

Influence of recrystallization and environment on tensile behavior of cold-rolled Ni₃Al(Zr) alloys

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Abstract: The effects of recrystallization and environment (vacuum versus air) on tensile properties of B-free Ni₃Al (Zr) alloys were investigated. The results indicate that the incompletely recrystallized and stress-relieved specimens show the most desirable ductility and ultimate tensile strength, and that the recrystallization treatment promotes susceptibility to the test environment of the alloys. It is found that the amount of ductile fracture is reduced by air for completely recrystallized specimens. The Auger analyses show that Zr atoms do not segregate to the grain boundaries (GBs) for specimens heat-treated at 1 100 °C, however Zr atoms segregate to the GBs for specimens heat-treated at 900 °C. These results imply that Zr-doping cannot suppress environmental embrittlement.

Key words: Ni₃Al; Ni₃Al(Zr); Zr-doping; recrystallization; tensile properties; environmental embrittlement

1 Introduction

Intermetallic compounds have long been the subjects of considerable interest for high temperature applications. In particular, Ni₃Al is one of the more promising intermetallic compounds due to its anomalous temperature dependence of the yield strength, good oxidation resistance and lower density compared with superalloys[1–4]. However, it has a propensity to brittle intergranular fracture in polycrystalline forms under air environment. Some studies by LIU et al[5–7] have shown that low ductility and brittle fracture in Ni₃Al is caused not only by intrinsic factors but also by extrinsic factors. Environmental degradation is found to be a major cause as an extrinsic factor in many ordered intermetallics including Ni₃Al.

AOKI and IZUMI[8] found that the addition of a small amount of boron to polycrystalline Ni₃Al significantly improves the intrinsic ductility and changes the fracture mode from intergranular to completely transgranular one, however low strength and low creep resistance at elevated temperature remains[9–11]. Fortunately, MISHIMA et al[12] found that zirconium increases the yield strength in B-doped Ni₃Al by solid

solution strengthening, and study showed that the creep rupture life of Ni₃Al (B) increases with the Zr addition. It is now generally recognized that a small amount of Zr addition ductilizes Ni and Ni-base superalloys by suppressing segregation of impurities such as S to grain boundaries (GBs) through sulfide formation. Furthermore, GUO et al[13], GEORGE et al[6] found the ductilization of boron-free Ni₃Al by Zr additions alone. Efforts are now underway to understand this ductilization mechanism better.

Heat treatment is another way to improving the intrinsic ductility and reducing the environmental embrittlement of intermetallics. SU et al [14] studied the effect of recrystallization on tensile properties of a Ni₃Al-based alloy at room temperature and found that the best ductility was attained in specimens that had been heat-treated to complete recrystallization. The ductile fracture mode remained unchanged when the test environment changed from vacuum to air. For Ni₃Al (Zr) alloy, information on the influence of recrystallization and environment on this material has not been reported yet.

The object of this paper is to describe the influence of recrystallization and environment on the tensile properties at room temperature for B-free Ni₃Al (Zr)

alloy, and to determine whether the heat treatment is an effective method for improving the intrinsic ductility. The ductility mechanism of Zr addition is also discussed.

2 Experimental

Four Ni₃Al(Zr) alloys were prepared by melting and casting in a vacuum induction furnace, the ingots were homogenized at 1 100 °C for 4 h followed by cold-rolled repeatedly into around 2 mm-thick sheets with intermediate annealing at 1 050 °C for 30 min. The nominal compositions were based on the formula Ni₇₇Al_{1-x}Zr_x, where *x* is the mole fraction of Zr, it is 0.2, 0.6, 1.0 and 1.5 respectively. The agreement between the nominal and analyzed chemical composition was fairly good. Tensile specimens with a gage section of 2 mm × 2.5 mm × 16 mm were cut from the sheet with the gauge length parallel to the rolling direction. A set of samples were annealed isochronally for 2 h at temperatures ranging from 800 °C to 1 100 °C, with an interval of 50 °C. After these heat treatments, the gauge sections of the specimens were polished through 1 200 grit to remove the thin layer formed during annealing.

