1200 K COMPRESSIVE PROPERTIES OF N-CONTAINING NIAL

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ABSTRACT

As part of a series of experiments to understand the role of N on the strength of NiAl, a heat of NiAl was enriched with N by melting and atomization to powder in a nitrogen atmosphere. Following consolidation of the powder by hot extrusion, 1200 K compressive properties were measured in air. Within the range of strain rates examined, 10^{-3} to 10^{-9} s^{-1}, the strength of the N-enriched NiAl was greater than that of a simple 15 μm grain size polycrystalline, binary NiAl alloy. For the most part the overall improvement in strength is ascribed to the fine grain size of the N-doped NiAl rather than the alloy chemistry; however, the alloy displayed a complex behavior exhibiting both weakening effects as well as strengthening ones.

INTRODUCTION

Cyromilling of NiAl has been identified as a means to impart elevated temperature creep resistance in this B2 crystal structure intermetallic [1]. By milling nickel aluminide powder in liquid nitrogen relatively large amounts of N (wt.% levels) can be incorporated on and beneath the exposed NiAl powder surfaces as very fine AlN particles. Upon densification of the cryomilled powder a cellular microstructure is produced, where a thin layer of nickel aluminide enriched with AlN particles surrounds nitride-free NiAl cores. Although the nitrides in cryomilled NiAl are the most likely source of strength, cryomilling must also place nitrogen into solid solution up to its solubility limit in NiAl. To date little is known about the effect of dissolved N on the elevated temperature strength of NiAl [2]. Nitrogen as a successful agent for improvement of creep resistance could have important consequences because it is one of the few alloying elements identified to date, which does not cause low temperature embrittlement of NiAl [3]. Hence a study of the 1200 K compressive properties of a N-doped NiAl has been initiated to determine if low levels of nitrogen can improve the elevated temperature strength.

EXPERIMENTAL PROCEDURES

Nitrogen doped, nominally stoichiometric NiAl (Heat P1810) was produced by Homogeneous Metals Inc. via a conventional vacuum + gas atomization technique except that nitrogen gas was substituted for the usual, inert Ar during melting and atomization. The prealloyed powder was vacuum sealed in a mild steel can and hot extruded at 1200 K and 16:1 reduction ratio. Extensive characterization of this extruded material has been reported in [3]. In summary, the composition of the alloy is Ni-49.9Al (±0.2 at.% Al) and contained 0.0057 carbon, 0.0347 oxygen, and 0.0904 nitrogen (all compositions in at.%). This concentration of nitrogen represents a two orders of magnitude increase over the N found in a typical lot of Ar-atomized, prealloyed NiAl powder. Transmission electron microscopy (TEM) examination [3] of cross sections taken from the extrusion revealed equiaxed ~4 μm diameter grains with some of the boundaries decorated by nanometer size particles. While energy dispersive analysis indicated that

all these particles were rich in Al and N, several of them seemed to also contain O. In addition, a few grains contained larger second phase precipitates, and microdiffraction techniques were able to identify the larger particles as AlN.

To further characterize the location of nitrogen in the material, both as-extruded and heat treated (1673 K/2h/water quench) samples were analyzed by Auger electron microscopy. Notched cylindrical specimens were fractured by impact in a preparation chamber and immediately transferred to the analytical chamber through a connecting valve without exposure to air. A beam energy of 10 keV and current of 1 nA were utilized to produce a beam diameter of less than 100 nm. The analyzer was a hemispherical capacitor operating at the retard ratio of 4 which imparted 0.5% energy resolution. The analytical chamber had a working pressure of ≤ 4.9 x 10^{-8} Pa, that permitted at least one hour of analysis time before there was detectable O or C contamination on the surface.

