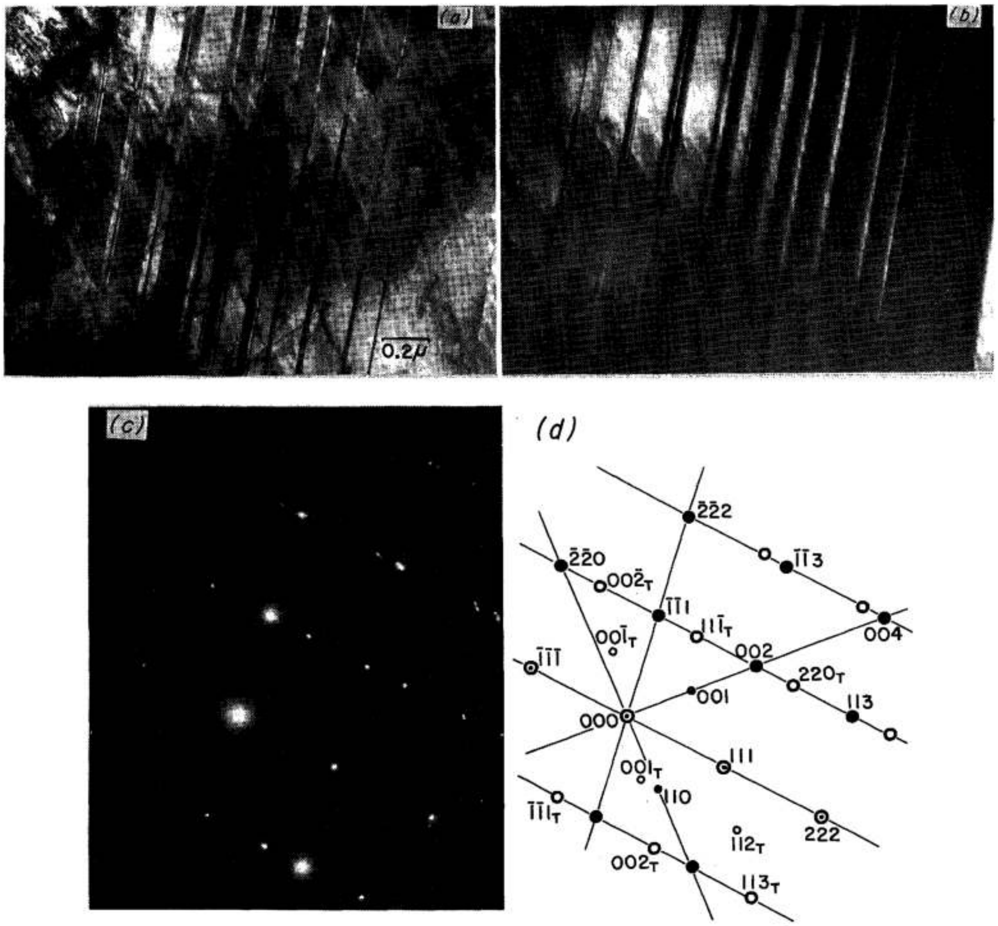

Photo. 3 Transmission electron micrographs of the internal twins in the α_2' $Ni_{34}Zn_{48}Cu_{18}$ martensite; (a) bright field image, (b) dark field image of the same area as (a) taken by the $(11\bar{1})_T$ reflection, (c) diffraction pattern from (a) with zone axis $[1\bar{1}0]$, and (d) indexed pattern showing the $(111)[11\bar{2}]_{fct}$ twinning. Suffix "*T*" means a twin spot.

similar to that in Photo. 1(a) appeared again below about 70 °C, although this process is not shown in the photograph. The temperature hysteresis, M_s-A_s, of the transformation was about 45 °C. These results reconfirm the thermoelastic nature of the martensitic transformation in this alloy†.

The microstructure of the α_2' $Ni_{34}Zn_{48}Cu_{18}$ martensite was studied by transmission electron microscopy. Photograph 2 represents a transmission electron micrograph of this martensite. In the diffraction pattern shown in Photo. 2(b), superlattice spots such as 001 and 110 are observed, although their intensity is very weak. This diffraction pattern is in good agreement with the previous result[6] of X-ray analysis for the AuCuI-type lattice having the axial ratio c/a of 0.88††.

Photograph 3(a) and (b) represent the bright field and dark field micrographs, respectively, showing the existence of internal twins in the α_2' $Ni_{34}Zn_{48}Cu_{18}$ martensite. The diffraction pattern shown in Photo. 3(c) with the zone axis $[1\bar{1}0]$ indicates the twin symmetry as indexed in

† The present authors[(6)~(8)] have shown that the volume change with the *bcc* to *fct* transformation is very small (within 0.1 %) and that the temperature hysteresis of the transformation is about 30~40 °C in Ni–Zn–Cu alloys.

†† Lattice parameters of the AuCuI-type lattice in $Ni_{34}Zn_{48}Cu_{18}$ martensite are $a=3.823$ and $c=3.356$ Å at 20 °C, i.e. c/a is about 0.88[(6)].

Photo. 3(d). From this result, it is seen that the twinning plane is the $(111)_{fct}$ plane of the AuCuI-type tetragonal lattice. Very weak streaks are observed in the [111] direction in the diffraction pattern of Photo. 3(c). These are quite similar to those found in the α_2' Ni–Al martensite[1][2]. An example of micrograph taken from the another area of a specimen is shown in Photo. 4. In this photograph, the width of internal twins is a little different from that observed in Photo. 3. These results indicate that the width of internal twins is variant in a range from 70 to 4000 Å depending on a local place of a specimen. According to Kajiwara[3] and Enami *et al.*[1], the magnitude of the twinning shear, S_t, on the $\{111\}\langle 11\bar{2}\rangle_{fct}$ system is calculated by $S_t=(2\eta^2-1)/\sqrt{2}\eta$, where η is the axial ratio c/a of the *fct* lattice. In the present α_2' $Ni_{34}Zn_{48}Cu_{18}$ martensite, c/a is about 0.88 and thereby S_t is calculated to be 0.44.

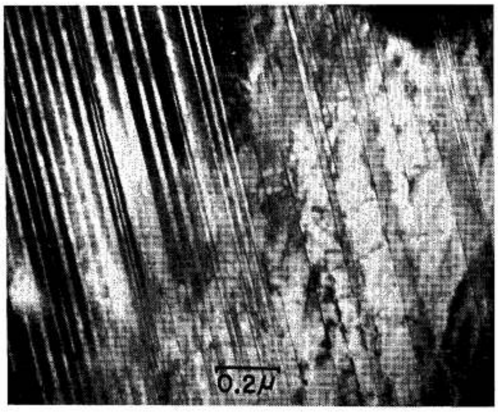

Photo. 4 Another example of internal twins in the α_2' $Ni_{34}Zn_{48}Cu_{18}$ martensite. Diffraction pattern of this area is quite similar to Photo. 3(c).

In summary, martensitic transformation in the Ni–Zn–Cu β_2' phase alloys was confirmed to be thermoelastic and the microstructure of the α_2' martensite was found to be the $\{111\}\langle 11\bar{2}\rangle_{fct}$ internal twins.

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