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Effect of atomic ordering on environmental embrittlement of (Co, Fe)$_3$V alloy in gaseous hydrogen①

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[Abstract] The diffusible hydrogen contents in precharged (Co, Fe)$_3$V alloy were measured. It is found that atomic ordering can not promote hydrogen penetration in the (Co, Fe)$_3$V alloy. The ultimate tensile strength (UTS) and ductilities in various condition were also investigated. The results show that the UTS and elongation of disordered alloy are higher than that of ordered one with fixed diffusible hydrogen content and (Co, Fe)$_3$V alloy with ordered structure is highly susceptible to the embrittlement in hydrogen gas. The factor which may affect the susceptibility to the embrittlement of (Co, Fe)$_3$V alloy in hydrogen gas is mainly due to that the atomic ordering may accelerate the kinetics of the catalytic reaction for the dissociation of molecular hydrogen into atomic hydrogen. However, it can not be roled out that atomic ordering intensifies planar slip and restricts cross-slip at the grain boundaries and enhances the susceptibility of the alloy to hydrogen embrittlement.

[Key words] (Co, Fe)$_3$V alloy; atomic ordering; environmental embrittlement; hydrogen gas
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1 INTRODUCTION

Since Kuruvilla and Stoloff[1] first reported that hydrogen embrittlement is much more severe for ordered alloys than for disordered alloys of identical composition, and several investigators[2~5] also reported the similar results later. It is suggested that the reactive element (usually as the minority component of ordered intermetallics) reacts with moisture (or water), and thereby atomic hydrogen can be released from H_2O into materials[6]; while the transition element (usually as the majority component of ordered intermetallics) plays a catalytic role to decompose H_2 gas, and thereby atomic hydrogen can be injected into materials[7~10]. The influence of atomic ordering on moisture-induced embrittlement is some ambiguous. Nishimura et al[4] found that the $Co_{60}Fe_{16.5}V_{23.5}$ alloy exhibits a typical environmental embrittlement in air in $L1_2$-ordered state, but the alloy exhibits no sign of environmental embrittlement in the disordered state. Our previous results showed that ordering of the (Co, Fe)$_3$V alloy[5] and Ni_4Mo alloy[11], which are composed of active elements V and Mo, has no, or a little influence on the moisture-induced environmental embrittlement. However, the influence of atomic ordering on gaseous hydrogen-induced embrittlement is very clear[8, 10].

There are three points of view to explain the effect of atomic ordering on the environmental embrittlement. Stoloff et al and Takasugi et al[2, 3] suggested that atomic ordering may promote hydrogen atoms to segregate at grain boundaries and lower the grain boundary cohesion through the intense planar slip and restricted cross-slip at the grain boundaries of the superlattice dislocation. Nishimura et al[4] suggested that the atomic-size cavities at grain boundaries of strongly ordered alloys serve as hydrogen trapping sites. Our previous study[5] suggested that atomic ordering of some intermetallics may accelerate the kinetics of the catalytic reaction for the dissociation of molecular hydrogen into atomic hydrogen on the surface of transition metals resulting in more severe embrittlement of the alloy. To clarify the effect of atomic ordering on environmental embrittlement of (Co, Fe)$_3$V alloy in hydrogen gas, there are four aspects investigated in this paper. Firstly, the diffusible hydrogen contents in precharged (Co, Fe)$_3$V alloys with disordered and ordered structure are measured. Secondly, (Co, Fe)$_3$V alloys with disordered and ordered structure were tensile tested dynamically at room temperature. Thirdly, the critical partial pressure of hydrogen gas causing brittle fracture in disordered and ordered (Co, Fe)$_3$V alloys is measured. Fouthly, the disordered and ordered alloys are tensile tested at a low pressure of dry hydrogen atmospheres when a hot tungsten filament is introduced.

2 EXPERIMENTAL

A 1.0 kg button of (Co, Fe)$_3$V alloy having the nominal composition of 60% Co-16.5% Fe-23.5% V (mole fraction) was arc melted in argon atmosphere using high-purity cobalt and master alloy of Fe-

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56.2V. To ensure the chemical homogeneity, the button was remelted three times. The button with a thickness of about 23 mm was hot rolled at 1 100 ℃ to 3 mm in thickness, and then cold rolled to about 1.5 mm.

