### DEVELOPMENT OF NIAL AND NIAL-BASED COMPOSITES FOR

### STRUCTURAL APPLICATIONS: A STATUS REPORT

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### **Abstract**

The pursuit of improved engine efficiency is placing ever increasing demands on current material systems. The operating conditions of the next generation of advanced jet engines are so demanding that the required increase in maximum long-term use temperature and the need for lower density materials necessitates the development of new material systems to replace current superalloy technology. The ordered intermetallic alloy NiAl is considered an attractive candidate due to its combination of high melting temperature, low density, high thermal conductivity, and excellent oxidation resistance. In this paper, the historical development of NiAl as a potential high-temperature structural material is reviewed and discussed in terms of current and envisioned applications. In addition, the properties of NiAl in single crystal, polycrystal, and composite form are compared to superalloys and other potential alternative materials. Although some key issues concerning the mechanical properties of NiAl are as yet unresolved, recent success in improving high-temperature strength and control of processing, along with a better understanding of the deformation mechanisms, warrants optimism for the eventual commercialization of this system.

#### Introduction

It is apparent that an incremental leap, rather than a gradual evolution, in high-temperature material requirements has become a national priority, necessitated by the desire for increased engine efficiencies. However, many of the initial optimistic goals for maximum long-term use temperatures have been tempered by the realization that significant improvements over current generation superalloys will involve more basic research and development than anticipated. Further development of  $\gamma$  based superalloys can result only in marginal improvements in operating temperatures due to the melting temperature limitation of the primary strengthening phase. Consequently, significant improvements in high-temperature capabilities will only be achieved through the development of new material systems. While the potential benefit gained through the use of these advanced materials is high, the risk and level of effort required for development to a point of being a viable replacement for superalloys, which have proven toughness, creep strength, and oxidation resistance, are proportionally high.

Of the numerous intermetallic compounds under investigation, NiAl is considered an especially attractive candidate due to its combination of high melting point (1910 K), low density (5.90 g/cm $^3$ ), and excellent oxidation resistance. The density advantage (2/3) that of a typical superalloy) is particularly attractive when NiAl is used in a rotating part. For instance, replacing superalloys with NiAl as a high-pressure turbine blade material would result in at least a 40% reduction in the turbine rotor weight (blades and disk) [1]. Another extremely important advantage of NiAl arises from its high thermal Because NiAl has a much higher thermal conductivity than conductivity [1,2]. superalloys, the temperature distribution in a high-temperature component would be more uniform, reducing the life-limiting hot spot temperature by as much as 50 K [1]. NiAl also posses a greater oxidation resistance than any other high-temperature alloy or coating material. This fact has long been recognized by the aerospace community since it has be used for many years as the principal constituent for coatings on superalloy turbine components [3]. Additionally, neither Ni or Al are considered strategic elements, and they are abundant at a low cost.

While it is useful to compare NiAl to conventional superalloys, it is important to realize that NiAl must also compete with other potential alternative materials. The ordered body-centered cubic crystal structure of NiAl results in a small slip vector (<001>) which allows low-temperature deformation to occur more readily than in many other high melting point intermetallics or ceramic systems. The small slip vector also allows for moderate room temperature ductility, especially in microalloyed single crystals [1,4]. Likewise, NiAl has a relatively low brittle-to-ductile transition temperature (BDTT), on the order of 500-700 K [1,5], although some alloying additions can increase this transition to near 1000 K [6]. Not only does ductility increase significantly at the BDTT but fracture toughness increases accordingly [7]. Because of this, NiAl has a very metallic-like behavior at relatively low temperatures compared to either ceramics, which remain brittle to near their melting temperatures, or compounds such as MoSi, which has a BDTT of approximately 1600 K [8]. NiAl is also stable as a single phase ordered compound over a wide composition range, from 44 to 59 atomic percent Ni at 700 K, and has significant yet relatively untapped potential for alloy development. Most alloying elements fall within three broad categories; either being highly soluble within NiAl, having limited solubility in NiAl and forming a second intermetallic phase that can be used as a strengthening agent, or forming a psuedobinary eutectic with NiAl which may be useful as both a high temperature strengthening and toughening agent. The excellent environmental resistance of NiAl at all temperatures is also in contrast to many intermetallic systems which suffer either from low temperature environmental problems, such as Fe-Al alloys, intermediate temperature oxidation (pesting) as in niobium aluminides, or are incapable of forming protective oxide coatings such as many silicide systems. Consequently, NiAl is one of the most promising intermetallic systems for replacing superalloys.

