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Effect of L1o → Ni_5Al_3 Reordering on Properties of Martensitic Ni-Al Alloys

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Abstract. L1o—>Ni_5Al_3 reordering and related properties in powder Ni-Al alloys consisting 64-65 at.%Ni have been examined by X-ray diffraction and dilatometric and damping capacity measurements. The Ni_5Al_3 formation occurs in the L1o matrix by simple reordering of atoms with a continuous increase of the c/a ratio. As a result, degradation of shape memory effect and decrease of damping capacity are observed after short-time annealing at 200-300°C.

1. INTRODUCTION

At the Ni rich side of Ni-Al phase diagram several ordered phases are known to exist [1]. The ordered B2 (CsCl type) structure shown in Fig. 1a is stable at high temperatures over a wide composition range of 40-68 at.%Ni. For Ni-rich compositions, excess Ni atoms distribute themselves randomly on the Al sublattice[2]. The B2 phase undergoes a thermoelastic martensitic transformation up on quenching to the tetragonal L1o ordered structure shown in Fig. 1b [3,4]. The Ms temperature for the transformation in Ni-Al varies sharply with Ni content, from - 280°C to 500°C over the composition range of 60-68 at.%Ni [5,6]. These alloys are therefore considered as promising shape memory alloys for operation at elevated temperatures [7,8]. However, the stability of the martensitic transformation and hence the shape memory effect has been shown to be dependent on the presence of the Ni_5Al_3 phase [9,10].

The Ni_5Al_3 (hereafter abbreviated as 5:3 following the notation of [11]) structure was first observed in a $Ni_{63.8}Al_{35.2}Co_1$ by Enami and Nenno [12]. They suggested an ordered orthorhombic unit cell of the Pt_5Ga_3 type, schematically presented in Fig. 1c. This unit cell was later confirmed in binary $Ni_{65.3}Al_{34.7}$ by Khadkikar and Vedula who determined the lattice parameters to be a=0.7475nm, b=0.3732nm and c=0.6727nm [13]. From these parameters, a basic nearly tetragonal lattice is apparent (a Å2b) and the small deviations from tetragonality are neglected in most cases[14-16]. Microstructural studies suggested that the 5:3 phase can form from the L1o structure by a simple reordering at temperatures as low as 300°C while the main morphology of the martensite plates and their internal twinning remains unchanged [17-19]. The purpose of present paper is to study the kinetics and mechanism of L1o—>B2 reordering and associated changes in special properties of Ni-Al martensitic alloys (shape memory effect and damping capacity).

2. EXPERIMENTAL

$Ni_{63.8}Al_{36.2}$ and $Ni_{64.8}Al_{35.2}$ alloys (hereafter abbreviated as 64Ni and 65Ni, respectively) were prepared by the powder metallurgy method. Using the approximation of Au and Wayman [5], the Ms temperatures for B2—>L1o transformation were estimated as 150°C and 250°C in the 64Ni and 65Ni, respectively. The powders were obtained by the joint deoxidisation of Al_2O_3 (99.98%) and NiO (99.99%) powders with CaH_2 at 1150°C, followed by separation from CaH_2 in a weak acid solution and drying. Rods 8mm in diameter were made by hot extrusion of the Ni-Al powders at 1100-1200°C at an area reduction ratio of 20:1 followed by homogenisation at 1200°C for 18ks and water quenching. Quenching baths consisting of an 80%water - 20%NaCl solution was maintained at room temperature. The specimens of 20x8x1.5mm in size for X-ray study and 10x4x4 mm in size for shape memory tests were prepared from rods by spark machining. Other specimens of 100x8x3 mm in size for damping capacity (DC) measurements were cut by a slow rate diamond saw. The ageing time is depicted in kiloseconds(ks) throughout this paper.

X-ray diffraction studies were made using FeKα radiation on a diffractometer equipped with a heating stage for 2θ scanning at temperatures up to 350^0C. A Mn-Cu balanced filter was used to suppress Kβ wavelength. The apparatus for DC measurement was described elsewhere [20].

