Ductility of Undoped Ni₃Al

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Ductility of binary Ni₃Al alloys having Al concentrations ranging from 23 to 26 mol% has been investigated using tensile tests. It was found that a recrystallized Ni-23Al alloy exhibits elongation of approximately 5%. Recrystallized Ni-23 ~ 26Al alloys prepared in the present investigation were confirmed to be γ' single phase by optical and transmission electron microscopy. Elongation of recrystallized alloys decreases with increasing Al concentration from 23 mol% to stoichiometry and recrystallized alloys containing more than 25% Al exhibit almost no elongation at 290 K.

This ductilization behavior in Ni-rich Ni₃Al alloys is explained by considering both Ni segregation to grain boundaries and decrease in ordering energy, caused by deviation away from stoichiometry.

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I. Introduction

Since the yield stress of intermetallic compound Ni₃Al increases with increasing temperature, Ni₃Al is well suited for use as high-temperature structural components. However, brittleness of grain boundaries in polycrystalline Ni₃Al prevents this material from being applied to a structural component at elevated temperatures. Much effort has been devoted to suppress the brittle fracture in Ni₃Al and it has been found that a small amount of boron addition to Ni₃Al is significantly effective in improving its ductility⁽¹⁾. However, several questions remain to be answered concerning the ductilization mechanism. For example, it is not clearly understood why ductility is improved only when boron is added to Ni-rich Ni₃Al, although boron tends to segregate to the grain boundaries of both Ni-rich and Al-rich Ni₃Al⁽²⁾.

In previous papers⁽³⁾⁽⁴⁾, we showed that ductility of Ni₃Al can be improved by macroalloying with only a few atomic percent of Pd and such ductilization behavior of Pd-doped Ni₃Al depends on Al concentration in a similar manner to that of B-doped Ni₃Al mentioned above. That is, the recrystallized alloy with the composition of Ni-23Al-2Pd exhibits elongation to fracture of 11%, whereas that with the composition of Ni-25Al-2Pd exhibits no ductility. On the basis of the above ductilization behavior and thermodynamic analyses, we pointed out that this ductilization of Pd doped Ni₃Al is attributable to decrease in ordering energy due to both Pd doping and decrease in Al content. Therefore, it is of great impor-

tance to consider the effect of variation in ordering energy by both the addition of ternary element and deviation from stoichiometry on the ductilization of Ni₃Al.

In a previous work⁽⁵⁾, we divided ternary elements in Ni₃Al into two categories, that is, a γ and a γ' former which are effective in lowering and raising ordering energy respectively, and moreover revealed that Ni-rich Ni₃Al macroalloyed with a γ former becomes ductile, whereas that macroalloyed with a γ' former remains brittle. Therefore, in the present investigation, we focus on the relationship between deviation away from stoichiometry and the ductilization of binary Ni₃Al alloys. Recently, Cahn *et al.*⁽⁶⁾⁽⁷⁾ and Enomoto *et al.*⁽⁸⁾ indicated that the ordering energy of Ni₃Al decreases with decreasing Al content. This implies that undoped binary Ni₃Al alloys with Al-poor composition exhibit ductility. Furthermore, Ackland and Vitek⁽⁹⁾ suggested that the grain boundary structure is affected by ordering energy; the grain boundaries are strong in weakly ordered alloys with low ordering energy, whereas they are weak in strongly ordered alloys with high ordering energy. However, they considered that ductility of an ordered alloy with off-stoichiometric composition is due to the segregation of constituent atoms to grain boundaries instead of variation in ordering energy, which is caused by deviation away from stoichiometry.

Therefore, the purpose of the present work is to investigate the ductility of recrystallized binary Ni₃Al alloys and to interpret the results in terms of variation in ordering energy and/or Ni segregation to grain boundaries. For this purpose, single phase Ni₃Al alloys were used on the basis of the Ni-Al equilibrium phase diagram obtained by a precise study employing microanalysis of diffusion couples and thermodynamic calculation (see figure 1 which is reproduced from reference⁽¹⁰⁾).

