NASA Technical Memorandum 86976

NASA TM- 86976

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NF00126

ALLOYS BASED ON NiAl FOR HIGH TEMPERATURE APPLICATIONS

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ABSTRACT

This paper presents some of the results obtained in an on-going study of NiAl alloys for potential high temperature applications. Alloys were prepared by powder metallurgy techniques. Flow stress values at slow strain rates and high temperatures were measured. Some promising ternary alloying additions (Hf, Ta and Nb) have been identified. The mechanism of strengthening in alloys containing these additions appears to be a form of particle dislocation interaction. Interesting effects of grain size and stoichiometry in binary alloys are also presented.

INTRODUCTION

NiAl is one of the interesting intermetallic compounds for potential use as a high-temperature structural material. The ordered structure is believed to provide high-temperature strength and the aluminum content provides the oxidation resistance. This paper presents some of the results of a broader study on the potential for NiAl and FeAl based alloys for high-temperature applications.

Stoichiometric NiAl has an ordered L2o (B2) crystal structure up to its congruent melting point of 1911°K (1638°C). Figure 1 shows the binary Al-Ni phase diagram [1]. The ordered B2 structure is maintained over the composition range from 45.0 to 58.5 at % at room temperature. This provides the potential for improving high temperature strength by solid solution alloying. However, very limited information on the alloying behavior of NiAl is available. A previous publication by these authors [2] contains some information on the potential for solid solubility of several ternary additions. Ti, Mn, Cr, Fe and Cu are found to have considerable solubilities in binary NiAl, whereas Nb, Hf, Ta, Mo, W and Zr are found to have very limited solubilities.

Deviations from stoichiometry on either side are accomodated by defect structures [3,4]. The defects on the nickel-rich side are believed to be antistructure defects (with excess nickel atoms occupying aluminum sites) and those on the aluminum-rich side are believed to be vacancies (with the nickel deficient sites remaining vacant). There is, however, some indication that even the stoichiometric alloy may contain a combination of both these types of defects and that the aluminum rich structure may contain a complex triple defect structure. Hence, within the single phase field of the ordered structure, mechanical properties are sensitive to deviations from stoichiometry [5]. At low temperatures, deviations from stoichiometry result in defect hardening. On the other hand, at high temperatures defects are believed to increase the diffusion processes and hence weaken the alloys.

Previous investigations of B2 aluminides have shown some peculiar grain size effects [6,7,8], in which fine grained material is observed to be stronger than coarse grained material even at temperatures
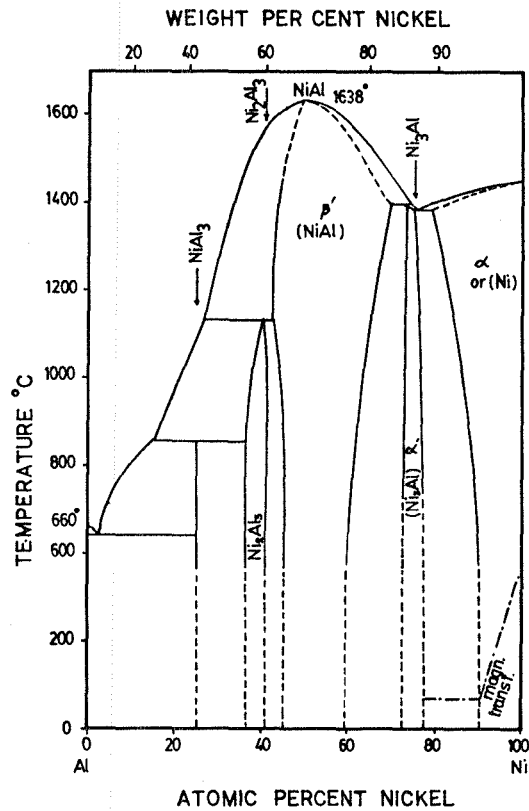
WEIGHT PER CENT NICKEL

Fig. 1. Binary Al-Ni Phase Diagram [1]

of the order of 0.7 Tm. In particular, this effect has been noted for extruded FeAl alloys [6]. The reasons for this behavior are unknown and must be related to the effects of ordering on grain boundary structure and high temperature deformation mechanisms.

