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ENVIRONMENTAL EFFECTS ON THE TENSILE PROPERTIES OF TWO Ni_3Si-BASED ALLOYS

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Introduction

There is considerable potential for structural intermetallic alloys based on the nickel-silicon system. This is due to their good corrosion resistance, reasonable room-temperature ductility, and excellent strength to temperatures of 600°C or more. Several previous studies have been performed on Ni_3Si [1–4] as well as $Ni_3(Si,Ti)$ [1,2,5,6] based alloys, yielding promising results. However, these alloys have been reported to suffer from environmental embrittlement at room as well as elevated temperatures [3–7]. The present study was performed to develop a further understanding of such effects. Toward this end, the tensile properties of two Ni_3Si based alloys were evaluated over a range of temperatures in environments including air, vacuum, and dry oxygen.

Experimental

Two Ni_3Si-based alloys were prepared from high-purity elemental starting materials by arc melting and drop casting into a water-chilled copper mold. The compositions of the two alloys were Ni-18.9Si and Ni-18.9Si-4Cr-1Mo (all compositions in this manuscript will be in at. % unless otherwise noted). Both alloys were doped with 50 ppm B (by weight). The ingots (125 mm long with a rectangular cross-section of 12.5 × 25 mm) were forged ~30% at 1050°C followed by annealing at 72 hours at 900°C. Optical metallography revealed remnant cast structures in the annealed condition. A second forging step (~25%) was performed to produce plates approximately 7 mm thick. The plates were annealed for 72 hours at 900°C. In both alloys a two-phase microstructure was observed with the major phase being the Ll_2-ordered Ni_3Si and the minor phase being fcc nickel solid-solution (see Fig. 1). The average grain sizes were measured (using the linear intercept method) to be 7 and 13 μm for the Ni-18.9Si and Ni-18.9Si-4Cr-1Mo alloys, respectively. Tensile samples were prepared from the annealed plates by electro-discharge machining (EDM) and were carefully polished to remove the damaged surface layer. Selected samples were subjected to a pre-oxidizing heat treatment as will be described in the next section. Tensile testing was performed at temperatures ranging from room-temperature (RT) to 1000°C at a constant crosshead speed and an engineering strain rate of 3.3×10^{-3} s^{-1}. The tests were performed in air, vacuum (~2×10^{-4} Pa), or in dry oxygen (6.7×10^4 Pa). For

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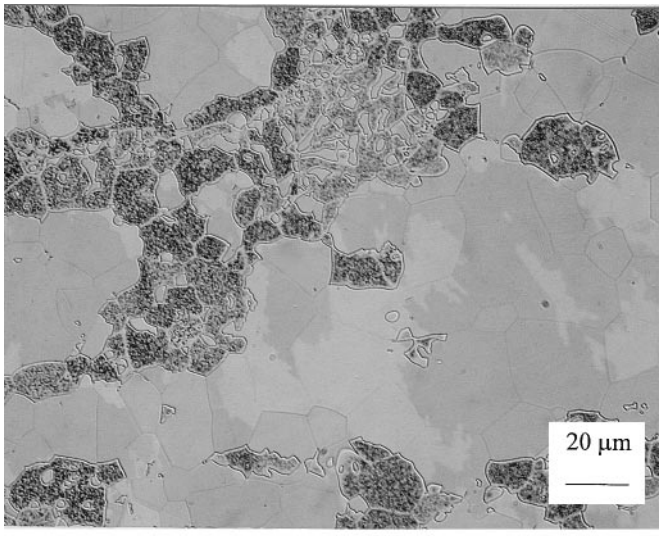
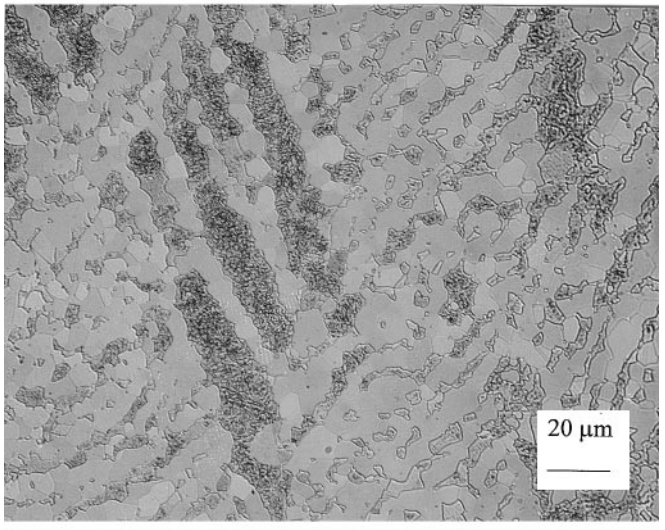