The tensile tests were performed under various pressure of hydrogen gas. Some tensile tests were conducted at room temperature (25 ℃). The hydrogen charging tests were performed in an aqueous electrolytic solution of 0.5 mol/L H_2SO_4 containing 0.05 g/L $NaAsO_3$. The $NaAsO_3$ was added to poison the hydrogen recombination reaction, and to enhance the hydrogen absorption rate. The specimens tested simultaneously with hydrogen charging were coated with lacquer only on the gage section and one end exposed for electrical contact. This was done to limit hydrogen absorption to the gage section only. The specimens were charged at various current densities during the test. If not illustrated, the nominal strain rate is $2 \times 10^{-3} s^{-1}$. Fracture surfaces were examined in a scanning electron microscope.

The contents of diffusible hydrogen in cathodically charged specimens were measured by the glycerol volumetric technique[12]. The glycerol bath was maintained at room temperature (about 11 ℃) and the length of the initial column of glycerol inside the collecting tube with an inner diameter of 3 mm was about 200 mm above the glycerol level of the bath. The height of the hydrogen column was measured after 48 h collecting and the content of hydrogen was calculated. The minimum scale of the height of the hydrogen column is 0.01 mL. Before collecting diffusible hydrogen, the specimens with size of 0.6 mm × 9 mm × 19 mm were electro-discharge machined from the sheets and polished by a finer abrasive paper to remove surface damage, then cathodically charged with hydrogen at various current density in the 0.5 mol/L H_2SO_4 solution (added 0.05 g/L $NaAsO_3$) kept at a constant temperature of 20 ℃.

3 RESULTS

3.1 Effect of atomic ordering on diffusible hydrogen contents

Fig. 1 shows the plots of diffusible hydrogen contents of $(Co, Fe)_3V$ alloys in disordered and ordered condition against the charging current density at 20 ℃ charging for 180 min. The hydrogen content increased with the charging current. An interesting result is that the diffusible hydrogen contents in disordered condition were as much as, or slightly higher than that in ordered condition.

Fig. 2 shows the kinetics of evolution of hydrogen at room temperature (11 ℃), as measured by the glycerol volumetric method, from specimens precharged at 20 ℃ for 180 min with the current density of 500 A/m². The result shows that there is no or a little difference in disordered and ordered condition.

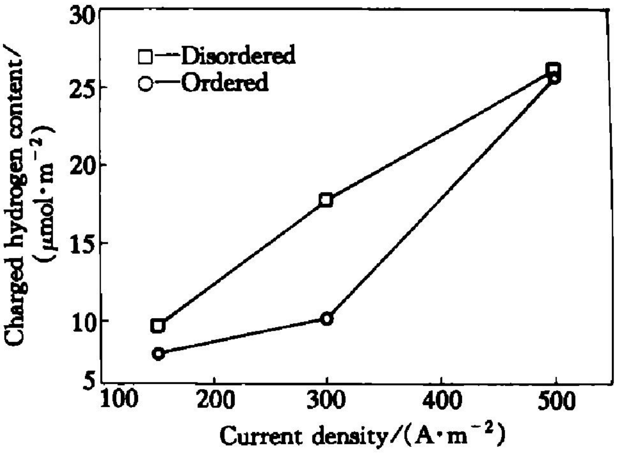

Fig. 1 Diffusible hydrogen contents against charging current density at 20 ℃ charging for 180 min

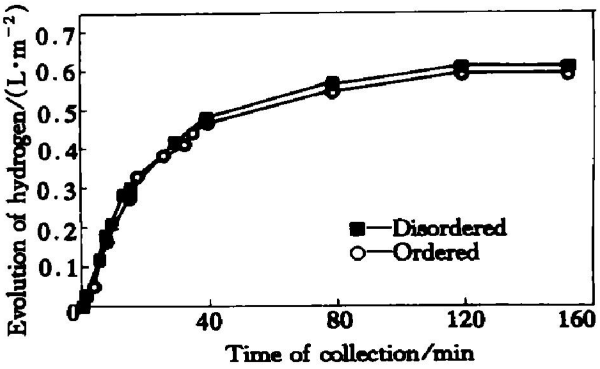

Fig. 2 Kinetics of evolution of hydrogen at room temperature (11 ℃) after charging at 20 ℃ for 180 min (current density 500 A/m²)

In general lattice diffusion of hydrogen is reported to be slower in $L1_2$-ordered state than in disordered state[13]. While it is possible that hydrogen penetrates in the alloy predominantly by grain-boundary diffusion. Unfortunately, the diffusion data along grain-boundary are not available at present. However, from our results, atomic ordering can not promote hydrogen to penetrate into the alloy.

