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## MOISTURE-INDUCED ENVIRONMENTAL EMBRITTLEMENT OF ORDERED INTERMETALLIC ALLOYS AT AMBIENT TEMPERATURES

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**ABSTRACT.** Recent studies have demonstrated that moisture-induced environmental embrittlement is a major cause of low ductility and brittle fracture in ordered intermetallics with high crystal symmetries (e.g., L1<sub>2</sub> and B2). The embrittlement involves the reaction of reactive elements in intermetallics with moisture in air and the generation of atomic hydrogen at crack tips. The loss in ductility at ambient temperatures is generally accompanied by a change in fracture mode from ductile appearance to brittle grain-boundary fracture in many L1<sub>2</sub> intermetallics, and to brittle cleavage in body-centered cubic (bcc)-ordered intermetallics. In a number of cases, the embrittlement was alleviated by alloy design through control of microstructure and alloy composition.

### 1. Introduction

Aluminides and silicides generally possess attractive high-temperature properties; however, brittle fracture and poor ductility at ambient temperatures have limited their use as structural materials for engineering applications [1-7]. For the past ten years, substantial efforts have been devoted to understanding brittleness in ordered intermetallics. As a result, significant progress has been made in understanding both intrinsic and extrinsic factors contributing to the low ductility and brittle fracture in these intermetallics.

This paper briefly reviews recent research on environmental embrittlement of ordered intermetallics in air and other atmospheres at ambient temperatures. The studies have demonstrated that environmental embrittlement — an extrinsic factor — is a major cause of brittle fracture and low ductility in many intermetallic alloys when tested in moist air at ambient temperatures [8-19]. The embrittlement involves decomposition of moisture in air and generation of atomic hydrogen at crack tips [9]. The loss in ductility is caused by hydrogen embrittlement. In many cases, the ductility reduction is accompanied by a change in fracture mode from ductile appearance to brittle grain-boundary fracture or cleavage fracture [8-19].

This review paper contains five sections. The introduction section is followed by a description of environmental effects on room-temperature ductility and fracture in bcc-type intermetallics. The third section summarizes the environmental effects in face-centered cubic (fcc)-type intermetallic alloys. The fourth briefly mentions alleviation of environmental embrittlement by alloy design. The last section provides a brief summary and remarks.

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## 2. Environmental Embrittlement of bcc-Type Ordered Intermetallics

The FeAl aluminide with the B2 structure is a good model material for study of environmental embrittlement in ordered intermetallics because of its high sensitivity to test environment at ambient temperatures [20]. Figure 1 and Table 1 show the tensile properties of the aluminide containing 36.5 at. % Al as a function of test environment at room temperature [9]. The yield stress is not sensitive to environment, whereas the ultimate tensile strength scales with tensile ductility, which, in turn, depends strongly on test environment. The aluminide with a coarse grain structure showed a ductility of 2.2% in air. The ductility of the aluminide increased to 5 to 6% when tested in vacuum or Ar + 4% H<sub>2</sub> environment. The specimens showed, surprisingly, a high ductility of 17.6% when tested in dry oxygen. The water-vapor test confirmed the low ductility found in the air tests, indicating that water vapor is the embrittling agent.

The FeAl aluminide shows a change in fracture mode with increasing ductility (Fig. 1) [9]. The aluminide exhibited mainly transgranular cleavage fracture when tested in air, whereas it showed mainly grain-boundary separation when tested in an oxygen environment. A mixed fracture mode was observed for the vacuum test. The occurrence of cleavage fracture, presumably along {100} planes, indicates that cleavage planes are more susceptible to embrittlement than are the grain boundaries. When the embrittling effect of moisture is removed by testing in dry oxygen, the fracture path follows the grain boundaries, which are the (intrinsic) weakest links in the aluminide.