(a)



(b)

Figure 1. The as-annealed microstructures of (a) Ni-18.9Si and (b) Ni-18.9Si-4Cr-1 Mo.

the tests performed in oxygen, a vacuum ($\sim 2 \times 10^{-4}$ Pa) was obtained in the testing chamber prior to backfilling with oxygen. Fracture modes were determined using a scanning electron microscope (SEM).

Results and Discussion

The yield stress of the two alloys is shown in Fig. 2 as a function of temperature for samples tested in air. At RT, the yield stress of Ni-18.9Si is 656 MPa, while that of Ni-18.9Si-4Cr-1Mo is distinctly

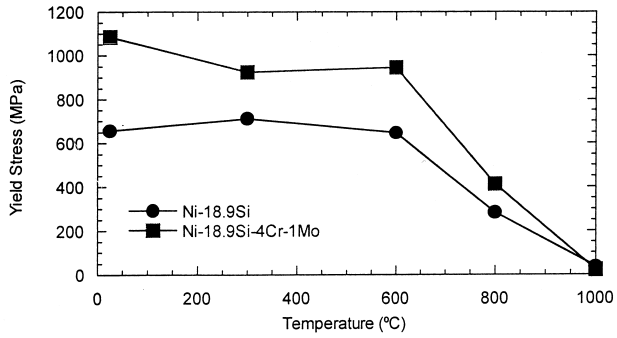


Figure 2. The yield stress as a function of temperature (tests performed in air).

higher at 1084 MPa. This difference reflects the solid-solution hardening effects of the Cr and Mo additions as well as possible Hall-Petch effects resulting from the difference in grain size. As the temperature is increased to 600°C, the yield stress of the Ni-18.9Si alloy is approximately constant, while a slight decrease is observed in the Ni-18.9Si-4Cr-1Mo alloy. At temperatures greater than 600°C the yield stress of both alloys decreases rapidly.

The ductility as a function of temperature is shown in Fig. 3 for samples tested in air. It can be seen that the RT ductilities of these alloys are reasonable. Indeed, a value of 18.9% is observed for Ni-18.9Si. This value drops to 8.8% for Ni-18.9Si-4Cr-1Mo. Unfortunately, many Ni-Si alloys exhibit an intermediate-temperature ductility minimum around 600°C. Of the two alloys in this study, Ni-18.9Si shows the sharpest decrease with the ductility falling to 1.6%. In contrast, that of Ni-18.9Si-4Cr-1Mo falls only to 3.0%. At temperatures greater than 600°C the ductilities of both alloys begin to increase. For example, a value of 25.9% was observed for Ni-18.9Si at 1000°C. For Ni-18.9Si-4Cr-1Mo the increase at higher temperatures is more pronounced, reaching as high as 193% at 1000°C. This value is comparable to those reported by Nieh and Oliver in their study of superplasticity in Ni-Si based alloys [8].

To determine whether environmental embrittlement was a factor at RT, tensile tests were run in vacuum as well as in air. The ductility of the Ni-18.9Si and Ni-18.9Si-4Cr-1Mo alloys tested in vacuum were found to be 18.7 and 8.9%, respectively. These are virtually indistinguishable from the values for samples tested in air, suggesting no environmental embrittlement is occurring at RT. In contrast, a study

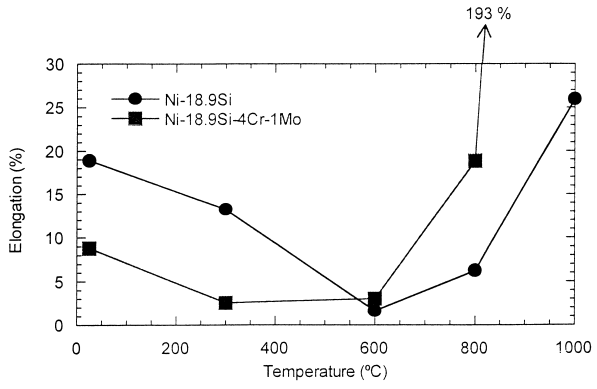


Figure 3. The ductility as a function of temperature (tests performed in air).