Tensile tests were performed at room temperature with an initial strain rate of $1.04 \times 10^{-3} \text{ s}^{-1}$ on a Gleeble 1500 test machine equipped with a vacuum chamber. Environmental effects were investigated under two conditions: ambient room air and a vacuum of about $5 \times 10^{-3} \text{ Pa}$. The microstructures and fracture surfaces of the tensile specimens were examined by optical and scanning electron microscopes(SEM), respectively. The studies of GBs were conducted using an EM420 transmission electron microscope(TEM) equipped with EDAX and LAS3000 auger electron spectroscopy(AES). The recrystallized fraction was estimated under a metallurgical microscope, and the grain sizes were measured by intercept method.

3 Recrystallization effect

3.1 Microstructure

Some typical optical micrographs of samples annealed for 2 h at temperatures ranging from 850 °C to 1 100 °C are given in Fig.1. It has been observed that

the microstructure evolution is dependent on temperature strongly.

The original GBs and deformation bands preferentially serve as effective nucleation sites at the early stage of recrystallization. In these regions new recrystallized grains can be observed(Fig.1(c)). With the proceeding of recrystallization, the volume fraction of recrystallized structure increases, and the whole microstructure changes from the deformation bands introduced by cold rolling to complete recrystallization by annealing at 1 050 °C. After annealing at 1 100 °C (Figs.1(b) and (f)), the equiaxed grain structure is obtained. The volume fraction of the recrystallized zone and recrystallized grain size under different treatment conditions are shown in Table 1. It shows that, with increasing the zirconium content, the recrystallization temperature decreases and the recrystallized grain size decreases.

It is noticed that in alloys C and D, a small amount of the Zr-rich phase is found to be present in the γ' matrix (Fig.2). These inclusions appear to be fragile and have a deleterious effect on ductility, but can be reduced by heat treatment[15].

3.2 Mechanical properties

Fig.3 illustrates the dependence of the yield strength on the heat-treatment temperature of four alloys. The yield strength decreases with increasing heat-treatment temperature (also recrystallization degree) for all four alloys. The maximum yield strength is attained for the unrecrystallized material, while the completely recrystallized material possesses the lowest yield strength. The high yield strength can be attributed to the intrinsic effect of strain-hardening arising from an increased dislocation density in the matrix due to the extrinsic influence of cold deformation. The course of recrystallization relieves the strain hardening.

It is also shown that the yield strength increases with an increase in Zr content except for alloy A (0.2%Zr, mole fraction), which is related to the solute strength. For alloy A, the degree of strain-hardening effect is probably very high and it is difficult to relieve in the course of heat treatment.

Fig.4 illustrates the variations of the elongation

Table 1 Volume fraction of recrystallized zone and recrystallized grain size for four Ni₃Al-Zr alloys at different heat treatment temperatures(HTT)(%)

Alloy	800 °C	850 °C	900 °C	950 °C	1 000 °C	1 050 °C	1 100 °C
A	0	0	0	0	20	50	80
B	10	50	60	70	90	100(30)	100(50)
C	20	40	60	70	90	100(25)	100(40)
D	20	40	50	80	100(15)	100(20)	100(30)

The numbers in the bracket are the grain size with the unit of μm .

