

Preliminary investigation of a NiAl composite prepared by cryomilling

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An attempt has been made to improve the high temperature mechanical strength of the B2 cubic crystal structure intermetallic NiAl by dispersion strengthening. Prealloyed Ni-51 (at. %) Al was cryomilled with a Y_2O_3 addition to form an yttria dispersoid within the intermetallic matrix. Following milling, the powder was hot extruded to full density and machined into test coupons. Compression testing between 1200 and 1400 K indicated that the cryogenic process yielded the strongest NiAl based material tested to date: creep resistance was six times better than NiAl and twice that of a NiAl particulate composite containing 10 vol. % TiB_2 . Surprisingly, transmission electron microscopy revealed that the second phase was inhomogeneously distributed. Furthermore, x-ray analysis indicated that the second phase was not Y_2O_3 but rather AlN.

I. INTRODUCTION

Although the B2 cubic crystal structure intermetallic phase NiAl has a relatively low density and excellent oxidation resistance, its use as a monolithic high temperature material is problematic. Such doubts stem from the lack of elevated temperature strength.¹ Following time-honored traditions in metallurgy, solid solution and precipitation hardening²⁻⁵ as well as both particulate composite⁵⁻⁸ and unidirectional fiber reinforcement⁹ approaches are being investigated to improve mechanical properties.

As opposed to the attempts involving large volume fractions of a second phase for strength, studies¹⁰⁻¹² are also underway to apply "dispersion strengthening" concepts to NiAl. The object in this case is to distribute a low volume fraction (<5%) of a thermodynamically stable material uniformly throughout a matrix as very small diameter (on the order of 30 nm) particles which can disrupt the passage of dislocations. Current efforts have focused on Rapid Solidification Technology (RST) to incorporate HfC, TiB_2 , and TiC as dispersoids in NiAl.¹⁰⁻¹² Compression testing of such materials indicates that HfC leads to effective strengthening at 1200 and 1300 K.^{13,14} In particular, HfC additions have resulted in behavior which is similar to that of Oxide Dispersion Strengthened (ODS) alloys: for example, (1) large increases in the stress exponent from 5 to ~20; (2) in some instances, apparent threshold stresses for creep [a stress below which no measurable creep

occurs]; and (3) departure side pinning of dislocations to particles.¹⁵⁻¹⁷

Prior to the recent RST work, Seybolt¹⁸ in 1966 produced ODS B2 crystal structure iron and nickel aluminides containing Al_2O_3 , ThO_2 , and Y_2O_3 . Of these materials only one thoriated intermetallic (NiAl + $3ThO_2$) would be classified today as dispersion strengthened, since the particle size(s) for the alumina and yttria containing aluminides was too coarse, on the order of 0.5 μm . Furthermore, only NiAl + $3ThO_2$ demonstrated significantly improved 1123 to 1450 K strength over the unreinforced matrix during slow tension testing (strain rates of $4.2 \times 10^{-5} s^{-1}$) and creep rupture testing [data presented in the form of Larson-Miller parameter; specific test temperature(s) was not defined]. Although this initial attempt to dispersion strengthen aluminides held some promise, the relatively low strength at and below 1200 K in comparison to superalloys precluded further development.

Over the past twenty years the ODS technology has undergone major changes primarily due to the advent of mechanical alloying,¹⁹ and the latest developments are described in Ref. 20. Advances in processing techniques and reproducibility have led to the development and production of commercial quantities of Al-base (Al-9021 and Al-9052), Fe-base (MA 956), and Ni-base (MA 754 and MA 6000) ODS alloys at IncoMAP. With the success of metallic systems, it is both logical and reasonable to apply mechanical alloying methods to

intermetallics in order to increase their strength. Vedula, Michal, and Figueredo²¹ have recently attempted to perse Y_2O_3 in B2 aluminides by mechanical alloying at room temperature. While they report success with FeAl-based materials, the results for NiAl were disappointing.

Concurrently with the efforts of Vedula *et al.*,²¹ we have been attempting to dispersion strengthen NiAl by use of a cryogenic milling process.²² This paper presents some results in terms of microstructure and mechanical properties for initial application of this technique to a B2 aluminide.