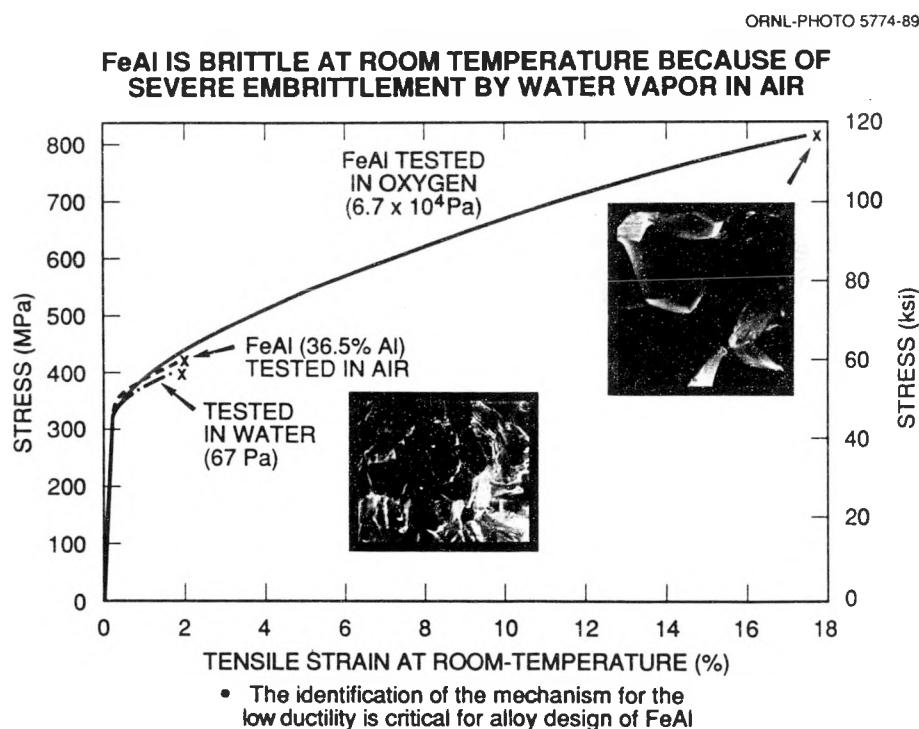


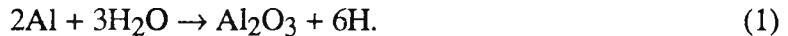
Figure 1. Tensile stress-strain curves comparing the effects of different environments on FeAl fracture behavior.

TABLE 1. Effect of test environment on room-temperature tensile properties<sup>a</sup> of FeAl (36.5% Al) [9,10]

Test environment (gas pressure)	Elongation (%)	Yield strength (MPa)	Ultimate tensile strength (MPa)
Air	2.2	360	412
Vacuum ( $< 1 \times 10^{-4}$ Pa)	5.4	352	501
Oxygen ( $6.7 \times 10^4$ Pa)	17.6	360	805
Ar + 4% H <sub>2</sub> ( $6.7 \times 10^4$ Pa)	6.2	379	579
H <sub>2</sub> O Vapor (67 Pa)	2.4	368	430

<sup>a</sup>All specimens were annealed 1 h/900°C + 2 h/700°C in vacuum.

The mechanism that has been postulated [9] for this type of environmental embrittlement is similar to what is observed in aluminum and its alloys [21,22]. In general, aluminum alloys are not embrittled by dry hydrogen; sometimes, however, they can be severely embrittled by moist air. The chemical reaction that is thought to cause this embrittlement is shown below [21]:



It is believed that the high-fugacity atomic hydrogen, produced in this reaction between the aluminum atoms and H<sub>2</sub>O in moist air, enters the metal at crack tips and causes hydrogen embrittlement. Since FeAl alloys contain relatively large concentrations of aluminum, it is postulated that a reaction similar to the one described above for aluminum alloys also takes place in FeAl [9]. Preliminary experiments using nuclear reaction analysis have shown that FeAl does, in fact, react with heavy water (presumably in a reaction analogous to the H<sub>2</sub>O dissociation shown above), producing deuterium which is then absorbed into FeAl [23]. The underlying mechanism of environmental embrittlement in FeAl may be similar to hydrogen embrittlement in other ordered intermetallics like Co<sub>3</sub>Ti, Ni<sub>3</sub>(Al<sub>0.4</sub>Mn<sub>0.6</sub>), (Fe,Ni)<sub>3</sub>V, and B-doped Ni<sub>3</sub>Al [13-19], the principal difference being the manner in which atomic hydrogen is generated and absorbed in the different studies (e.g., reaction with moist air [9] versus cathodic hydrogen charging [17]). Consistent with this, Table 1 shows that the yield strength of FeAl is insensitive to test environment, a common observation also in other studies of hydrogen embrittlement [13-19]. The best ductility (17.6%) is obtained in a dry oxygen environment, indicating that the reaction of aluminum atoms with oxygen competes with the moisture reaction in Eq. 1, thereby reducing the generation of atomic hydrogen from the moisture in air. It is surprising that even the residual moisture in the vacuum test is enough to cause significant embrittlement compared with the oxygen test.

The environmental embrittlement in FeAl occurs along cleavage planes rather than grain boundaries, suggesting a possible reduction of the cohesive strength by absorbed hydrogen [9-12]. This is supported by recent first-principles total-energy calculations, which indicate that interstitial hydrogen draws electrons to itself and reduces the cleavage strength and energy of FeAl by as much as 20 to 70% (depending on the hydrogen concentration) [24]. Recent studies of the prestrain effect also support the decohesion mechanism. In this study, FeAl specimens containing 35 at. % Al were first strained in dry oxygen to different levels, followed by further straining to fracture in moist air. As

shown in Table 2, all the specimens fractured almost at the same fracture strength, independent of prestrains or total strains. Note that the fracture strength in air is lower than the maximum strength obtained by prestraining in dry oxygen. This result can be interpreted as follows: hydrogen released from moisture reduces atomic bonding and causes crack propagation at a relatively lower strength at crack tips.

For FeAl containing more than 38% Al, its low ductility is essentially caused by two mechanisms: (1) intrinsic grain-boundary weakness and (2) environmental embrittlement [11,12]. The first mechanism dominates the ductility and fracture when Fe-40% Al is tested at room temperature in air or in dry oxygen (see Table 3). To eliminate the intrinsic grain-boundary problem, boron at a level of 300 wt ppm was added to the 40% Al alloy. Boron tends to segregate strongly to grain boundaries and suppresses intergranular fracture in FeAl [11]. As shown in Table 3, the boron-doped 40% Al alloy tested in air showed mainly transgranular fracture rather than grain-boundary fracture, as was seen in the boron-free alloy. The increase in ductility resulting from boron doping is around 3%, which generally agrees with the data reported by Crimp et al. [25,26] and Gaydosh et al. [27]. The boron-doped alloy showed a distinctly higher ductility (16.8%) when tested in the oxygen environment. This result clearly demonstrates that boron-doped FeAl containing 40% Al, just like the lower aluminum alloys, exhibits environmental embrittlement in air, and that this embrittlement can be reduced by testing in a dry oxygen atmosphere.