A portion of the extruded bar stock was wire electrodischarged machined into cylindrical compression samples 5 mm in diameter by 10 mm in length. All specimens had their long axis parallel to the extrusion direction, and they were tested with the as-machined surface finish. Elevated temperature mechanical behavior at 1200 K in air was determined both under constant velocity and constant load conditions. Selected compression tested samples were mounted longitudinally and metallographically prepared. The specimens were examined by light optical microscopy in both the unetched and etched states. A solution of 50 ml HF + 150 ml H_2O mixed with 100 g molybdic acid was utilized as a swab etchant.

RESULTS

Auger Analysis

Auger analysis of coarsened precipitates in the heat treated NiAl-N alloy confirmed that the majority of the particles are AlN. However, the presence of O, as well as N, in a few of the particles also indicates that a number of small aluminum oxy-nitrides exist (Fig. 1(a)). Attempts to directly analyze the particles in the as-extruded material were somewhat ambiguous due to the fine size of the second phase particles. Finally, characterization of regions of the NiAl grain boundaries in both the as-extruded and heat treated samples that were free from the second phase particles did not reveal any traces of third elements (Fig. 1(b)). Thus, even in a highly nitrogen-doped NiAl, no evidence for grain boundary segregation of N or any other interstitial element is apparent.
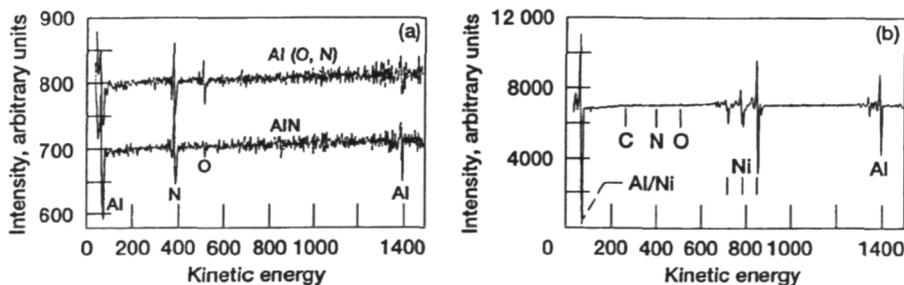

Fig. 1. Auger spectra from features in the N-doped NiAl: (a) AlN and Al(N,O) particles, and (b) particle-free grain boundary.

Mechanical Properties

The true compressive stress - strain diagrams for N-doped NiAl determined by constant velocity testing at 1200 K are given in Fig. 2(a) as a function of approximate strain rate. In general, similar behavior was obtained under all imposed deformation rates, where rapid work hardening occurred through ~1.5% strain and then was succeeded by continuous flow at a more or less constant stress. Near duplicate testing at ~2 x 10^{-6} s^{-1} (Fig. 2(a)) yielded the expected results with the slower test being slightly weaker. The 1200 K creep behavior of N-doped NiAl compressed under constant load conditions is given in Fig. 2(b) as a function of the initial stress. Both tests exhibited normal behavior with primary and secondary creep regimes.

The relationship between flow stress (σ) and strain rate ($\dot{\varepsilon}$) of N-doped NiAl at 1200 K is given in Fig. 3(a), where the flow stress was taken at 3 percent strain from the stress-strain diagrams (Fig. 2(a)) and from the steady state regime of the creep curves (Fig. 2(b)). These data demonstrate several unusual aspects compared to polycrystalline NiAl. For example, two power law regimes are indicated in this figure. The fastest strain rate results gave a stress exponent, n, of ~9, while the intermediate rates are described by n = 4.6; neither of these stress exponents are consistent with the commonly accepted value for NiAl of about 6 [2]. Lastly, the lowest stress creep test (20 MPa, Fig. 3(b)) resulted in behavior inconsistent with either the fast or intermediate strain rate results.
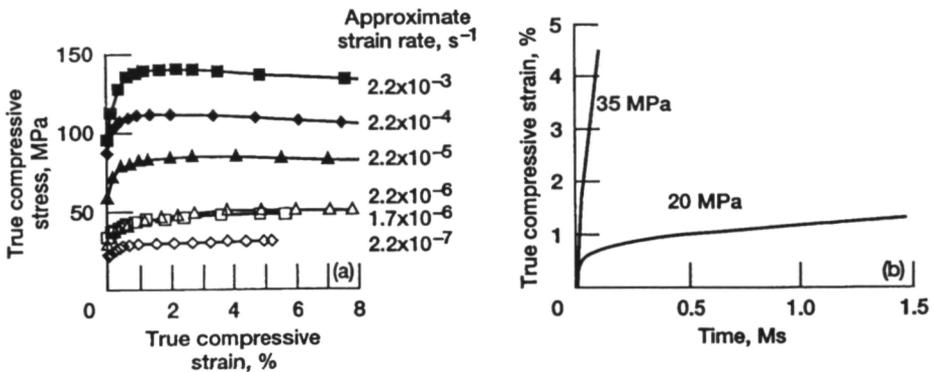