3.2 Tensile properties tested simultaneously with hydrogen charging

Fig. 3 shows the tensile properties of hydrogen charging $(Co, Fe)_3V$ alloys with disordered and ordered structure with different current density. It shows that ultimate tensile strength (UTS) and elongation are decreased with increasing current density in both disordered and ordered condition. The tensile properties tested at strain rate of $5 \times 10^{-5} s^{-1}$ with current density of 150 A/m² were also shown. With decreasing the strain rate, the UTS and elongation of disordered and ordered $(Co, Fe)_3V$ alloys both decreased similarly. The UTS of $(Co, Fe)_3V$ alloy with disordered structure is about 100 MPa higher than that with ordered structure, and the elongation of

(Co, Fe)$_3$V alloy with disordered structure is also about 4% higher than that with ordered structure at any current density and strain rate except testing in the solution without current. In fact, atomic ordering can not promote hydrogen to penetrate into the alloy at static state. Therefore, at dynamic state, the susceptibility to hydrogen embrittlement for both disordered and ordered alloys with fixed diffusible hydrogen content is comparable. The difference may result from the different dislocation structures. The intense planar slip and restricted cross-slip at the grain boundaries of the superlattice in the ordered alloy can promote hydrogen atoms to segregate at the grain boundaries and lower the grain boundaries cohesion[2, 3].

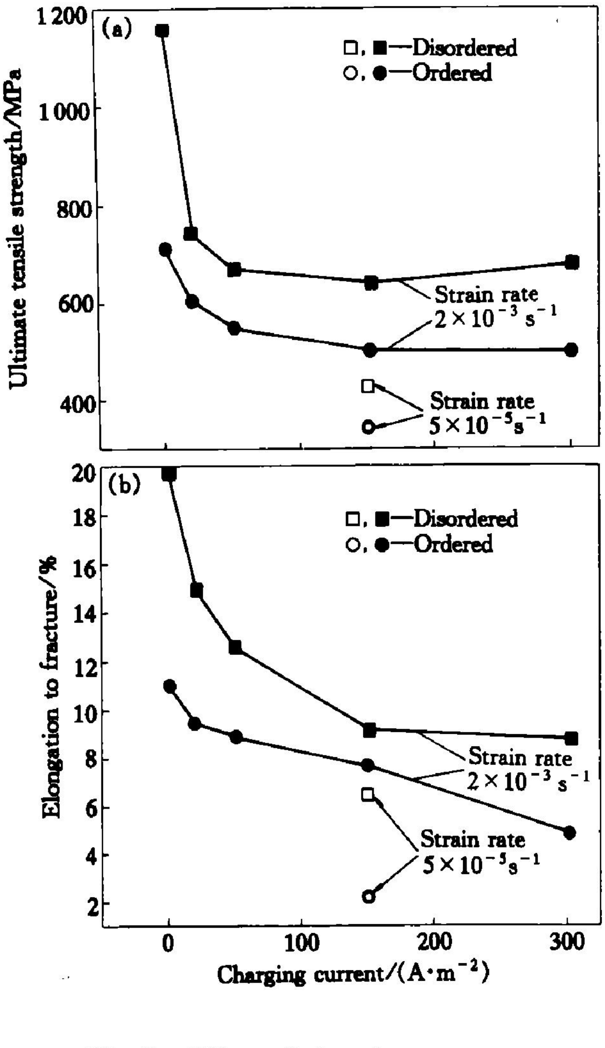

Fig. 3 Effect of charging current on ultimate tensile strength (a) and ductilities (b) of disordered and ordered (Co, Fe)$_3$V alloys

The fracture surface morphologies of the hydrogen charging (Co, Fe)$_3$V alloys with different current density are shown in Fig. 4. When being tested in the aqueous electrolytic solution without any current (as shown in Fig. 4(a) and (d)), the fractograph exhibits predominantly intergranular fracture with ductile dimple fracture around the rim in both disordered and ordered condition. When being tested at current density of 20A/m^2 (as shown in Fig. 4(b) and (e)) or 300A/m^2 (as shown in Fig. 4(c) and (f)), the fracture surface of disordered alloy shows some regions of ductile tearing and a large secondary crack, while that of ordered alloy shows mainly intergranular fractograph. The different fractography between disordered and ordered alloy may be corresponding to the different dislocation structure too. The intense planar slip and restricted cross-slop at the grain boundaries of the superlattice in the ordered alloy may result in intergranular fracture. The dislocation in the disordered alloy can easily cross-slip and promote hydrogen redistribution, leading to microcrack formation in the vicinity of the main crack. Secondary cracks are quite common in hydrogen embrittlement of steels[14, 15].