This paper discusses some of the observations of potential strengthening mechanisms in NiAl based alloys. These observations form part of an overall program at NASA Lewis Research Center to develop NiAl alloys for high temperature applications. In particular, the effects of ternary additions, grain size and deviations from stoichiometry will be discussed.

MATERIALS AND PROCEDURE

Powder metallurgy processing was found to be a convenient method for processing these alloys.

Ternary alloys were prepared from blends of prealloyed NiAl and elemental ternary additions. Consolidation was achieved by either hot extrusion or hot isostatic pressing of canned powder. Alloys were heat treated after consolidation in order to ensure maximum homogeneity. Grain sizes of these ternary alloys were typically in the range of 25 to 50 μm. Specific details of the processing with ternary additions are presented elsewhere [2]. Compositions of alloys reported in the previous publications are presented in Table I. New alloys containing 2 at% Ti, Ta and Nb were later prepared and are discussed in this paper. Compositions of these alloys are presented in Table II.

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TABLE I. Gross Chemical Composition of Alloys From Reference 2
(Atomic %)

Specimen	Ni	Al	Ternary	Fe[1]
HIPPED ALLOYS				
NiAl	55.28	44.60	--	0.001
NiAl-Ti	49.89	47.18	2.16 Ti	0.330
NiAl-Ta	51.12	46.39	1.17 Ta	1.310
NiAl-Nb	49.12	46.28	1.00 Nb	3.630
NiAl-Mn	50.03	47.22	2.52 Mn	0.002
NiAl-Mo	49.70	47.18	2.92 Mo	0.002
HOT EXTRUDED ALLOYS				
NiAl-Fe	45.19	49.54	5.27 Fe	
NiAl-Mo	41.84	53.73	4.43 Mo	
NiAl-W	41.87	53.63	4.50 W	
NiAl-Re	41.98	53.59	4.42 Re	
NiAl-Mn[2]	53.00	42.00	5.00 Mn	
NiAl-Hf	45.32	53.63	1.05 Hf	

1 Impurity
2 Intended Composition

TABLE II. Intended Gross Chemical Compositions of Second Alloy Series
(Atomic %)

Specimen	Ni	Al	Ternary
NTi2	50.00	48.00	2.00 Ti
NNb2	50.00	48.00	2.00 Nb
NTa2	50.00	48.00	2.00 Ta

Fine grain sizes (< than 10 μm) were obtained in the binary alloys by reextruding at a lower temperature (1073°K) after initial extrusion at a higher temperature (1350°K). This was carried out for binary alloys having compositions of 48 at% Ni, 50 at% Ni and 52 at% Ni. Coarse grains were obtained by annealing extruded specimens in argon for varying lengths of time up to 144 hours at 1625°K and 1723°K. Deviations from stoichiometry were obtained by using different compositions of prealloyed powders.

Microstructures of alloys were observed using optical and electron microscopy.

High temperature testing was accomplished using constant strain rate compression testing of small cylindrical specimens (approximately 5 mm by 10 mm) on an Instron machine in air at temperatures ranging from 1100°K to 1400°K. Specimens were normally tested to about 10% reduction in heights and flow stress was recorded. Load - deformation information was converted to true stress - true strain information neglecting the slight barreling of the specimens. Flow stress remained

fairly constant during the plastic deformation. Values of the maximum flow stress and corresponding strain rate were used to compare the high temperature behavior of various specimens.

RESULTS AND DISCUSSION

The results will be discussed in the light of potential strengthening mechanisms resulting from: (a) alloying additions, (b) grain boundaries and (c) deviations from stoichiometry.

