Effects of Boron and Carbon Additions on Environmental Embrittlement of a Ni$_3$(Si, Ti) Alloy at Ambient Temperature

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The effects of additions of a small amount of boron and carbon on environmental embrittlement of a Ni$_3$(Si, Ti) alloy are investigated by means of room temperature tensile tests in various kinds of atmospheres and at various strain rates. The additions of boron and carbon to the Ni$_3$(Si, Ti) alloy suppress the embrittlement in air and distilled water, and slightly reduce the embrittlement in H$_2$ gas. The beneficial effect of boron and carbon on environmental embrittlement may be attributed to the boron (and carbon) segregation to grain boundaries where these atoms compete their site occupancy and/or their diffusion path with hydrogen atoms, resulting in the change in the fracture mode from intergranular to transgranular. Distinction in the embrittlement between air (or distilled water) and H$_2$ gas is considered to be due to the difference in the decomposition kinetics into hydrogen atoms.

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I. Introduction

Recent studies on mechanical properties of ordered intermetallics demonstrate that a number of ordered intermetallics are very susceptible to environmental embrittlement in the ordinary environment such as air at ambient temperature when tensile tested at ordinary deformation rates$^{13-15}$. L1$_2$-type Ni$_3$Si alloys have been considered to have high potential as high temperature structural materials because they have superior mechanical, physical and chemical properties. However, they had been suffering from embrittlement at ambient temperatures. The brittleness of Ni$_3$Si has recently been overcome by macro alloying (i.e. addition of titanium)$^{607}$ and also by micro alloying (i.e. doping of boron and carbon)$^{60}$. However, the ductilized Ni$_3$(Si, Ti) alloys have also been observed to be susceptible to the environmental embrittlement at ambient temperature$^{607}$. It was shown that the tensile elongation of Ni$_3$(Si, Ti) alloys was reduced when tested in air$^{79}$. However, the addition of a small amount of boron (and also carbon) to Ni$_3$(Si, Ti) polycrystals was found to be very effective in suppressing the embrittlement in air$^{1298}$; in boron-doped Ni$_3$(Si, Ti) polycrystals, the tensile elongation in air was identical to that in vacuum$^{1299}$. More quantitative and detailed studies should be performed on environmental embrittlement of Ni$_3$(Si, Ti) alloys with and without boron and carbon additions to make clear the mechanisms of this alloying effects.

In this study, environmental embrittlement of L1$_2$-type Ni$_3$(Si, Ti) polycrystals with and without a small amount of boron and carbon (as a material parameter) is investigated by tensile tests in various kind of environmental media and at various strain rates (as an experimental parameter). Main results are discussed from the point of view of the interaction between doping atoms and hydrogen atoms, and also the kinetic process of decomposition into hydrogen atoms.

II. Experimental Procedure

The Ni$_3$(Si, Ti) alloys with a base composition of 79.5 mol% Ni, 11 mol% Si and 9.5 mol% Ti were used in this study. Starting raw materials were 99.9 mass% Ni, 99.999 mass% Si and 99.9 mass% Ti. Three alloy ingots, i.e. Ni$_3$(Si, Ti), Ni$_3$(Si, Ti) doped with 50 mass ppm boron (B) and Ni$_3$(Si, Ti) doped with 0.05 mass% carbon (C) were prepared by arc melting. Alloy preparation, heat-treatments of homogenization and recrystallization and tensile specimen preparation were done by following the same procedures as those in the previous studies$^{607-609}$. The average grain diameters measured by a linear intercept method were 50 μm for undoped and boron-doped Ni$_3$(Si, Ti) alloys, and 31 μm for carbon-doped Ni$_3$(Si, Ti) alloy. Chemical analysis of the materials showed that the compositions were fairly in agreement with the nominal ones. It should be noted that boron-doped and carbon-doped Ni$_3$(Si, Ti) alloys contained very small volume fraction of second phase particles preferentially at their grain boundaries, indicating that boron and carbon concentrations of alloys used in this study were slightly beyond the solubility limits in Ni$_3$(Si, Ti)(L1$_2$ phase)$^{708-709}$. However, it was demonstrated that ductility/brittleness property of this alloy did not depend on second phase particles but was primarily affected by solute atoms of boron and carbon within grain interior or at grain boundaries$^{59-111}$. Residual hydrogen contents in the samples before tensile testing were analyzed by the ‘argon carrier fusion-thermal conductivity’ method, and they were shown to be approximately 0.4 mass ppm independent of alloy compositions. This level of hydrogen content is assumed to be insufficient to influence the
mechanical properties of Ni$_3$(Si, Ti) alloys.

