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### STRAIN AGING BEHAVIOR IN NiAl MICROALLOYED WITH INTERSTITIAL AND SUBSTITUTIONAL SOLUTES

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#### ABSTRACT

Dynamic strain aging has been investigated in polycrystalline NiAl alloys containing combined additions of interstitial and substitutional impurities. The results indicate that strain aging can be enhanced in polycrystalline alloys containing concentrations of silicon or iron in excess of 0.15 at.% in addition to conventional levels of carbon. This co-doping leads to very dramatic strain aging events, comparable to those typically observed in single crystals. This effect will be discussed with respect to conventional theories of strain aging.

#### INTRODUCTION

Recent research efforts have established that the intermetallic compound NiAl is subject to the phenomenon of strain aging due to elastic interactions between dislocations and interstitial solutes, namely carbon [1-16]. Though this phenomenon can be minimized through the selection of the proper gettering elements [9,12,15], prior investigators have suggested that it can also be enhanced via small additions of various substitutional species [11]. In NiAl single crystals, strain aging manifests itself dramatically in the form of yield stress plateaus, upper yield points, flow stress transients upon an upward change in strain rate and the Portevin-LeChatelier effect. In polycrystals, however, such manifestations are typically more subtle. In this study, strain aging has been investigated in polycrystalline NiAl alloys containing combined additions of carbon and some common substitutional impurities. The emphasis of this investigation is to identify the role of substitutional impurities on the strain aging behavior of polycrystalline NiAl alloys.

#### EXPERIMENTAL PROCEDURE

Polycrystalline NiAl alloys in the form of vacuum induction melted (VIM) ingots were prepared from elemental constituents. The resulting VIM ingots were placed in mild steel extrusion cans and extruded at 1200 K at a reduction ratio of 16:1. Post extrusion chemical analyses were conducted using the techniques deemed the most accurate for the particular elements. The results of these analyses are listed in Table 1. Cylindrical compression specimens and round button-head tensile specimens were EDM wire cut or centerless ground from the extruded rods so that the gage lengths were parallel to the extrusion direction. Sample dimensions were 3.1 mm for the tensile gage diameters and 30.0 mm for the tensile gage lengths and 5.0 mm for the compression sample diameters and 10.0 mm for the lengths. All tensile specimens were electropolished prior to testing in a 10% perchloric acid-90% methanol solution that was cooled to 208 K. During some of the compression tests, strain was measured using a clip on strain gage extensometer.

All tensile and compression tests were performed using a screw driven load frame at constant crosshead velocities corresponding to an initial strain rate of  $1.4 \times 10^{-4} \text{ s}^{-1}$ . Testing was accomplished as follows: the temperature dependence of flow stress was determined by testing all as-extruded alloys in air between 300 and 1100 K by heating the samples in a clamshell type resistance furnace where temperature gradients were controlled to  $\pm 2 \text{ K}$ . During this phase of testing, the strain rate sensitivity (SRS) was also determined by increasing the strain rate by a factor of ten from the base strain rate at fixed plastic strain intervals. The quantity extracted from these experiments was the SRS,  $s = \Delta\sigma/\Delta \ln \dot{\epsilon}$ .

Table 1: Chemical Analyses of NiAl Alloys

Material	at. %				at. ppm			
	Ni	Al	Si	Fe	C	O	N	S
CPNiAl-1	50.10	49.69	0.15	0.00	147	70	<9	<7
CPNiAl-2	50.11	49.84	0.02	0.00	186	94	<9	<8
CPNiAl-3	50.22	49.69	0.02	0.00	431	154	<15	<13
CPNiAl-4	49.51	50.45	0.00	0.00	195	146	<15	<7
NiAl-Fe	50.09	49.28	0.01	0.30	572	148	<9	<13
NiAl-Si	49.49	50.18	0.30	0.00	192	149	<15	<7

Al, Fe, & Ni Analysis performed using analytical wet chemistry/titration techniques, relative accuracy  $\pm 1\%$   
 Si Analysis performed on an Ultraviolet/Visible Spectrophotometer, Shimadzu, Model UV-160, relative accuracy  $\pm 10\%$   
 C & S Analysis performed on a Simultaneous Carbon/Sulfur Determinator, LECO Corp., Model CS-244, relative accuracy  $\pm 10\%$   
 N & O Analysis performed on a Simultaneous Nitrogen/Oxygen Determinator, LECO Corp., Model TC-136 or Model TC-436, relative accuracy  $\pm 10\%$

## RESULTS

### Chemistry and Microstructures

Within experimental accuracy ( $\pm 0.2$  at.% for Ni and Al), the Ni and Al contents of both alloys are not significantly different from each other. The major differences between the materials are the residual C, O, N and S contents and the presence of Si and Fe as alloying additions. The microstructures of all the NiAl alloys were similar as observed by optical microscopy and consisted of fully dense recrystallized grains. Nominal linear intercept grain sizes were  $20 \pm 2 \mu\text{m}$ .