Environmental embrittlement is also the major cause of low ductility in  $\text{Fe}_3\text{Al}$  [10] at ambient temperatures. Table 4 shows the tensile properties of  $\text{Fe}_3\text{Al}$  (28% Al) heat treated to produce either the  $\text{D}0_3$  or  $\text{B}2$  structure and then tested in various environments at room temperature. Both crystal structures showed essentially the same dependence on test environment. The air tests produced a ductility of about 4%. When tested in vacuum, the tensile elongation increased three-fold to about 12%. Similarly high values of ductility (~ 12%) were obtained in dry oxygen and somewhat lower values (~ 8%) in a mixture of  $\text{Ar} + 4\% \text{H}_2$ . The water vapor tests, on the other hand, resulted in ductilities even lower than those obtained in the air tests, although the pressure in the water vapor tests was comparable to the vapor pressure of moisture in the air tests.

TABLE 2. Effect of prestrain in dry oxygen on room-temperature tensile properties of FA-317 (35% Al) tested in air

Pre-strain in oxygen			Follow-on test in air	
Yield strength (MPa)	Maximum stress (MPa)	Strain (%)	Fracture strength (MPa)	Total elongation <sup>b</sup> (%)
<sup>a</sup>	--	0	442	0 + 3.4 = 3.4
349	412	2.6	425	2.6 + 0.5 = 3.1
351	487	4.3	427	4.3 + 0 = 4.3
342	578	7.8	442	7.8 + 0 = 7.8

<sup>a</sup>For FA-317, yield strength = 347 MPa.

<sup>b</sup>Total elongation due to pre-strain and follow-on straining at room temperature.

TABLE 3. Effect of test environment on room-temperature tensile properties of FeAl (40 at. % Al) with and without boron [11]

Test environment	Strength (MPa)		Ductility (%)	Fracture mode <sup>a</sup>
	Yield	Ultimate		
<b>No boron</b>				
Air	390	405	1.2	GBF
Oxygen <sup>b</sup>	402	537	3.2	GBF
<b>Doped with 300 wt ppm boron</b>				
Air	391	577	4.3	TF
Oxygen <sup>b</sup>	392	923	16.8	TF

<sup>a</sup>GBF = grain-boundary fracture; TF = mainly transgranular fracture (cleavage).

<sup>b</sup>Oxygen pressure:  $6.7 \times 10^{-4}$  Pa.

TABLE 4. Room-temperature tensile properties of Fe<sub>3</sub>Al (28 at. % Al) tested in various environments [10]

Test environment (gas pressure)	Elongation (%)	Yield strength (MPa)	Ultimate strength (MPa)
<b>(A) B2 Structure Produced by Annealing 900°C/1 h + 700°C/2 h</b>			
Air	4.1	387	559
Vacuum ( $\sim 10^{-4}$ Pa)	12.8	387	851
Ar + 4% H <sub>2</sub> ( $6.7 \times 10^4$ Pa)	8.4	385	731
Oxygen ( $6.7 \times 10^4$ Pa)	12.0	392	867
H <sub>2</sub> O vapor ( $1.3 \times 10^3$ Pa)	2.1	387	475
<b>(B) D0<sub>3</sub> Structure Produced by Annealing 850°C/1 h + 500°C/5 d</b>			
Air	3.7	279	514
Vacuum ( $\sim 10^{-4}$ Pa)	12.4	316	813
Oxygen ( $6.7 \times 10^4$ Pa)	11.7	298	888
H <sub>2</sub> O vapor <sup>a</sup>	2.1	322	439

<sup>a</sup>Air saturated with water vapor was leaked into the test chamber.

These results clearly indicate that  $\text{Fe}_3\text{Al}$  alloys are also susceptible to moisture-induced environmental embrittlement, just like the  $\text{FeAl}$  alloys. It is interesting to note that there is no difference between the ductilities obtained in the oxygen and vacuum tests (Table 4). This is quite different from the case of  $\text{FeAl}$  alloys where the best ductility was obtained in dry oxygen [9]. Since a dry oxygen environment is not needed to completely eliminate environmental embrittlement in  $\text{Fe}_3\text{Al}$ , it appears that the  $\text{Fe}_3\text{Al}$  alloys are less susceptible to moisture-induced embrittlement than are the  $\text{FeAl}$  alloys. Presumably, this is a result of their lower aluminum contents. The environmental effect has also been studied recently in several  $\text{Fe}_3\text{Al}$  and  $\text{FeAl}$  alloys tested in different atmospheres and at different strain rates [28].

In addition to the iron aluminides,  $\beta$ -brass ( $\text{CuZn}$ ) also showed some degree of environmental embrittlement [29,30]. For instance,  $\text{CuZn}$  typically exhibits a 55% elongation to failure in air and about 6% elongation in distilled water. The embrittlement here is due to stress-corrosion cracking in distilled water.

