



Effect of Multi-Elements Substitution on the Mechanical Properties of Intermetallic Compound

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ABSTRACT

It is well known that various elements substitute for a certain sub-lattice of intermetallic compounds. There have been various experimental investigations of the effects of substituted elements on mechanical properties, however, there are few reports describing the effects of multi-element substitution. In the present study, $L1_2$ -type compounds A_3B (Ni_3Al and $Co_3(Al,W)$) were selected as model compounds because their substitution behavior is well known. It was reported that various elements such as Ni, Co, Cu, Pd and Pt occupy the A-site, whereas Al, Si, Ga, Ge, Ti, V, Nb, Ta, Mo, and W occupy the B-site. These elements are expected to introduce local lattice distortion, which may affect the motion of dislocations over a wide range of temperatures. Several alloys composed of five or more elements including Ni, Co, Al, Mo, and W, were prepared using an Ar-arc melting machine and heat-treated. Several alloys were found to include an $(Ni, Co)_3(Al, Mo, W, \dots)$ - $L1_2$ compound as a constituent phase. The nano-hardness of these $L1_2$ phases was higher than that of the high-strength $Co_3(Al,W)$ - $L1_2$ compound, confirming that multi-element substitution is an effective way to improve the mechanical properties of an intermetallic compound without decreasing the phase stability.

INTRODUCTION

Intermetallic compounds have attracted recent attention after the successful utilization of TiAl as the base material for structural applications in jet engines. Conventional intermetallic compounds such as Ni_3Al are still attractive for structural use as precipitates in the Ni solid solution matrix. It is well known that many elements

substitute preferentially into a particular sub-lattice in intermetallic compounds. For example, it is well known that Co, Pd, and Pt substitute for the A-site (Ni-site), whereas W, Si, Ga, Ge, Ti, Mo, and Ta substitute for the B-site (Al-site) in Ni₃Al [1]. These elements substitute for a certain constituent element (Ni or Al) because they have similar bonding characteristics with the counterpart element in another site (Al or Ni). Intermetallic compounds are expected to provide the possibility of unique alloy design due to such substitution behavior, but the mechanical properties and phase stability after substitution with many elements are not well understood. Once an element occupies a part of the sub-lattice, lattice distortion may arise, and it results in the increase of applied stress for the motion of dislocations.

The other advantage of multi-element substitution is the enhancement of phase stability by increasing mixing entropy. A simple expression of the mixing entropy of an intermetallic compound A_aB_b composed of two sublattices (A and B) by Bragg-Williams approximation is as follows [2]:

$$\Delta S_{conf} = -R \left(\frac{a}{a+b} \sum_{i=1}^{n_A} (X_i^A \ln X_i^A) + \frac{b}{a+b} \sum_{i=1}^{n_B} (X_i^B \ln X_i^B) \right) \quad (1)$$

where R is the gas constant, X_i^k is the molar fraction of element i in sublattice k ,

and n_k is the number of elements occupying sub-lattice k of the compound.

Table 1 shows the estimated mixing entropy for several cases. With increasing elemental substitution in the sub-lattices, the mixing entropy increases. This increase in the entropy contributes to phase stability at high temperatures.

In this research, we investigated the mechanical properties of multi-element intermetallic compounds with various elemental substitutions, using L1₂-Co₃(Al,W) as a model. The purpose was to obtain a multi-element L1₂ intermetallic compound and to investigate the effects of multi-element substitution on mechanical properties and phase stability.

EXPERIMENTAL DETAILS

Two series of alloys were produced by Arc melting under an Ar atmosphere. In Equi-series alloys, the total concentration of A-site elements such as Co and Ni is 75 at.% and that of B-site elements such as Al and W is 25 at.%. The other alloy series, named the 41Ni series, consisted of L1₂ single-phase alloys, the compositions of which were determined based on the results of the investigation of the Equi-series alloys. The composition of 41Ni-Std. was determined from the Co-Ni-Al-W quaternary phase diagram reported by Shinagawa et al. [3]. The nominal ingot compositions are shown in Table 2. Samples were water quenched after heat treatment at 1200 °C for 48 hours and subsequently heat-treated at 700 °C for 168 hours. In both heat treatments, the samples were sealed in an evacuated quartz ampule.

Field emission electron probe microanalysis (FE-EPMA: JEOL, JXA-8530F) was used to observe the microstructure and to determine the composition of the equilibrium phases. X-ray diffraction (XRD: PHILIPS, X'Pert Pro) with Cu-K α was carried out at room temperature to determine the crystal structure of the phases. The mechanical properties of the phases were investigated using a nano-indenter (Hysitron, TI-950 Triboindenter) with a load of 10,000 μ N.

Table 1 Calculated ΔS_{conf} values in A_3B -type compounds by Equation (1), with an assumed random distribution of atoms in each site. The amount of each element occupying the same site is the same.

Number of the elements in the A-site	1	1	2	2	2
Number of the elements in the B-site	1	2	2	3	4
ΔS_{conf}	0	0.17R	0.69R	0.79R	0.87R

Table 2 Nominal compositions of the alloys used in the present study.