### Mechanical Properties

The temperature dependence of the SRS is presented in Figure 1. In agreement with prior observations, distinct SRS minima were observed in the temperature range 600 to 800 K with SRS becoming negative for NiAl-Si. Coincident with this region of reduced SRS were flow stress transients upon an upward change in strain rate for NiAl-Fe and serrated yielding for NiAl-Si and CPNiAl-1 (Figure 2a). The flow stress serrations observed in NiAl-Si and CPNiAl-1 were preceded by a small critical onset strain,  $\epsilon_c$ . In a recent investigation, serrated yielding was observed in single crystal alloys containing the same concentrations of C and Si as NiAl-Si and CPNiAl-1 [9,11,12,17]. No such flow stress transients or flow stress serrations were observed in CPNiAl-3 or CPNiAl-4 (Figure 2b). By plotting the temperature and strain-rate dependence of  $\epsilon_c$ , it is possible to derive several kinetic parameters related to the mechanism of strain aging. Following McCormick's formulation [18],  $\epsilon_c$  is related to T and  $\dot{\epsilon}$  by the relation:

$$\epsilon_c^{m+\beta} = K\dot{\epsilon} \exp(Q/RT) \quad (1)$$

where Q is the activation energy for the onset of serrated flow, R is the gas constant, K is a constant, and the exponent (m+ $\beta$ ) is related to the concentration of vacancies and the mobile dislocation density. The exponent (m+ $\beta$ ), determined from the slope of a plot of  $\ln \dot{\epsilon}$  versus  $\ln \epsilon_c$  at constant temperature for NiAl-Si was  $1.76 \pm 0.2$  (Figure 3a). The activation energy is then determined from a plot of  $\ln \epsilon_c$  versus  $1/RT$  (i.e.,  $Q = \text{slope} \times (m+\beta)$ , see Figure 3b). This method produces an activation energy of 95 kJ/mol in NiAl-Si which is in good agreement with the activation energies determined for static strain aging in polycrystalline NiAl (70 to 76 kJ/mol) [8-10] and the activation energies for dynamic strain aging in single crystal NiAl [2,3,6,9,12]. Due to a lack of experimental data, it was not possible to estimate the activation energies for strain aging in NiAl-Fe.

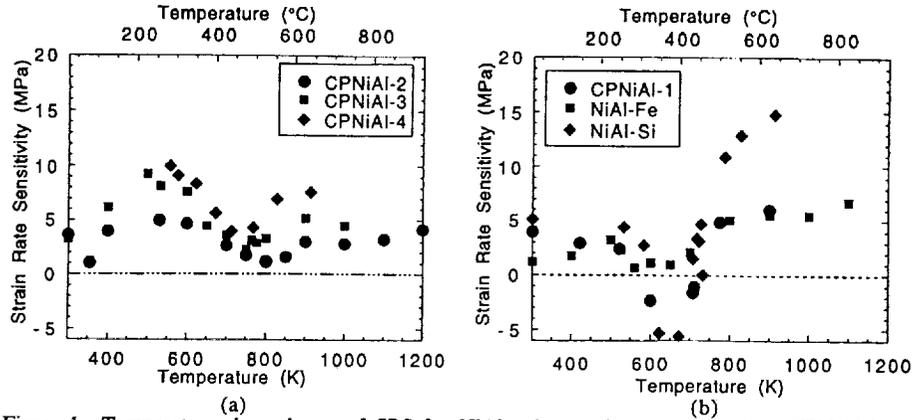


Figure 1. Temperature dependence of SRS for NiAl polycrystals: (a) CPNiAl-2, CPNiAl-3 and CPNiAl-4; and (b) CPNiAl-1, NiAl-Fe, and NiAl-Si. Note the significantly reduced SRS values in (b).

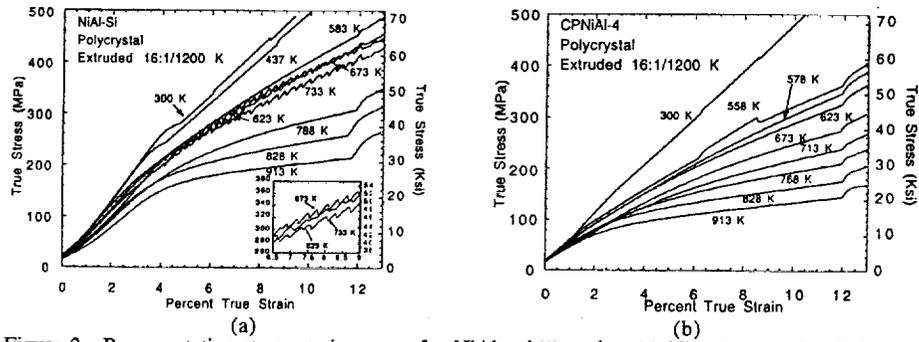


Figure 2. Representative stress-strain curves for NiAl polycrystals: (a) NiAl-Si; and (b) CPNiAl-4. Flow stress transients as observed for NiAl-Si at 583 K were observed in NiAl-Fe and CPNiAl-2 between 560 and 800 K.