II. EXPERIMENTAL PROCEDURES

Dispersion strengthened NiAl was prepared by ball milling a slurry of NiAl and Y_2O_3 powders in liquid nitrogen medium, a process known as cryomilling.²² The operation was performed in a modified Model 1-S Szegvari 10-liter attritor, where the vessel was chilled by a continuous flow of liquid nitrogen through the "water cooling" jacket. In addition, liquid nitrogen was introduced into the milling chamber throughout the run to maintain the level of the slurry bath. Thermocouple probes, suspended in the bath, served to monitor the temperature of the slurry and the level of the bath. The powder charge consisted of 995 g of Ni-51 at. % Al, supplied as -325 mesh powder by Homogeneous Metals, Inc., and 5 g of Y_2O_3 , furnished as $<10 \mu\text{m}$ diameter particles by Research Chemicals. At the completion of the 16-h milling cycle, the mill was allowed to warm to room temperature under dry argon. The cryomilled powder was then vacuum canned in mild steel and hot extruded at 1505 K and various reduction ratios.

Cylindrical compression specimens, whose length was parallel to the extrusion direction, were electrodischarge machined from the 16:1 extrusion and ground to final size: $\sim 5 \text{ mm}$ in diameter by about 10 mm in length. Constant velocity compression tests at crosshead speeds ranging from 2.12×10^{-3} to $8.47 \times 10^{-7} \text{ mm/s}$ were conducted in air at 1200 to 1400 K in a universal test machine to $\sim 8\%$ strain. The autographically recorded load-time charts were converted, assuming conservation of volume, to true compressive stresses, strains, and strain rates via the offset method.^{23,24} Selected as-fabricated materials and compression tested specimens were microstructurally characterized by standard light optical and scanning electron microscopy procedures.

Transmission electron microscopy (TEM) of as-extruded materials was undertaken on sections perpendicular to the extrusion axis through a combination of electrodischarge machining ($200 \mu\text{m}$ thick), mechanical grinding ($100 \mu\text{m}$), and dimpling to $20 \mu\text{m}$, followed by ion milling. None of the attempts to electrolytically thin in 10% perchloric acid-methanol solution was successful.

III. RESULTS

Figure 1 illustrates the typical microstructure found in the as-extruded materials where both transverse and longitudinal sections strongly suggest that the distribution of strengthening phase and matrix is quite inhomogeneous. In fact, the structure appears to consist of small, pure NiAl (light gray) regions, elongated in the extrusion direction, which are separated by particle-rich aluminide. This image is reinforced by the TEM results (Fig. 2) where most grains have a mantle of particles [Fig. 2(a)]. In spite of this behavior, the material is fully dense and crack-free within grains, at grain-to-grain junctions, and at interfaces between particle and matrix [Fig. 2(b)]. Due to the uneven partitioning, it was difficult to measure the particle size. However, as can be envisioned from Fig. 2(b), the average diameter of the second phase is quite small, certainly

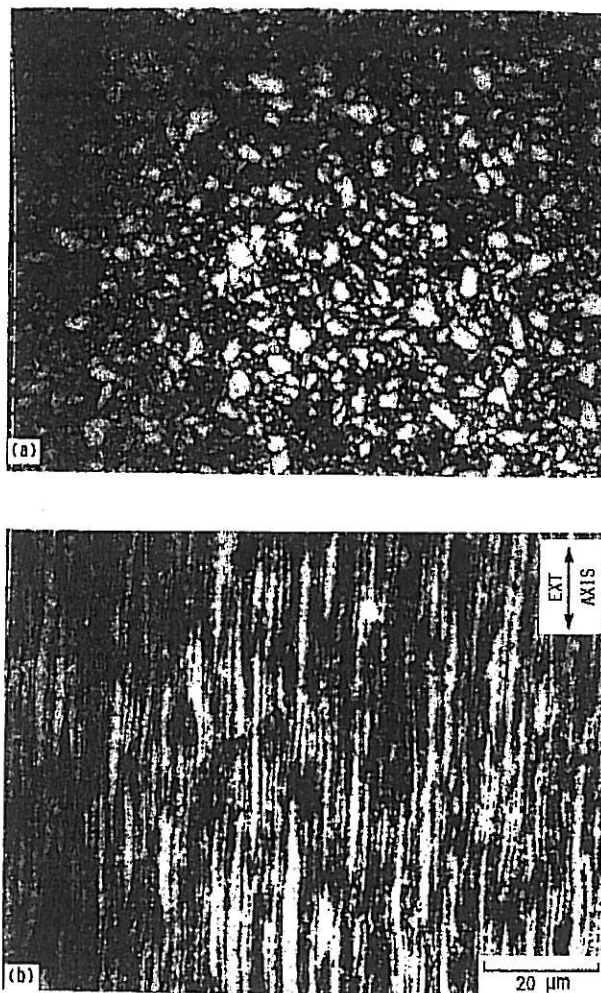


FIG. 1. Light optical photomicrographs of as-extruded (1505 K-16:1) cryomilled NiAl: (a) transverse and (b) parallel to the extrusion axis. Aluminide etched with 33 HNO₃, 33 acetic acid, 33 H₂O plus 1 HF.