(A) Alloying Additions

The alloying additions used could be classified on the basis of microstructural evaluation [2]. Extent of homogeneity in the specimens was evaluated by EDAX analyses. The alloys containing Ti, Mn and Fe were essentially shown to be homogeneous single phase alloys with no evidence of undissolved ternary powders. Alloys containing Ta, Nb, Hf and Re showed a significant amount of undissolved ternary powder in spite of a certain amount of dissolution and alloys containing Mo and W showed a negligible amount of dissolution.

The alloying additions which have poor solubility in the matrix, in general, appear to provide more strengthening at high temperatures than those with large solubilities. This trend was clearly indicated in the results presented previously and reproduced in Figure 2 [2]. Compositions of the alloys shown in this figure are tabulated in Table I. The alloys containing Ti, Mn and Fe did not show any significant improvements over binary alloys in compressive creep tests conducted in air at 1300°K. These are single phase alloys and the small amount of strengthening observed is probably due to solid solution effects. The alloys containing Ta, Nb and Hf exhibited very substantial strengthening compared to the binary alloys. These alloying additions only dissolved to a very small extent in the matrix NiAl, as indicated by the presence of undissolved ternary additions even after very long homogenization treatments.

This same trend is observed in the second series of alloys (NTi2, NNb2, NTa2) tested in hot compression at 1300°K. Figure 3 compares these alloys with binary data obtained from [2]. Compositions of this series of alloys are given in Table II. The alloys containing Ta and Nb are much stronger than the binary alloy and the alloy containing Ti.

The strength of the stronger alloys (Ta and Nb containing alloys) appears to be more temperature dependent than that of the binary alloys. This is illustrated in Figure 4 which shows that although the Ta alloy is significantly stronger (about twice as strong at constant strain rate) than the binary at 1400°K, its superiority over the binary alloy is much more at 1200°K (about ten times as strong at constant strain rate). This difference in temperature dependence suggests that whatever the actual mechanism of high temperature deformation in these alloys, the activation energy for the mechanism increases with the alloying addition.
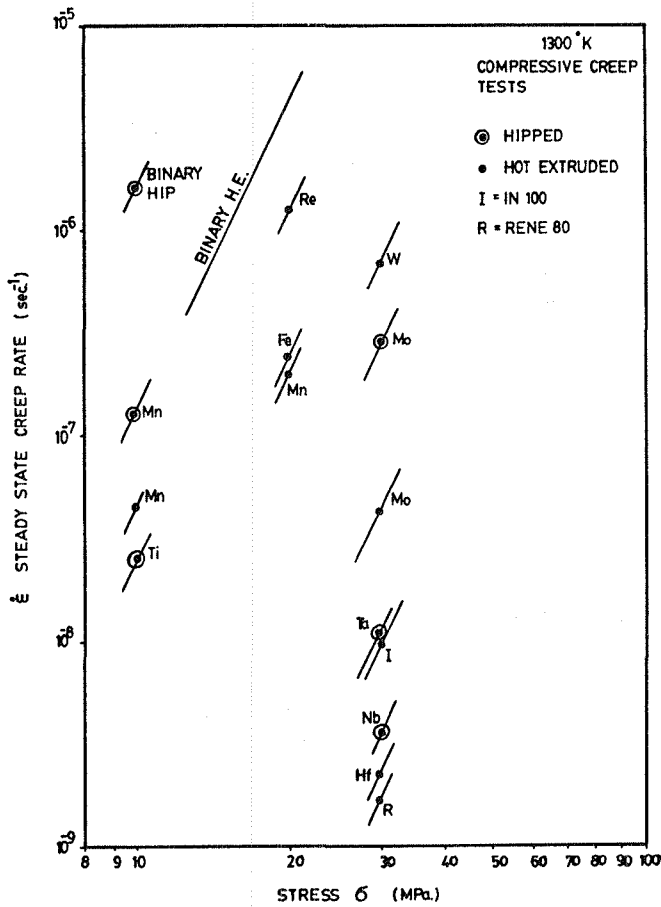
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Fig. 2. Comparison of Compressive Creep Behavior of Several Ternary NiAl Alloys and Conventional Superalloys at 1300°K [2]. The ternary alloying addition is indicated at the data point.
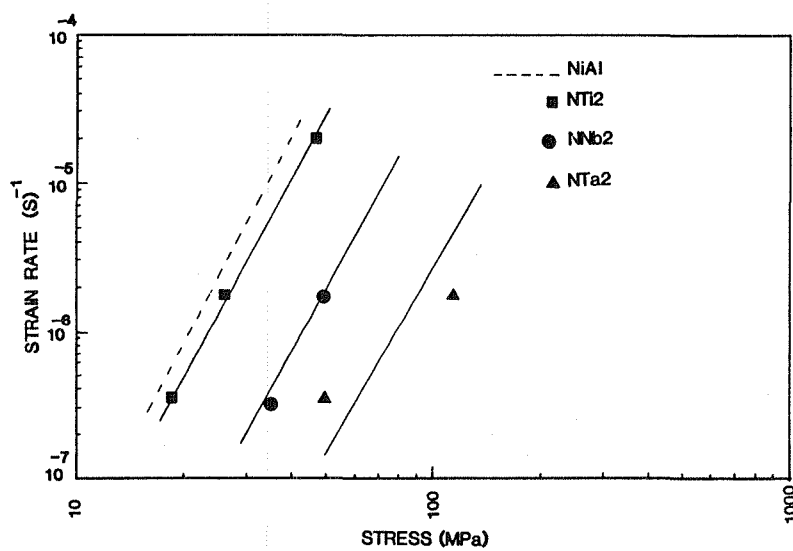