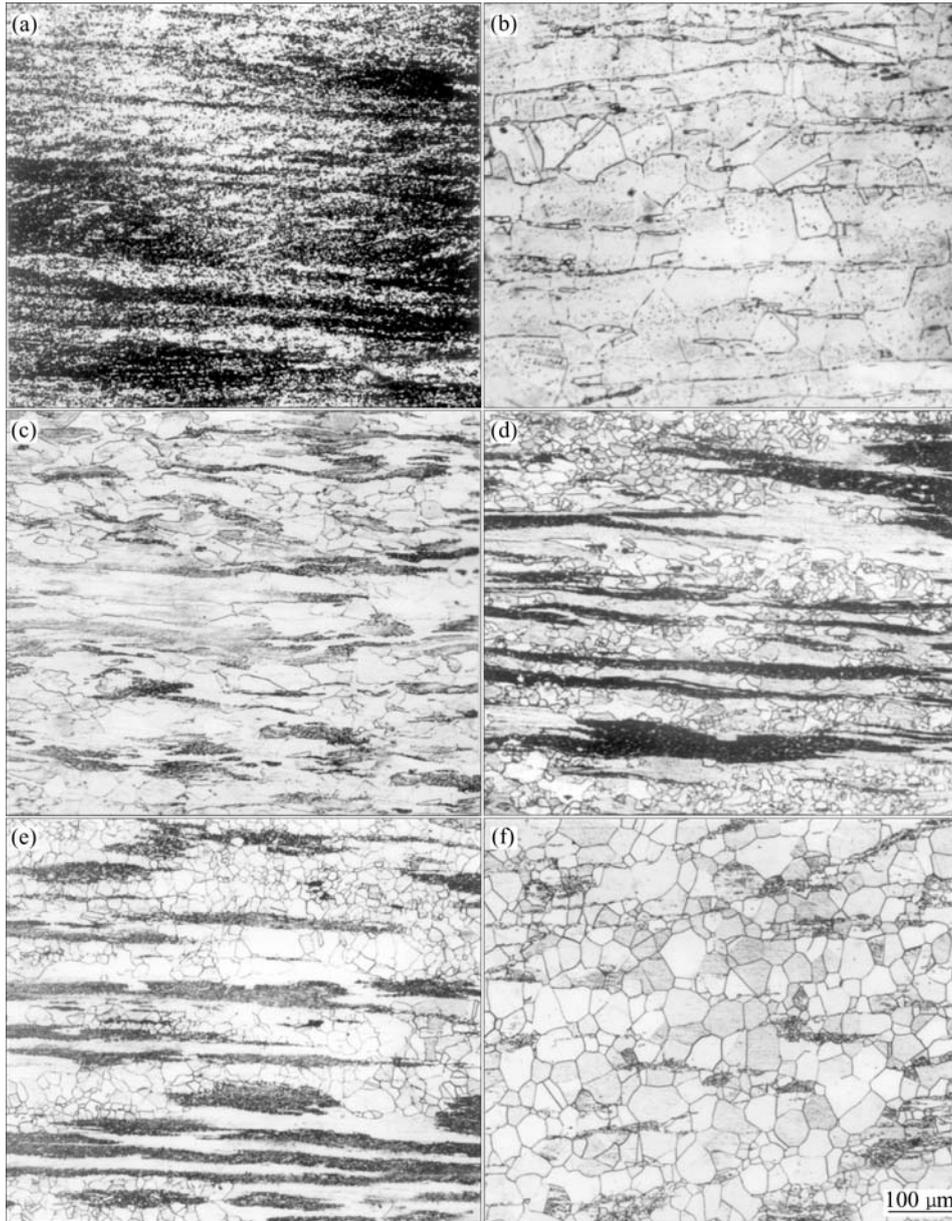


Fig.1 Microstructures of Ni₃Al-Zr alloys at different heat treatments: (a) Alloy A, 900 °C, 2 h, AC; (b) Alloy A, 1100 °C, 2 h, AC; (c) Alloy B, 850 °C, 2 h, AC; (d) Alloy B, 900 °C, 2h, AC; (e) Alloy B, 950 °C, 2 h, AC; (f) Alloy B, 1100 °C, 2 h, AC

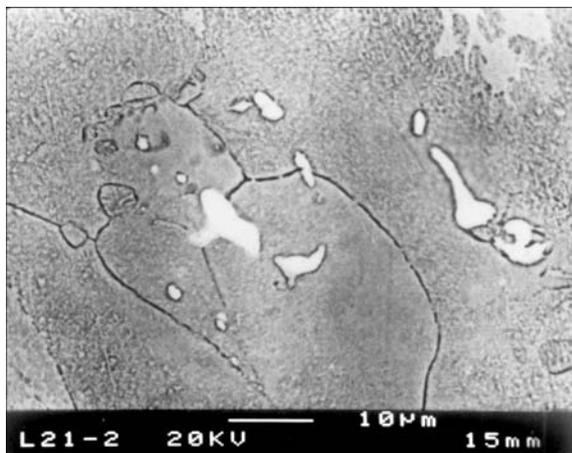


Fig.2 SEM micrograph of alloy B

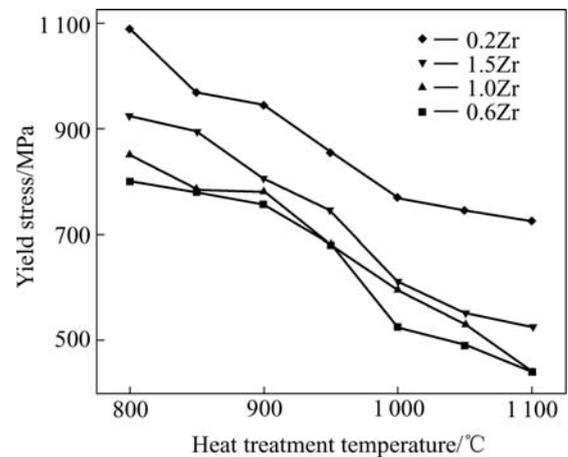


Fig.3 Yield strength at room temperature as function of heat-treatment temperature for Zr-doped Ni₃Al alloys