3.3 Critical pressure of hydrogen gas

Fig. 5 shows the dependence of ultimate tensile strength and elongation of disordered and ordered (Co, Fe)$_3$V alloys on the pressure of hydrogen. These data were obtained by the following experimental procedure: at first the vacuum chamber was evacuated to pressure lower than 3×10^{-2}Pa and backfilled with dry hydrogen, then released from hydrogen-storage materials (the purity is 99.9999%) to the desired pressure. As shown in Fig. 5, for disordered alloy there is a little change in UTS and ductility with increasing H_2 pressure, until the pressure reaches a critical value, at which the UTS and ductility drop precipitously. However, for the ordered alloy the UTS and elongation are decreased gradually with increasing hydrogen pressure. The critical pressure causing the reduction of UTS and ductility is more than 4 orders larger in disordered (Co, Fe)$_3$V alloy than in ordered one, illustrating that (Co, Fe)$_3$V alloy with ordered structure is highly susceptible to gaseous hydrogen-induced environ- mental embrittlement. Furthermore, at more than 4×10^4Pa pressure of hydrogen employed, the UTS and ductility of (Co, Fe)$_3$V alloy in disordered state are still higher than those in ordered state. The difference of both disordered and ordered alloy tested at as high as 4×10^4Pa pressure of hydrogen is the same as that of hydrogen charging test.

Accompanying this drop in the UTS and ductility with increasing H_2 pressure there is a change from predominantly transgranular fracture in vacuum (as shown in Fig. 6(a) and (c)) to predominantly intergranular fracture in 0.1MPa H_2 (as shown in Fig. 6(b) and (d)) in both disordered and ordered alloys.

3.4 Effect of an external source of atomic H

Atomic H can, in principle, be generated by several means, For example, by the dissociation of H_2O or H_2 or hydrogen charging. However, if an ion gage is used to measure gas pressures, its hot tungsten