Fig. 3. Comparison of 1300°K Hot Compressive Flow Stress Behavior for additions of Ti, Ta and Nb at 2 at% level.
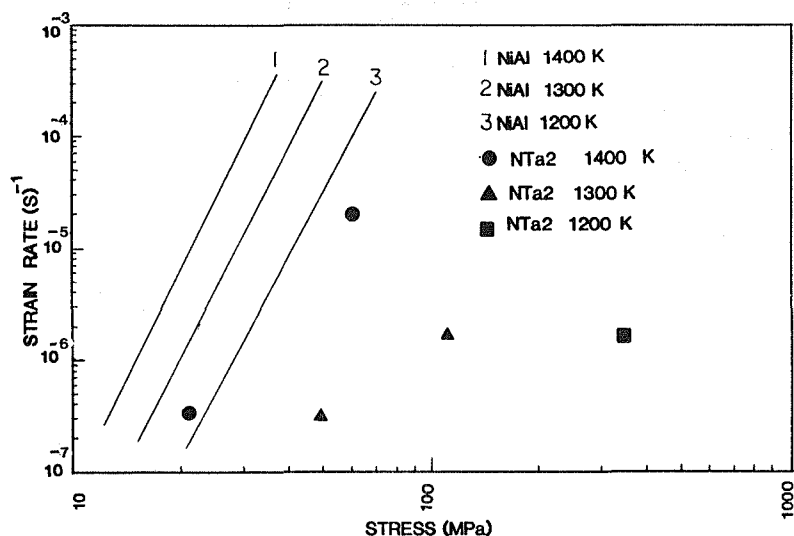
Fig. 4. Comparison of Hot Compresssive Flow Stress Behavior of Binary Stoichiometric NiAl [8] with Ni(50 at%)-Al(48 at%)-Ta(2 at%) at three temperatures.