# Historical Development of NiAl

As shown in Figure 1, NiAl has been investigated as a potential high temperature structural material for nearly four decades. Most of the early studies were performed at government labs or on contract by the Air Force, with the majority of these early works never reaching the open literature. These early studies were exploratory in nature and concerned primarily with determining whether NiAl or NiAl-based alloys had potential as high-temperature refractory compounds. Later studies focussed on the processing of NiAl along with a systematic investigation of the effect of metallurgical variables on mechanical behavior. During the early 1960's, NiAl was considered to have potential as a general high temperature structural material, and by the mid 1960's was identified as a potential candidate material for use as the leading edge in a superalloy turbine vane [2]. Unfortunately, by the end of the 1960's no solution was found for the low-temperature brittleness and consequently industrial and governmental interest waned. It was at this point that research in NiAl shifted primarily to universities. Studies from about 1968 through 1980 focussed on understanding the deformation mechanisms, after which interest again diminished. In the mid-1980's the discovery that B additions could dramatically improve ductility in Ni<sub>3</sub>Al, along with the development of new processing techniques, rekindled interest in developing ductile intermetallic materials and NiAl research again flourished and has since grown steadily.

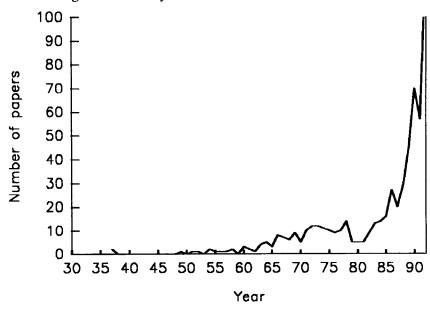


Figure 1. The number of published papers on NiAl and NiAl related topics, as recorded in NASA's RECON database, illustrates the dramatic increase in NiAl research over the past 10 years.

As in the early years of NiAl research, NiAl is again considered a generic high-temperature structural material either as a monolithic or as a matrix material in composites. Perhaps more importantly, NiAl is also being developed for very specific applications (Figure 2). Industrial interest in NiAl monolithics is being lead by General Electric (GE), whose interest is in high-temperature turbine blade materials [1]. NiAl composites are being considered by NASA in such programs as HITEMP (High Temperature Engine Materials Program) and EPM (Enabling Propulsion Materials) which is an independently funded component of the HSCT (High Speed Civil Transport) program. In these programs, NiAl composites are competing with MoSi<sub>2</sub> and superalloy-based composites as candidate materials for the HSCT exhaust nozzle. In addition, NiAl research is being performed at almost every major university in this country as well as many universities abroad.

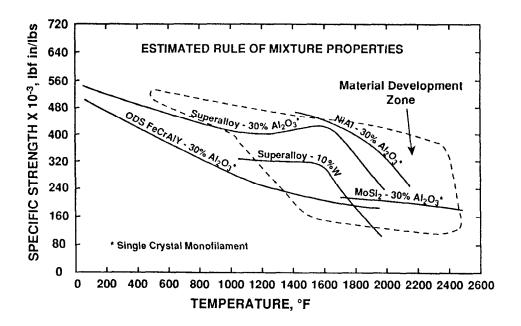


Figure 2. Estimated values of specific strength for candidate metal and intermetallic matrix composite systems demonstrating feasibility of reaching HSCT goals.

# **Processing**

NiAl is routinely fabricated into either single crystal, polycrystalline, or composite form. While processing of NiAl is relatively easy, processing in such a way to yield reproducible properties is more difficult. The mechanical properties of NiAl are extremely sensitive to stoichiometry, interstitial contaminants, lattice defects, and solute concentrations [9]. Although the mechanical properties of NiAl have been studied for several decades, a disparity exists in the reported properties of nominally identical materials. Many of these inconsistencies can be traced to uncontrolled processing variables or chemical control which altered the properties of the alloy. Since mechanical property variation due to the presence of impurities, or slight deviations in stoichiometry, can mask the effects of the intended variables, erroneous conclusions have occasionally been drawn concerning the effect of metallurgical variables on mechanical properties. As investigators have become more aware of these problems, improvements in processing have arisen.