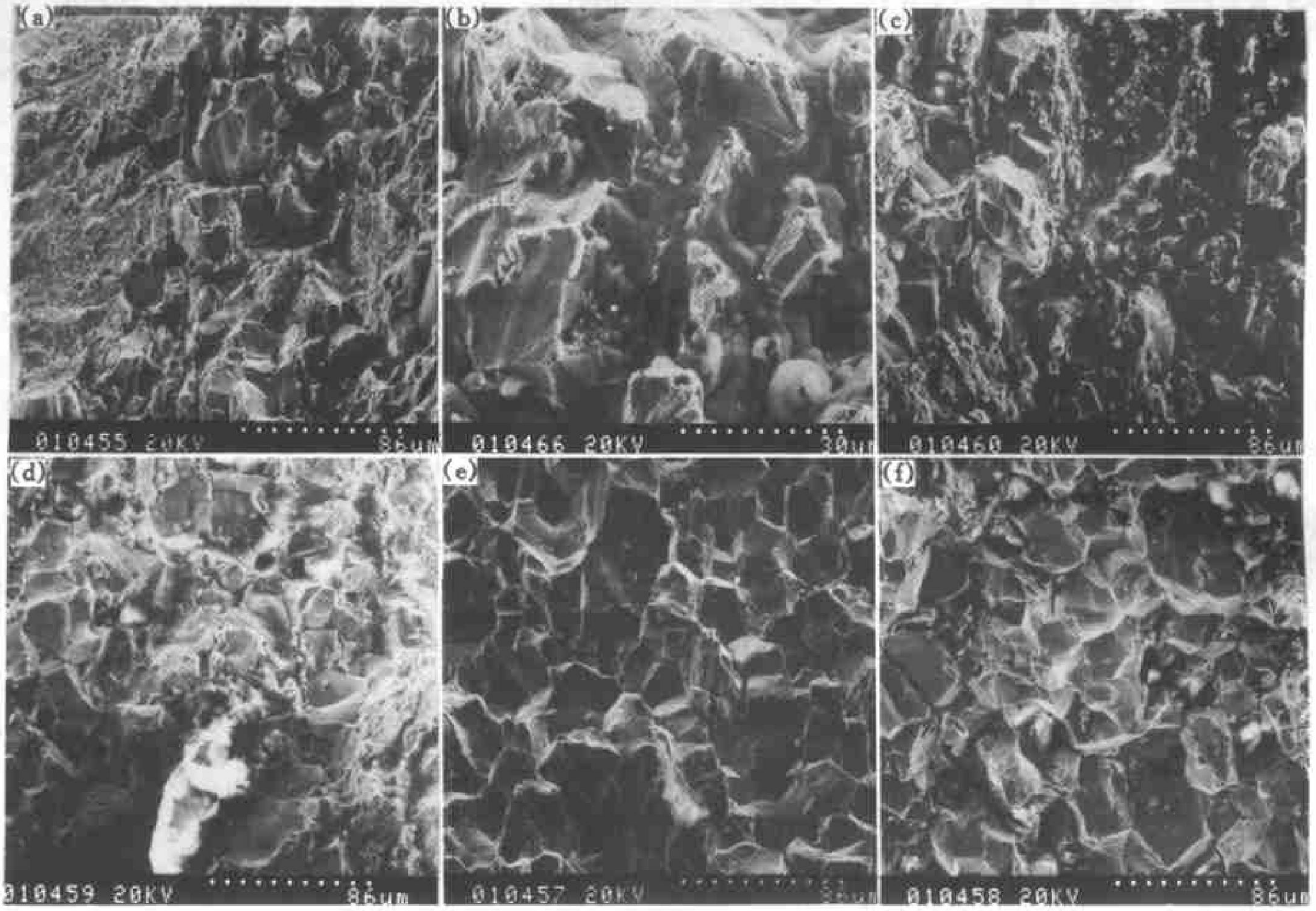

Fig. 4 Fracture surface morphologies of hydrogen charging (Co, Fe)$_3$V alloys
(a) —With disordered structure; $J = 0\,A/m^2$; (b) —With disordered structure; $J = 20\,A/m^2$; (c) —With disordered structure; $J = 300\,A/m^2$; (d) —With ordered structure; $J = 0\,A/m^2$; (e) —With ordered structure; $J = 20\,A/m^2$; (f) —With ordered structure; $J = 300\,A/m^2$

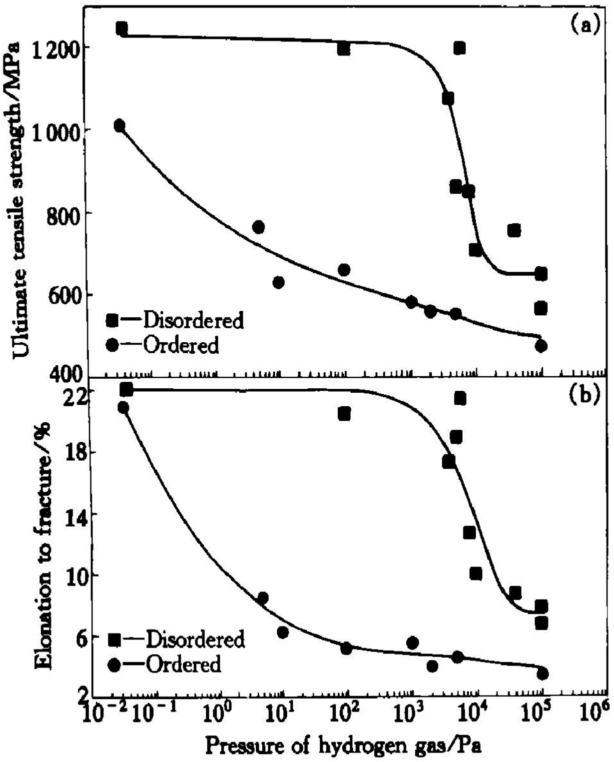

Fig. 5 Effect of H_2 pressure on ultimate tensile strength (a) and ductilities (b) of (Co, Fe)$_3$V alloys

filament can dissociate molecular H_2 into atomic H. Table 1 summarizes the effects of the hot tungsten filament on the room temperature tensile properties of fully disordered and ordered (Co, Fe)$_3$V alloys. When the ion gage was turned off, the ductility of the fully disordered alloy at low hydrogen pressure (5×10^3 Pa) is as high as 18.8%, while fully ordered (Co, Fe)$_3$V displays brittle fracture with very limited ductility (4.6%), indicating that atomic ordering has strong effect on environmental embrittlement. When the ion gage was turned on, the ductility of the alloys both in the fully disordered and ordered states is nearly identical, indicating that if the degree of hydrogen dissociation is fixed, the sensitivity of the ordered or disordered alloys to hydrogen embrittlement is comparable.