3. RESULTS AND DISCUSSION

Fig. 2 is the XRD scan of the as-quenched 64Ni. At room temperature, alloy shows the L1o pattern with the fundamental $(111)_{L1o}$, $(200)_{L1o}$, $(220)_{L1o}$, $(022)_{L1o}$, $(311)_{L1o}$, $(222)_{L1o}$ and superlattice $(110)_{L1o}$, $(201)_{L1o}$ peaks. The $(002)_{L1o}$ fundamental peak is not seen indicating the possibility of the preferred grain orientation in extruded specimens. On heating to 300^0C, the reverse martensitic transformation occurs resulting in the B2 pattern with the $(110)_{B2}$, $(200)_{B2}$, $(211)_{B2}$, $(220)_{B2}$ fundamental and $(100)_{B2}$, $(111)_{B2}$ superlattice peaks.

Although the As temperature for the L1o—>B2 transformation in the 65Ni was estimated as 230-250^0C, this alloy does not transform to B2 on heating in X-ray diffractometer up to maximum temperature available. Moreover, after heating to 300^0C and cooling at a rate of 20^0/min, the shift of angular positions of the $(200)_{L1o}$, $(220)_{L1o}$, $(022)_{L1o}$ and $(311)_{L1o}$ peaks has been observed indicating the change in lattice parameters: decreasing of *a* and increasing of *c*. Taking into account that the Ni_5Al_3 structure in tetragonal approximation exhibits a higher *c/a* ratio than that of the L1o [18-19], the reordering from L1o ordered type to 5:3 one seems to occur on heating retarding the transformation to the B2 structure. Thus, two alternative transformations are possible on heating of as-quenched specimens: L1o—>5:3 or L1o—>B2. So as the L1o—>5:3 transformation needs atomic diffusion while the L1o—>B2 is diffusionless, the real transition path is expected to depend on the heating rate and the value of Ms for L1o—>B2 transformation. On heating with a conventional rate, the 64Ni transforms to the B2 structure while the 65Ni having the higher As transforms to 5:3 before reaching the As.

As seen from Fig. 2, the L1o—>5:3 transformation needs only ordering of the randomly distributed Ni atoms in the Al sublattice by short-range diffusion. So as the 5:3 phase is stable over the composition range of 62.5-67.5 at.%Ni [14-16], long-range diffusion is not necessary for this reordering, and the L1o—>5:3 reaction can occur at relatively low temperatures. Fig. 3 shows the evolution of $(220)_{L1o}$, $(022)_{L1o}$ and $(311)_{L1o}$ peaks in the 65Ni with isothermal annealing at 230^0C and 300^0C. The continuous shift of the angular positions of the peaks that corresponds to a smooth change of *c/a* ratio from 0.864 (the L1o structure) to 0.902 (the 5:3 structure) is observed. These data suggest a homogeneous mechanism for the L1o—>5:3 reordering over the whole volume of the specimen. In the intermediate stage of ageing, the excess Ni atoms are evidently partially ordered in the Al sublattice. The as-quenched 65Ni alloy also exhibits the small (220) peak of the Ni_3Al phase meaning that this composition belongs to the (B2+Ni_3Al) region at 1200^0C (quenching temperature). However, the amount of the Ni_3Al is negligible and does not vary with further annealing at temperatures lower than 300^0C. Thus, Ni_3Al does not seem to be involved in reactions among the B2, L1o and 5:3 phases on ageing at moderate temperatures.

Despite a minor difference in the arrangement of atoms, the L1o and 5:3 phase show quite different behaviour of lattice parameters. Table I lists the *c/a* ratio of the L1o structure and that of the well developed 5:3 (the latter is in tetragonal approximation) for different compositions. In the 64Ni, the 5:3 structure formation was simulated by the special treatment described in [21]. The calculated *c/a* ratio remains higher in the 5:3 structure in every composition and increases with increasing Ni content in both the L1o and 5:3. Fig. 4 presents temperature dependence of lattice parameters for the L1o and 5:3 structures. The L1o structure shows a sharp linear increase of *a* and a decrease of *c/a* with increasing temperature while lattice parameters in 5:3 depend slightly on temperature. The former dependence may indicate an instability relative to a Bain distortion into the B2 structure and the latter seems to follow the temperature dependence of the degree of order in the 5:3 structure reported to be weak in the 20-300^0C temperature interval [16].

Table I

The *c/a* ratio in the L1o and 5:3 structures.