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II. Experimental

Raw materials used for alloying in the present investigation were 99.95 mass% nickel and 99.998 mass% aluminum. Button ingots of binary Ni₃Al alloys were prepared in the composition range of 23–26 mol%Al by arc-melting the raw materials four times to attain chemical homogeneity on a water-cooled copper hearth in an argon gas atmosphere at a pressure of approximately 93 kPa. A mass loss after the arc-melting was smaller than 0.01% for all the specimens. Since the plates sliced from the as-cast buttons could not be cold-rolled, the plates with the dimension of 15 mm in thickness $\times$ 10 mm in width $\times$ 40 mm in length were cold-pressed by approximately 20% reduction, encapsulated in a vacuum of 10^{-3} Pa with a sponge Zr getter, and annealed at 1323 K for 86.4–172.8 ks for homogenization and recrystallization. The annealing temperature was determined by considering the fact that γ' phase field in the phase diagram, as shown in Fig. 1, is the widest around 1323 K. Furthermore, from the phase diagram, the composition of all the specimens used in the present study is found to be in γ' single phase region in the temperature range from 1173 to 1473 K. The recrystallized alloy plates (except for a Ni–23Al alloy) were again cold-pressed by approximately 20% reduction, encapsulated into a vacuum quartz tube and subjected to recrystallization annealing in order to obtain grain size of 100 μm or so. On the other hand, since the Ni–23Al alloy recrystallized by the above process (i.e., cast $\rightarrow$ cold-pressing $\rightarrow$ annealing) could be cold-rolled by approximately up to 50% reduction, recrystallized specimens of Ni–23Al having various grain sizes ranging from approximately 6 to 260 μm were obtained by the subsequent annealing. Tensile specimens having gauge section of $1 \times 2 \times 16 \text{ mm}^3$ were spark-machined from the

as-cast and recrystallized plates. After the surface layer was removed by electropolishing at a voltage of 12 V and 273 K in a solution of 95 parts methanol plus 5 parts sulfuric acid, tensile tests were performed at ambient temperature in a vacuum of 10^{-2} Pa and in air using an Instron-type machine at an initial strain rate of $5.2 \times 10^{-4} \text{ s}^{-1}$.

An optical and a scanning electron microscope were employed to examine the microstructures and fractured surfaces of tensile specimens respectively. To examine as to whether or not γ phase precipitates at grain boundaries in a tensile specimen of the Ni–23Al alloy, transmission electron microscope (TEM) observation was performed using a JEM-2000EX transmission electron microscope operated at 200 kV ($\lambda = 0.00251 \text{ nm}$). The grain boundary character was also determined by analyzing sets of Kikuchi patterns (camera length of 0.2 m) taken from adjacent grains. Thin foils for TEM observation were prepared using jet-electropolishing in the same condition as in the case of electropolishing.

III. Results

1. Mechanical properties

Figure 2 shows the results of the tensile tests performed using an as-cast and two recrystallized specimens with the composition of Ni–23Al. As shown in this figure, the as-cast specimen having a coarse-grained columnar structure, which contains γ phase, oriented normal to the tensile axis exhibits almost no elongation, whereas the two

Fig. 1 Partial phase diagram of the Ni–Al system, reproduced from Ref. (10).

Fig. 2 Tensile stress-strain curves of as-cast and recrystallized Ni–23Al alloys.

recrystallized specimens consisting of equiaxed grains with different grain sizes exhibit elongation of approximately 5%. The difference in the ductility between the as-cast specimen and recrystallized specimens suggests that ductility of Ni₃Al depends on grain size, grain shape, grain boundary character and so forth. In addition, discontinuous yielding, corresponding to propagation of Lüders bands, is observed in the recrystallized specimen with fine-grains (9.2 μm), whereas it is not observed in the recrystallized specimen with coarse-grains (116 μm). This suggests that the extent of the discontinuous yielding region depends on the grain size, in agreement with the results previously reported by Schulson *et al.*⁽¹¹⁾⁽¹²⁾ and Chiba *et al.*⁽¹³⁾ Figure 3 shows the elongation (to fracture) of recrystallized Ni-23Al alloys with various grain sizes, together with that of recrystallized Ni-23Al-2Pd alloys quoted from references⁽³⁾⁽⁴⁾, as a function of the inverse square root of grain size. As shown in this figure, the ductility of the two alloys does not seem to depend on the grain size ranging from approximately 10 to 200 μm . In addition, Ni-23Al alloys exhibit elongation of 2–5%. On the other hand, the Ni-23Al-2Pd alloy exhibits elongation of more than 7%. This indicates that the recrystallized Ni-23Al is further ductilized by Pd doping. The total tensile elongations of recrystallized specimens with the average grain size of about 100–150 μm are plotted in Fig. 4 as a function of aluminum concentration. As shown in this figure, ductility changes from 5.2 to 0.3% as the aluminum concentration is increased from 23 to 25 at%. Additionally, specimens containing more than 25% Al exhibit almost no elongation at 290 K. It is concluded from these results that deviation from stoichiometry toward aluminum poor composition has a strong influence on the ductility of Ni₃Al in a

Fig. 3 Variation in elongation of Ni-23Al and Ni-23Al-2Pd⁽³⁾⁽⁴⁾ alloys as a function of the square root of grain size.

Fig. 4 Room temperature tensile elongation as a function of aluminum concentration.

similar manner to that of boron-doped Ni₃Al.

