Mechanical Properties and Ductilization Mechanism of Pd-Doped Ni₃Al†

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The ductility and temperature dependence of 0.2 % flow stress for Al-poor Ni₃Al macroalloyed with Pd has been investigated using tensile and compression tests. It has been shown that ductility of Al-poor (23 mol % Al) Ni₃Al is improved by the addition of only 1 atomic percent Pd and "recrystallized Ni-23Al-2Pd exhibits elongation of 11 %. TEM observations on the microstructure of melt-spun ribbons indicated that the ordering energy of Al-poor Ni₃Al is degraded by Pd addition. Furthermore, from the compression tests, it has been found that the temperature dependence of 0.2 % flow stress in Ni-poor Pd doped Ni₃Al is much more significant than that in Al-poor one. In addition, it was suggested that the anisotropy of antiphase-boundary (APB) energy for Al-poor Ni₃Al was lowered by Pd addition, indicating degradation of ordering energy. Therefore, the present results discuss the ductilization mechanism by considering correlation between dislocation reactions at grain boundaries and degradation of ordering energy.

Keywords: Alloys, Deformation, Ductility, Transmission electron microscopy, Ductilization mechanism.

INTRODUCTION

It can be of great benefit to use the intermetallic compound Ni₃Al as a structural material at elevated-temperatures, because of its excellent high-temperature strength properties and its resistance to oxidation[1-4]. However, brittleness of the polycrystalline Ni₃Al has been the major obstacle to practical use as a high-temperature structural component. Since the addition of boron to Ni₃Al was found to be significantly effective in improving the ductility[5], considerable efforts have been devoted to understanding of brittle nature in Ni₃Al. Both experimental studies and modeling analyses have suggested that high ordering energy[6] and large difference in valency[7] (or electronegativity[8]) between constituent atoms in A₃B L1₂ ordered alloys result in intrinsic weakness of grain boundaries.

Vitek *et al.*[9] and Sob *et al.*[10] have calculated theoretically atomic structures of grain-boundaries in L1₂ ordered alloys. According to their calculation, the grain-boundary structure is affected by ordering energy, namely the grain-boundaries are strong in weakly ordered alloys with low ordering energy, whereas they are weak in strong ordered alloys with high ordering energy. Furthermore, Kin and Yoo[11] have proposed a

model to explain intergranular fracture in ordered alloys. They showed that the number of allowed dislocation reactions at grain-boundaries is significantly larger at a disordered alloy than at an ordered one, which is related to a stress concentration due to the dynamic pile-up of slip dislocations. In addition, it was revealed that such substitution behaviour of Pd in Ni₃Al was related to degradation of ordering energy on the basis of thermodynamical studies[12,13]. Based on these investigations, we proposed that the ductility improvement of Ni₃Al by Pd addition was attributable to degrading the ordering energy. Therefore, experimental evidence showing the degradation of ordering energy is needed to confirm the above proposed ductilization mechanism. Besides the ductility, it is assumed that the temperature dependence of 0.2 % flow stress is affected by a change in antiphase-boundary (APB) energy of Ni₃Al which is associated with a variation in ordering energy. Accordingly, the purpose of the present investigation is to examine the microstructures of melt-spun ribbons and the temperature dependence of 0.2 % flow stress as well as ductility in Pd doped alloys in order to obtain knowledge concerning the variation in ordering energy of Ni₃Al by Pd addition and to discuss the correlation between ductility and degradation of ordering energy.

