

1300 K COMPRESSIVE PROPERTIES OF A REACTION MILLED NiAl- AlN COMPOSITEJ. Daniel Whittenberger¹, Eduard Arzt² and Michael J. Luton³¹ NASA Lewis Research Center, Cleveland, OH 44135² Max-Planck-Institut für Metallforschung, Stuttgart, FRG³ Exxon Research and Engineering, Annadale, NJ 08801

ABSTRACT

Cryomilling (high intensity mechanical ball milling in a liquid nitrogen bath) of the B2 crystal structure nickel aluminide leads to a NiAl- AlN composite containing about 10 vol pct second phase which is dispersed as very small diameter (< 50 nm) AlN particles in a mantle surrounding particle-free NiAl grains. The AlN particles are the result of reaction milling, where nitrogen incorporated into the matrix during cryomilling reacts with Al during subsequent thermomechanical processing to form a composite. Compressive testing at 1300 K of such materials densified by either hot extrusion or hot isostatic pressing have indicated that strength at relatively fast strain rates ($> 10^{-7}$ s⁻¹) is dependent on the method of consolidation; however no clear dependency on densification technique appears to exist at slower rates. In addition deformation at 1300 K occurs by two distinct mechanisms, where at high strain rates the stress exponent is greater than 13 while at slower rates ($< 10^{-7}$ s⁻¹) a much lower stress exponent (~ 6) was found.

INTRODUCTION

The B2 crystal structure, nominally equiatomic intermetallic NiAl is of interest for high temperature structural applications due to its high melting point, low density and inherent oxidation/corrosion resistance in comparison to Co-, Fe- and Ni-base superalloys. Unfortunately, the poor elevated temperature mechanical properties of this aluminide leave much to be desired. A recent report [1], however, indicates that cryomilling (ball milling in liquid nitrogen [2]) of NiAl powder followed by hot extrusion can lead to a material which is at least 6 times stronger than the unprocessed nickel aluminide at 1300 K. It was speculated that the enhanced deformation resistance was due to the observed nonuniform microstructure where a thin mantle containing a high density of small (< 50 nm) diameter AlN particles surrounded essentially particle-free grains. Because dislocations would be unable to easily move through the particle-rich regions by either glide or climb mechanisms, a high strength elevated temperature composite was produced.

The objective of this paper is (1) to further characterize the effects of cryomilling and consolidation on the NiAl powder and (2) to present additional 1300 K mechanical property data, including long term creep results, on cryomilled NiAl densified by hot extrusion and hot isostatic pressing.

EXPERIMENTAL PROCEDURES

Prealloyed, gas atomized Ni-51(at pct)Al was cryomilled with a 0.5 wt pct Y_2O_3 addition in a modified Model 1-S Szegvari 10 liter attritor, as the original intention of the work [1] was to produce a yttria dispersion strengthened nickel aluminide. After 16 h of milling, the charge was allowed to warm to room temperature under dry argon and subsequently handled in air. The cryomilled powder was then vacuum canned in steel and densified by either

1. Hot isostatically pressing at 1323 K - 207 MPa for 5 h or 1623 K - 207 MPa for 5 h, or

2. Extrusion at 1505 K with reduction ratios of 8:1, 12:1 or 16:1. Cylindrical compression specimens, whose length was parallel to the extrusion direction for the extruded materials, were electro-discharge machined and ground to final size: ~ 5 mm in diameter by about 10 mm in length. Compressive stress - strain behavior was determined at 1300 K in air in a universal test machine running under constant velocity conditions at crosshead speeds ranging from 2.12×10^{-3} to 9.47×10^{-7} mm/s. The autographically recorded load - time charts were converted, assuming conservation of volume, to true compressive stresses, strains, and strain rates via the offset method [3]. Constant load compressive creep testing at 1300 K in air was also undertaken to determine the long term (up to 1000 h) strength of the cryomilled NiAl. Lastly, selected as fabricated materials and compression tested specimens were microstructurally characterized by standard light optical & scanning electron microscopy (SEM) and X-ray procedures.

