Strain Rate Effect on Oxygen-Induced Embrittlement of PM Ni₃Al at Intermediate Temperatures

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The influence of the strain rate on the embrittlement of hot isostatically pressed powder metallurgy (PM) Ni₃Al alloys with boron additions has been studied at temperatures between 623–773 K. Tensile testing has been carried out in air at strain rates in the range of 10^{-5} to 10^{-1} s⁻¹. The influence of powder particle size on ductility loss has also been investigated. Results indicate that high elongations to failure are achieved when the intermetallic is tested at the highest strain rate, namely 8×10^{-1} s⁻¹ but no ductility is observed when tests are carried out within a low strain rate range. This effect is explained in terms of a reduction of oxygen-induced embrittlement when strain rate is higher than oxygen diffusion rate at the crack tip. On the other hand, the decrease in the initial particle size of the intermetallic produces the same effect on ductility as the increase in the strain rate. A microstructure of fine particles in PM Ni₃Al reduces the oxygen embrittlement.

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I. Introduction

Environmental embrittlement has been described for Ni₃Al with and without boron additions tested in air or oxygen between 773 and 1073 K. The phenomenon is accompanied by a change in the fracture mode from ductile transgranular to brittle intergranular^{(1)–(8)}. Oxygen has been identified as the embrittlement agent since the same intermetallic tested in vacuum shows ductile behaviour^{(5)–(7)(9)}.

It should be noted that oxygen embrittlement takes place at intermediate temperatures in polycrystalline Ni₃Al but not in single-crystal. This fact has been associated with the relatively large diameter of the oxygen atom which can penetrate along grain boundaries at intermediate temperatures but cannot pass through the lattice of L1₂-type intermetallics⁽¹⁰⁾.

Liu and White⁽²⁾ suggest that embrittlement is due to a dynamic process involving localized high-stress concentration, elevated temperatures, and gaseous oxygen. Adsorption or absorption of oxygen at the crack tip produces the weakening of the Ni–Al or Al–Al bonds and facilitates microcrack propagation. Furthermore, Hippsley and DeVan⁽¹¹⁾ studied the crack growth in the temperature range of 873–1033 K, and they propose a discontinuous step-wise mechanism in which the oxygen diffusion along grain boundaries causes enough local embrittlement for the crack to jump forward by a slight discrete increment.

Other authors have suggested that, although this embrittlement is mainly related to a dynamic process involving oxygen, this is not the only reason and some intrinsic characteristic of the material contributes to the process as well^{(12)–(15)}. For instance, a peculiar variation of both yield

stress and strain hardening rate with temperature is considered. The generally accepted theory is that both parameters increase with increasing temperature in the intermediate temperature range⁽¹⁶⁾. More recent studies show that for small strains (about 1%) work hardening rate increases in the temperature range of the yield stress anomaly⁽¹⁷⁾⁽¹⁸⁾. However, at 1.5% strain, these authors find that maximum work hardening rate takes place at 500 K and then decreases with increasing temperature. A similar behaviour of work hardening rate variation with temperature in Ni₃Al has been observed in other works^{(19)–(23)}. All the above indicates that larger ductilities are obtained in materials having lower yield stress and a higher value of both the work hardening rate and fracture stress⁽¹³⁾⁽²³⁾.

The embrittlement phenomenon is especially dramatic in PM Ni₃Al due to the weakness of the particle boundaries as has been observed in a previous work⁽²⁴⁾. Nevertheless, the synthesis of this material by a powder metallurgical route is considered interesting and potentially useful in the manufacturing of complex parts with final shapes. Furthermore, the use of this method eliminates the thermomechanical treatment which must be carried out at temperatures above 1273 K due to the special characteristics of this intermetallic, such as the increase in yield stress with temperature.

The purpose of this work is to study the effect of the strain rate and the powder particle size on the ductility of Ni₃Al processed by a powder metallurgical route in the range of 623–773 K. Additionally, the embrittlement phenomenon is analysed.

II. Experimental Procedure

Rapidly solidified powders were produced by argon

gas atomization of a Ni_3Al cast alloy doped with boron. The powder was sieved and sorted into different size fractions. Particle size fractions of 50–100 and 100–200 μm were canned in cylindrical steel capsules of 30 mm in diameter. Then, they were outgassed at 2 Pa and 673 K for 2 h, and sealed. The consolidation by hot isostatic pressing (HIP) was conducted at 150 MPa for 2 h at 1373 K. The chemical composition of the material was determined as Ni-24.1Al-0.3B (at%), using inductive coupling plasma (ICP).