TABLE 1
The RT and 600°C Fracture Modes of Samples Tested in Air and Vacuum

	RT		600°C	
Alloy (at.%)	Air	Vacuum	Air	Vacuum
Ni-18.9Si	TG	TG	IG	IG
Ni-18.9Si-4Cr-1Mo	IG	IG	IG	IG

IG = predominantly intergranular fracture, TG = predominantly transgranular fracture.

of a boron-free Ni-22.5Si alloy by Liu and Oliver found that environmental embrittlement occurred at RT [9]. A later study by Liu et al. showed that the addition of boron could eliminate this embrittlement [4]. Moreover, a study by Takasugi et al. reported an RT environmental embrittlement in $Ni_3(Si,Ti)$ alloys which also could be alleviated by the addition of boron [5]. Since both of the alloys in the present study were boron-doped, it is believed that any potential environmental effects at RT were eliminated.

The fracture modes of the two alloys at RT are listed in Table 1 for samples tested in both air and vacuum. The Ni-18.9Si alloy exhibited mostly transgranular fracture, while the Ni-18.9Si-4Cr-1Mo alloy exhibited mostly intergranular fracture. These fracture modes were found to be essentially independent of test environment.

Perhaps the most difficult hurdle in the development of Ni-Si alloys is overcoming the intermediate-temperature ductility minimum. This minimum has been observed in many systems based on $L1_2$-ordered phases such as Ni_3Si [3] and $Ni_3(Si,Ti)$ [5,6], as well as Ni_3Al [10–13]. It is generally associated with oxygen-induced environmental embrittlement. To better understand the role of environment in this effect, tensile tests were performed on the alloys of this study at 600°C in air, vacuum, and dry oxygen. The results are shown in Fig. 4. For Ni-18.9Si, the ductilities are seen to be quite low regardless of test environment. Curiously, a slightly lower ductility was measured in the sample tested in vacuum relative to those tested in air or oxygen. This point will be discussed later. In the Ni-18.9Si-4Cr-1Mo case, significant differences can be seen between test environments. The ductility increases from 3.0 to 9.0% when the test environment is changed from air to vacuum. The component in air responsible for this environmental embrittlement is oxygen, as evidenced by the fact that the ductility of the sample tested in dry oxygen is essentially the same as the one tested in air.

The fracture modes of the two alloys tested at 600°C are also listed in Table 1. It can be seen that the fracture was mostly intergranular for both alloys when tested in either air or vacuum. Intergranular fracture is consistent with oxygen-assisted environmental embrittlement [14,15].

As described above, the 600°C ductility of Ni-18.9Si-4Cr-1Mo is superior to that of Ni-18.9Si. This superiority arises from the presence of Cr which is instrumental in the rapid development of a protective

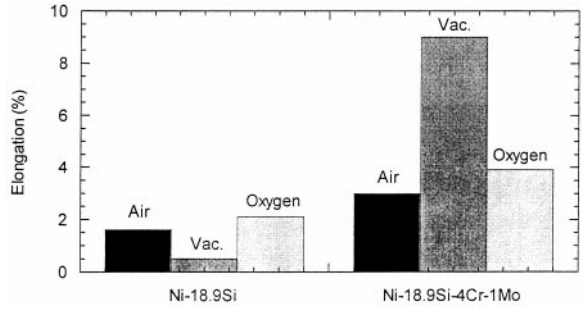


Figure 4. The intermediate-temperature (600°C) ductility of samples tested in various environments.