EXPERIMENTAL

With 99.95 mass % nickel, 99.998 mass % aluminum and 99.98 mass % palladium, alloy buttons of about 140 g with the nominal compositions of Ni-23Al-XPd (X = 0, 1 and 2) for tensile tests and Ni-25Al-XPd (X = 0, 1, 3 and 5) and Ni-(25-X)Al-XPd (X = 1 and 2) for compression tests were prepared by arc-melting the raw materials in argon atmosphere. Tensile specimens having a gauge section of 1 mm × 2 mm × 16 mm were spark-machined from the plates sliced from the as-cast alloy buttons and subsequently electropolished to remove the surface layer. Specimens for compression tests with a dimension of 3 mm × 3 mm × 7 mm were cut using a wheel-cutter from the alloy button homogenized at 1473 K for 36 ks. Tensile tests at ambient temperature and compression tests at temperatures ranging from liquid nitrogen temperature to 1173 K were performed in a vacuum of 6.6×10^{-3} Pa using an Instron-type machine at an initial strain rate of 5.2×10^{-4} and 1.2×10^{-3} s^{-1}, respectively. Besides the as-cast specimens, recrystallized specimens with the composition of Ni-23Al-2Pd were used for the tensile tests in order to examine the dependence of ductility on the solidification morphology. The recrystallized specimens were obtained by the following procedure. Plates sliced from the as-cast alloy button, about 3 mm in thickness × 10 mm in width × 50 mm in length, were cold-rolled by about 40 % reduction (used roll diameter of 200 mm), encapsulated into 1.3×10^{-3} Pa with sponge Zr getter and annealed at 1323 K for 172.8 ks for homogenization and recrystallization. The plates having recrystallized grains were again cold-rolled by about 50 % reduction for tensile specimens and by about 65 % reduction for microstructre observation. Finally, after the recrystallization annealing, the specimens for tensile test and TEM observation with a grain size of 53 and 2.9 μm, respectively, were obtained by the similar manner to that described above. Transmission electron microscope of thin foils were prepared from recrystallized specimens and melt-spun ribbons with the composition of Ni-25Al and Ni-23Al-2Pd to examine the micro-structure. A scanning electron microscope was employed to examine the fracture surfaces.

RESULTS AND DISCUSSION

The results on the tensile tests for the as-cast binary Ni-23Al and ternary Ni-23Al-XPd (X = 1 and 3 at. %) are shown in Fig. 1. Although the binary specimen exhibits almost no elongation, significant improvement in ductility of Ni₃Al is achieved by the addition of only 1 atomic percent Pd in the Al-poor (23Al) Ni₃Al. Further, it should be noted that Pd doped specimens exhibit elongation of about 7 %. It is found from these results that good cold-workability obtained for Pd doped Ni₃Al is attributable to the improved tensile ductility. Fig. 2 shows the nominal stress-strain curves for Pd-doped recrystallized specimens with various grain sizes. As shown in this figure, the maximum elongation to fracture of 11 % was obtained in the specimen with the composition of Ni-23Al-2Pd, after a discontinuous yielding, corresponding to the propagation of Lüders bands along the gauge[14,15], whereas those with the composition of Ni-25Al-2Pd exhibited no elongation. This result suggests that deviation from stoichiometry toward the
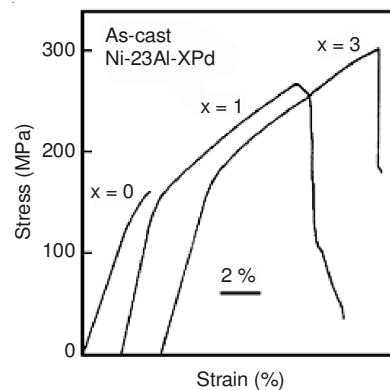

Fig. 1. Tensile stress-strain curves, showing the effect of Pd addition on the ductility of ascast Ni₃Al
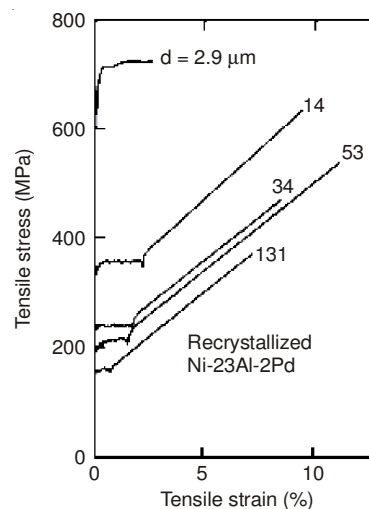

Fig. 2. Nominal stress-strain curves for recrystallized Ni-23al-2Pd with various grain sizes