(Fig.4(a)) and the ultimate tensile strength(UTS) (Fig.4(b)) of four alloys with heat-treatment temperatures. The elongation begins to increase with an increase in heat-treatment temperature (recrystallization degree), and reaches a maximum (peak), and then tends to decrease with further increasing heat-treatment temperature (Fig.4(a)). The ultimate tensile strength basically decreases with increasing recrystallization degree.

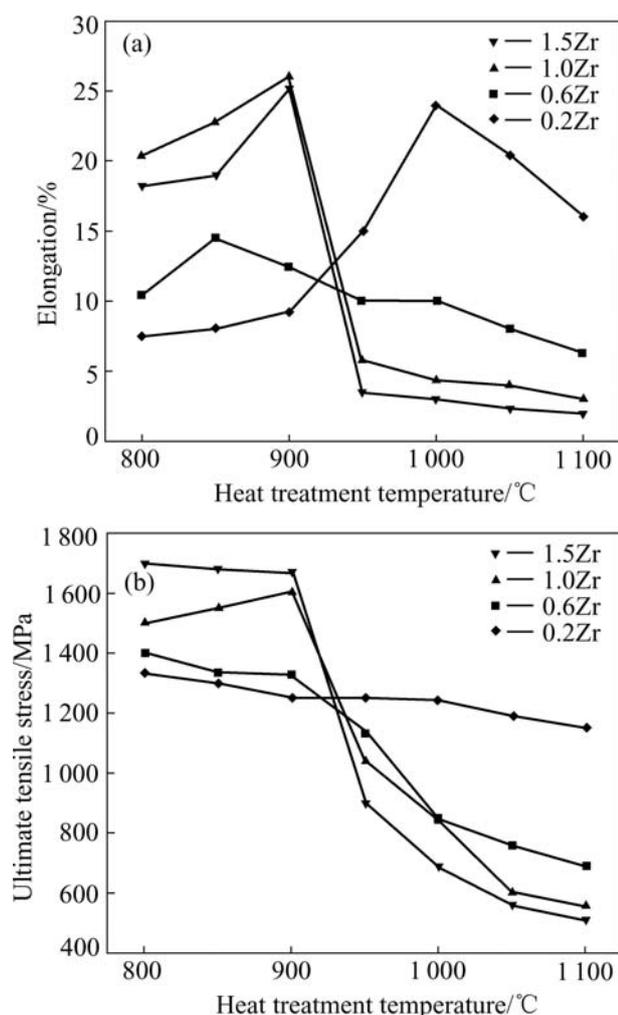


Fig.4 Variations of elongation(a) and ultimate tensile stress(b) at different heat-treatment temperatures for Zr-doped Ni₃Al alloys

It was found that the greatest ductility corresponded to stress-relieved specimens with incompletely recrystallized microstructure, and the completely recrystallized microstructures coincided with the least desirable properties for all alloys.

It should be pointed out that, when the heat-treatment temperature is higher than 950 °C, the elongation and UTS decrease with the increase of Zr amount. That perhaps relates to the increase of the Zr-rich phase, or the increase of the transverse grain boundaries where hydrogen atoms diffuse more easily.

3.3 Fracture behavior

Fig.5 illustrates the variations of the fractograph patterns observed in alloy B treated at different temperatures. The transgranular fracture with dimple-like patterns is dominant when the volume fraction of recrystallization is small (Figs.5(a) and (b)). The intergranular fracture patterns tend to be more dominant with increasing heat-treatment temperatures (Fig.5(c)). The specimens show complete intergranular fracture patterns when heated to complete recrystallization (Fig.5(d)).

Reminding that, the fracture patterns are basically correlated to the elongation (or the UTS) itself. Related to the Fig.4, as the elongation (or the UTS) value increases the fracture patterns change from intergranular to transgranular.