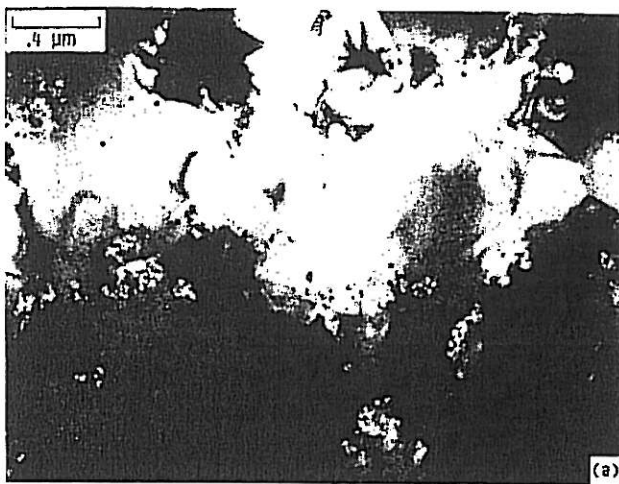


FIG. 2. Transmission electron photomicrographs of as-extruded (1505 K-16:1) cryomilled NiAl illustrating the (a) small grain size and (b) inhomogeneous particle distribution.

less than 50 nm. Also the amount and distribution of particles have negated efforts to determine the grain size; in any case, from Figs. 1 and 2, the large grains are perhaps 1 μm in diameter by 10 μm in length.

Another distinct observation from the photomicrographs is the amount of visible second phase material. Clearly, such a large volume fraction was not expected based on the addition of 0.5% Y₂O₃ to the aluminide during milling. Selected area diffraction patterns and Guinier x-ray diffraction analysis indicated that the majority of the second phase was AlN, although there was, in one instance, an indication that a small amount of Y₃Al₅O₁₂ was also present (Fig. 3). The fraction of AlN within the matrix was indirectly estimated from the original composition and the lattice parameter of the remaining NiAl. After extrusion the average lattice parameter was 0.28856 nm, and following a 120-h anneal at 1000 K this was reduced slightly to 0.28837 nm. Comparison of this span of values to the lattice parameter-

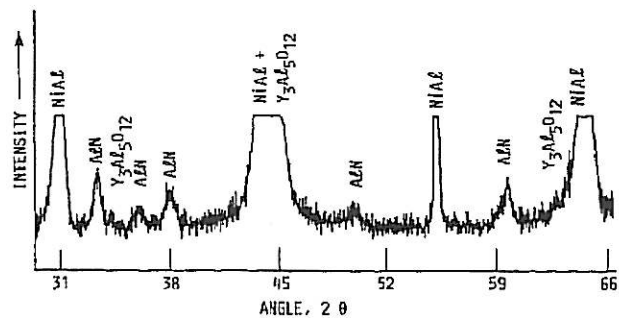


FIG. 3. X-ray intensity as a function of angle (2θ) for as-extruded (1505 K-8:1) cryomilled NiAl irradiated with Cu K_α.

composition data in Refs. 25-27 indicates that the matrix contains about 48 at. % Al. From the starting aluminide powder composition (51 at. % Al) and densities of AlN (3.26 Mg/m³, Handbook value) and Ni-48Al (5.987 Mg/m³²⁸), the volume fraction of AlN within the matrix was estimated to be about 10%.

While the amount of AlN and its distribution would classify this material as a particulate composite rather than a dispersion strengthened NiAl, our difficulty during extrusion indicated that it was quite strong. For example, for 1420 K, 16:1 conditions NiAl powder^{1,29} requires a breakthrough pressure of ~1080 MPa while a NiAl-10TiB₂ (vol. %) particulate composite powder³⁰ required 1230 MPa. Our attempt to extrude the cryomilled powder under these conditions was unsuccessful with the press stalling at its upper limit of 1310 MPa. Fortunately, increasing the temperature to 1505 K allowed extrusion of this material, although the 1240 MPa pressure needed for a 16:1 reduction ratio was close to the maximum.