Al-poor composition, as well as the additions of Pd, is responsible for the ductility. Since the microstructure in these samples was confirmed to be completely a single phase, the occurrence of the ductility in Pd-doped Ni₃Al is not related to the presence of the γ-phase which blunts crack propagation along the γ'-γ' boundaries[16]. In addition, fractured surface of the tensile specimen exhibiting the maximum elongation to fracture of 11 % consists of intergranular and transgranular fracture. Fig. 3 shows the SEM fractograph of the recrystallized tensile specimen described in Fig. 2. As shown in this fractograph, intergranularly fractured surfaces are mainly observed.
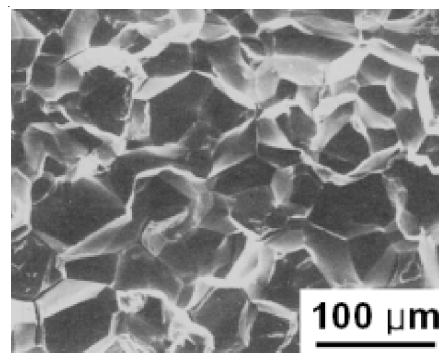

Fig. 3. SEM fractograph for the recrystallized Ni-23Al-2Pd alloy exhibiting elongation of 11 %

A TEM micrograph of the recrystallized Ni-23Al-2Pd alloy with the average grain size of 2.9 µm is shown in Fig. 4. A loop of APB (antiphase-boundary) is found within a grain, indicating the sign of degradation of ordering energy. Further indications of degradation of ordering energy by Pd doping are observed in Figs. 5(a) and (b). A few APB loop can be seen in the melt-spun ribbon with stoichiometric Ni₃Al (Fig. 5(a)), whereas a fine APD structure can be seen in that of Ni-23Al-2Pd (Fig. 5(b)) of which the ductility is improved (Fig. 2). These observations strongly suggest that the ordering energy of Ni₃Al can be degraded by Pd doping in the Al-poor composition.
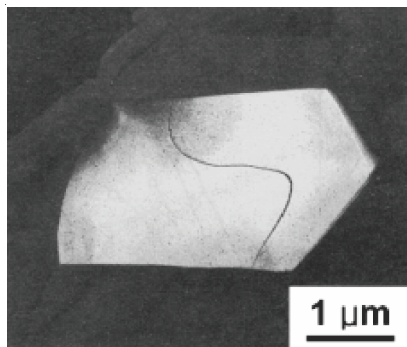

Fig. 4.   TEM micrograph of the recrystallized Ni-23Al-2Pd alloy with grain size of 2.9 µm
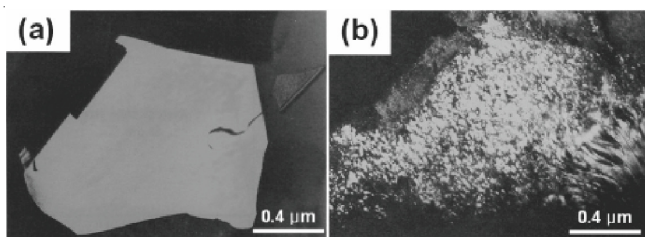

Fig. 5.   TEM micrographs of melt-spun ribbons with the composition of (a) Ni-25Al and (b) Ni-23Al-2Pd

Fig. 6 shows the temperature dependence of the 0.2 % flow stress in the Pd doped specimens of the compositions of (75-X) Ni-25Al-XPd (X = 1, 3 and 5) and 75Ni-(25-X)Al-XPd (X = 1 and 2), together with Ni-25Al for comparison. The flow stresses for all of the tested alloys are found to increase with increasing temperature below the peak. Especially, the flow stress level of the Pd doped alloys with Al stoichiometric composition (Fig. 6(a)) is higher than that of the binary alloy over a temperature range from 77 K to the peak. At temperatures ranging from 400 to 600 K, on the other hand, the flow stress level for the alloys of Ni stoichiometric composition (Fig. 6(b)) is almost comparable with that for binary alloys in spite of the different flow stress level at 77 K. In addition, it is found that the temperature dependence of 0.2 % flow stress in Fig. 6(a) is much more significant than that in Fig. 6(b).