RESULTS AND DISCUSSION

Cryomilled NiAl

The starting prealloyed gas atomized Ni-51Al powder was uniformly spherical, about $60 \mu\text{m}$ in diameter, with each particle composed of multiple grains (Fig. 1(a)). Cryomilling broke the spheres into pieces and small flakes and significantly reduced the average size (Fig. 1(b)). Examination of the cross section of the larger cryomilled pieces revealed that they were, in reality, agglomerations of the small flakes. No second phase particles were visible on the surface or in the cross sections of either the as-gas atomized or as-cryomilled powder. Wet chemical analysis of the as received, gas atomized powder showed it to contain about 32.4 wt pct Al, 4 ppm W and 135 ppm O. Spectrographic comparison of the Al levels of the cryomilled aluminate and the as received powder showed them to be nearly identical. On the other hand the oxygen content of the cryomilled powder had increased to 0.58 wt pct while the nitrogen level was 1.98 wt pct.

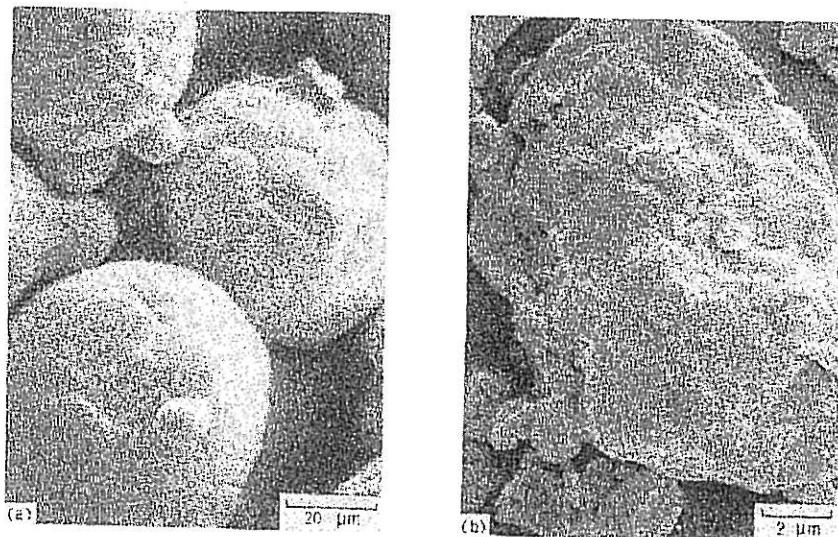


FIG. 1. Scanning electron photomicrographs of as-gas atomized (a) and cryomilled (b) NiAl powder.

X-Ray diffractometer scans [4] of the as-cryomilled powder only revealed a slight shifting to high angles and peak broadening in comparison to those for the gas atomized powder. After 1505 K extrusion, however, distinct AlN peaks were found in the X-ray spectra [1,4], and second phase particles within the densified material were observed by light optical, scanning electron and transmission electron microscopy [1]. Because AlN was not detected in the as-gas atomized or as-cryomilled powder but was readily visible after exposure to elevated temperature, we believe that the present materials are examples of the use of reaction milling to form a high temperature composite: i.e. the nonequilibrium interstitial/solid solution alloying which occurs as a result of high energy mechanical milling leads to a precipitation reaction during subsequent thermomechanical processing. Furthermore, at least in this instance, reaction milling is capable of introducing relatively high volume fractions of refractory second phases. For example based on the measured powder compositions prior to and following cryomilling, the present NiAl-AlN composites contain about 1.8 vol pct alumina and 10.3 vol pct aluminium nitride in a Ni-47.3(at pct)Al matrix.