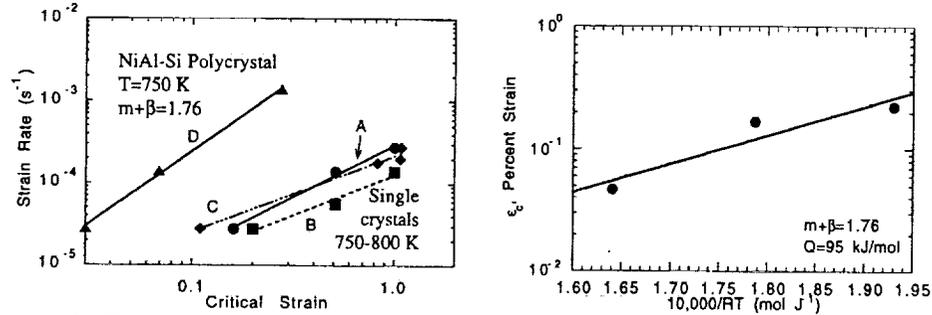


Figure 3. The influence of  $\dot{\epsilon}$  and  $T$  on the critical strain for the onset of serrated flow,  $\epsilon_c$  for polycrystalline NiAl-Si: (a)  $\ln \dot{\epsilon}$  vs  $\ln \epsilon_c$  and (b)  $\ln \epsilon_c$  vs  $10,000/RT$ . Data previously collected for single crystals [9,12] has been included in (a) for comparison purposes.

The typical temperature dependence of the 0.2% offset yield stress,  $\sigma_{0.2}$ , normalized with respect to the elastic modulus,  $E$ , is summarized in Figure 4. The normalized flow stress generally decreased with increasing temperature for all alloys. However, in NiAl-Fe and NiAl-Si, an apparent plateau was observed at intermediate temperatures while no such peaks or plateaus were observed in CPNiAl-3 or CPNiAl-4. Similar peaks have been observed previously in single crystal and polycrystalline alloys exhibiting manifestations of DSA [3,9,11-14,17].

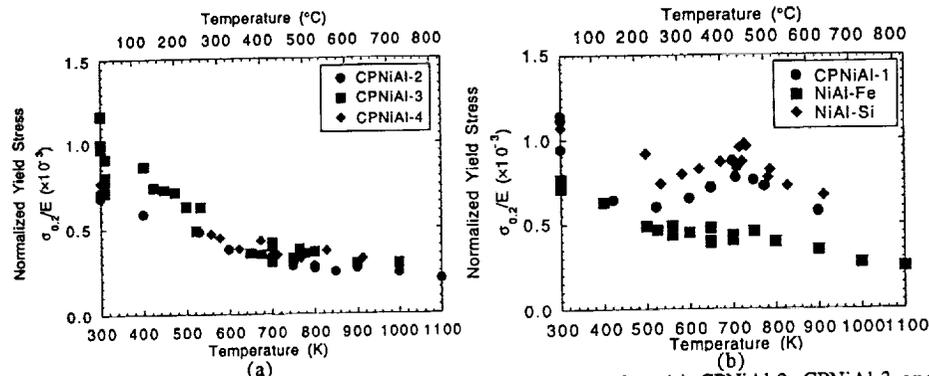


Figure 4 Temperature dependence of  $\sigma_{0.2}/E$  for NiAl polycrystals: (a) CPNiAl-2, CPNiAl-3 and CPNiAl-4; and (b) CPNiAl-1, NiAl-Fe, and NiAl-Si. Note the significantly reduced SRS values in (b).