4 Environmental effect

4.1 Tensile properties

The mechanical properties of alloy C were examined by tensile tests at room temperature in vacuum and air (Fig.6). The yield strength decreases with an increase in heat-treatment temperature, regardless of atmosphere. These results show that the yield strength is not susceptible to air. The ultimate tensile strength and the elongation are reduced by air (versus vacuum). In the other words, the completely recrystallized specimen exhibits a more serious susceptibility to environmental embrittlement. These results might be ascribed to the fact that, a number amount of GBs are parallel to the tensile axis and there is little normal stress on GBs in the partially recrystallized specimens used in this study. For the completely recrystallized polycrystalline sample, the equiaxed grain structure not only gives rise to a normal stress on GBs but also provides transverse boundaries which enhance the entry rate of hydrogen atoms into the alloy, since grain boundary diffusion is much faster than bulk one.

4.2 Fracture behavior

Fig.7 shows the fracture patterns of samples that were tested at room temperature in vacuum and air respectively. For the specimens heat-treated at 900 °C, 950 °C and 1100 °C, these two fracture patterns at vacuum and air are quite similar and show mostly ductile transgranular fracture patterns (Figs.7(a) and (b)). The fracture surfaces of specimens are slanted at about 45° to the tensile axis, approximately corresponding to the plane of maximum shear stress. These results correspond well with the result that two samples show almost identical and high values of the elongation and UTS, as shown in Fig.6. Figs.7(e) and (f) show very interesting fracture patterns of samples that were treated at 950 °C

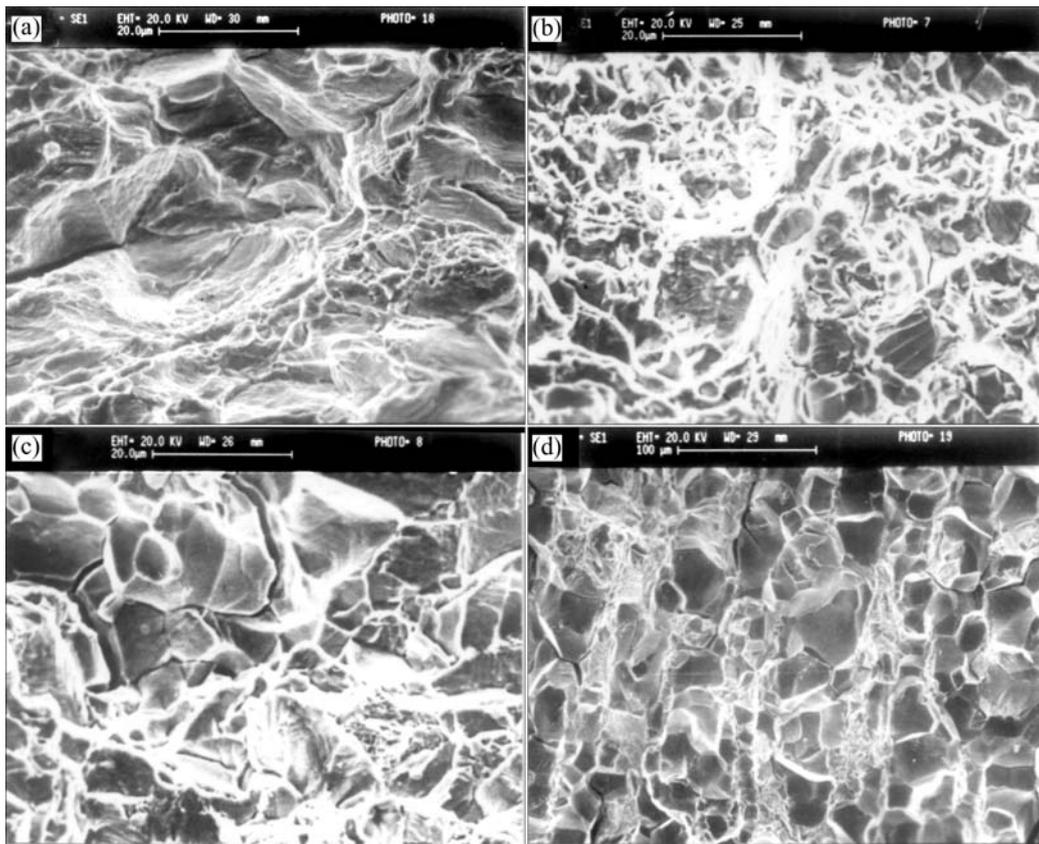


Fig.5 Fractographs of alloy B after different heat treatments tested at room temperature: (a) 850°C, 2 h, AC; (b) 900 °C, 2 h, AC; (c) 950 °C, 2 h, AC; (d) 1 100 °C, 2 h, AC