### 3. Environmental Embrittlement of fcc-Type Ordered Intermetallics

A number of  $\text{Ll}_2$ -ordered intermetallic alloys also show environmental embrittlement in moist air at room temperature. Izumi and his group at Tohoku University have done extensive work on characterization of deformation and fracture in  $\text{Co}_3\text{Ti}$  and its alloys [13,14,18,31]. They observed environmental embrittlement in  $\text{Co}_3\text{Ti}$  both with and without boron additions (Fig. 2) [13,31]. The alloy specimens with and without hydrogen charging showed a substantial reduction in room-temperature ductility when tested in air.  $\text{Co}_3\text{Ti}$  alloys also exhibited severe embrittlement when tested in hydrogen-gas environments [13,15,18]. With decreasing ductility, their fracture mode changed

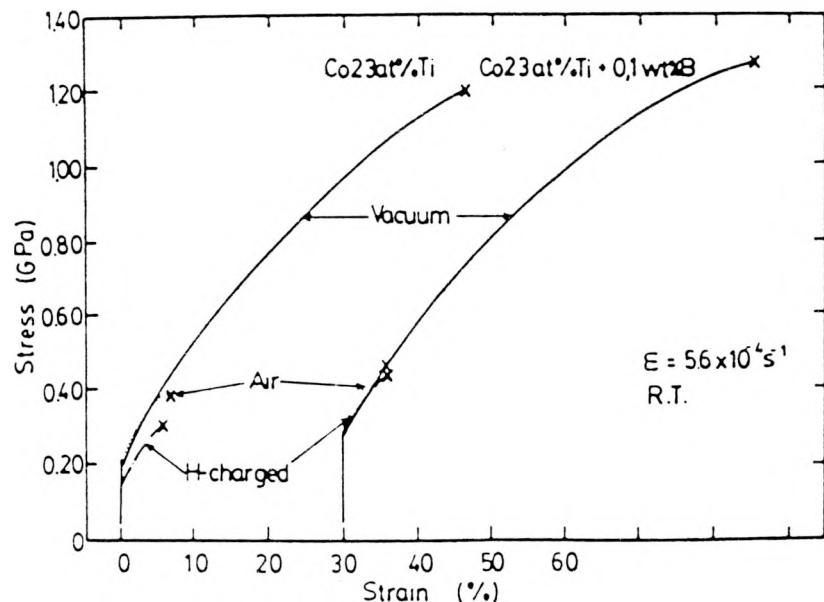


Figure 2. Effect of test environment on room-temperature stress-strain curves of  $\text{Co}_3\text{Ti}$  (23 at. % Ti) with and without 0.2 wt % B [13].

from transgranular to intergranular. The embrittlement was attributed to hydrogen, which promotes brittle intergranular fracture. The environment embrittlement is not affected by boron doping but is influenced by alloy stoichiometry of  $\text{Co}_3\text{Ti}$ . The alloy is much less susceptible to environmental embrittlement when titanium is reduced from 23 to 21 at. % [13].

Similar to the  $\text{Co}_3\text{Ti}$  alloys, a  $(\text{Co},\text{Fe})_3\text{V}$  alloy has been found recently to be susceptible to environmental embrittlement at room temperature [32-33]. As indicated in Fig. 3,  $(\text{Co}_{78}\text{Fe}_{22})_3\text{V}$  showed ductile transgranular fracture, with a tensile ductility of 35.8% in vacuum. The room-temperature ductility reduced to 20% in air and 15.3% in distilled water. The reduction in ductilities is accompanied by a change in fracture mode from ductile transgranular to mixed transgranular and intergranular fracture. The grain-boundary fracture was observed mainly at corners of the fracture surface, indicating that moisture-induced hydrogen diffuses from surface to interior, mainly through the grain boundaries, and causes intergranular fracture. Note that the yield strength and work hardening behavior are insensitive to test environment. The environmental embrittlement in  $(\text{Co},\text{Fe})_3\text{V}$  was completely eliminated by increasing strain rate from  $3.3 \times 10^{-5}$  to  $3.3 \times 10^{-1}\text{s}^{-1}$  [33].