2. Microstructure and fractography

Microstructural observations of the two recrystallized Ni-23Al alloys revealed that the two alloys consist of a γ' single-phase without any second-phase γ . Figure 5 shows optical micrographs taken from gauge parts of recrystallized tensile specimens of Ni-23Al prior to tensile tests. Figure 5(a) and (b) correspond to the fine-grained specimen and the coarse-grained specimen respectively. The two specimens, as shown in these figures, have a single-phase structure containing no second-phase γ at grain boundaries or within grains; the existence of a γ phase at a grain boundary is thought to be effective in blunting crack propagation along the grain boundary⁽¹⁴⁾, resulting in ductility improvement of Ni₃Al. In addition, TEM observations on the microstructures of the recrystallized Ni-23Al alloys revealed that there exists no discernible γ phase. Typical TEM micrographs of the recrystallized Ni-23Al alloy are shown in Fig. 6(a) and (b), where a $\Sigma 25$ grain boundary (a) and a $\Sigma 5$ grain boundary (b) in the tensile specimens with the grain size of 226 μm strained by 2.5% and with that of 99 μm strained by 5.1%, respectively, at room temperature are exemplified. Although a number of dislocations appear to be nucleated at the grain boundary, no obvious existence of a γ phase is observed along the grain boundary. Grain boundaries other than the $\Sigma 25$ and $\Sigma 5$ were observed in order to confirm whether or not a γ -phase exists at grain boundaries. No detectable γ phase was found in the present TEM observation. Therefore, we conclude that the occurrence of the ductility in Ni-rich Ni₃Al is not related to the presence of a γ phase blunting crack propagation

Fig. 5 Optical microstructures of recrystallized tensile Ni-23Al specimens with the grain size of (a) $9.2\ \mu\text{m}$ and (b) $116\ \mu\text{m}$.

along the γ' - γ' boundaries.

Fracture behavior of recrystallized Ni-23Al exhibiting elongation of approximately 5% was studied using scanning electron microscopy. Figure 7(a) and (b) show the fractured surface of Ni-23Al with the grain size of $9.2\ \mu\text{m}$ and $116\ \mu\text{m}$ respectively. The smooth grain boundary facets (in part, deformation marks and transgranular fracture) are seen in the both fractographs.

IV. Discussion

In this paper we have first demonstrated that binary Ni_3Al alloys exhibit ductility when Al concentration deviates from stoichiometry to substoichiometry. It has been pointed out by several authors⁽⁹⁾⁽¹⁵⁾ that deviation from stoichiometry in ordered alloys such as Ni_3Al changes grain boundary structure. That is, segregation of a surplus A or B atom in A-rich or B-rich $\text{A}_3\text{B-L1}_2$ compound, respectively, to grain boundary was considered to produce boundaries similar to those in pure f.c.c. metal⁽⁹⁾⁽¹⁵⁾. There have been extensive studies to clarify either the grain boundary structure or the grain boundary chemistry of boron-doped and undoped Ni_3Al with both stoichiometric and off-stoichiometric compositions. It is believed from these studies that Ni-enrichment is introduced at grain boundaries in Ni-rich Ni_3Al without

Fig. 6 Transmission electron micrographs taken from recrystallized Ni-23Al tensile specimens with the grain size of $226\ \mu\text{m}$ strained by 2.5%(a) and with that of $99\ \mu\text{m}$ strained by 5.1%(b), showing (a) a $\Sigma 25$ grain boundary and (b) a $\Sigma 5$ grain boundary. A and B are Kikuchi patterns taken from the grains a and b respectively.

Fig. 7 Scanning electron micrographs of the fractured surface of recrystallized tensile Ni-23Al specimens exhibiting elongation to fracture of (a) 4.9% (grain size, 9.2 μm) and (b) 5.2% (grain size, 116 μm).

boron. In addition, no Ni-enrichment has been reported in the alloy containing more than 25% Al. Consequently, whether or not the occurrence of ductility in the present recrystallized Ni-rich Ni₃Al is related to the Ni segregation to grain boundaries is an important consideration. Therefore, first of all we will discuss the present results on the ductility of binary Ni₃Al by considering the Ni segregation to grain boundaries and subsequently the variation in ordering energy by deviation away from stoichiometry.

1. Occurrence of ductility vs. Ni segregation

Kruisman *et al.*⁽¹⁵⁾ investigated the atomic structure of stoichiometric and non-stoichiometric grain boundaries in the A₃B-L1₂ ordered crystal structure. According to their investigation, the energies of the antisite defects are $E_{A-B} = 2.213$ eV, when B is replaced by A, and $E_{B-A} = -1.55$ eV when A is replaced by B. Therefore, it is energetically unfavorable in the bulk to deviate away from the stoichiometry towards the surplus of A; this trend leads to segregation of A to the boundaries and A-rich boundaries will be created. Furthermore, they pointed out that boundaries in an A-rich compound are much less likely to fracture in a brittle manner than are those in stoichiometric or B-rich compound, because the former is relatively undistorted and the latter is highly distorted. Accordingly, the boundaries possessing distorted structures are more susceptible to brittle fracture, because the local resistance to shear and/or to the transmission of slip through grain boundaries is much

higher in the distorted than in the undistorted boundary structures.