The strength of the NiAl-AlN composite was confirmed by compression testing, and true stress-strain diagrams determined at 1200 to 1400 K are presented in Fig. 4. For all conditions these curves indicate rapid work hardening over the initial 1.5% strain, followed by a plateau, 2 to 4% strain wide, where flow continues at essentially a constant stress, and lastly slow strain softening. Figure 5 illustrates and compares the true stress-strain rate behavior for the composite to that for Ni-48.3Al^{7,8} where the stress σ and strain rate $\dot{\epsilon}$ were evaluated at 3% strain. In terms of a log-log format, the data exhibit a linear dependency at each test temperature (Fig. 5); hence the flow stresses and strain rates were fitted to standard power law equations

$$\dot{\epsilon} = A\sigma^n \quad (1)$$

and

$$\dot{\epsilon} = B\sigma^n \exp(-Q/RT) \quad (2)$$

where A and B are constants, n is the stress exponent, Q is the activation energy for creep, R is the gas constant, and T is the absolute temperature. Results of this

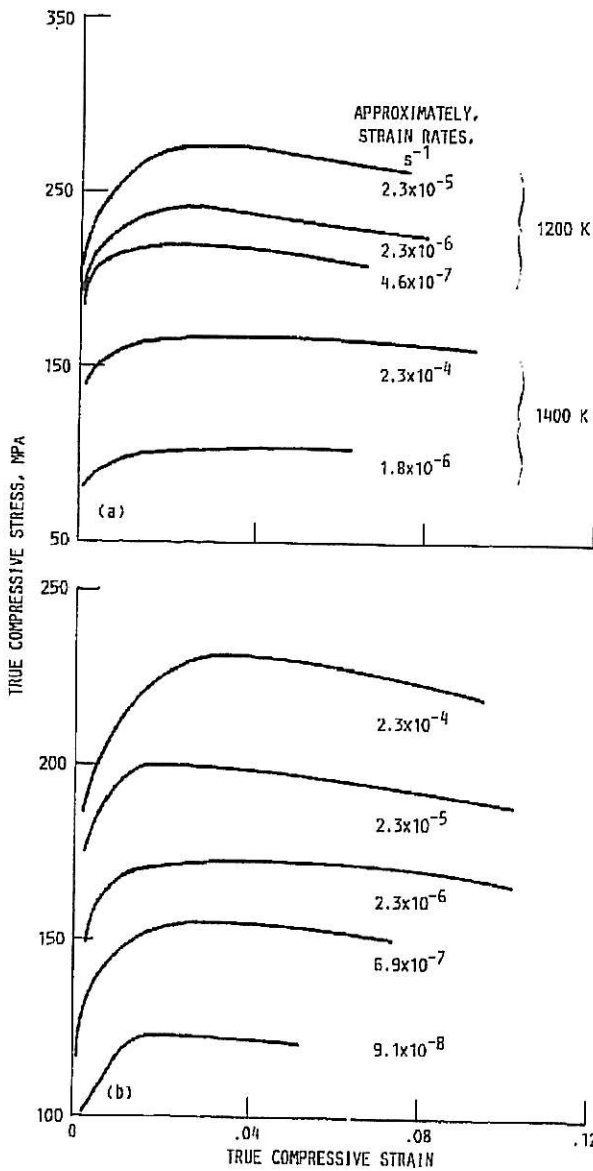


FIG. 4. True compressive stress-strain curves for cryomilled NiAl tested at (a) 1200 and 1400 K and (b) 1300 K.

regression analysis, along with the coefficient of determinations R_d^2 , are given in Table I.

Selected specimens were materialographically examined after testing. Figure 6 illustrates the typical post test structure. Light optical examination [Fig. 6(a)] revealed that the specimens were crack-free and the air exposed surface had not suffered any unusual oxidation. Scanning electron microscopy (SEM) of tested samples [Fig. 6(b)] found the structure to be identical to the as-extruded material, where AlN appeared as dark particles in the light gray Ni-48Al matrix. Examination utilizing both secondary and backscattered electron modes on unetched specimens revealed that the interfaces between AlN and NiAl were intact, and no cavi-