Tensile tests were carried out at room temperature by an Instron machine. Four environmental media, namely, vacuum (with a vacuum of approximately $8 \times 10^{-4}$ Pa), air (with a humidity ranging between 65 and 80%), distilled water and hydrogen gas (H$_2$) (with extremely high grade of hydrogen gas) were used in this study. Evacuation and introduction of H$_2$ gas were repeated three times before the tests. Effect of strain rate on the tensile behavior was also investigated at initial strain rates between $6 \times 10^{-3}$/s and $6 \times 10^{-2}$/s in each environmental medium. Tensile elongation was obtained by measuring cross head displacement and load was measured by load cell. Fracture surfaces were observed by a scanning electron microscope (SEM).

III. Results

1. Mechanical Behavior

Figure 1 shows the effects of environmental media and strain rate on tensile elongation [Fig. 1(a)] and tensile strength; the 0.2% yield strength and the ultimate tensile strength (UTS) [Fig. 2(b)] of the undoped Ni$_3$(Si, Ti) alloy. The elongation was considerably influenced by the environment, and the magnitude of the elongation decreased in the following order: in vacuum, in air, in water and in H$_2$ gas. The elongations of specimens deformed in vacuum were always beyond 30% at all the strain rates tested in this study. In contrast, specimens deformed in air showed a pronounced strain rate depend-
ence. The elongation increased from 3% to 28% with increasing strain rate from the lowest strain rate to the highest one. Thus, a sharp "brittle-to-ductile" transition occurred in a strain rate range between $10^{-3}$/s and $10^{-1}$/s for Ni$_3$(Si, Ti) alloy deformed in air. Specimens deformed in distilled water did not show any ductility at the lowest strain rate, but the ductility increased with increasing strain rate to $10^{-3}$/s, and the elongation reached approximately 4% at the highest strain rate. On the other hand, specimens deformed in H$_2$ gas was so brittle that they fractured prior to macroscopic yielding at all the strain rates. The obtained 0.2% yield strength was insensitive not only to the environmental media but also to the strain rate. In contrast, the UTS depended on the environmental media and the strain rate in the same way as elongation did.

Figure 2 shows tensile test results of boron-doped Ni$_3$(Si, Ti) alloy. A marked effect of boron addition was recognized. The specimens deformed in vacuum, air and distilled water showed constantly large elongation (i.e. approximately 30%) even at the lowest and the intermediate strain rate, but it appeared to decrease with increasing strain rate to the highest strain rate. This indicates that the embrittlement in air and distilled water was completely suppressed by addition of a small amount of boron to the Ni$_3$(Si, Ti) alloy. However, ductility of specimens deformed in H$_2$ gas was still very low although it increased with increasing strain rate. At the highest strain rate, elongation was about 3%, indicating that the boron addition to this alloy is effective also in reducing the em-

![Fig. 1](image1.png)

![Fig. 2](image2.png)

Fig. 1 The effect of the environmental media and the strain rate on (a) the tensile elongation and (b) tensile strength, i.e. the 0.2% yield strength and the ultimate tensile strength (UTS) of Ni$_3$(Si, Ti) alloy.

Fig. 2 The effect of the environmental media and the strain rate on (a) the tensile elongation and (b) tensile strength, i.e. the 0.2% yield strength and the ultimate tensile strength (UTS) of Ni$_3$(Si, Ti) alloy doped with 50 mass ppm B.
brittlement in H₂ gas. The 0.2% yield strength of this alloy was again insensitive not only to the environmental media but also to the strain rate, while the UTS and elongation depended on the environmental media and the strain rate.

Figure 3 shows the test results of the carbon-doped Ni₃(Si, Ti) alloy. The order of magnitude of tensile elongation was same to that of undoped alloy. Specimens deformed in vacuum showed large elongation (~30%), which slightly decreased at the lowest strain rate. Elongation of the specimens deformed in air showed marked strain rate dependence, that is, elongation increased steadily from 16% to 35% with increasing strain rate from the lowest strain rate to the highest one. Elongation of the specimens deformed in distilled water showed a similar strain rate dependence to that deformed in air, although elongation in distilled water was smaller than that in air at each strain rate. On the other hand, specimens deformed in H₂ gas were very brittle even at the highest strain rate. Comparison of Fig. 3 with Figs. 1 and 2 indicates that the addition of carbon to Ni₃(Si, Ti) alloy moderately reduces the embrittlement in air and distilled water but does not reduce the embrittlement in H₂ gas at all. The 0.2% yield strength of this alloy was again insensitive to both the environmental media and the strain rate, while UTS depended on them, which was correlated well with that of the elongation.