Tensile tests were carried out using flat specimens prepared by electro-spark machining from billets. The damaged surface layer was removed by grinding. Samples had a section of 8 mm², a curvature radius (r_c) of 3 mm and a gauge length of 6.5 mm. The tests were conducted in air at room temperature and in the temperature range of 623–773 K using a 10000 N load cell at initial strain rates of $\dot{\epsilon}=3 \times 10^{-5}$, 3×10^{-4} , 3×10^{-2} and $8 \times 10^{-1} \text{ s}^{-1}$. The microstructural characterization of specimens and their fracture surfaces were carried out by optical microscopy (MO) and scanning electron microscopy (SEM). Metallographical etching was done using a solution of $\text{CH}_3\text{COOH}:\text{HNO}_3:\text{HCl}=8:4:1$

III. Results

The microstructure of PM Ni_3Al consolidated with both particle sizes of 50–100 and 100–200 μm is equiaxed and consists of the ordered $\text{L1}_2\text{-Ni}_3\text{Al}$ phase. The metallographical section of 50–100 μm particle size compacted material, in which the original powder particles containing grains are visible, is shown in Fig. 1. Since the grains rarely exceed the particle size, it can be concluded that the material of smaller particle size results in finer grain size.

Figure 2 shows the tensile parameters for both types of samples as a function of temperature at a strain rate of $3 \times 10^{-4} \text{ s}^{-1}$. As can be seen, tensile strength and elongation to failure are higher for the material of smaller particle size than for the material of larger particle size, as has been described in a previous work⁽²⁴⁾. The figure also shows a high ductility loss for both particle sizes at tem-

peratures above 473 K. This temperature dependence of the tensile parameters was similarly observed at the other strain rates.

To gain an insight into the effects of the strain rate on the tensile strength, the yield stress and the elongation to failure are plotted in Fig. 3 at 623 K for the 50–100 μm particle size material. A significant increase in elongation to failure and tensile strength with the increase in strain rate are visible whereas the yield stress remains practically unvaried. It is observed that the alloy reaches the maximum elongation values ($\sim 12\%$) at the two highest strain rates. However, as the strain rate decreases the elongation decreases, approaching zero at the slowest strain rate of $3 \times 10^{-5} \text{ s}^{-1}$. On the other hand, the influence of strain rate on ductility is more remarkable as the test temperature increases, as shown in Fig. 4, where the elongation to failure vs the temperature is plotted at different strain rates for the 50–100 μm particle size material. A completely brittle behaviour is exhibited at 773 K at 3×10^{-4} and $3 \times 10^{-5} \text{ s}^{-1}$. However, some ductility is observed at the highest strain rates, achieving an elongation to failure of 5% at $8 \times 10^{-1} \text{ s}^{-1}$ and 3% at $3 \times 10^{-2} \text{ s}^{-1}$.

A similar influence of the strain rate on ductility has

Fig. 2 Tensile properties vs test temperature for the intermetallic of 50–100 and 100–200 μm particle sizes, tested at a strain rate $\dot{\epsilon}=3 \times 10^{-4} \text{ s}^{-1}$.

Fig. 1 Metallographic section of 50–100 μm particle size material showing original powder particles with grains inside.

Fig. 3 Variation of tensile properties with strain rate for the intermetallic of 50–100 μm particle size at 623 K.

been found for 100–200 μm particle size material as seen in Fig. 5. It can be observed that the elongation to failure decreases from 5% at 623 K to 1% at 773 K at the strain rate of $8 \times 10^{-1} \text{ s}^{-1}$. However, the material becomes brittle at 693 K at the strain rate of $3 \times 10^{-4} \text{ s}^{-1}$. From the comparative analysis of Figs. 4 and 5, it turns out that for a given experimental condition the elongation to failure is higher for the 50–100 μm particle size material than for the 100–200 μm material.

Macroscopically, the fracture mode was always brittle and samples fractured without necking. The OM observations of the specimen surfaces showed a large number of cracks which were perpendicular to the tensile axis and associated with the particle-boundaries. The crack density decreases with decreasing strain rate (Fig. 6). For a given strain rate, the crack density is higher in the lower particle size material. Therefore, it can be inferred that the elongation to failure increases with increasing crack density.

Fracture analysis by SEM indicates that failure is always interparticle, irrespective of test temperature and strain rate (Fig. 7). This fracture mode is usually observed in PM material consolidated by HIP. The interparticle failure in this case may have been associated with the presence of aluminum and nickel oxides formed on the powder particle surfaces during atomization, which prevented the material flow during further consolidation. Such oxides particles might cause the nucleation and coalescence of voids that provoke the interparticle failure. At higher magnifications intergranular and transgranular regions on the fracture surfaces are visible (Fig. 8). The latter regions are related to the presence of dimples and slip bands. The density of these regions is higher in samples tested at high strain rates.