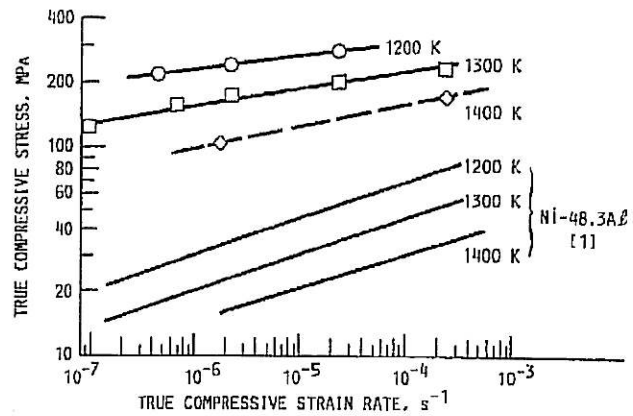


FIG. 5. True compressive stress-strain curves for cryomilled NiAl and NiAl¹ tested between 1200 and 1400 K.

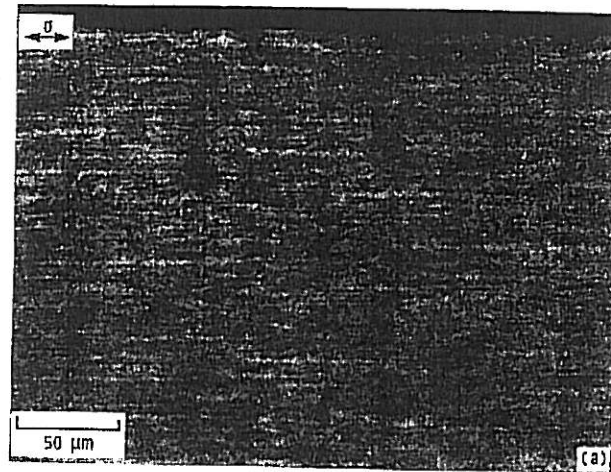


FIG. 6. Microstructure of an unetched NiAl-AlN composite tested at 1300 K and a nominal strain rate of 2.3×10^{-3} s⁻¹ to 10.2% strain. (a) Light optical and (b) backscattered electron mode in the SEM.

ties or microcracks were visible at magnifications as high as 20 000 times.

TABLE I. Power law and temperature compensated-power law fits of true compressive flow stress-strain rate data for NiAl composites.

Volume pct 2nd phase	Temperature, K					
	1200			1300		
	A, s^{-1}	n	R_{adj}	A, s^{-1}	n	R_{adj}
10AlN	1.20×10^{-46}	16.9	0.999	5.08×10^{-34}	12.5	0.975
10TiB ₂ [#]	3.14×10^{-27}	10.81	0.988	2.05×10^{-24}	12.76	0.986
Ni-34Cr (ds) @ 1273 K ³⁰				2.98×10^{-47}	25.5	...
Composition, at. %						
Ni-48.3 ¹	3.93×10^{-15}	5.70	0.998	4.30×10^{-14}	5.68	0.993
Ni-40Al-10Ti ⁶	1.71×10^{-13}	2.89	0.934	4.14×10^{-11}	2.25	0.988
Ni-35Al-15Ti @ 1173 K ²	2.06×10^{-13}	2.35	0.999			
Ni-35Al-15Ti @ 1327 K ²				3.53×10^{-14}	3.24	0.924

Volume pct 2nd phase	Temperature range, K	B, s^{-1}		$Q, kJ/mol$	R_{adj}
		n	n		
10AlN	1200-1400	7.30×10^{-7}	12.0	644.5	0.946
10TiB ₂ [#]	1200-1300	3.14×10^{-10}	11.63	426.8	0.980
Composition, at. %					
Ni-48.3Al ¹	1100-1400	0.19	5.80	318.5	0.996
Ni-40Al-10Ti ⁶	1200-1300	2.52	2.46	278.7	0.950
Ni-35Al-15Ti ²	1171-1419	1.33×10^{-3}	3.53	275.2	0.869

IV. DISCUSSION

Although application of the cryogenic milling process to NiAl did not yield a classical dispersion strengthened material, the process did produce a composite aluminide with very interesting mechanical properties. Clearly, the NiAl-AlN is much stronger than an unreinforced Ni-48.3Al (Fig. 5), and it is more deformation resistant than a NiAl-10TiB₂ particulate composite (Fig. 7). Additionally, NiAl-AlN has a strength advantage at slower strain rates over Ni₂AlTi-NiAl precipitation hardened materials (Ni-35Al-15Ti and Ni-40Al-10Ti in Fig. 7). However, the present AlN containing composite is not as strong as a directionally solidified NiAl-Cr eutectic containing 34 vol. % Cr³¹ or single crystal Ni base superalloys such as MAR-M247 and its variants.³² For completeness, the flow stress-strain rate data for the NiAl-based materials have been fitted to Eqs. (1) and (2), and the appropriate parameters are listed in Table I.