On a light optical level the microstructure of all consolidated materials appears as dark outlined "grains," where the outline is the AlN dispersed mantle surrounding particle free regions [1]. In the case of the extruded materials cigar shaped particle free grains, whose length increases and width decreases with increasing reduction ratio (Fig. 2(a), [1]) are observed. The grain structure of the hipped NiAl-AlN (Fig. 2(b)) is more or less equiaxed consisting of a duplex distribution of large ($\sim 10 \mu\text{m}$) and small ($\sim 1 \mu\text{m}$) approximately spherical AlN-free grains.

Compressive Properties

Stress-Strain Behavior -- True 1300 K compressive stress - strain diagrams for the cryomilled aluminate powder extruded at 1505 K and 8:1 reduction ratio or hot isostatically pressed at 1623 K are presented in Fig. 3. The extruded composite (Fig. 3(a)) rapidly work hardens over the first one percent of

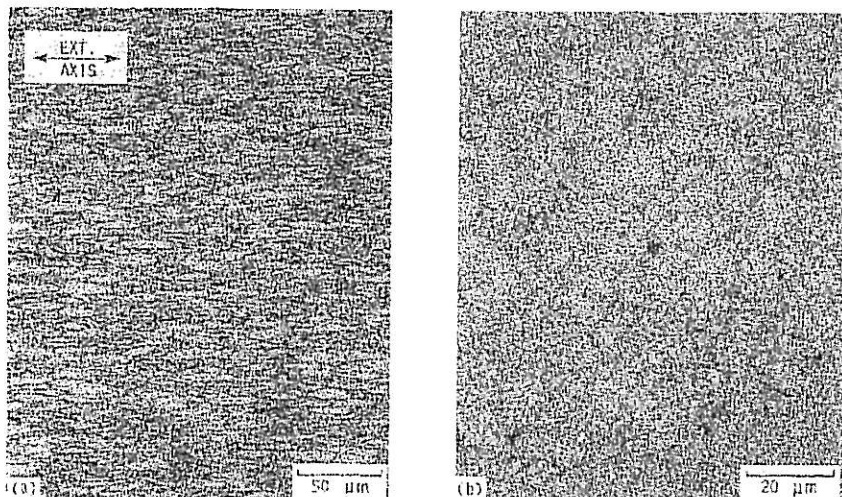


FIG. 2. Light optical photomicrographs of cryomilled NiAl after (a) extrusion at 1505 K and 8:1 and (b) hot isostatic pressing at 1623 K -207 MPa - 5 h.

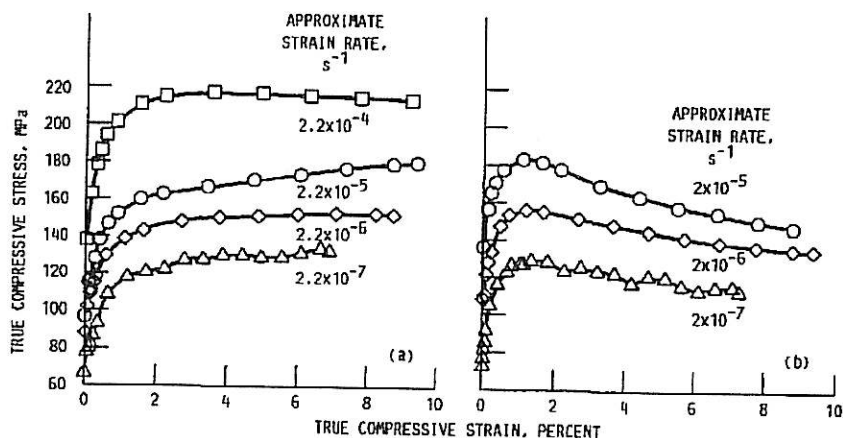


FIG. 3. True 1300 K compressive stress - strain curves for cryomilled NiAl (a) extruded at 1505 K and 8:1 and (b) hipped at 1623 K - 207 MPa - 5 h.

deformation then transitions into continued, but gradual strain hardening except for the fastest strain rate test. At a strain rate of $2 \times 10^{-4} \text{ s}^{-1}$, work hardening leads to a broad stress maximum ranging from about 2 to 4 percent strain, and this is followed by minor strain softening. The hipped composite also displays rapid work hardening during the initial deformation, but this leads to stress maxima at approximately one percent strain and then strain softening. Comparison of the relative strengths of these two consolidation procedures reveal that the hipped material is stronger than the extrusion for the first 3 percent strain; beyond this level, however, the 8:1 extruded composite is the more capable due to its continuous work hardening.