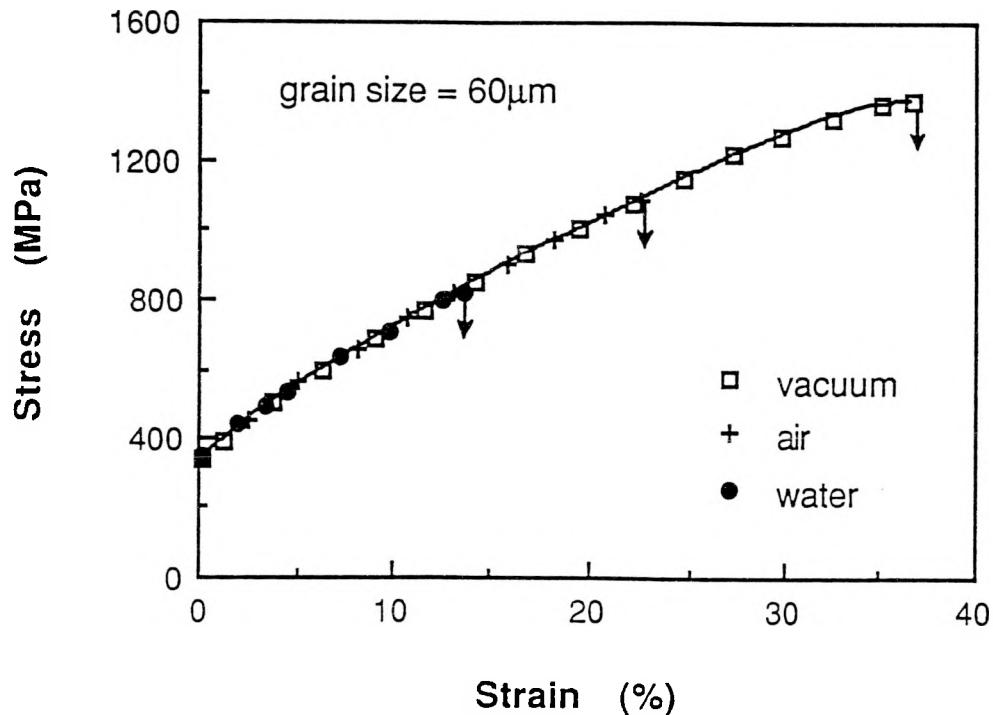


Figure 3. Effect of test environment on stress-strain curves of  $(\text{Co}, \text{Fe}_3)\text{V}$  tested at room temperature [33].

Recently, Takasugi et al. [34,35] and Liu et al. [36] have studied the effect of test environment on room-temperature tensile properties of  $\text{Ni}_3(\text{Si},\text{Ti})$  and  $\text{Ni}_3\text{Si}$ , respectively.  $\text{Ni}_3\text{Si}$  showed no appreciable plastic deformation when tested in air but an elongation of 7.5% when tested in dry oxygen (Table 5). This result demonstrates that  $\text{Ni}_3\text{Si}$  is prone to environmental embrittlement at ambient temperatures. Since the elimination of the

environmental effect by testing in dry oxygen does not lead to extensive ductility (e.g., 30% or above) and complete suppression of intergranular fracture in the silicide, the environmental effect appears not to be the sole source of grain-boundary brittleness in  $\text{Ni}_3\text{Si}$ . This is further indicated by comparison of the tensile data of  $\text{Ni}_3\text{Si}$  and  $\text{Ni}_3(\text{Si},\text{Ti})$ . As shown in Table 5,  $\text{Ni}_3(\text{Si},\text{Ti})$ , like  $\text{Ni}_3\text{Si}$ , is also susceptible to environmental embrittlement. The  $\text{Ni}_3(\text{Si},\text{Ti})$  alloy, however, exhibited a considerable ductility (7%) when tested in moist air at room temperature. It exhibited excellent ductility (29%) when tested in vacuum, indicating that the titanium addition enhances intrinsic grain-boundary properties (such as grain-boundary cohesion) of  $\text{Ni}_3\text{Si}$ , as suggested by Takasugi and Izumi (37,38). The effect of boron additions on environmental embrittlement will be discussed in the next section.

TABLE 5. Effect of Test Environment on Room-Temperature Tensile Properties of  $\text{Ni}_3\text{Si}$  (22.5 at. % Si) and  $\text{Ni}_3(\text{Si},\text{Ti})$  Alloys<sup>a</sup>

Alloy	Test environment	Tensile ductility (%)	Yield strength, MPa (ksi)	Ultimate strength, MPa (ksi)
$\text{Ni}_3\text{Si}$	Air	~ 0 <sup>b</sup>	<sup>b</sup>	627 (91.0)
$\text{Ni}_3\text{Si}$	Vacuum	4.7	677 (98.3)	853 (123.8)
$\text{Ni}_3\text{Si}$	Oxygen	7.5	685 (99.4)	1040 (151.0)
$\text{Ni}_3(\text{Si},\text{Ti})$	Air	7	606 (88)	813 (118)
$\text{Ni}_3(\text{Si},\text{Ti})$	Vacuum	29	586 (85)	1323 (192)
B-doped $\text{Ni}_3(\text{Si},\text{Ti})^c$	Air	36	599 (87)	1323 (192)
B-doped $\text{Ni}_3(\text{Si},\text{Ti})^c$	Vacuum	34	599 (87)	1323 (192)

<sup>a</sup>Alloys containing 9.5 at. % Ti [34].

<sup>b</sup>Fracture prior to macroscopic yielding.

<sup>c</sup>Doped with 50 ppm boron [34].

In addition to  $\text{Co}_3\text{Ti}$ ,  $(\text{Co},\text{Fe})_3\text{V}$ ,  $\text{Ni}_3\text{Si}$ , and  $\text{Ni}_3(\text{Si},\text{Ti})$ , the environmental effect was observed in other  $\text{Ll}_2$ -ordered intermetallics, such as  $\text{Ni}_3(\text{Al},\text{Mn})$  [14] and Be-doped  $\text{Ni}_3\text{Al}$  [39]. The titanium aluminide,  $\text{TiAl}$ , has the  $\text{Ll}_0$ -ordered structure, which is also a derivative of the fcc structure. Recently, Nakamura [40] has found that the bend ductility of  $\text{TiAl}$  (50 at. % Al) is highly susceptible to environmental embrittlement at room temperature as shown in Fig. 4. The aluminide fractured almost immediately after macroscopic yielding when bend testing in air. It showed, on the other hand, a significant plastic strain when testing in vacuum. The bend strain fell between the two limits when tested in hydrogen atmosphere. All these results are essentially consistent with the moisture-induced environmental embrittlement observed in  $\text{FeAl}$ .