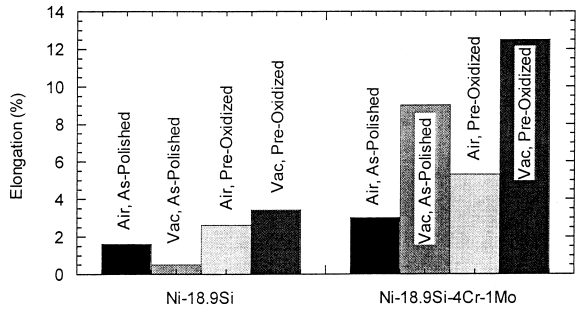


Figure 5. The intermediate-temperature (600°C) ductility of both as-polished and pre-oxidized samples tested in air and vacuum.

oxide layer at the surface, thus inhibiting the oxygen-induced embrittlement. This beneficial effect of Cr has been reported previously for Ni_3Si [3] as well as Ni_3Al [11] alloys. The use of a pre-oxidizing heat treatment to develop a protective surface layer has been shown to be effective in reducing elevated-temperature embrittlement in alloys based on Ni_3Al [14,16]. To further explore this concept for Ni_3Si-based alloys, as-polished samples were subjected to a heat treatment of 4 hours at 700°C in air prior to testing. The exposed samples were then tensile tested in both air and vacuum at 600°C. The results are shown in Fig. 5. The ductility of both alloys in air was seen to be greater in the pre-oxidized state, with the larger increase being found in the Ni-18.9Si-4Cr-1Mo alloy. These results would suggest that an oxide surface layer can indeed inhibit the environmental embrittlement at 600°C, and that Cr plays a significant role in the development of this layer. For both alloys, pre-oxidized samples tested in vacuum resulted in the highest 600°C ductilities observed in this study. This suggests the following conclusion: neither pre-oxidation nor testing in vacuum ($\sim 2 \times 10^{-4}$ Pa) is sufficient by itself to fully eliminate the intermediate-temperature ductility minimum. In fact, it is inconclusive that even a combination of the two techniques will fully eliminate the effect.

For the Ni-18.9Si alloy, the ductility of pre-oxidized samples increased when tested in vacuum instead of air. This is a role reversal from the as-polished samples where the ductility was reported earlier to *decrease* when tested in vacuum. The following explanation is offered for this counterintuitive result. When an as-polished sample is tested in air at 600°C an oxide layer develops prior to the running of the test while the sample is sitting at-temperature. When this same as-polished sample is tested in vacuum no protective oxide layer can develop and even the low levels of oxygen present are sufficient to embrittle the sample. In the pre-oxidized state this is not a concern and the vacuum test exhibits the higher ductility. The above behavior is not observed for as-polished Ni-18.9Si-4Cr-1Mo where the presence of Cr accelerates the formation of protective oxide films. It is clear from this discussion that many factors must be carefully considered when interpreting elevated-temperature environmental test results for these and other similar alloy systems.

Conclusions

The tensile properties of two boron-doped Ni_3Si-based alloys, Ni-18.9Si and Ni-18.9Si-4Cr-1Mo, were evaluated over a range of temperatures and test environments. The findings of this study are summarized below:

1. The yield stress of both alloys was found to be a weak function of temperature from RT to 600°C. The Ni-18.9Si-4Cr-1Mo alloy was considerably stronger than the Ni-18.9Si alloy. The yield stress of both alloys fell sharply at temperatures above 600°C.
2. The room-temperature ductilities and fracture modes of both alloys were found to be independent of test environment. The Ni-18.9Si alloy had a ductility of 18.9% and a predominantly transgranular fracture mode. The Ni-18.9Si-4Cr-1Mo alloy had a somewhat lower ductility of 8.8%, accompanied with an intergranular fracture mode.
3. An intermediate-temperature ductility minimum was observed in both alloys around 600°C resulting in an intergranular fracture mode. In the Ni-18.9Si alloy low ductilities were found in all test environments. In the Ni-18.9Si-4Cr-1Mo alloy, however, a considerable increase in ductility was observed when tested in vacuum. The ductility in oxygen was found to be similar to that in air, confirming that an oxygen-induced embrittlement is responsible for the ductility minimum.
4. The intermediate-temperature ductility of both alloys tested in air was found to improve when pre-exposed in air for 4 hours at 700°C. This was attributed to the formation of a protective surface oxide. This effect is apparently enhanced in the Cr-containing alloy. The greatest ductilities were observed when pre-oxidized samples were tested in vacuum, suggesting that neither pre-oxidation nor testing in vacuum is sufficient to eliminate all environmental effects.

Acknowledgments

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