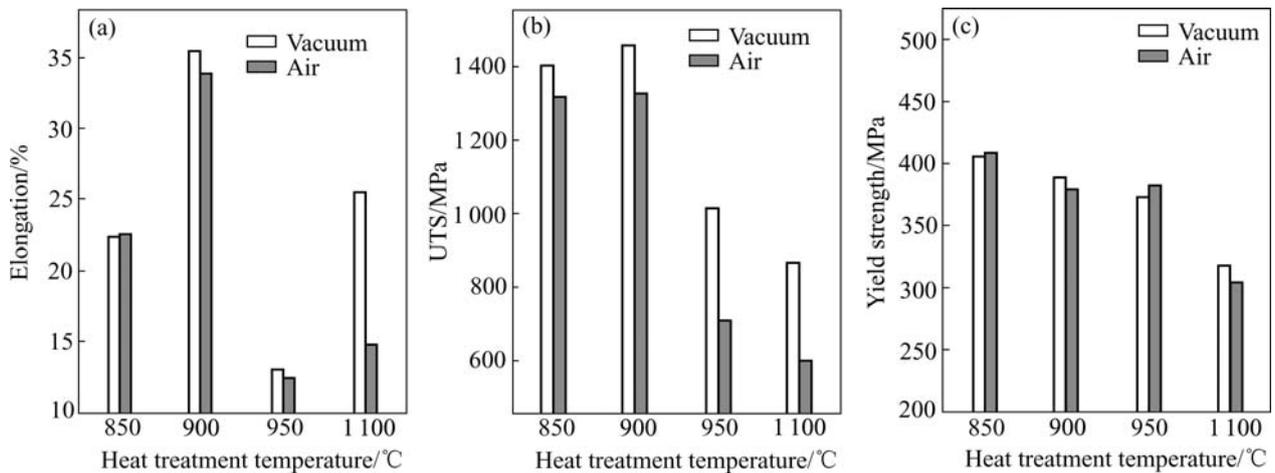


Fig.6 Variations of elongation(a), ultimate tensile strength(b) and yield strength(c) of alloy C versus heat treatment temperature in vacuum and air

and 1 100 °C in vacuum and in air. The specimens tested in vacuum exhibit a mixture of intergranular and transgranular fracture patterns (Figs.7(a) and (e)). However, the samples tested in air show almost all intergranular fracture ones, and the grain-boundary facets are smooth and free from deformation marks, indicating the brittleness of grain boundaries (Figs.7(d) and (f)).

The fracture surface of the specimens is perpendicular to the tensile axis. These consist with the relatively high elongation (and UTS) in vacuum, and the low elongation (and UTS) in air. All these results verify the conclusion mentioned before that Ni₃Al (Zr) alloy is embrittled by air at room temperature.