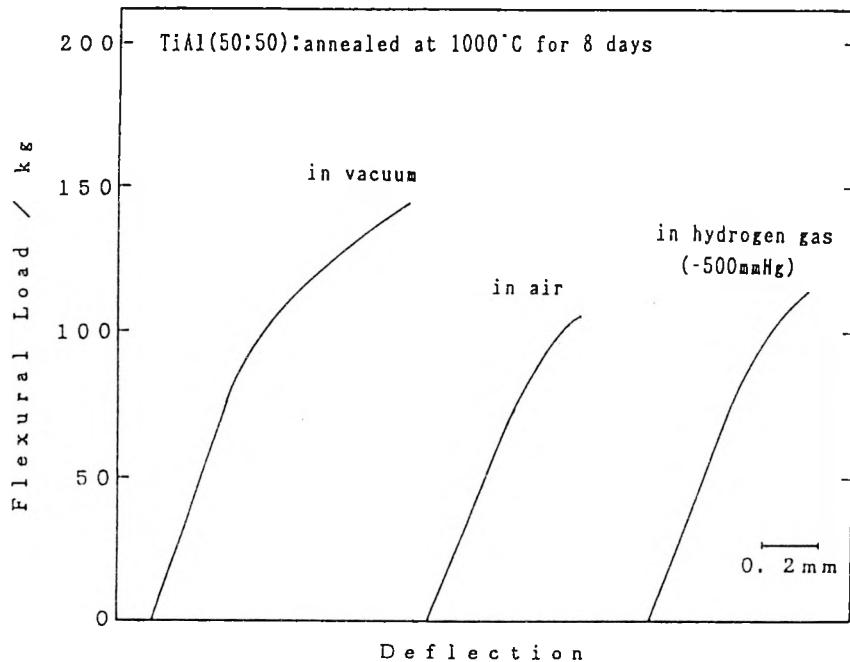


Figure 4. Effect of test environment on load-deflection curves of TiAl (50% Al) bend tested at room temperature [40].

#### 4. Alloy design of ordered intermetallics

As shown in the foregoing sections, environmental embrittlement is a major cause of the brittle fracture and low ductility of many ordered intermetallics at ambient temperatures. The environmental problem has to be solved satisfactorily in order to use intermetallic alloys as engineering materials. There are possible ways to alleviate this problem:

- (1) to control surface composition to reduce generation of hydrogen from the moisture/intermetallic reaction [Eq. (1)],
- (2) to reduce bulk and grain-boundary diffusion of hydrogen by alloying additions,
- (3) to reduce the solubility limit of hydrogen in the material,
- (4) to refine microstructure (such as grain size) to reduce stress concentration, and
- (5) to lower yield strength.

All these are metallurgical means possible to reduce generation of hydrogen at alloy surfaces, to slow down penetration of hydrogen into the material, and to reduce stress concentration at microcrack tips.

Recently, considerable efforts have been devoted to alleviating environmental embrittlement in intermetallic alloys. The most interesting one is to solve the environmental embrittlement in  $\text{Co}_3\text{Ti}$  by alloying. In this study, Izumi and Takasugi [15,18] added individually a variety of alloying elements to  $\text{Co}_3\text{Ti}$  containing 23 at. % Ti. As indicated in Fig. 5, the elements Y, Ta, Cr, Mo, W, and Ge at a level of 3 at. % appear not to significantly affect environmental embrittlement, whereas the elements Fe and Al completely suppress the embrittlement. This result has demonstrated that the environmental embrittlement in intermetallics can be effectively reduced or completely

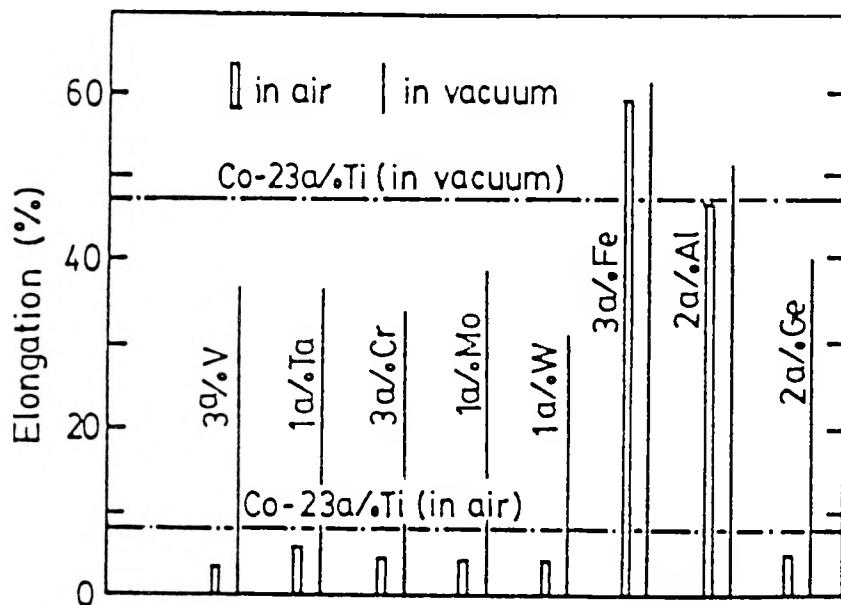


Figure 5. Effect of alloy addition on room-temperature tensile elongation of  $\text{Co}_3\text{Ti}$  (23 at. % Ti) tested in air and vacuum [15,18].

eliminated by alloy additions. The beneficial effect of iron has been attributed to creation of a more homogeneous electronic distribution at grain boundaries where some of the Co-Ti bonds are replaced by Co-Fe bonds. This suggestion appears to be reasonable; however, it is difficult to explain why aluminum is as effective as iron in reducing the embrittlement.