Polycrystalline NiAl is typically produced by extrusion of powder or cast precursor material. Powder processes generally result in higher impurity levels and can result in higher flow stresses than cast and extruded material. When grain size is controlled, powder extrusion is a very reproducible fabrication technique. Extrusion of small cast ingots greatly reduces contamination compared to powder extrusions and has resulted in reproducible tensile ductilities for NiAl studied by a number of different investigators.

Development of NiAl single crystals is being lead by GE Aircraft Engines in an attempt to achieve the high-temperature creep strengths necessary to compete with current superalloys. Using a modified Bridgeman process, single crystals measuring 10.2 cm x 2.5 cm x 3.8 cm have been successfully grown. Using a combination of electro-discharge machining, electro-chemical machining, and grinding processes, GE is able to fabricate small, single crystal, high-pressure turbine blades [1].

Fabrication techniques for producing continuous fiber-reinforced NiAl is under investigation by several research groups. Included in possible processing routes are powder cloth, foil/fiber, and thermal spraying. The choice of reinforcing fiber is limited by the requirements of high temperature strength as well as compatibility with the matrix. The compatibility requirement refers to both mechanical compatibility (similar coefficients of thermal expansion (CTE)) and to chemical compatibility with the matrix. Additionally, the fiber must be readily available in quantities sufficient for developmental studies. At present, single crystal Al<sub>2</sub>O<sub>3</sub> fibers are the best choice for meeting these requirements. Composite properties are highly dependant on the nature of the interfacial bond between the NiAl matrix and the reinforcing fibers. In a recent study [10] it was reported that fiber/matrix bonding, which plays a major role in controlling the mechanical properties of the composite, can be altered through changes in processing.

### **Properties of NiAl**

# Tensile Behavior

A comparison of the yield stress of NiAl, Ni<sub>3</sub>Al, and several superalloys is shown in Figure 3. Although the magnitude of the yield stress is sensitive to many metallurgical properties, all studies agree that, unlike Ni<sub>3</sub>Al, the yield stress of NiAl decreases or remains constant with increasing temperature. As shown in Figure 3, the yield stress of polycrystalline NiAl is significantly lower than both commercial superalloys and Ni<sub>3</sub>Al. At temperatures below about 600 K, [001] single crystal NiAl is stronger than both polycrystalline and single crystal superalloys, although NiAl suffers from low toughness at these temperatures. Above about 600 K, the ductility and toughness of NiAl dramatically increases, but as shown in Figure 3, only at the expense of strength. A significant improvement in flow strength is possible through alloying, with the most potent strengthening by precipitation of Ni<sub>2</sub>AlX (where X=Hf,Nb,Ti,Zr,V,Ta) phases, referred to as Heusler or  $\beta$ ' phases. As shown in Figure 3,  $\beta$ ' containing alloys have flow stresses approaching that of a common turbine blade material such as Rene'80. Unfortunately, strength improvements to-date have come at the expense of ductility and no acceptable balance of properties has been achieved.

Tensile ductility and fracture toughness are crucial issues influencing the potential of NiAl. It took over 20 years to repeat the observation of Rozner and Wasilewski of measurable room temperature tensile ductilities [11,12]. Now with current advances

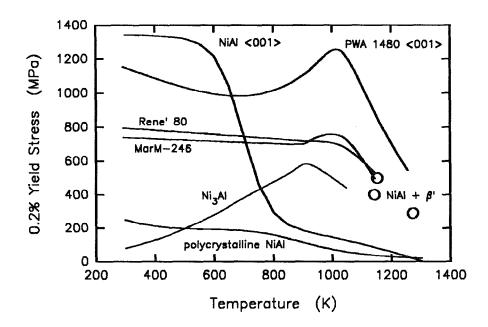


Figure 3. 0.2% offset yield stress as a function of temperature for NiAl, Ni<sub>3</sub>Al, and several commercial superalloys.