Recent studies have revealed that many ordered

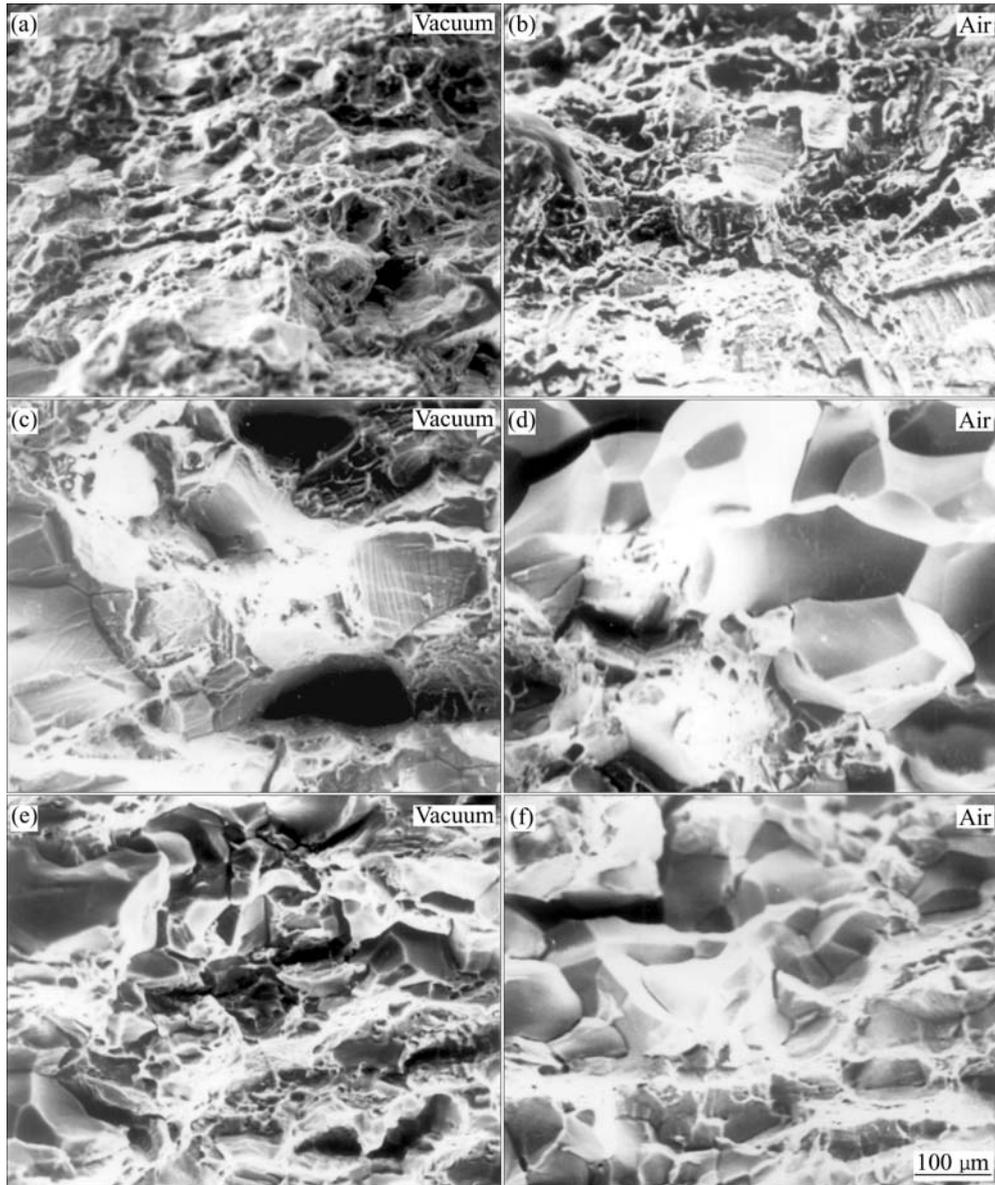


Fig.7 Fractographs of alloy C deformed at room temperature in vacuum and air: (a), (b) 900 °C, 2 h, AC; (c), (d) 950 °C, 2 h, AC; (e), (f) 1100 °C, 2 h, AC

intermetallics containing aluminum are very susceptible to environmental embrittlement. The phenomenon of environmental embrittlement in aluminides[16, 17], as well as in aluminum-based alloys is explained by following chemical reaction:



Aluminum atoms in the aluminides react with moisture in air, resulting in the generation of atomic hydrogen that causes embrittlement, which has been borne out by test results of YIN et al[18] in 1991. Because $\text{Ni}_3\text{Al}(\text{Zr})$ alloy also contains the reactive element Al, we believe that above reaction should occur in this alloy also.

Our results indicate that the stress-relieved, incompletely recrystallized microstructure in some way

minimizes the environmental effect, and elongated grains or unrecrystallized rolled bands may disrupt the entrance of hydrogen by providing a minimum number of transverse grain boundaries. We can also conclude that the $\text{Ni}_3\text{Al}(\text{Zr})$ alloy still has a tendency for environmental embrittlement.