Constant velocity testing of the NiAl-AlN composite which had been densified by 16:1 reduction at 1505 K [1] yielded true 1300 K stress - strain diagrams which are similar to those for the 8:1 extrusion tested at a strain rate of about $2 \times 10^{-4} \text{ s}^{-1}$ (Fig. 3(a)); i.e. a stress maxima at about 3 pct strain followed by slow strain softening. In addition to the absence of extended work hardening, the higher reduction ratio composite was much stronger than the 8:1 extrusion or, for that matter, the 1623 K hipped product. For instance at $2 \times 10^{-5} \text{ s}^{-1}$ the maximum strengths are about 200, 180 and 160 MPa for the 16:1 extrusion, 1623 K hipped compact and 8:1 extrusion (value at 3 pct strain) respectively.

Constant Load Creep Tests -- True compressive creep curves for NiAl-AlN composites extruded at 1505 K and an 8:1 reduction ratio are presented in Fig. 4, and two creep tests results for materials hot isostatically pressed at 1623 K or extruded at 16:1 and 1505 K are given in Fig. 5. In all cases the composites almost immediately (within the first few hours) deform about 1 percent with the application of stresses ranging from 77 to 125 MPa. Following this period of rapid deformation, work hardening was sufficient to cause normal transient creep behavior leading to rates which either very slowly decreased with time (1623 K hipped material tested at 85 MPa, Fig. 5) or became constant (1505 K, 16:1 extrusion tested at 102 MPa, Fig. 5).

Flow Stress - Strain Rate Behavior -- True Compressive flow stress - strain rate data taken from the 1300 K constant velocity tests at 3 pct strain (Fig. 3 & [1]) and the nominal steady state creep data from the 1300 K constant load tests (Figs. 4 and 5) are presented in Fig. 6. Following convention, the flow

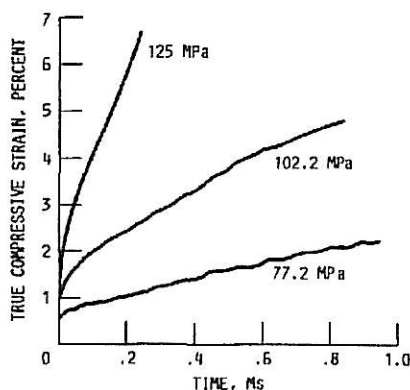


FIG. 4. True compressive 1300 K creep curves for cryomilled NiAl extruded at 1505 K and 8:1.

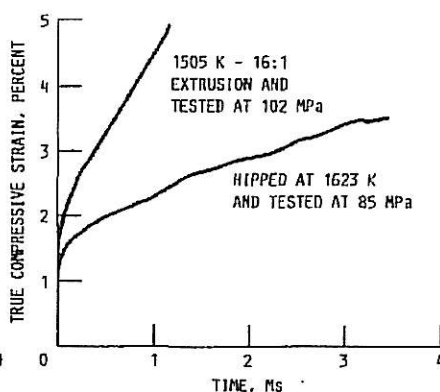


FIG. 5. True compressive 1300 K creep curves for several cryomilled NiAl materials.

stresses σ and strain rates $\dot{\epsilon}$ were fitted to the standard power law equation, $\dot{\epsilon} = A\sigma^n$, by linear regression techniques where A is a constant and n is the stress exponent. The graphical results of such fits and the values for the stress exponent also are given in Fig. 6. The data for 1505 K, 16:1 material (Fig. 6(a)) and the 1505 K, 8:1 extrusion (Fig. 6(b)) indicate that two deformation regimes exist with a boundary at a strain rate of $\sim 10^{-7} \text{ s}^{-1}$. Due to the limited data for the 1623 K hipped material (Fig. 6(c)), the presence of two separate regions is less certain.