NiAl forms subgrains during elevated temperature plastic deformation,¹ and its stress exponent and activation energy of creep (Table I) are close to the expected values (i.e., $n = 5$; $Q =$ activation energy for diffusion) for a dislocation climb controlled mechanism. Because the equilibrium subgrain size is inversely proportional to stress,³³ maintaining a small, stable grain size in NiAl can and does lead to elevated temperature strengthening,²⁹ and this is reflected by increases in the stress ex-

ponents in Eqs. (1) and (2). Although precipitation of Ni₂AlTi as a result of Ti additions (Fig. 7, Table I) can strengthen, such alloying results in a large decrease in the stress exponent. Thus the usual subgrain forming deformation mechanism seems to be subverted, and the strength of these alloys does not extend to the low strain rates typical of the creep regime. Additions of "inert" particles, such as TiB₂ and AlN, to the matrix greatly

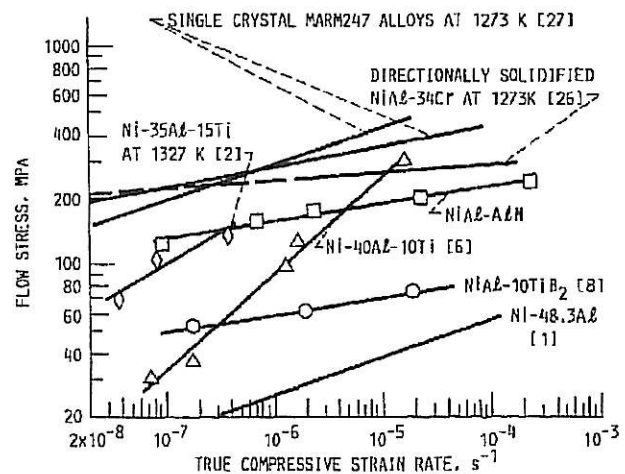


FIG. 7. Comparison of the 1300 K flow stress-strain rate properties of several materials.

increase both the stress exponents and activation energy. While this type of behavior could result from an apparent "threshold stress," this is not the case for NiAl-TiB₂ composites⁸ based on the stress-strain rate curves, size of the particles, and post deformation dislocation structures. Similarly, the current 1200 and 1300 K flow stress-strain rate data for NiAl-AlN do not indicate a "threshold stress."

We can offer some speculation as to reasons for the enhanced strength of the cryomilled NiAl over other two-phase, discrete particle NiAl-based materials. This cryomilled aluminide can be considered to be comprised of particle-free and particle-rich regions which remain compatible both internally and along boundaries; thus neither is free to deform without the cooperation of neighboring regions. The small grain size within the particle-free regions can limit the effective size of subgrains and lead to strengthening.²⁹ Possibly this concept can be extended to the particle-rich region; however, both the number and size of particles [Fig. 2(b)] would seemingly make the movement of even single dislocations difficult. Therefore the establishment of any type of equilibrium substructure within the particle-rich regions would appear to be improbable. More likely strength within the particle-enriched zones derives from dislocation-particle interactions, perhaps through Orowan looping or the maintenance of a cold work-like structure.

Much work needs to be undertaken before any real understanding of the NiAl-AlN composite can be achieved. Some of the questions remaining include the following: (1) the thermodynamic stability of the AlN particles, (2) temperature-time-stress dependent growth of the particles in the matrix, (3) nature of dislocation-AlN behavior in regions densely populated with ~50 nm particles, (4) effect of AlN on oxidation/corrosion resistance, and (5) tensile properties where necking and cavitation can affect the results. Additionally, there are questions concerning the processing; for instance, why do large amounts of AlN form during cryogenic milling of NiAl while little is produced during production of dispersion strengthened Al? Also, much room for improvement in the technology exists; a uniform distribution of AlN in the NiAl matrix could result in greatly improved mechanical properties.

V. SUMMARY

The initial attempt to fabricate an oxide dispersion strengthened aluminide by a cryogenic milling was unsuccessful; however, a NiAl composite containing a relative high volume fraction of AlN was produced. This material possesses the best elevated temperature slow plastic mechanical properties measured to date for either precipitation hardened or particulate composite NiAl-based systems and deserves further study.

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