Therefore, if the Ni segregation to grain boundaries in the present recrystallized Ni₃Al alloy is enhanced with increasing Ni concentration from stoichiometry towards the surplus of Ni, the ductility is expected to be improved by the decrease of distortions on the basis of the consideration by Kruisman *et al.*⁽¹⁵⁾ In fact, as shown in Fig. 4, elongations of Ni-23Al and Ni-24Al are approximately 5 and 1.3%, respectively, whereas elongation of Ni-25Al is only 0.3%. Thus, the difference in ductility may be described by considering the Ni segregation to grain boundaries. However, as discussed previously, if we consider the fact that the addition of Pd to Ni-rich Ni₃Al improves the ductility⁽³⁾⁽⁴⁾, the ductility improvement of the recrystallized Ni₃Al alloy cannot be interpreted only in terms of Ni segregation criterion. That is, in the recrystallized Ni-23Al-2Pd alloy exhibiting elongation of 11%, the number of formed antisite defects, if any, is almost the same as that in recrystallized Ni-23Al exhibiting elongation of 5%, because ALCHEMI technique has revealed that Pd substitutes for the Ni site in Ni₃Al independent of the composition of the host alloy⁽¹⁶⁾. This implies that almost the same amount of Ni segregates to grain boundaries in the two alloys. Therefore, we find it difficult to describe the ductility behavior of Ni₃Al only in terms of Ni segregation criterion.

2. Ductility vs. ordering energy

As mentioned above, Ackland and Vitek⁽⁹⁾ have calculated the grain boundary structure in L1₂ ordered alloys. They pointed out that in strongly ordered alloys such as Ni₃Al with stoichiometric composition the relaxation in the boundary region is hard to occur, resulting in the presence of columns of cavities in the boundaries, whereas in weakly ordered alloys such as Cu₃Au with either stoichiometric or non-stoichiometric composition the relaxation is substantial, leading to chemical disorder in the boundary region. Therefore, the principal feature of the boundary structures in L1₂ compounds seems to be determined by the ordering energy. On the other hand, Cahn *et al.*⁽⁷⁾ and Enomoto and Harada⁽⁸⁾ indicated that the ordering energy of Ni₃Al decreases with decreasing Al concentration. Therefore, we should consider the possibility that not only Ni segregation but also the variation in ordering energy, by deviation from stoichiometry, affects grain boundary structure of Ni₃Al.

Besides the structural change in grain boundaries, if ordering energy is lowered, grain boundary dislocations become easily moved⁽¹¹⁾⁽¹⁷⁾⁻⁽¹⁹⁾. As the result, a great number of dislocation reactions at grain boundaries becomes available⁽²⁰⁾. This leads to the reduction in the stress concentration at grain boundaries produced by piling-up of dislocations and to ductility improvement. King and Yoo⁽²⁰⁾ assessed the availability of reactions between dislocations and grain boundaries in ordered alloys. They considered 30 possible absorption reactions and 1800 different transmission or transformation reac-

Table 1 Numbers of allowed dislocation reactions in $L1_2$ alloys⁽²⁰⁾. Note that the number of available reactions depends on the value of Σ ; and the number of reactions is always larger if Σ is an integer multiple of 3.

	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)	

tions. In Table 1 are summarized the numbers of possible reactions. In this Table, it should be noted that the number of available reactions is always larger at disordered grain boundaries rather than at ordered grain boundaries. Therefore, we can conclude that the lower the ordering energy, the easier becomes movement of grain boundary dislocations, which results in ductility improvement.

V. Conclusions

Ductility of binary Ni_3Al alloys was investigated using recrystallized tensile specimens having Al concentrations ranging from 23 to 26 mol%. The obtained results are summarized as follows.

(1) Recrystallized Ni-23 ~ 26Al alloys prepared in the present investigation are found to be a γ' single phase by optical and transmission electron microscopy.

(2) Recrystallized Ni-23Al alloys exhibit elongation of approximately 5%, whereas the as-cast one remains brittle.

(3) Ductility of recrystallized alloys decreases with increasing Al concentration from 23 mol% to stoichiometry. Recrystallized alloys containing more than 25 mol%Al exhibit almost no elongation at 290 K.

(4) Not only Ni segregation to grain boundaries but also variation in ordering energy, by deviations away

from stoichiometry, should be considered to explain the ductility improvement of binary Ni_3Al .

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