2. Fracture behavior

Figure 4 shows fracture surfaces of the undoped Ni₃(Si, Ti) alloy deformed in vacuum, air, distilled water and H₂ gas at the lowest strain rate (6 × 10⁻⁴/s). The specimen deformed in vacuum fractured in a ductile manner showing transgranular dimple patterns with a small area fraction of grain boundary fracture. The specimens deformed in air and distilled water fractured mainly along grain boundaries with a small area fraction of the transgranular dimple fracture. Finally, the specimen deformed in H₂ gas showed almost complete grain boundary fracture. Thus, the fracture mode of undoped Ni₃(Si, Ti) alloy is quite consistent with the tensile behavior shown in Fig. 1; the higher elongation and UTS were accompanied by transgranular fracture while the lower elongation and UTS were accompanied by grain boundary fracture.

Figure 5 shows the effect of strain rate on fracture mode of undoped Ni₃(Si, Ti) alloy deformed in air, indicating that the tensile elongation was very dependent on the strain rate (Fig. 1). It is evident that the area fraction of transgranular ductile fracture increased with increasing strain rate, which is consistent with the tensile behavior shown in Fig. 1.

Figure 6 shows fracture surfaces of boron-doped Ni₃(Si, Ti) alloy deformed in each environmental medium at the lowest strain rate (6 × 10⁻⁴/s). A distinctive result in this alloy is that the specimen deformed in air showed mainly transgranular dimple patterns, while the specimen deformed in H₂ gas showed grain boundary fracture. Consistency of the fracture mode with the tensile behavior shown in Fig. 2 is again noticed; the large elongation of the specimen deformed in air is accompanied by transgranular fracture while the small elongation of the specimen deformed in H₂ gas is attributed to the brittle grain boundary fracture.

Fracture mode of the carbon-doped Ni₃(Si, Ti) alloy was similar to that observed in the boron-doped Ni₃(Si, Ti) alloy. For example, the specimens deformed in vacuum and air at a strain rate of 6 × 10⁻⁴/s showed mainly transgranular dimple fracture, while the specimens deformed in H₂ gas showed mainly grain boundary fracture. The grain boundary fracture of the carbon-doped Ni₃(Si, Ti) alloy was more prevailing than the boron-doped alloy in each environmental media and at each strain rate.

IV. Discussion

The main results obtained in this study are summarized as follows; 1) tensile elongation of the Ni₃(Si, Ti) alloys is sensitive to strain rate, regardless of the environmental media or boron (and carbon) doping. This result suggests that the embrittlement is associated with the dynamic process of hydrogen competing with the applied deformation rate. 2) the embrittlement of the Ni₃(Si, Ti) alloys in H₂ gas was much more severe than in air, regardless of boron (and carbon) doping or strain rate. 3) the addition of boron to the Ni₃(Si, Ti) alloy completely suppresses the embrittlement in air and distilled water in a wide range of strain rate. Similarly, the addition of carbon to the
Ni$_3$(Si, Ti) alloy reduces the embrittlement in air and distilled water.

It has been recognized that environmental embrittlement in ordered intermetallics as well as the ordinary materials occurs through some microscopic processes involving decomposition, permeation and condensation of hydrogen atoms, and bond breaking process resulting in the final fracturing of materials$^{(10-15)}$. It has been assumed that the specimens deformed in air are embrittled by atomic hydrogen decomposed from moisture (i.e. ‘H$_2$O molecule’). It has been suggested that active element (M$_{\text{active}}$) (such as Si or Ti in this alloy) reacts with moisture in air by the following reaction;

$$\text{M}_{\text{active}} + \text{H}_2\text{O} \rightarrow \text{M}_{\text{active}} \text{O} + 2\text{H}, \quad (1)$$

and thereby releases atomic hydrogen (H) from H$_2$O into material interior$^{(12-13)}$, although this reaction may proceed via some metastable reactive products (processes)$^{(14)}$. Whereas, the specimens deformed in H$_2$ gas are embrittled by atomic hydrogen decomposed from ‘H$_2$ molecule’. In this case, it has been assumed that transition element (M$_{\text{transition}}$) (such as Ni in this alloy) may play a catalytic role, i.e. the catalyst of the following reaction:

$$\text{H}_2 \rightarrow [\text{M}_{\text{transition}} \text{(catalyst)}] \rightarrow 2\text{H}, \quad (2)$$

and thereby atomic hydrogen (H) can be released from H$_2$ gas and penetrates into the material interior$^{(13-16)}$, although this reaction may also proceed via some metastable reactive products (processes). The fact that the tensile behavior in air is different from that in H$_2$ gas, but rather similar to that in distilled water, implies that the embrittlement in air is not caused by the decomposition of a low partial pressure of H$_2$ gas contained in air but is caused by the decomposition of ‘H$_2$O molecule’ contained in air. Also, the fact that the embrittlement in the Ni$_3$(Si, Ti) alloys was much more severe in H$_2$ gas than in air (and also distilled water), implies that the decomposition process from H$_2$ molecule (i.e. eq. (2)) is much more active (i.e. rapid) than the decomposition process from ‘H$_2$O molecule’ (i.e. eq. (1)).