	Alloy	
Structure	63.8 at.pct Ni	64.8 at. pct Ni
L1o	0.854	0.864
5:3	0.894	0.902

Shown in Fig.5 are length changes on heating of the 64Ni and 65Ni specimens subjected preliminary compression deformation of 1-2%. The 64Ni shows one way shape memory effect associated with

L1o—>B2 reverse martensitic transformation while the 65Ni does not exhibit any significant shape changes on heating because of L1o—>B2 transformation is suppressed by L1o—>5:3 one. Fig. 6 shows DC of the L1o phase in the 64Ni and 65Ni and its evolution with L1o—>5:3 transition in the 65Ni. An approximately 50% decrease of DC in the fully ordered 5:3 structure is observed while its amplitude dependence remains principally the same as that in the L1o phase. High DC in martensitic alloys is known to associate with mobility of internal twin boundaries and their arrangement in microstructure. Present results indicate that L1o—>5:3 reordering reduces mobility of twin boundaries inherited from L1o. A more significant decrease of DC is expected after ageing at 400-500°C when coalescence of 5:3 plates and change of their internal twinning was reported [16].

4. CONCLUSIONS

1. Annealing of Ni-Al martensitic alloys at 230-300°C results in the 5:3 (Ni_5Al_3) formation. The 5:3 structure forms from the L1o one by simple reordering with a continuous change of the lattice tetragonality.
2. The L1o—>5:3 reaction results in degradation of shape memory effect and decrease of damping capacity.

Abbreviations

64Ni - $Ni_{63.8}Al_{36.2}$ alloy
65Ni - $Ni_{64.8}Al_{35.2}$ alloy
DC - Damping Capacity

B2 - the NiAl structure of the NaCl type
L1o - the NiAl structure of the CuAu type
5:3 - the Ni_5Al_3 structure of the Pt_5Ga_3 type

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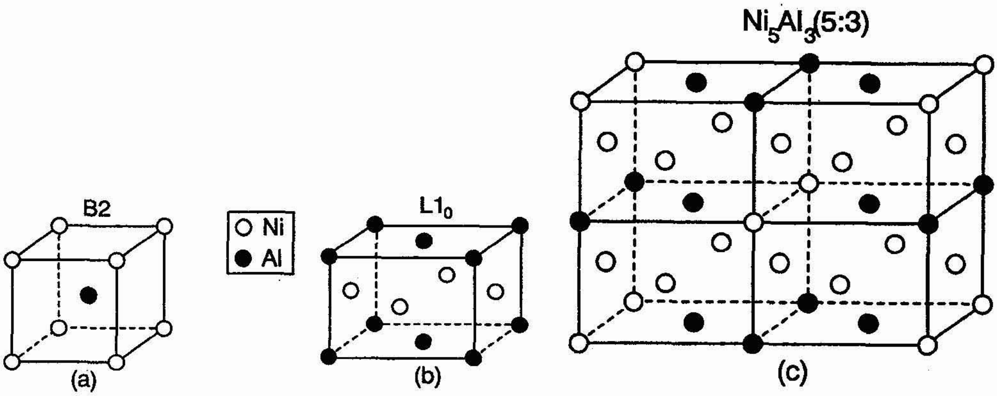

Figure 1: Crystal structures of various phases in Ni-rich Ni-Al alloys.