While it could be argued that the transition is simply an artifact due to the change from constant velocity to constant load testing, we do not believe this to be the case. For example several constant velocity data points clearly deviate from the extrapolation of the high stress exponent region for the 1505 K - 16:1 extruded material (Fig. 6(a)), and, secondly, good agreement exists between both experimental procedures at a flow stress of $\sim 125 \text{ MPa}$ for the 1505 K - 8:1 extruded material (Fig. 6(b)). Therefore on basis of the present results (Fig. 6), it appears that plastic flow in the NiAl-AlN composites at 1300 K can take place via two distinct mechanisms: under fast deformation conditions strain rate is highly dependent on stress (ie. stress exponents > 13 signifying a low temperature like behavior), while at slow strain rates ($\leq 10^{-7} \text{ s}^{-1}$) more normal high temperature creep processes ($n \approx 6$) occur.

The densification technique does make a difference in terms of strength at fast strain rates, with the cryomilled NiAl extruded at 1505 K and 16:1 (Fig. 6(a)) being significantly stronger than the other two methods (Fig. 6(b,c)) having equal resistance to deformation. Below 10^{-7} s^{-1} , the composite flow stress seems to be less dependent on the method of consolidation, where extrapolations of the 16:1 extruded (Fig. 6(a)) and 1623 K hipped (Fig. 6(b)) composites indicated similar strengths while the 8:1 material (Fig. 6(c)) appears to be slightly weaker.

Materialography

As the majority of the compression tested specimens are intended for transmission electron microscopy studies, only a few samples have been sacrificed for examination by light optical and SEM techniques. With only two exceptions little difference could be detected between as densified and as