Fig. 2. *Compressive response of N-doped NiAl at 1200 K: (a) true stress - strain diagrams as a function of nominal strain rate and (b) creep curves for several engineering stresses.*

Post-Test Microstructure

Since previous studies of binary NiAl [4,5] and HfC-dispersion strengthened NiAl [6,7] had also displayed unusual $\sigma - \dot{\varepsilon}$ behavior, which was ascribed to changes in the microstructure during testing, a large number of the compression tested samples were polished and examined. After relatively fast deformation (Fig. 4(a)) the resulting grain structure and grain size of 3.8 μm were identical to the as-extruded state. As the imposed strain rate decreased, clear evidence for grain growth could be seen (Fig. 4(b,c)), but the majority of the structure was still quite small (~4.2 μm). Finally, under the slowest conditions (Fig. 4(d)) extensive regions of the original as-extruded grain structure were being replaced by much larger grains. Based on these observations, it appears that the AlN particles were effective in pinning the grain boundaries and for the most part, were successful in maintaining a small grain structure. Only in the lowest stress, longest term experiment (Fig. 4(d)) was the as-extruded structure widely replaced by large grains.
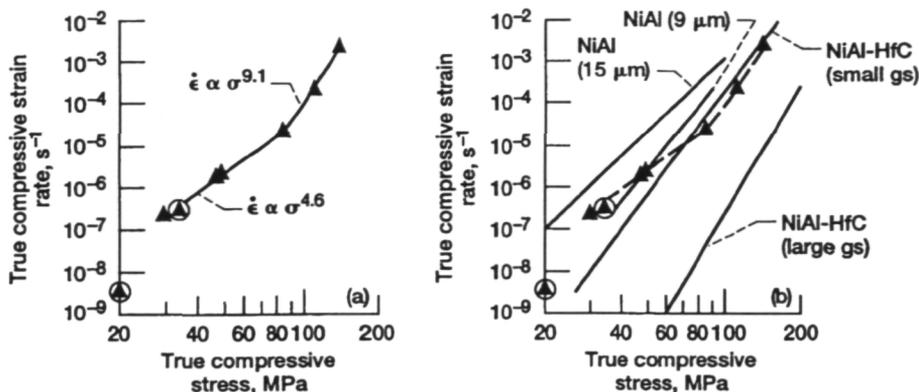
Fig. 3. True 1200 K compressive stress - strain rate properties of: (a) N-doped NiAl and (b) comparison of N-doped NiAl to several other forms of NiAl. Encircled data points taken from constant load creep tests.