Alloy Designation	Nominal composition (at. %)							
	Ni	Co	Al	W	Mo	Nb	Ta	
Equi-Series	Mo	37.5	37.5	8.3	8.3	8.3	-	-
	Mo-Nb	37.5	37.5	6.3	6.3	6.3	6.3	-
	Mo-Ta	37.5	37.5	6.3	6.3	6.3	-	6.3
41Ni-Series	Std.	41.1	38.5	10.9	9.5	-	-	-
	Mo	41.3	38.7	9.0	5.4	5.6	-	-
	Mo-Nb	41.4	38.2	6.3	4.3	4.5	5.3	-
	Mo-Ta	40.2	39.6	6.5	4.3	4.9	-	4.5

1. Microstructure and phase composition

Fig. 1 shows backscattered electron images (BSE-images) of heat-treated Equi- (a) Mo, (b) Mo-Nb and (c) Mo-Ta alloys. The XRD results confirmed $L1_2$ peaks in all alloys. Microstructural observation indicated at least three phases in equilibrium in the Equi-Mo alloy and four phases in the Equi-Mo-Nb and Equi-Mo-Ta alloys. By combining these results, compositions were selected for 41Ni series to ensure $L1_2$ phases in each alloy. The confirmed $L1_2$ phases are indicated in Fig. 1, while the other phases (labelled #1-#11) were not confirmed. Fig. 2 shows BSE-images of heat-treated 41Ni-(a) Std, (b) Mo, (c) Mo-Nb, and (d) Mo-Ta alloys. XRD confirmed superlattice reflections in all alloys of $2\theta \approx 25^\circ$ or 35° , corresponding to an $L1_2$ structure. Although there was a very small particle of unknown phase only near the grain boundary in some samples, it can be concluded that all alloy had high volume fractions of the $L1_2$ phase. The compositions of the $L1_2$ phases in these alloys were determined by FE-EPMA and are shown in Table 3. The amount of Al was much smaller than that of a typical Co-based $L1_2$. This might be attributed to enhanced phase stability due to increased mixing entropy resulting from the additional elements.

2. Mechanical properties of the $L1_2$ phase

Fig. 3 shows the results of nanoindentation hardness tests conducted on 41Ni-series alloys, together with those of the homogenized $L1_2$ ternary $Co_3(Al, W)$ (Co-9.2Al-11.4W in at.%) in a Ni-free Co-10Al-12W alloy produced by Miura et al [4]. Fig. 3 shows a comparison of nano-hardness and reduced elastic modulus of each alloy. It is obvious that the hardness of the alloys is widely distributed; however, the reduced elastic modulus of each alloy is almost the same as the reported Young's modulus of about 260 GPa for $Co_3(Al, W)$ [5], and the deviation is quite small.

As is shown in Tables 2 and 3, the sum of the amounts of Co and Ni is higher than 75 at.% in all alloys; that is, the $L1_2$ phases are off-stoichiometric. In the $L1_2$ - Ni_3Al phase, it is known that the concentration of constitutional vacancies is quite small, even with an off-stoichiometric composition, and the solid solution strengthening is governed by the kind and the amount of elements occupying each site. It was also found that the solid solution strengthening effect of elements that substitute for the B-site is quite large. In the present study, the total amount of elements in the B-site was evaluated by

subtracting the Al concentration from 25 at. % (shown in Fig. 4). Clearly, the nano-hardness of the 41Ni-series alloys is mainly governed by the amount of substitution at the B-site. Note that the elements occupying the B-site included not only W, Mo, Nb, and Ta, but also Ni and Co in the present study. It is quite interesting that the Ni-free Co-Al-W phase had a much lower hardness value, and its deviation from the rest of the 41Ni-series might be attributed to the absence of Ni from the A-site.

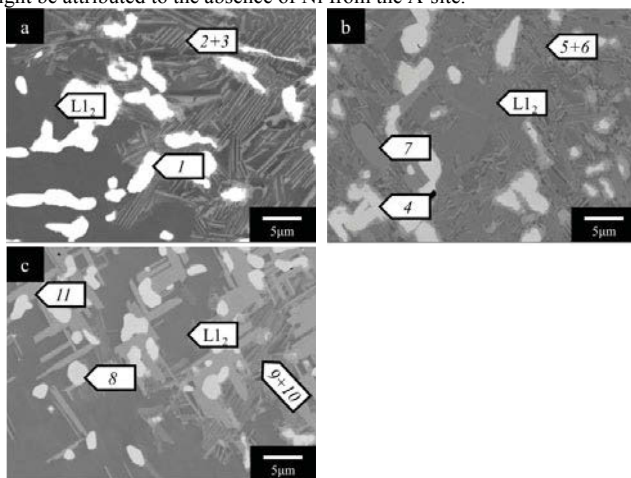


Fig. 1 BSE images of the microstructures of Equi-(a) Mo, (b)Mo-Ta, and (c)Mo-Nb alloys annealed at 700°C for 168h after heat-treatment at 1200°C for 48h. (The numbers in the figure indicate phases other than L1₂.)