Mechanical properties: The brittleness of the grain boundary for Ni₃Al is considered to be inherent nature because of its high ordering energy[6] and large difference in valency[7] (or electronegativity[8]) between constituent atoms. Therefore, it is of great interest in the present investigation that the addition of only 1 atomic percent Pd to Al-poor Ni₃Al results in improving the ductility. However, current models[7,8] do not elucidate
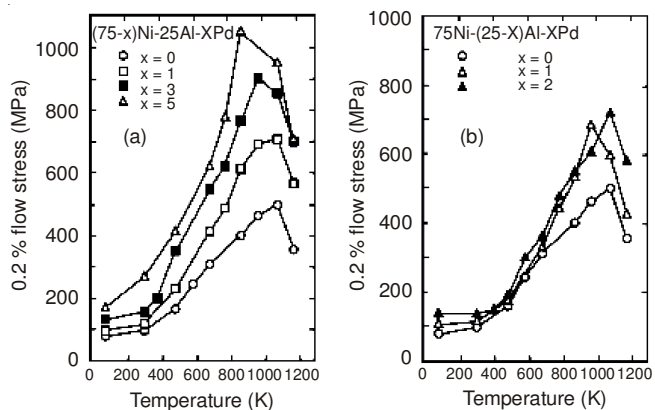

Fig. 6.   Temperature dependence of 0.2 % flow stress for (a) (75-X)Ni-25Al-XPd (X = 0, 1, 3 and 5 at. %) and (b) 75Ni-(25-X) Al-XPd (X = 0, 1 and 2 at. %)

the ductility improvement of Ni₃Al at least in two points. That is, the substitution behaviour that Pd has a strong tendency to occupy the Ni site and the value of the electronegativity of Pd, which is higher (2.20) than that of Ni (1.91) or Al (1.61). According to the current models, these two points are disadvantageous for ductilization of Ni₃Al. Furthermore, the two models[7,8] have suggested that the ductility of A₃B L1₂ compound can be improved by increasing the strength of the chemical bonding across the grain boundary, resulting in the increment of the fracture stress of the grain boundary. However, atomistic calculations[17] have indicated that the cohesive strength of grain boundaries are comparable for ductile Ni and brittle Ni₃Al, suggesting that the inherent brittleness of grain boundaries of Ni₃Al should be related to dislocation reactions at grain boundaries rather than the strength of the chemical bonding. Although the above two models[7,8] do not consider any dislocation reaction which is related to slip accommodation at a grain boundary, Schulson & Xu[14] and Kin & Yoo[11] pointed out that if movement of grain boundary dislocations is facilitated, slip propagation across the grain boundary becomes easy, resulting in the suppression of crack initiation at a grain boundary and improvement in ductility. It is evident from thermodynamical analysis[12,13] and the present observation on the microstructures of melt-spun ribbons that the ordering energy of ductilized Pd doped Al-poor Ni₃Al is degraded. Grain boundary dislocations can easily move within a grain boundary plane of Ni₃Al with degraded ordering energy, because the movement of grain boundary dislocations results in disordering in the plane. Thus, the present results experimentally demonstrated that the ductilization of Ni₃Al by macroalloying is due to the above mechanism concerning dislocation reactions at grain boundaries.

A further point to note is that as shown in Fig. 6(b), 0.2 % flow stress for Ni-25Al increases with increasing temperature ranging from 77 to 1073 K, whereas that in Ni-23Al-2Pd remains constant in the same temperature range. On the contrary, the slope of positive temperature dependence in the latter alloys is much steeper in the temperature range from about 600 K to the peak temperature than in that of the former alloys. This phenomena may be related to lowering the anisotropy of APB energy[18], indicating the degradation of ordering energy of Ni₃Al by Pd addition.

Correlation between substitution behaviour and ordering energy: Gaurd and Westbrook[2] carried out an extensive investigation of the substitution behaviour of ternary element in Ni₃Al from an analysis of ternary phase diagram data. According to them, Co and Cu substitute exclusively for the Ni site, Si, Ti, V and Mn exclusively for the Al site and Cr, Fe and Mo for both sites. In addition, the theoretical consideration, based upon the Brags-Williams model of nearest neighbour approximation, on substitution behaviour of ternary elements was presented by Ochiai *et al.*[19]. They indicated that the substitution behaviour of ternary elements in A₃B L1₂ ordered intermetallic compounds could be predicted by the change in total bonding energy of the host compound by a small addition of a ternary element at stoichiometry, which is reduced to the following expression:

$$K = \frac{V_{AC}}{V_{AB}} - \frac{V_{BC}}{V_{AB} - P} \qquad (1)$$

where P is the asymmetric index[19,20], which depends only on the nature of the host compound and V_{AB}, *etc.* is the interaction parameters, formulated as