DISCUSSION

The role of grain size on the elevated temperature mechanical properties of binary NiAl is somewhat complicated due to competing deformation mechanisms. Under lower temperature/higher strain rate conditions it has been shown [5] that the creep strength of NiAl can be enhanced by decreasing the grain size. It has also been demonstrated [8] that under higher temperature/slow strain rate conditions NiAl can be significantly weakened by a fine grain size. Strengthening via reduction in grain size derives from a dislocation climb control mechanism [9], while grain size weakening is a result of deformation by accommodated grain boundary sliding [10]. Because of these conflicting relationships between strength and grain size, rather strange behavior can arise during testing of binary NiAl [4]. For instances, {1} grain growth during straining at 2×10^{-7} s^{-1} at 1400 K can lead to a flow stress which is greater than that observed for an equivalent 1300 K test, and {2} the lack of grain growth in fine grain size NiAl at either 1300 or 1400 K can lead to materials that are much weaker than expected based on the dislocation climb mechanism.

The situation is further complicated when the grain structure of dispersion strengthened NiAl evolves during testing. Constant load 1300 K creep studies of a HfC-dispersed NiAl revealed a deformation regime where stain rate was independent of the applied stress, while 1300 K constant velocity testing indicated that a threshold stress for creep existed [6]. Both of these phenomena were traced to microstructural instabilities [7].

Some insight on the possible role of structure on the strength of N-doped NiAl can be obtained through comparison of its properties (Fig. 3(b)) with those of binary and dispersion strengthened NiAl possessing stable microstructures during testing. In Fig. 3(b) the curve for 15 μm grain size NiAl [4] represents a typical large grain size, binary polycrystalline aluminide. This strength level can be improved by simply decreasing the grain size to 9 μm [5]. The superposition [7] of a fine grain size (~5 μm) and dispersion strengthening in NiAl-HfC seems to produce additional resistance to deformation, and finally the conversion of the dispersed NiAl-HfC to large grain microstructures (> 40 μm) provides the greatest improvement in strength [7].
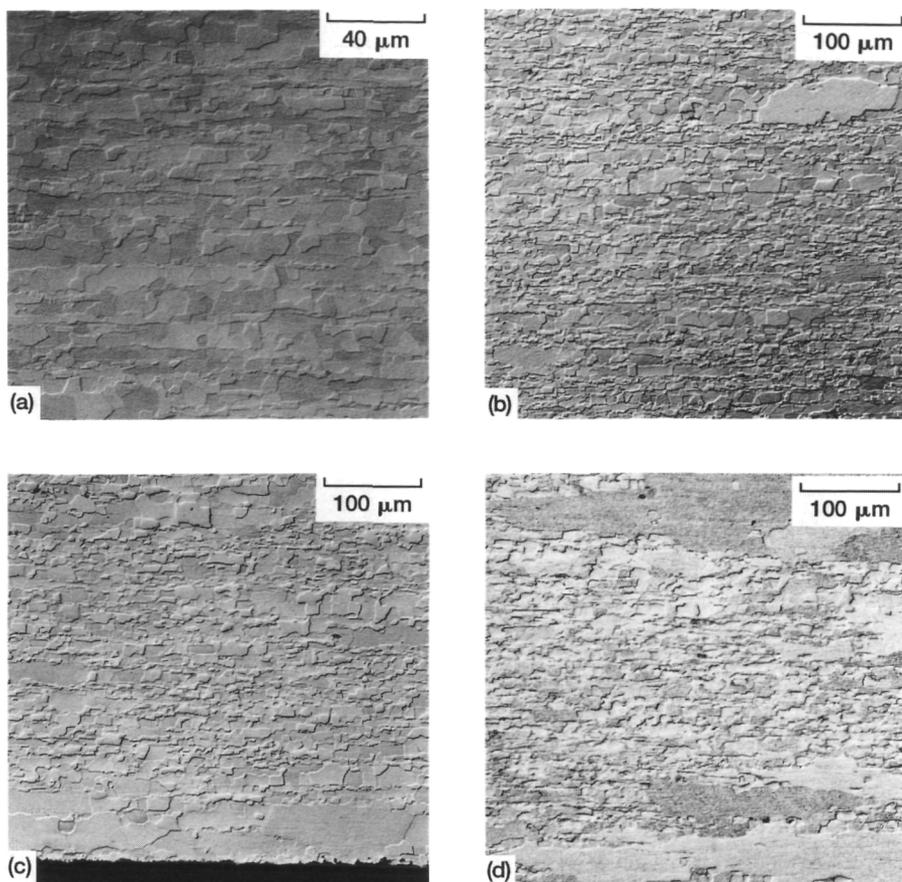
Fig. 4. Typical post-test microstructures of 1200 K tested N-doped NiAl: (a) compressed at 2.2 x 10⁻⁴ s⁻¹ to 9.2 % strain, (b) compressed at 1.7 x 10⁻⁶ s⁻¹ to 5.6 % strain, (c) compressed at 2.2 x 10⁻⁷ s⁻¹ to 5.2 % strain, and (d) crept at 20 MPa to 1.3 % strain over 1.5 Ms. Compression (extrusion) axis is horizontal; differential interference lighting of etched samples.