The mechanism of strengthening for the alloys containing Ta and Nb appears to be some form of interaction between dislocations and fine precipitates which are richer in the alloying addition. This is indicated quite strongly by the TEM microstructure of the deformed Ta-containing alloy illustrated in Figure 5. Typical bowing of dislo- cations between sub-micron sized particles is obvious. These particles are found to be rich in Ta and are probably a ternary intermetallic of Ni, Ta and Al. These fine precipitates appear to have formed during the slow cooling of the specimen after homogenization treatment, since homogenization in these alloys does result in a certain amount of dissolution of the ternary addition and since the solubility of this ternary element is expected to decrease at lower temperatures. A more detailed TEM investigation is needed in order to clearly understand the nature, the mechanism of formation and role of these precipitates.

(B) Grain Size and Stoichiometry

A wide range of grain sizes have been obtained using the technique of a second extrusion at a lower temperature. Typical grain sizes obtained by reextrusion followed by annealing are illustrated in Figure 6. (Note the factor of 20 difference in magnifications). Grain sizes obtained for the three alloys studied under different annealing conditions are presented in Table III.

An interesting aspect of the grain growth of these alloys appears to be that it is slow in the beginning but becomes much more rapid after some time resulting in a deviation from the standard power law grain growth kinetics. Figure 7 for grain growth at 1723°K illustrates this type of behavior. This appears to be indicative of some form of abnormal grain growth and, in fact, optical microstructures do reveal a bimodal distribution of grains in the coarse grained specimens.

6
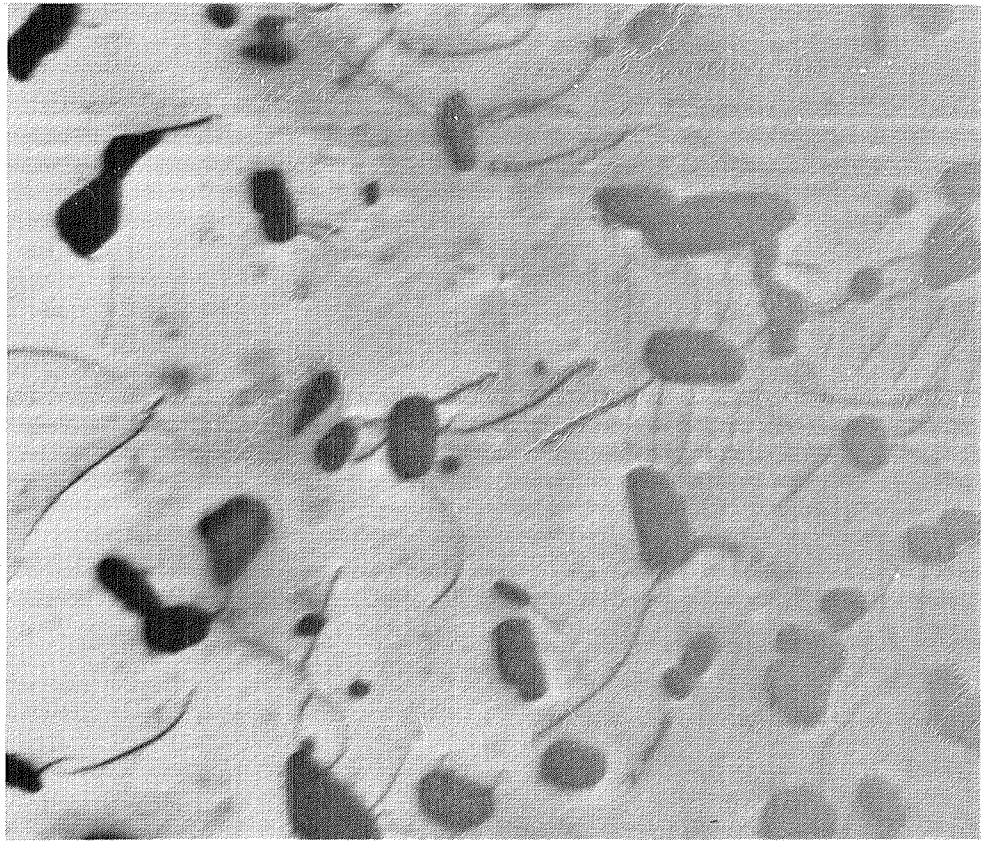
1 μm

Fig. 5. Transmission Electron Micrograph of NiAl-2-at% Ta
specimen deformed in Hot Compression at 1300°K to
about 7% strain illustrating dislocation pinning at
precipitation as a possible strengthening mechanism.