Considering the beneficial effect of additions of boron and carbon on environmental embrittlement of the Ni$_3$(Si, Ti) alloys, it should be noted that the addition of boron to Ni$_3$(Si, Ti) single crystals with similar chemical composition, Ni$_3$Si$_2$Ti$_{11}$, had no effect in suppressing the embrittlement in air and H$_2$ gas$^{(17)}$. This observation implies that boron and carbon may affect some kinetic processes of hydrogen associated with grain boundaries. It is very likely that boron and carbon atoms interact with hydrogen atoms for their site occupation and/or diffusion path at grain boundaries. In other words, the beneficial effect of additions of boron and carbon to the Ni$_3$(Si, Ti) alloy cannot be attributed to scavenging action of these doping elements in lattice (i.e. grain interior), although these elements may affect decomposition and subsequent absorption processes from molecule (i.e.
and enriching at grain boundaries. Therefore, in order to reduce the embrittlement in \( \text{H}_2 \) gas by alloying technique, the element affecting (i.e. reducing) the decomposition process of eq. (2) may be effective.

It was shown that carbon has a moderate effect in reducing environmental embrittlement of the \( \text{Ni}_3(\text{Si}, \text{Ti}) \) alloys. Carbon is considered to segregate to grain boundaries of this alloy because of similar atomic diameter and electronic nature to boron. However, in order to clarify whether moderate effect of carbon on this embrittlement is due to moderate grain boundary segregation of carbon atoms or due to moderate capability of carbon atoms interfering with the site occupation and/or diffusion of hydrogen at grain boundaries, the direct detection of hydrogen atoms as well as carbon atoms is required. This kind of direct observation is also needed for the boron-doped \( \text{Ni}_3(\text{Si}, \text{Ti}) \) alloys.

Specimens deformed in \( \text{H}_2 \) gas fractured mainly before the macroscopic yielding while specimens in air and distilled water fractured after the yielding, although the embrittlement in both environments is considered to be so called "hydrogen embrittlement". The embrittlement in both environmental media is suggested to be due to the reduction of the grain boundary cohesion. In the embrittlement in \( \text{H}_2 \) gas, high content of hydrogen is equilibrated at grain boundaries and is considered to be enough to cause the grain boundary fracturing before the yielding. In the embrittlement in air, hydrogen content decomposed (and then absorbed) from moisture in air (or distilled water) is not sufficient to cause the fracturing before the yielding. That is, their hydrogen contents are assumed to be below the critical hydrogen content causing the grain boundary fracture. In this case, the activated dislocations offer the rapid path of hydrogen atoms or collect hydrogen atoms by their sweeping, resulting in the fracturing at the stage of plastic deformation.

V. Conclusion

The effects of additions of a small amount of boron and carbon on environmental embrittlement of \( \text{L}_1_2 \)-type \( \text{Ni}_3(\text{Si}, \text{Ti}) \) alloys were investigated by room temperature tensile test. The following results were obtained.

1) The addition of boron to the \( \text{Ni}_3(\text{Si}, \text{Ti}) \) alloy results in complete suppression of the environmental embrittlement in air and distilled water, and it has a slight effect on suppressing the embrittlement in \( \text{H}_2 \) gas.

2) The addition of carbon to the \( \text{Ni}_3(\text{Si}, \text{Ti}) \) alloy results in moderate suppression of the embrittlement in air and distilled water, but no suppression of the embrittlement in \( \text{H}_2 \) gas.

3) Distinction in the embrittlement behavior between air (or distilled water) and \( \text{H}_2 \) gas may be due to the difference in the decomposition kinetics into atomic hydrogen. It was suggested that the decomposition process of \( \text{H}_2 \) molecule at the alloy surface was much more active than the decomposition process of \( \text{H}_2\text{O} \) molecule at the alloy surface.

4) The beneficial effect of boron (and carbon) on en-

Fig. 5 Fracture surfaces of \( \text{Ni}_3(\text{Si}, \text{Ti}) \) alloy deformed in air at strain rates of \( 6 \times 10^{-7}/\text{s} \), \( 1.2 \times 10^{-7}/\text{s} \) and \( 6 \times 10^{-9}/\text{s} \).
Environmental embrittlement of the Ni$_3$(Si, Ti) alloy may be attributed to their segregation to grain boundaries where these atoms compete their site occupation and/or diffusion path with hydrogen atoms, which is considered to cause the fracture mode change from intergranular to transgranular fracture.

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