At strain rates exceeding 2×10^{-5} s^{-1}, the ~4 μm grain size N-doped nickel aluminide is stronger than both binary alloys and even the small grain size HfC-dispersed NiAl (Fig. 3(b)). However, due to the change in deformation mechanism, it can be seen that extrapolation of the fast strain rate behavior into the lower strain rate regime predicts a much stronger material than is actually found. Such irregularities can not offhandedly be ascribed to an error from the mixing of data obtained by two different testing procedures, because both methods gave similar flow stresses for a strain rate of about 2.5×10^{-7} s^{-1} (Fig. 3). Instead, the strength of the N-doped alloy decreases in the lower stress regime according to a stress exponent of 4.6 and becomes weaker than the 9 μm binary, at least through a strain rate of 2×10^{-7} s^{-1}. The result from the 1200 K - 20 MPa creep test, however, does not indicate continued weakening at lower strain rates. These

observations and comparisons in combination with the microstructural observations (Fig. 4) allow some conjecture as to the operating deformation mechanisms in N-doped NiAl at 1200 K.

At the three fastest tests it is likely that N-doped NiAl is strengthened by its small ~4 μm grain size (Fig. 4(a)). Furthermore, since its strength exceeds that of the ~5 μm grain size NiAl-HfC and both materials possess like stress exponents of 9.1, it appears that grain size strengthening could be more important than dispersion hardening at faster strain rates. Unfortunately, the small grain size (Figs. 4(b,c)) also leads to activation of an accommodated grain boundary sliding mechanism [10] at strain rates below 2×10^{-5} s^{-1}, which decreases the stress exponent and weakens the N-doped alloy. Once significant grain growth takes place (Fig. 4(d)), however, the material would become composite-like with load shifting from the small grain areas to the stronger large grain regions. This seems to be the case (Fig. 3), where the 1200 K - 20 MPa creep test exhibits much greater resistance to deformation than that predicted by extrapolation of the $n = 4.6$ regime. More recent work [11] indicates that this explanation is likely and that strengthening of the large grain material actually occurs by the presence of a fine subgrain structure that is stabilized by the AlN particles. Therefore, it appears that all the strengthening/weakening effects displayed by the present lot of N-doped NiAl at 1200 K can be ascribed to the microstructure of the alloy rather than its chemistry.

SUMMARY OF RESULTS

Compression testing of a ~4 μm grain size NiAl doped with about 900 appm N at 1200 K has demonstrated that this alloy has superior elevated temperature strength between 10^{-3} and 10^{-9} s^{-1} compared to typical binary nickel aluminides. In general, the improvement can be ascribed to the grain structure rather than the N content. A small grain size provided considerable strengthening under fast deformation conditions, but the same small grain size promoted relative weakening under slower rates. Under low stress creep testing grain growth occurred in the N-doped NiAl, and the resultant material was somewhat stronger than polycrystalline, binary NiAl.

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