IV. Discussion

As mentioned before, the embrittlement process in Ni₃Al can be due to extrinsics, intrinsic factors, or a combination of both. To shed light on the cause of the ductility loss in Ni₃Al, a comparison of the mechanical behaviour and fracture surfaces with the unaffected

Fig. 4 Elongation to failure at 623 and 773 K at different strain rates for the intermetallic of 50–100 μm particle size.

Fig. 5 Elongation to failure at different temperatures and strain rates for the 100–200 μm particle size material.

(room temperature tests) and the embrittled (intermediate temperature tests) materials has been carried out. From Fig. 2, it is deduced that the 50–100 μm particle size material tested at $3 \times 10^{-4} \text{ s}^{-1}$ can withstand greater stresses with higher elongations to fracture at room temperature than at 623 K (1000 MPa and 21% against 600

Fig. 6 Surfaces of samples of 100–200 μm particle size tested at 623 K showing cracks. (a) $\dot{\epsilon} = 3 \times 10^{-2} \text{ s}^{-1}$, $\epsilon = 5\%$ and (b) $\dot{\epsilon} = 3 \times 10^{-4} \text{ s}^{-1}$, $\epsilon = 1\%$.

Fig. 7 Fracture surfaces of tensile tested samples at 623 K and $\dot{\epsilon}=3 \times 10^{-2} \text{ s}^{-1}$ showing interparticle failure. (a) Material of 50–100 μm particle size and (b) 100–200 μm particle size.

Fig. 8 Detail of the fracture surface of samples tested at 623 K for the 50–100 μm particle size material. (a) $\dot{\epsilon}=8 \times 10^{-1} \text{ s}^{-1}$ and (b) $\dot{\epsilon}=3 \times 10^{-4} \text{ s}^{-1}$.

MPa and 3%, respectively). It is interesting to note that interparticle failure has been observed at both temperatures despite these differences in elongation to failure. Assuming that interparticle fracture takes place when a critical stress is exceeded, the material should break at the same stress for both temperatures, although with a lower elongation for the higher temperature due to the increase in the yield stress as the test temperature increases. However, this strong decrease in tensile strength has not been observed when the same material has been tested at $8 \times 10^{-1} \text{ s}^{-1}$ (see Fig. 3). Consequently, intrinsic factors seems not to be the only causes of embrittlement. Thus, embrittlement must be related mostly to extrinsic factors (oxygen embrittlement), or perhaps a combined effect of intrinsic and extrinsic factors.

The oxygen induced embrittlement is also manifested by the strong dependence of elongation to failure on strain rate, as deduced from Figs. 4 and 5. As can be seen, for a given temperature the elongation to failure decreases as the strain rate decreases, as it does in the case of increasing temperature at a given strain rate. Therefore, the higher the test temperature the lower the difference in ductility, irrespective of the powder particle size. These results can be explained considering the presence of oxygen in the environment and its diffusion

to the crack tip.

In the case of the 50–100 μm particle size material tested at 623 K, an elongation to failure three times higher is attained when the strain rate is increased from 3×10^{-4} to $8 \times 10^{-1} \text{ s}^{-1}$ (Fig. 3). This increase in elongation is accompanied by an increase in crack densities on the sample surfaces, indicating that crack generation is favored over its propagation. This might occur if the material region ahead of the crack tip thoroughly hardens so that propagation of any crack generated on the surface is prevented. Therefore, at the highest strain rates the failure is caused by a high stress level (of about 1000 MPa) and the embrittlement phenomenon does not take place. On the other hand, the same material tested at low strain rates breaks at a very low stress, 600 MPa only (Fig. 3), and the surface examination reveals the presence of very few cracks, which indicates that crack propagation is favored over its generation.

Other evidence of the fact that oxygen embrittlement is not involved during deformation at high strain rates is given by the study of fracture surfaces. Although fracture is always interparticle, samples tested at the highest strain rates, (*i.e.* with higher elongations to failure) show a number of larger intergranular and transgranular regions than for samples broken at the lowest strain

rates. Therefore, in order to prevent the embrittlement process in this material at this temperature, it would be necessary to raise the strain rate above a critical value so that oxygen diffusion to the crack tip is slower than the strain rate imposed during the tensile test.