TABLE III. Grain Size Data for Binary NiAl
(Micrometers)

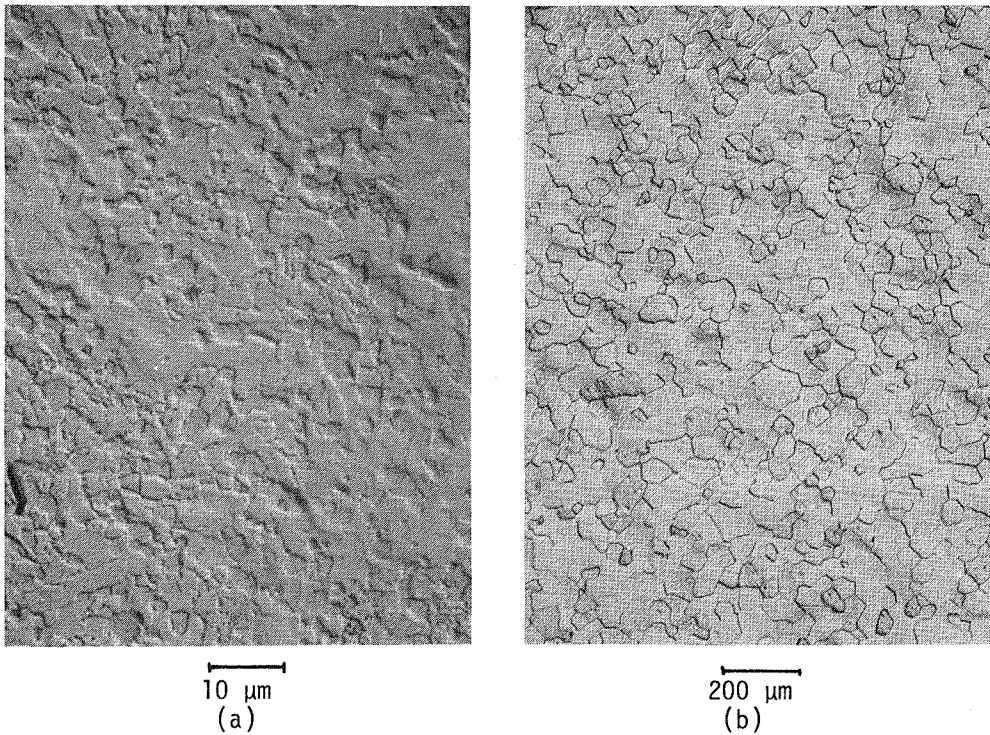| Composition	Annealing Temperature	Time (hrs)				
		0	0.5	3.0	10.0	144.0
48 at% Ni	1350°C	3	12	--	13	--
	1450°C	3	13	15	15	45
50 at% Ni	1350°C	2	15	--	19	28
	1450°C	2	17	20	20	48
52 at% Ni	1350°C	5	11	--	12	40
	1450°C	5	16	18	20	92

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10 μm
(a)

200 μm
(b)