Similar results have been reported by GAO et al[19] for B-free binary Ni-22.6Al(mole fraction, %) alloys. SU et al[14] have studied the effect of recrystallization on environmental embrittlement of a multicomponent Ni_3Al -base alloy doped with 0.02%B(mass fraction). It was found that the ductility increases and the susceptibility to environmental embrittlement decreases with increasing the recrystallized fraction. The fracture modes were ductile and transgranular, and no intergranular fracture was observed. These are quite

different from the results obtained in the present study. The differences might be explained in terms of the boron effect. Boron can reduce the diffusion of atomic hydrogen in Ni₃Al[20]. Therefore, the recrystallized Ni₃Al alloy doped with boron is less sensitive to the test environment and shows a fracture mode other than intergranular fracture. For the B-free Ni₃Al(Zr) alloy used in this study, the recrystallization treatment generates many transverse grain boundaries that are susceptible to hydrogen embrittlement, bringing on the fact that the amount of intergranular fracture increases with increasing the degree of recrystallization. It is concluded that the addition of Zr cannot reduce the environmental embrittlement of Ni₃Al alloy.

5 Zr alloying effect

From the obtained results we know that the elongation of the completely recrystallized alloy A is around 16.4% in air (Fig.4(b)), which is similar to the result achieved by GEORGE et al[6] in polycrystalline specimens produced by deforming and recrystallizing a single crystal of Ni-22.7Al-0.3Zr. The ductility is considerably higher than that of binary Ni₃Al (about 3.1%[21]). The result mentioned above confirms that Zr significantly improves the ductility of the Ni₃Al alloy. While the exact mechanism is not clear, we might suggest that the mechanism by which Zr improves the ductility of the Ni₃Al alloy is different from that by boron.

In literatures, several ideas have been suggested to account for the increasing ductility by Zr addition. One assumption, proposed by GEORGE et al[7], is that Zr appears to both alleviate environmental embrittlement and enhance GB cohesion, but they could not clearly indicate the mechanism. However, we have confirmed that Zr cannot alleviate environmental embrittlement in this study. CHUANG et al[22] proposed that Zr eliminates the segregation of harmful impurity element including sulphur to GBs. It is argued that even if the GBs are relatively free of embrittlement impurities, polycrystalline Ni₃Al still exhibits brittle intergranular fracture.

To investigate whether Zr improves the ductility of the Ni₃Al alloy by segregating to GBs, we performed Auger analyses on GBs of alloy B. We found that Zr does not segregate to GBs when treated at 1 100 °C (Fig.8(b)), however, for the specimen treated at 900 °C, Zr does segregate to GBs though the amount is small (Fig.8(a)). Therefore, if Zr does strengthen GBs in the Ni₃Al alloy, its mechanism is not clear. The other possibility is that, instead of strengthening GBs, Zr somehow changes the slip behavior of Ni₃Al, so reduces the effective stress concentration at GBs, or Zr

contributes to an increase of the fraction of special boundaries, such as low angle boundary(LAB), Σ 3 GBs, which are more resistant to fracture[23]. The last possibility is that, Zr increases the lattice parameter of the Ni₃Al alloy tremendously, and thereby the activation energy decreases. All possibilities require further investigation.

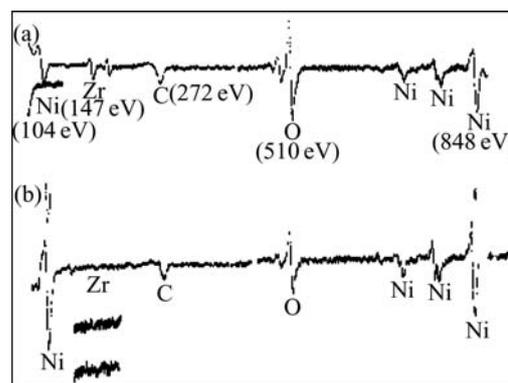


Fig.8 AES spectra taken from intergranular(IG) region for alloy B at 900 °C, 2 h, AC(a) and 1 100 °C, 2 h, AC(b)

6 Conclusions

1) The yield stress decreases with an increase in the degree of recrystallization. The completely recrystallized specimens have the lowest yield stress. The highest elongation is obtained in the stress-relieved specimens with incompletely recrystallized microstructure.

2) The amount of ductile fracture reduces for completely recrystallized specimens, and the ductile fracture mode remains unchanged for the incompletely recrystallized samples when tested from vacuum to air.

3) The increase in recrystallization degree results in an increase in the susceptibility to environmental embrittlement, and the completely recrystallized samples exhibit the most serious environmental embrittlement.

4) The Ni₃Al (Zr) alloys still have a tendency for environmental embrittlement, and Zr appears to have no effect on suppressing environmental embrittlement.

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