Previous works on the embrittlement at intermediate temperatures for this and other intermetallics indicate that intrinsic factors can play an additional role in the loss of ductility^{(10)–(15)(23)}. For example, Schulson *et al.*⁽¹⁵⁾ suggest the possibility that grain boundary sliding may be an important mechanism in crack nucleation, subsequently facilitating oxygen embrittlement. On the other hand, Fujita *et al.*⁽¹⁴⁾ associate the ductility loss in Ni₃Al with weak grain boundaries even when the intermetallic is doped with boron. Finally, some authors of this work (Pérez and Adeva⁽²³⁾) studying the tensile behaviour of Ni₃Al ribbons doped with boron between room temperature and 673 K, in vacuum, have observed a ductility loss at temperatures above 473 K caused by a decrease in the work hardening rate. The fact that the work hardening rate measured at 673 K is lower than at room temperature implies that at 673 K the material is softer ahead of the crack tip. The crack will propagate at lower stress levels, and fracture will take place with lower elongation. Intrinsic properties of materials have also been invoked to explain the ductility loss with increasing temperature in other intermetallics such as Ni₃Si⁽¹⁰⁾ and Ti₃Al based alloys⁽²⁵⁾. Hence, it is useful to compare elongations to failure in condition in which oxygen embrittlement is prevented (at intermediate temperatures and high strain rates) with those obtained after testing at room temperature. In this work it has been observed that the 50–100 μm particle size material tested at 623 K at high strain rates has a fracture behaviour similar to that observed at room temperature tested at a common strain rate of 10^{-4} s^{-1} despite the lower elongation to failure (12% in comparison to 21% at room temperature, Figs. 2 and 4). This 9% ductility loss observed at 623 K is attributed to the combined effect of a higher yield stress and a lower work hardening rate.

With respect to the operating mechanisms in oxygen induced embrittlement, DeVan *et al.*⁽¹¹⁾ have observed that crack propagation occurs in successive steps. They propose that critical oxygen concentration must be present at the crack tip to make the material ahead brittle and facilitate the crack growth, which then stops in an unembrittled zone. On the other hand, Xu and Schulson⁽²⁶⁾ conclude that a catastrophic crack propagation occurs at room temperature in this intermetallic when the triaxiality at the crack tip exceeds a critical value. This feature is favoured in the cracks nucleated at the edge of the sample. The work by Liu and White⁽²⁾ proves that cracks nucleate on the surface of the sample and the crack whose propagation produces the fracture extends from one edge of the sample to the other. This process has also been observed in the present work.

Another important aspect of this study is the influence of the alloy particle size on the ductility loss. Although the effect of grain size on oxygen embrittlement of Ni₃Al

has scarcely been studied, Liu and Oliver⁽⁷⁾ observed that the equiaxed grain structure is quite prone to dynamic embrittlement. However, their study shows that this phenomenon can be reduced by controlling the grain shape from equiaxed to columnar grain structure. A columnar grained structure with parallel grain boundaries to the tensile axis may minimize the normal stress across grain boundaries and, therefore, it may suppress nucleation and propagation of cracks along the grain boundaries. The PM Ni₃Al studied in this work can be considered to be of equiaxial structure. However, it has been observed that the material with the smallest particle size shows the highest level of ductility in the overall temperature range and strain rates studied (Figs. 4 and 5). Thus, embrittlement is shifted toward higher temperatures in the alloy with the smaller grain and/or particle size. The reduction in the particle size of this material seems to reduce the dynamic embrittlement in two ways: (1) Lengthening the pathway that oxygen must take in order to pass through the particle boundary and/or (2) Reducing the discontinuous crack advance distance⁽²⁷⁾. Therefore, the effect of decrease in the particle size is similar to the increase in the strain rate. It can be concluded that the embrittlement phenomenon can be reduced in a PM Ni₃Al using powders of fine particle size.

V. Conclusions

- (1) A clear correlation between strain rate and elongation to failure in PM Ni₃Al has been observed when it is tensile tested in air at intermediate temperatures. In general, the greater the strain rate the higher the elongation to failure.
- (2) The elongation to failure is higher in the 50–100 μm particle size material than in the 100–200 μm , regardless of testing temperature.
- (3) Oxygen is the main cause of the embrittlement. If the oxygen diffusion to the crack tip is lower than the strain rate imposed during the tensile test the embrittlement process will be prevented.
- (4) Intrinsic properties of this intermetallic also contribute to the decrease in elongation to failure, *e.g.* by decreasing the work hardening rate of this material with increasing temperature.
- (5) The oxygen embrittlement can be reduced in PM Ni₃Al by decreasing the powder particle size and by increasing the strain rate.

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