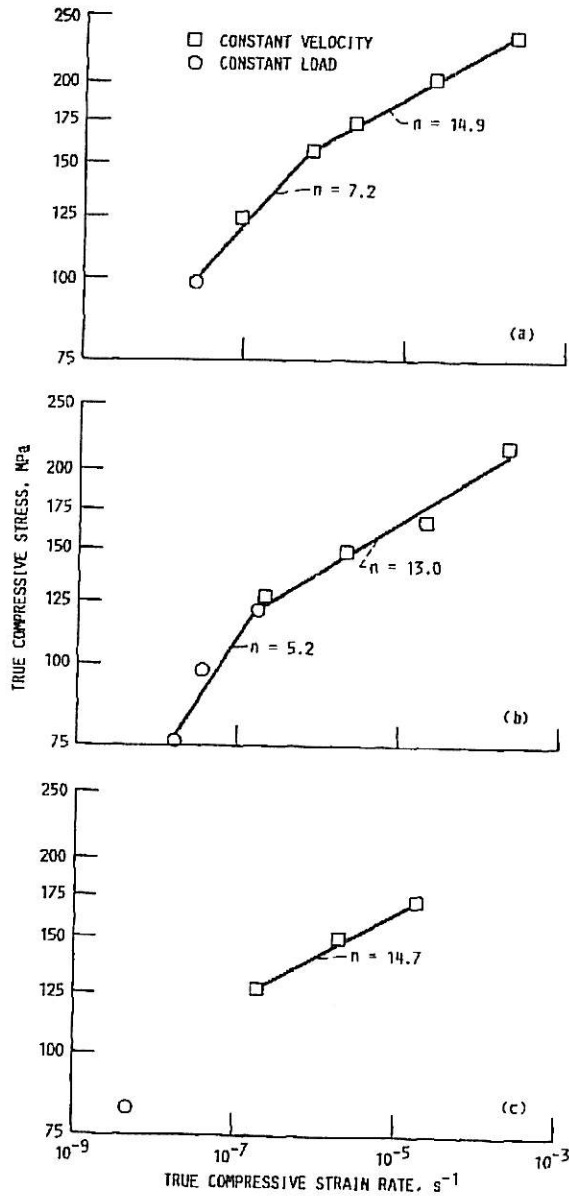


FIG. 6 True compressive 1300 K stress - strain rate behavior for cryomilled NiAl as functions of test and densification methods (a) extruded at 1505 K and 8:1, (b) extruded at 1505 K and 16:1 and (c) hipped at 1623 K -207 MPa - 5 h.

tested microstructures. In several cases porosity was found near the air exposed surfaces both after relatively long term (Fig. 7(a)) and short term (Fig. 7(b)) testing. Electron microprobe examination of the specimen shown in Fig. 7(a) revealed the existence of an Al concentration gradient between the oxide/matrix interface (low Al) and the sample interior; therefore it is likely that the pores are Kirkendall voids. These result from the Al diffusion to the surface to reform the alumina scale which is being continuously cracked and spalled during compressive deformation. It should be noted, however, that this behavior was not consistent, as porosity was not observed in other long and short term specimens. Secondly, a few samples possessed cracks which appeared to start from the center of the specimen base, run parallel to the compression axis for a short distance (at most 2 mm), turn 90° (perpendicular to the stress), and either continue to the free surface or simply end. Neither porosity nor cracking had been previously observed after compression testing of 1505 K, 16:1 extruded material [1].

SUMMARY OF RESULTS

Cryomilling of the B2 crystal structure intermetallic NiAl leads to the production of a NiAl-AlN composite via a reaction milling process. Compressive testing at 1300 K of such composites densified by both hot extrusion and hot isostatic pressing have indicated that strength at relatively fast strain rates ($>10^{-7} \text{ s}^{-1}$) is dependent on the method of consolidation; however no clear dependency appears to exist at slower rates. Furthermore 1300 K deformation occurs by two distinct mechanisms, where at high strain rates stress exponents greater than 13 were observed while $n \approx 6$ for $< 10^{-7} \text{ s}^{-1}$.

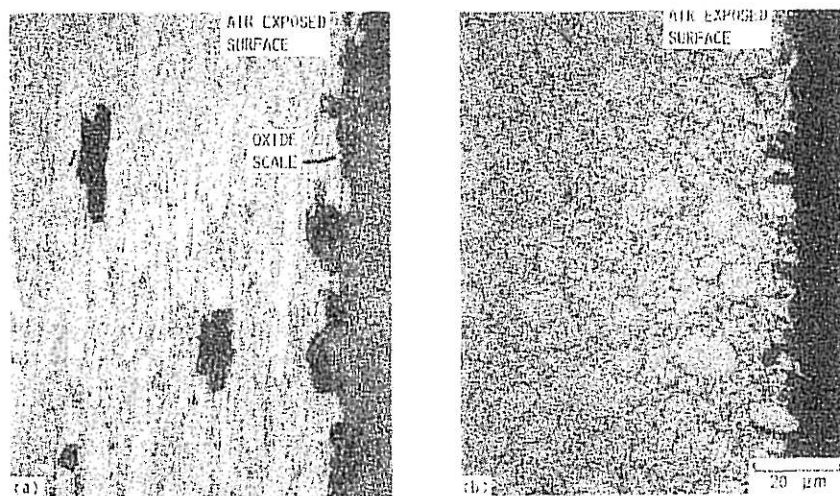


FIG. 7. Microstructure near air exposed surfaces for NiAl-AlN composites tested at 1300 K. (a) extruded at 1505 K and 8:1 and tested at 100 MPa to 4.8 pct strain over 0.8 Ms, (b) hipped at 1623 K -207 MPa - 5 h and tested at a nominal strain rate of $1.8 \times 10^{-5} \text{ s}^{-1}$ to 8.8 pct strain in 7.2 ks.

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