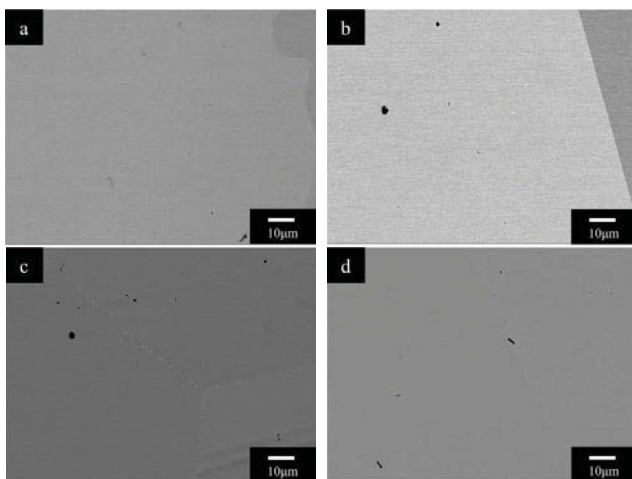


Fig. 2 BSE images of the microstructures of 41Ni-(a) Std, (b)Mo, (c)Mo-Nb, and (d) Mo-Ta alloy annealed at 700 °C for 168h after heat treatment at 1200 °C for 48h.

Table 3 Equilibrium compositions of the L₁₂ phase in the 41Ni-series at 700 °C.

Sample	Measured composition (at. %)							
	Ni	Co	Al	W	Mo	Nb	Ta	Co+Ni
Std.	41.5	40.0	9.6	8.9	-	-	-	81.5
Mo	40.7	39.1	9.4	5.0	5.8	-	-	79.8
Mo-Nb	41.0	39.6	6.1	3.9	4.3	5.1	-	80.6
Mo-Ta	40.1	40.5	6.3	4.3	4.5	-	4.3	80.6

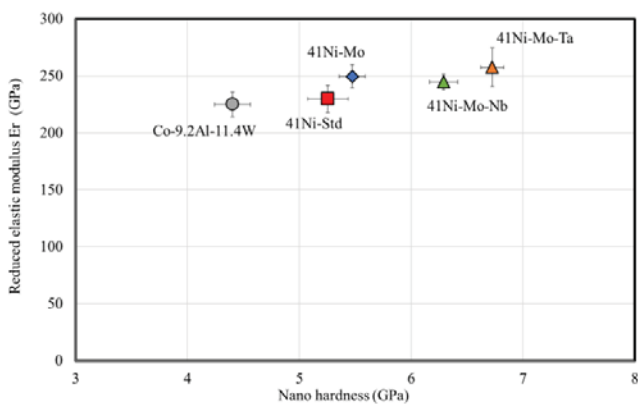


Fig. 3 Summary of nano-hardness and reduced elastic modulus for the L₁₂ phase of each alloy.

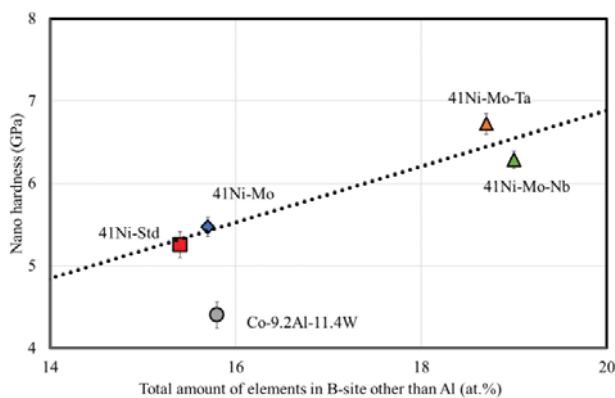


Fig.4 Relationship between nano-hardness and total amount of elements in the B-site other than Al (at. %).

The high strength of high entropy alloys, which are random solid solution alloys consisting of multiple principal elements, can be explained [6] according to the formation of short-range ordering, short-range clustering or lattice distortion due to the varying atomic radii of the constituent elements. However, it is not clear whether we can adopt these mechanisms to explain the strengthening behavior of $L1_2$ intermetallics. In the present study, an ordered structure was confirmed by XRD, but the existence of a higher order structure cannot be ruled out. Further research investigating the local atomic arrangement is necessary to understand the nature of the strengthening mechanisms of intermetallic phases with multi-element substitution.

CONCLUSION

Phase equilibrium and the mechanical properties of multi-element $L1_2$ intermetallic compounds were investigated. The effect of substitution elements on the strength of (Ni,Co)-Al-X (X:Mo, Mo&Nb, Mo&Ta) alloys is quite large; however, the change in elastic modulus is small. The substitution of Nb, Mo, and Ta for Al in $Co_3(Al, W)$ effectively stabilized the Co-based $L1_2$ compound. The present results suggest that multi-element substitution is one method of obtaining high-strength, high-stability intermetallic compounds.

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