Boron has been found to be effective in reducing environmental embrittlement of grain boundaries in certain  $\text{Ll}_2$  intermetallics. As shown in Table 5, undoped  $\text{Ni}_3\text{Si}$  and  $\text{Ni}_3(\text{Si},\text{Ti})$  are prone to environmental embrittlement, whereas boron-doped  $\text{Ni}_3(\text{Si},\text{Ti})$  is insensitive to test environment at room temperature [34,35]. As a matter of fact, the boron-doped  $\text{Ni}_3(\text{Si},\text{Ti})$  showed excellent ductility (34 to 36%) when tested in both air and vacuum. This result clearly indicates that boron is very effective in alleviating environmental embrittlement in  $\text{Ni}_3(\text{Si},\text{Ti})$ . Carbon-doped  $\text{Ni}_3(\text{Si},\text{Ti})$  also exhibited an excellent ductility, independent of test environment at room temperature. Boron and carbon are known to segregate strongly to grain boundaries in  $\text{Ni}_3(\text{Si},\text{Ti})$ , and their beneficial effect may come from reducing diffusion through reduction in site occupation by hydrogen at the boundaries [35].

$\text{Ni}_3(\text{Al},\text{Mn})$  [14] and beryllium-doped  $\text{Ni}_3\text{Al}$  [39] showed environmental embrittlement in air, whereas boron-doped  $\text{Ni}_3\text{Al}$  is not sensitive to test environment and strain rate (Fig. 6) [41]. The difference between beryllium and boron doping is that beryllium occupies substitutional sites while boron takes interstitial sites in the aluminide. Also, beryllium is not known to segregate to  $\text{Ni}_3\text{Al}$  grain boundaries. Boron, on the other hand, does not alleviate environmental embrittlement in  $\text{Co}_3\text{Ti}$ , as reported by Takasuki and Izumi [13]. In this case, it is possible that boron does not segregate to grain boundaries in  $\text{Co}_3\text{Ti}$ . Auger study is required to verify this point.

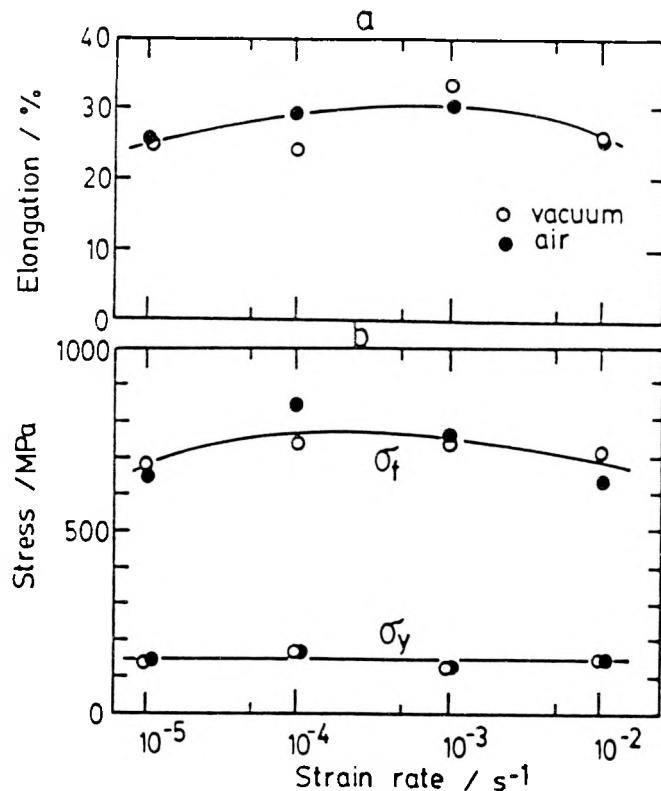


Figure 6. Effect of strain rate on tensile properties of boron-doped  $\text{Ni}_3\text{Al}$  (24 at. % Al) tested at room temperature in air and vacuum [41].

$\text{Fe}_3\text{Al}$  and  $\text{FeAl}$  exhibited severe embrittlement when tested in moist air at ambient temperatures [9-12,28,42,43]. Recent effort on alloy design of  $\text{Fe}_3\text{Al}$  by McKamey et al. [42,44,45] showed that the ductility of the aluminide can be substantially improved by increasing aluminum content from 25 to 28% and by adding chromium at a level of 2 to 6%. The increase in aluminum concentration sharply decreases the yield strength of the aluminide. The chromium additions double the tensile ductility when there are oxide scales formed on specimen surfaces during hot rolling or subsequently heat treatment in air [46]. As the oxide scales are removed by electropolishing, there is no apparent difference in tensile ductilities of  $\text{Fe}_3\text{Al}$  with and without the chromium additions. Refinement of grain structure and control of degree of recrystallization have been proven to be effective in improving the room-temperature ductility of  $\text{Fe}_3\text{Al}$  and  $\text{FeAl}$  alloys tested in moist air [27,42,43,47,48]. Preoxidation and formation of protective oxide scales on surface also reduce environmental embrittlement of iron and nickel aluminides in air or hydrogen environments [17,47].