Fig. 6. Comparison of Optical Microstructure of the range of grain sizes
of Binary Alloys used in this study. (a) As-Extruded Stoichio-
metric NiAl (1000X); (b) Stoichiometric NiAl annealed at 1723°K
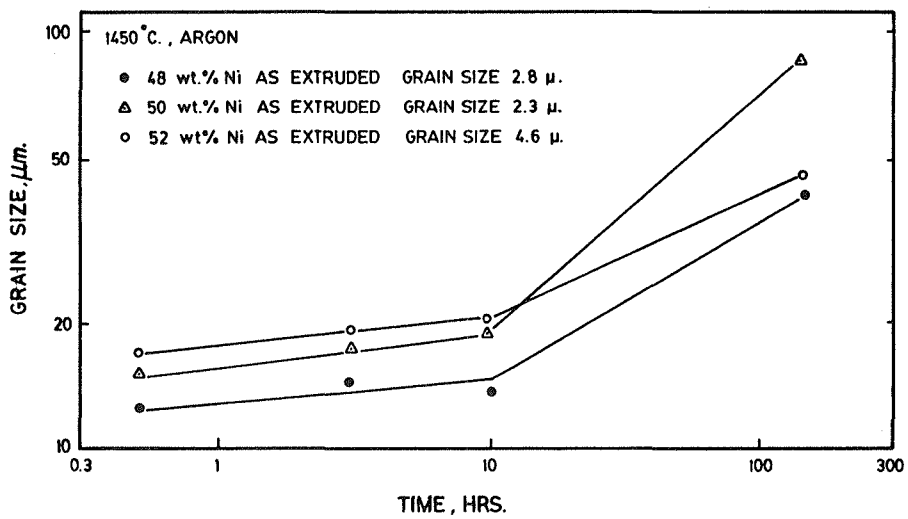in argon for 144 hrs. (50X).

Fig. 7. Grain Growth Kinetics at 1723°K (1450°C) in
Argon for Binary NiAl Alloys Prepared for
this study.

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The hot compressive flow behavior of these alloys under slow strain rates exhibits some very unusual effects of grain size. Figure 8 compares the flow curves of the three compositions of binary NiAl at 1300°K and 3 x 10^{-6} sec^{-1}. The fine grained (2μm) stoichiometric alloy (50 Ni) is twice as strong as the coarse grained (48 μm) stoichiometric alloy. This is unusual since at high temperatures and slow strain rates metals normally do not exhibit grain boundary strengthening. The explanation for this behavior is not obvious although it seems to agree with some other results of this nature in ordered alloys [6,7,8]. Figure 9 is a typical TEM micrograph of the stoichiometric alloy and shows the presence of subgrain boundaries which are likely to play a key role in the explanation of the observed effects of grain size.

Strengthening due to grain boundaries is, however, observed to a very significant extent only in the stoichiometric alloy. The other alloys containing 48 Ni and 52 Ni do not exhibit the same magnitude of the effect, although the fine grained material is still slightly stronger. Once again, the explanation for this is not clear, although it must be related in some way to the effect of ordering on grain boundary structure and deformation mechanisms. A complication may be introduced by the possibility of grain boundary contamination during the annealing treatment in argon in view of the susceptibility of these alloys to grain boundary pest phenomenon [9].
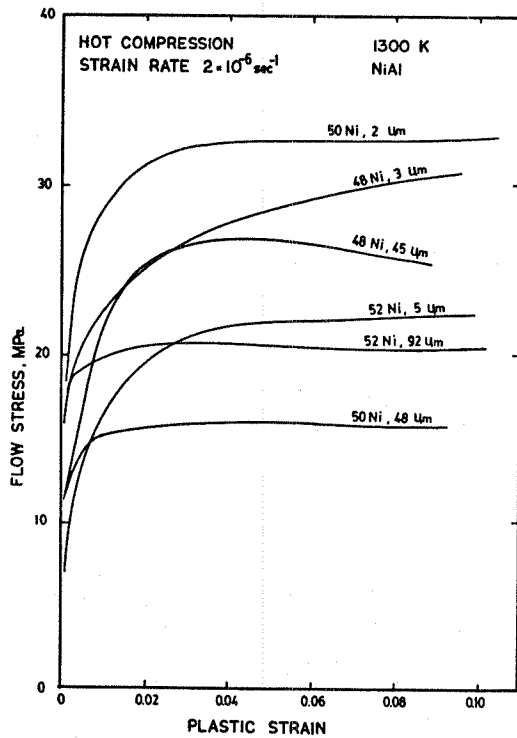

Fig. 8. Effect of Grain Size and
Stoichiometry on Hot
Compressive Flow Curves
of Binary NiAl at 1300°K.