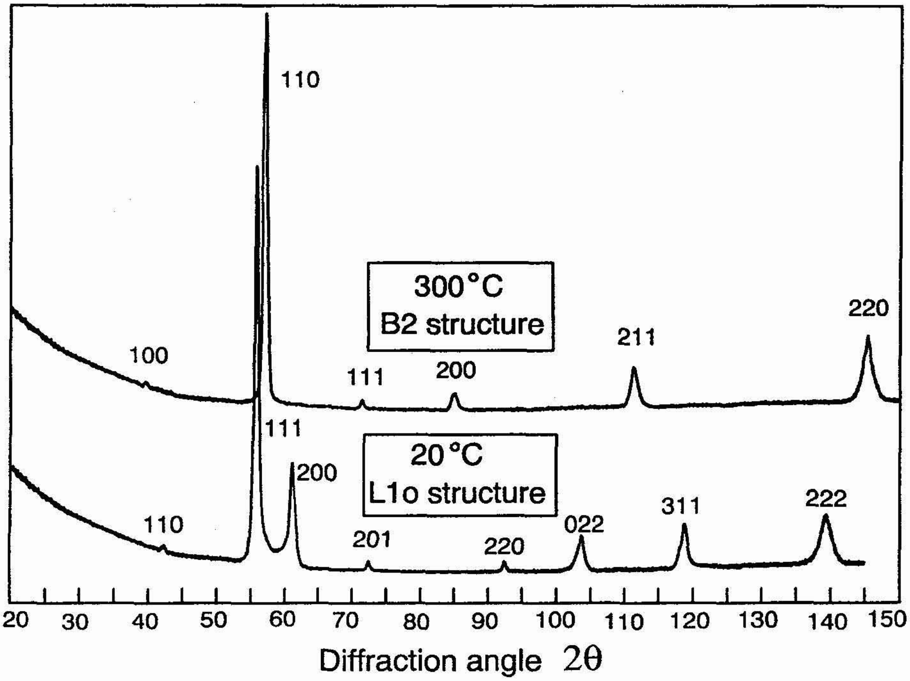

Figure 2: X-ray diffraction patterns for the as-quenched 64Ni at 20^0C and 300^0C showing reversible L1o—>B2 transformation.