## 5. Summary and Concluding Remarks

Recent studies have demonstrated that environmental embrittlement is a major cause of low ductility and brittle fracture in many ordered intermetallics. Surprisingly, the embrittlement occurs when intermetallic alloys are tensile tested in air at conventional

strain rates at ambient temperatures. It involves the reaction of reactive elements (such as Al, Si, Ti, V, etc.) in intermetallics with moisture in air, and the generation of atomic hydrogen. The embrittlement is a dynamic process involving continuous hydrogen generation and crack propagation during tensile tests.

Both bcc- and fcc-ordered intermetallics show severe environmental embrittlement at ambient temperatures. In the case of iron aluminides with bcc-ordered crystal structures, the embrittlement occurs along cleavage planes, resulting in brittle cleavage fracture. The brittle cleavage was suppressed when FeAl alloys were tested in dry oxygen instead of moist environments. In the case of L1<sub>2</sub> intermetallics, the loss in ductility is accompanied by a change in fracture mode from ductile appearance to brittle grain-boundary separation. The fcc-ordered intermetallics prone to environmental embrittlement include Co<sub>3</sub>Ti, (Co,Fe)<sub>3</sub>V, Ni<sub>3</sub>Si, Ni<sub>3</sub>(Si,Ti), Ni<sub>3</sub>(Al,Mn), Be-doped Ni<sub>3</sub>Al, and TiAl.

Environmental embrittlement as discussed here is similar to traditional hydrogen embrittlement [49], except that, in this case, hydrogen is released from moisture. The underlying mechanisms suggested for hydrogen embrittlement in ordered intermetallics can be grouped into three categories: (1) reduction of atomic bonding across cleavage planes, (2) reduction of cohesive strength across grain boundaries, and (3) influence of dislocation activities and crack-tip plasticity. Environmental embrittlement in the bcc-ordered iron aluminides occurs along cleavage planes rather than grain boundaries, suggesting the reduction of cleavage strength by absorbed hydrogen [9-12]. This is supported recently by first-principles total-energy calculations, which indicate that absorbed hydrogen significantly reduces the cleavage strength and energy of FeAl (by as much as 20 to 70%, depending on the hydrogen concentration) [24]. Superdislocations have been suggested to be the carrier for enhanced diffusion of hydrogen to crack tips [50]. In the case of fcc-ordered intermetallics [13-19,34,35] such as Ni<sub>3</sub>(Al<sub>0.4</sub>Mn<sub>0.6</sub>), Co<sub>3</sub>Ti, (Fe,Ni)<sub>3</sub>V, (Co,Fe)<sub>3</sub>V, and Ni<sub>3</sub>(Si,Ti) alloys, hydrogen embrittlement takes place mainly along grain boundaries, suggesting the reduction of cohesive strength along the boundaries. Fast diffusion [51,52] and segregation [53] of hydrogen to grain boundaries have been detected experimentally in conjunction with hydrogen embrittlement in conventional metals and alloys, but not yet in ordered intermetallics. In situ transmission electron microscope (TEM) studies of crack-tip plasticity indicate that hydrogen causes the dislocation velocity and crack growth rate to increase significantly in Ni<sub>3</sub>Al and Fe<sub>3</sub>Al alloys [54,55]. This observation basically supports the mechanism of decohesion in the presence of hydrogen at crack tips.

Limited effort has been devoted to alleviating environmental embrittlement in ordered intermetallics. Izumi and Takasugi [15] found that the embrittlement in Co<sub>3</sub>Ti can be completely eliminated by alloying with 3% Fe or Al. Boron is effective in reducing environmental embrittlement of grain boundaries in Ni<sub>3</sub>Si and Ni<sub>3</sub>(Si,Ti), but not in Co<sub>3</sub>Ti. The beneficial effect of boron is believed to be due to the fact that boron tends to segregate to grain boundaries and thus reduces the site occupation by hydrogen at the boundaries. In other words, the segregation of boron may slow down the penetration of hydrogen along the boundaries. The environmental embrittlement in iron aluminides was reduced by control of alloy composition, surface condition, and microstructure [42-48]. A tensile ductility as high as 20% has been achieved for Fe<sub>3</sub>Al alloys tested in moist air at room temperature [42,43,48].

It should be noted that the environment affects not only ductility, but also alloy preparation and fabrication. For instance, iron aluminides showed hair-line cracks on cutting surfaces when water was used as a coolant during cutting processes [54]. The cracking is caused by hydrogen generated from the reaction of iron aluminides at the cutting edge with water coolant. It can be eliminated by either control of cutting parameters or change of coolant (e.g. use of an oil coolant). Iron aluminides also absorb moisture from environments, resulting in the formation of porosities (like the formation of

pin holes in aluminum alloys) during melting and casting. The porosity density can be dramatically reduced either by casting in an inert-gas environment or by adding alloying additions [47].

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