Fig. 9. Transmission Electron
Micrograph of As-Extruded
Binary Stoichiometric
NiAl specimen illustrating
the presence of Sub-grain
Boundaries.

Some limited results at different temperatures presented in Figure 10 further illustrate the complexity of this behavior. The stoichiometric alloy which exhibits a large grain boundary strengthening effect at1300°K does not exhibit such a dramatic effect of grain boundary strengthening at the lower temperature of 1100°K, although grain boundary strengthening should normally be expected to be more important at lower temperatures. The non-stoichiometric 52 Ni alloy, however, appears to show the generally expected trend of grain boundary weakening at the higher temperature of 1400°K.

These results illustrate the complex interactions between high temperature deformation, defect structures, ordering and grain size which need to be unraveled by carefully controlled studies.
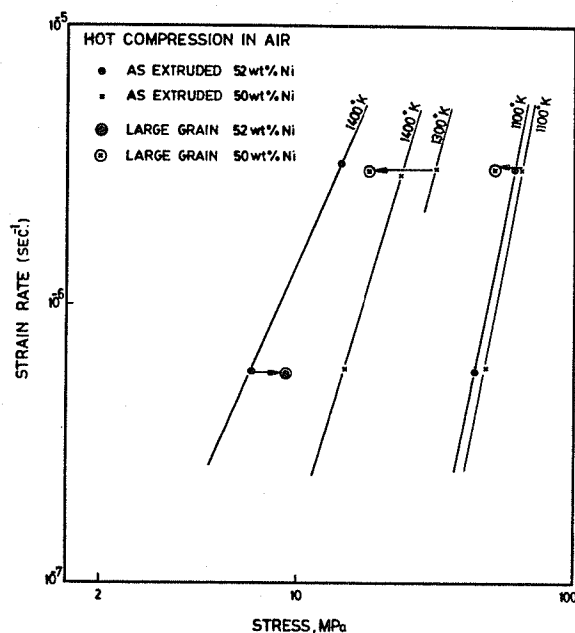

Fig. 10. Hot Compressive Flow Stress Behavior of Binary
NiAl Alloys illustrating some of the interesting
effects of temperature, grain size and stoichiometry.

CONCLUSIONS

The results presented in this paper show that a potentially useful strengthening mechanism for high temperature applications of NiAl alloys is by second phase strengthening. In particular, small additions of Nb, Ta and Hf are found to exhibit this kind of strengthening to a significant extent. However, the mechanism of strengthening needs to be more clearly understood and optimized.

Some very interesting effects of grain size and stoichiometry have been observed, which need to be investigated more carefully before any explanations can be offered. In particular, the presence of grain boundary strengthening in the stoichiometric alloy even at fairly high temperatures is very unusual.

ACKNOWLEDGEMENT

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1. Report No. NASA TM-86976	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle Alloys Based on NiAl for High Temperature Applications		5. Report Date
		6. Performing Organization Code 505-33-1A
7. Author(s) K. Vedula, V. Pathare, I. Aslanidis and R.H. Titran		8. Performing Organization Report No. E-2513
		10. Work Unit No.
9. Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135		11. Contract or Grant No.
		13. Type of Report and Period Covered Technical Memorandum
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		
		14. Sponsoring Agency Code

16. Abstract

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17. Key Words (Suggested by Author(s)) Aluminides Creep Intermetallic	18. Distribution Statement Unclassified - unlimited STAR Category 26		
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of pages	22. Price*

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