$$V_{AB} = H_{AB} - \frac{(H_{AA} + H_{BB})}{2}, \ etc. \qquad (2)$$

where H_{AB}, *etc.* is the bond energy for A-B pairs, *etc.* If K > 0, ternary element (C) tends to substitute for the Al site in 75Ni-(25-X)Al-XC, whereas if , it does for the Ni site in (75-X)Ni-25Al-XC. Accordingly, substitution behaviour is thought to be affected by the difference in the extent of interaction between Ni-C and Al-C bond pair, namely if the interaction between Al(Ni) and the C element, *i.e.*, $V_{AlC}(V_{NIC})$, is stronger than that between Ni(Al) and the C element, *i.e.*, $V_{NIC}(V_{AlC})$ the C element tends to substitute for the Ni(Al) site. Fig. 7 shows the substitution behaviour of various ternary transition elements in Ni₃Al in terms of the correlation between the bond energy ratios of V_{NIC}/V_{NIAl} and V_{AlC}/V_{NiAl}[19]. The solid line, corresponding to K = 0, divides the substitution behaviour into two types. The elements situated below the solid line substitute for the Ni site (corresponding to K < 0) and those above the solid line substitute for the Al site (corresponding to K > 0). Furthermore, the dotted line, which is derived by setting P equal to 1 in eqn. 1, divides the ternary elements which have a tendency to occupy the Ni site into two types. The elements situated below the dotted line, has a strong tendency to substitute for the Ni site independent of the composition of the host elements. On the other hand, the elements situated between the solid line and the dotted line substitute for the Ni site and the Al site if ternary alloying element, C, is added in (75-X) Ni-25A1-XC and 75Ni-(25-X)Al-XC, respectively, meaning that the substitution behaviour of such elements depends on the composition of the host elements. Consequently, one can predict the substitution behaviour of ternary element, C, in Ni₃Al by considering the difference in interaction between the Ni-C and Al-C bond pairs. It should be noted in this figure that Pd is situated farthest below both the solid line and the dotted line, meaning that Pd tends to substitute for the Ni site independent of the composition of the host elements.

In addition, it is found that the interaction between Al and Pd, *i.e.*, Al-Pd bond energy, is the strongest of all the other pair bond energies. Enomoto *et al.*[12] have indicated from their
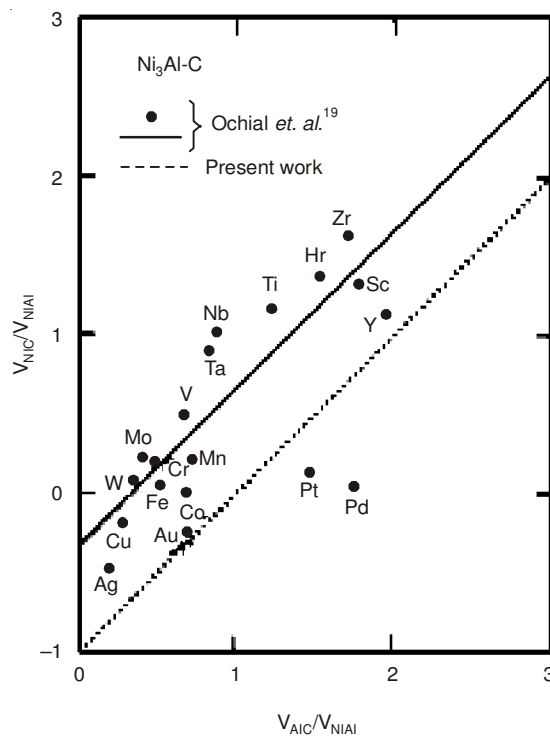