in processing and chemistry control, limited (1-3%) room temperature ductility in NiAl is routinely achieved. Unfortunately, the limited ductilities reported do not represent a true change from brittle to ductile behavior. Because NiAl deforms predominately by <001> dislocations [9,13] only three independent slip systems are available for deformation [14]. This is less than the five necessary for generalized plastic deformation to occur. Consequently, at low temperatures, binary stoichiometric alloys fail in a brittle intergranular manner with little or no tensile ductility. The highest tensile ductilities are generally obtained with low yield stress, high purity, stoichiometric NiAl. Unless future alloying is successful in altering the slip vector such that strain incompatibilities do not occur, there is little hope of achieving significantly higher tensile strains at low temperature. However, with increasing temperature the yield stress of NiAl decreases and tensile ductility and fracture toughness dramatically increases above 550-700 K. The change to ductile behavior is thought to be the result of the onset of thermally activated deformation processes thereby allowing accommodation of strains at the grain boundaries.

The use of W, Mo, and  $Al_2O_3$  fibers in NiAl has been successful in increasing the flow stress of NiAl [10]. A requirement for the increase in flow stress is that effective load transfer occurs from the matrix to the fibers. Strong interfacial bonds result in increased high-temperature strength but also degrade low-temperature toughness. Conversely, a weak interfacial bond improves ambient temperature toughness but provides no strengthening. Another consequence of using  $Al_2O_3$  fibers is that due to the CTE mismatch between the matrix and fiber, residual tensile stresses are generated in the matrix and can result in premature matrix failure. Although NiAl composites have a great potential, it is the least mature approach for improving the properties of NiAl.

# Creep Resistance

High temperature creep deformation in NiAl is satisfactorily described by type M, or dislocation climb controlled creep. Stoichiometric variations are relatively unimportant, especially between 45 and 52 at.% Al. Diffusional creep mechanisms become important at low stresses and above 0.7T<sub>m</sub>. Various strategies have been attempted to improve creep properties and include solid solution and precipitate strengthening, eutectic strengthening, use of single crystals, and composite strengthening. General Electric has been successful in developing  $\beta$ ' alloys such that they approach the stress-rupture resistance of Rene' 80 [1]. Although single crystals are being studied for their high-temperature properties, creep studies of binary NiAl have shown that the creep rate of [001] single crystal NiAl is identical to that of the polycrystalline material. This implies that creep is controlled by lattice properties and that grain boundaries play a secondary role in controlling creep resistance. Numerous studies have reported improved high-temperature creep resistance with Ti and Hf-based Heusler phases. Another approach is via a reaction milling processes termed Cryomilling. In this process, NiAl powders are ball milled in a liquid nitrogen bath resulting in a NiAl composite containing about 10 vol.% of AlN particles. Compression creep testing at 1300 K indicated that the density compensated strength of the polycrystalline NiAl/AlN was about equal to the Ni-base single crystal alloy NASAIR 100. Unfortunately, improvements in strength by any of the above mentioned techniques invariably decreases ductility and toughness by raising the yield stress above the fracture stress.

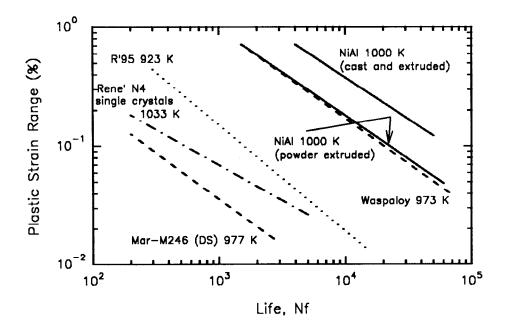


Figure 4. Comparison of high-temperature fatigue lives of NiAl to commercial superalloys.