## DISCUSSION

It is desirable to determine the species responsible for strain aging. This can be accomplished by analyzing the data generated in this study using equation (1). Typically, when  $(m+\beta)$  is in the range 0.5 to 1 an interstitial specie is responsible for strain aging whereas when  $(m+\beta)$  is in the range 2 to 3, a substitutional specie is responsible. In a prior study of strain aging in single crystals,  $(m+\beta)$  values were observed to lie in the range 0.93 to 1.27 suggesting an interstitial mechanism [9,12]. The results generated in this study are inconclusive. It was noted above that the value for the exponent  $(m+\beta)$  in NiAl-Si was  $1.76 \pm 0.20$  which suggests that either a substitutional specie is causing strain aging or that some other mechanism is operative. Additional inferences can be made by comparing the calculated activation energy data for serrated flow in NiAl-Si with the available diffusion data for NiAl and with the strain aging activation energy data generated in prior investigations [2,3,6,9,10,12]. Average activation energies for the diffusion of substitutional solutes are  $225 \pm 39$  kJ/mol regardless of composition [19]. The activation energies for strain aging reported in prior investigations lie in the range 66 to 134 kJ/mol. The experimentally determined activation energy of 95 kJ/mol in NiAl-Si is at least consistent with the prior results and is within the classical range for the diffusion of interstitial solutes in bcc metals.

In agreement with prior investigations on single crystals [9,11,12], SRS minima, flow stress transients, yield stress plateaus, and serrated yielding have been observed in NiAl polycrystals at intermediate temperatures indicating the occurrence of strain aging. Chemical composition was observed to influence the manifestations of strain aging as follows. (1) At intermediate temperatures (*i.e.*, ~600 to 800 K) the SRS minimum decreases to slightly lower levels and to lower temperature ranges with increasing Si concentration and with small Fe additions. (2) Within the same temperature range,  $\sigma_{0.2}/E$  remains relatively unchanged with increasing C concentration and increases significantly with increasing Si concentration. No noticeable increase was observed in NiAl-Fe but there was a detectable increase in scatter. (3) Serrated flow was observed in NiAl-Si and CPNiAl-1 while flow

stress transients were observed in NiAl-Fe and CPNiAl-2. No such behavior was observed in the other alloys. These observations appear to support the hypothesis of Weaver *et al.* [9,11,12] who observed an increase in serration size in single crystal alloys with increasing Si content and flow stress transients during strain rate change tests of alloys containing high C contents but lower Si contents. After analyzing the available data using equation (1), they suggested that strain aging in NiAl was the result of complex interactions between dislocations and residual C and Si atoms. Recent studies at the Oak Ridge National Laboratory indicating a two-fold increase in Si concentration at dislocation cores [20] and at Johns Hopkins University [21] indicating the preferential segregation of C to dislocations would seem to support these ideas.

From the results presented above, it is impossible to devise a definitive mechanism by which substitutional and interstitial impurities can cause strain aging. In references [9,11,12], it was suggested that strain aging could be the result of interaction solid solution hardening (ISSH) and/or increased lattice distortions caused by the presence of substitutional and interstitial solutes. In light of the observations at ORNL [20] and Johns Hopkins [21], it is suggested that Si preferentially segregates to dislocations and attracts C resulting in small Si-C complexes (*i.e.*, small agglomerates or precipitates) which lock dislocations more strongly than Si or C atoms along. Further evidence in support of this hypothesis were provided in diffusion couple studies between NiAl, Ni<sub>3</sub>Al, and SiC [22,23] which suggested that Si may diffuse as fast as or faster than C in NiAl and may result in the formation of complex Ni-Al-Si-C phases. This suggests that some clustering of C with Si, Ni, and Al may occur resulting in an expansion of the DSA regime and stronger pinning. It is understandable that Fe-C complexes could operate in the same manner, however, the overall effects will be minimized. Recent theoretical results suggest that Si will only occupy Al lattice positions [24] whereas other substitutional elements such as Fe or Ga will tend to occupy the site of the stoichiometrically deficient host element [24,25]. Assuming that C atoms occupy octahedral sites, it is theorized that the substitution of smaller Si atoms for Al will result not only in a reduction in the size of the octahedral interstices but also into more localized distortions of the lattice. Similarly, in the cases of Fe or Ga which occupy the stoichiometrically deficient host element sites, the overall distortions in the lattice will be minimized because the tetragonal distortions created by interstitial atoms can be partially accommodated resulting in reduced strain aging effects. Recently, serrated yielding has been reported to occur over a smaller temperature range in both Fe-doped and in Ga-doped single crystal alloys [26] which suggests that there might be some validity to this potential mechanism though more work is needed.

## CONCLUSIONS

Three of the six polycrystalline NiAl alloys examined in the present study exhibit flow stress plateaus, serrated flow and/or flow stress transients during strain rate change experiments in the temperature range 600 to 800 K. These observations are consistent with the occurrence of DSA. Compositional analyses suggest that DSA is the result of a complex interaction between substitutional solutes, interstitial solutes and dislocations. In this case Si atoms have been shown to strongly enhance the occurrence of strain aging in polycrystalline NiAl alloys. Similar additions of Fe in place of Si appear to have the same effect but in a reduced capacity. It is suggested that strain aging results from the formation of substitutional-interstitial aggregates.

## ACKNOWLEDGMENTS

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