Fig. 7. Substitution behaviour of ternary addition in Ni₃Al. ● marks and soid line are referred from the data evaluated by Ochiai *et al.* the dotted line is derived from the equation in reference[19]

theoretical calculation using cluster variation method that the existence of various types of substitution behaviour can be interpreted simply from the relative magnitude of each atom bond pair energy. They concluded that since the probability of forming Ni-C pairs of strong attractive interaction is increased in the L1₂ ordered lattice than in the solid solution of phase, a ternary element, C, is partitioned in at two phase equilibrium. The similar result was obtained from the experimental investigation by Jia *et al.*[13]. They showed that when a ternary C element tends to substitute for the Al site in Ni₃Al, the addition of the C element stabilizes, whereas when a C element tends to substitutes for the Ni site, is stabilized by the addition of the C element. This means that ordering energy of Ni₃Al is changed by the addition of ternary elements. Accordingly, the strong Pd-Al bond pairs are thought to be formed more readily in the phase rather than the phase. Pd, which has a strong tendency to substitute for the Ni site independent of the composition of the host elements, is preferentially partitioned in the phase at two phase equilibrium, which leads to stabilizing the phase. Therefore, it may be concluded that ordering energy of Ni₃Al is degraded by the addition of the element which substitutes for the Ni site regardless of having or not having the composition dependence of the host elements and the addition of Pd to Ni₃Al is the most effective in degrading the ordering energy.

Furthermore, it should be noted that improvement in ductility of Ni₃Al by macroalloying with Pd can be achieved only with the composition of Al hypo-stoichiometry. Recently, previous workers[21,22] and Enomoto *et al.*[12] have indicated that the ordering energy of Ni₃Al decreases with decreasing Al content, suggesting that the degradation of ordering energy of Ni₃Al is enhanced by Pd-doping to Al hypo-stoichiometric Ni₃Al.

Correlation between ordering energy and ductilization: In order to explain the intrinsic brittleness of polycrystalline Ni$_3$Al, Kin and Yoo[11] have shown that many of the possible dislocation reactions at grain-boundaries, absorption and/or transmission, become energetically unfavorable if chemical coordination must be maintained. They assesed the availability of reactions between dislocation and grain-boundaries in ordered alloys. In Table-1 the numbers of possible reactions are summarized[11]. It should be noted that the number of available reactions depends on the values of Σ and is always larger if Σ is an integer multiple of 3. A more important result is that the number of available reactions is always larger at disordered grain-boundaries rather than at ordered grain-boundaries. Accordingly, the number of dislocation reactions at chemically ordered boundaries becomes restricted, which results in the reduction in number of the possible deformation modes in the region of strongly ordered grain-boundaries.

TABLE-1
NUMBERS OF ALLOWED DISLOCATION
REACTIONS IN L1$_2$ ALLOYS

	Absorption		Transmission	
	$\Sigma = 3N$	$\Sigma \neq 3N$	$\Sigma = 3N$	$\Sigma \neq 3N$
Disordered (fcc)	12	6	288	216
Ordered (pc)	3	0	72	72
	(Possible 30)		(Possible 1800)	

Therefore, we can find from the above consideration that the grain-boundary brittleness of ordered alloys is related to ordering energy; namely the higher the ordering energy, the stronger becomes the tendency for grain boundaries to exhibit brittle intergranular fracture.

Consequently, it can be concluded in the present work that improvement in ductility of Pd-doped Ni$_3$Al with Al poor composition is attributable to degradation of the ordering energy by the addition of Pd, combined with decrease in Al content.

Finally, we would like to point out that if this line of reasoning is correct, it is possible to improve the ductility of Ni$_3$Al by the addition of ternary elements which has a relatively strong tendency to substitute for the Ni site, for instance, Pt, Au, Ag, Cu, Co and so forth, with the composition of 75Ni-(25-X)Al-XC.

Conclusion

Ductility and temperature dependence of 0.2 % flow stress for Ni$_3$Al macroalloyed with Pd have been investigated. The obtained results are summarized as follows: Pd-doped Ni$_3$Al is successfully rolled by 10-40 % reduction in the as-cast condition. Ductility of Al-poor (23Al) Ni$_3$Al is improved by addition of 1 atomic percent Pd. Recrystallized 75Ni-23Al-2Pd shows 11 % elongation to fracture, while recrystallized 73Ni-25Al-2Pd does no elongation. The improvement in ductility of Pd-doped Ni$_3$Al with Al poor composition is thought to be attributable to degrading the ordering energy by Pd addition, combined with decrease in Al content. TEM observations for melt-spun ribbons and compression tests support that the ordering energy of Al-poor Ni$_3$Al is degraded by Pd addition, consistent with the proposed ductilization mechanism.

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