# Fatigue Behavior

Research on the fatigue behavior of NiAl remains in its infancy. Only three studies concerning NiAl fatigue [15,16,17] and a equally small amount on other B2 compounds are available. Consistent with other properties thus far discussed, the fatigue behavior of NiAl is sensitive to processing technique. The fatigue life of hot isostatic

pressed (HIP) NiAl prealloyed powders at 1000 K was approximately an order of magnitude less than cast and extruded material. Interestingly, 1033 K fatigue lives of Ni-49.9Al-0.1Mo [001] oriented single crystals [15] were nearly identical to that reported for polycrystalline stoichiometric NiAl [16] and the lives followed the expected Coffin-Manson strain life behavior. Figure 4 compares the 1000 K lives of NiAl to polycrystalline and single crystal superalloys. The lives of NiAl at high strain ranges at 1000 K exceeds those of superalloys due to NiAl's high ductility. However, at lower strain ranges or on a stress basis, NiAl does not compare favorably due to its low yield stress. Compared with other B2 compounds for which room temperature data has been reported, however, NiAl has superior fatigue resistance [16]. NiAl composite fatigue has been reported in only one study [10]. Due to the low ductility of the matrix, there was some concern that the matrix/fiber interface might act as initiation sites for cracks. To explore this possibility, fatigue tests at several stress levels were performed on NiAl reinforced with continuous fiber Al<sub>2</sub>O<sub>3</sub> at room temperature. While the presence of fibers did limit the initial loading strain to that less than the fiber failure strains, the presence of fibers did not degrade the fatigue resistance at a given stress level.

#### Oxidation Resistance

The excellent oxidation resistance of NiAl has been known for many years. This behavior stems from the easy formation and slow growth rate of a protective  $Al_2O_3$  scale. It is well known that rare-earth or oxygen-active dopants have a beneficial effect on the oxidation resistance of NiAl and superalloys. The alloying additions most intensively studied are Y, Hf, and Zr. The beneficial effects under cyclic oxidation conditions are most pronounced when the alloying addition is present at about the 0.1 at.% level.

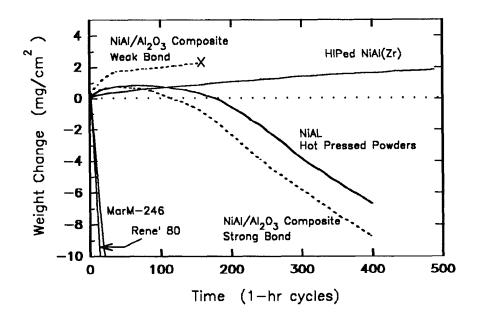


Figure 5. 1200 K cyclic oxidation data showing superior performance of NiAl and NiAl/Al<sub>2</sub>O<sub>3</sub> composites compared to commercial superalloys Rene' 80 and MarM-246.

Cyclic oxidation testing is significantly more severe than isothermal oxidation and more closely approximates actual service conditions. In Figure 5 weight gain vs. cycles for

several superalloys, NiAl, and NiAl/Al<sub>2</sub>O<sub>3</sub> composites is presented. As seen in this figure, the cyclic oxidation resistance of NiAl is vastly superior to superalloys at high temperatures. Although NiAl forms a protective oxide scale, during the cooling portion of the cycle, the differences in the thermal expansion coefficients between metal and oxide results in high stresses at the metal/oxide interface which can lead to spalling. Various alloying elements can be added to NiAl to improve the oxide adherence and thus improve cyclic oxidation resistance. In NiAl/Al<sub>2</sub>O<sub>3</sub> composites, the presence of a weak interfacial bond is detrimental to the cyclic oxidation resistance. In this case protective oxide scales that formed in the interface were damaged during cool-down due to the thermal clamping of the matrix. On each subsequent heating cycle fresh matrix was exposed to the atmosphere and thus provided a regenerating source for oxidation.

#### **Conclusions**

The development of NiAl has progressed significantly since the initial exploratory research on this intermetallic in the 1950's. Great strides have been made recently with the greatest progress occurring in the area of increased creep strength and improved ductility of single crystals. In addition, a better understanding of the temperature dependent flow and fracture behavior and oxidation resistance of NiAl has also occurred in the last several years. However, low-temperature properties (ductility and toughness) remain unsolved technical challenges.

Fortunately, interest and research on NiAl has been growing at an exponential rate over the last several years and will continue to do so based on current plans of many research labs and universities. Consequently, the relative success in overcoming the remaining obstacles will probably decide the fate of NiAl for the immediate future. If present limitations can be overcome either by true material improvements or by redesign to accommodate NiAl's deficiencies, then the future of NiAl appears very promising.

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