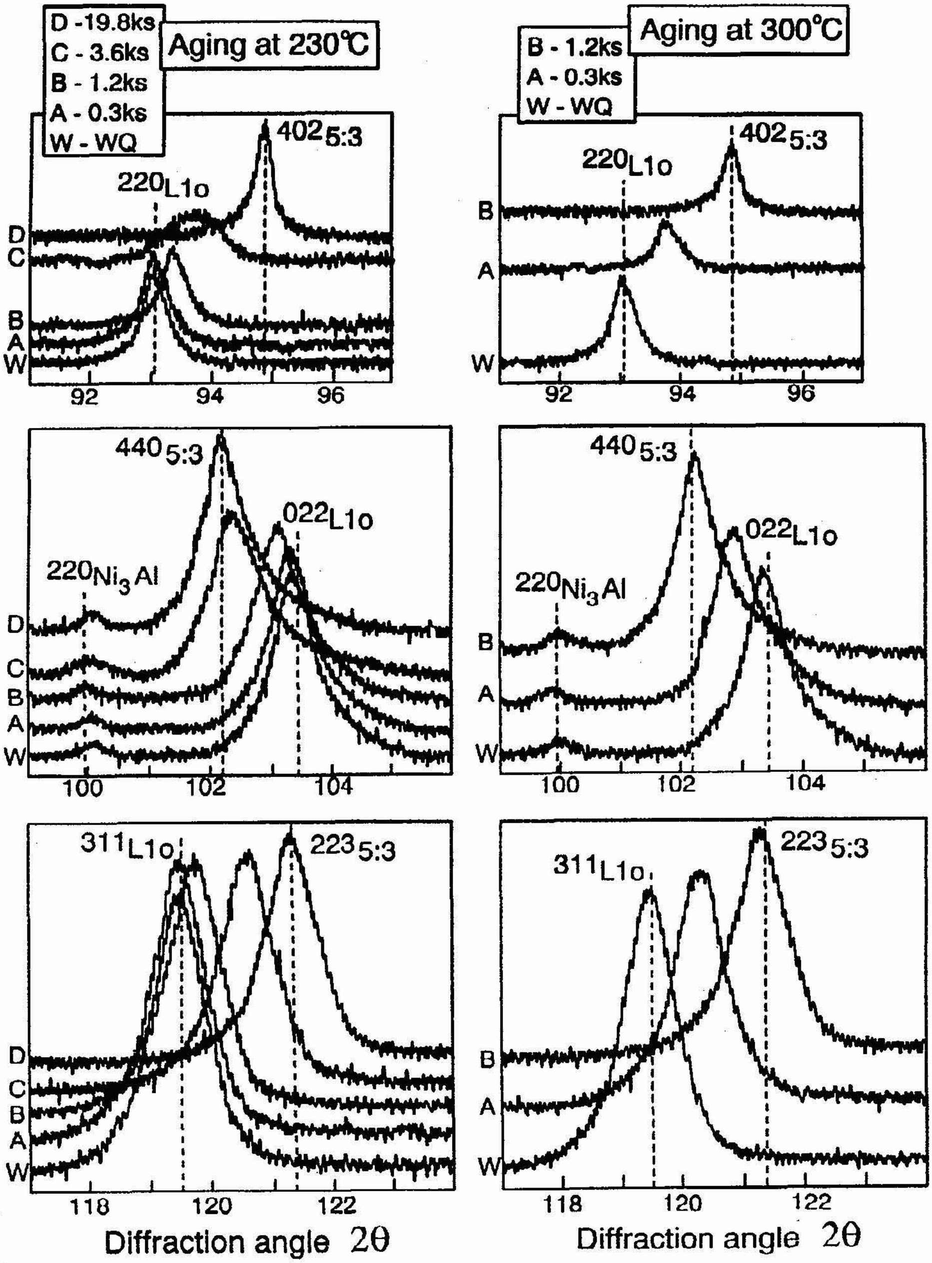

Figure 3: Evolution of X-ray diffraction scans in the 65Ni with agings at 230°C and 300°C showing L1o—>5:3 transition.

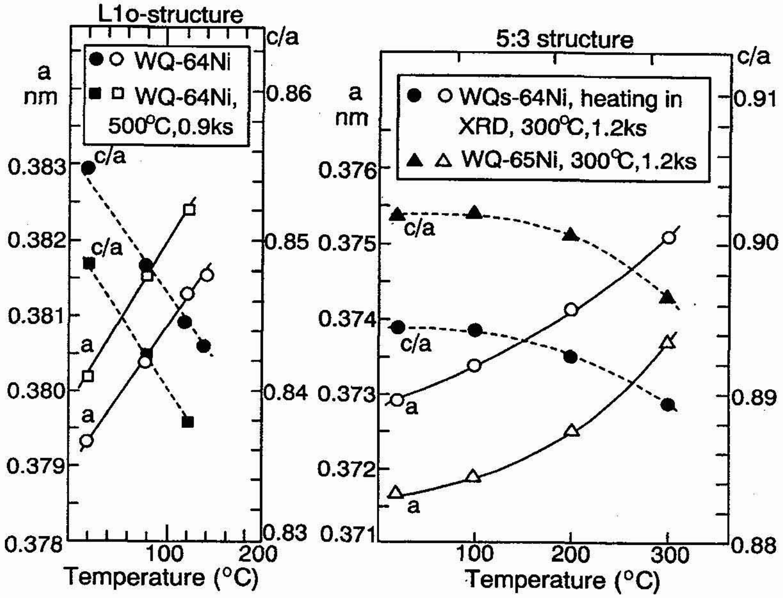

Figure 4: Temperature dependence of lattice parameters for the L1o and 5:3 structures.

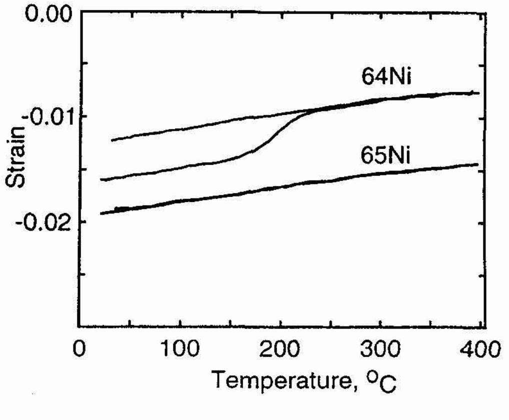

Figure 5: Length changes on heating of the 64Ni and 65Ni specimens preliminary subjected compression deformation.

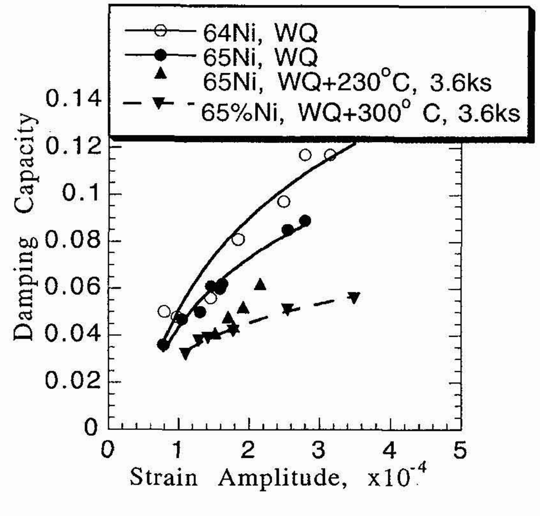

Figure 6: Damping capacity of the L1o and 5:3 structures. Aging of the 65Ni at 230°C for 3.6ks corresponds to the intermediate stage of L1o—>5:3 reaction. Aging at 300°C corresponds to the full L1o—>5:3 reordering.