Fig. 7 shows the fracture surface morphologies of (Co, Fe)$_3$V alloy tensile tested at room temperature at low hydrogen pressure of 5×10^3 Pa with the ion gage turned on or off. When the ion gage was turned off, the fracture surface of the fully disordered alloy exhibits ductile transgranular fracture (as shown in Fig. 7(a)); while the fracture surface of the fully ordered specimen is found to be almost intergranular (as

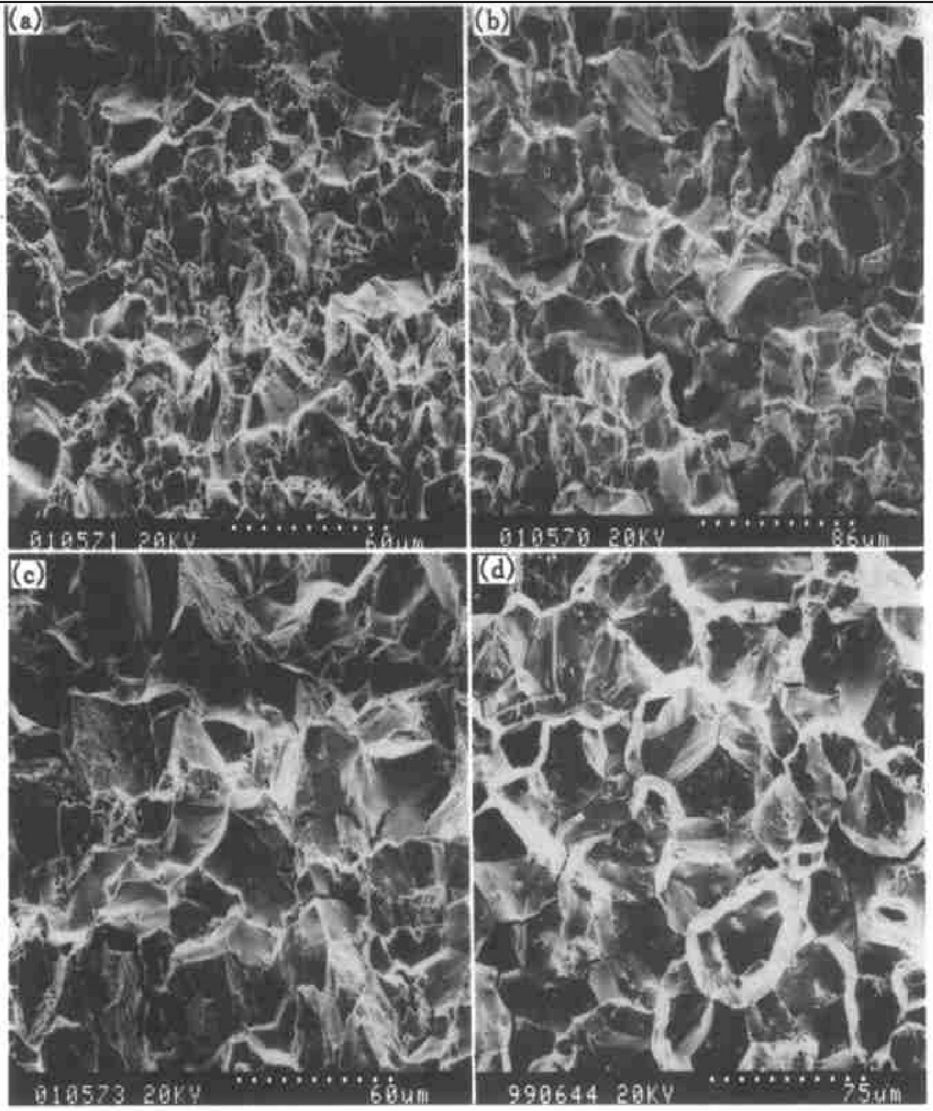

Fig. 6 Fracture surface morphologies of (Co, Fe) $_3$V alloys
(a) —With disordered structure, in vacuum; (b) —With disordered structure, in 0.1 MPa H_2;
(c) —With ordered structure, in vacuum; (d) —With ordered structure, in 0.1 MPa H_2

Table 1 Effects of hot tungsten filament and atomic ordering on tensile properties of (Co, Fe) $_3$V alloy ($\dot{\varepsilon} = 2 \times 10^{-3} s^{-1}$)

Alloy	With ion gage turned off		With ion gage turned on	
	δ/ %	σ_b/ MPa	δ/ %	σ_b/ MPa
Disordered	18.8	861	5.6	547
Ordered	4.6	552	4.5	588

shown in Fig. 7(b)) . When the ion gage was turned on, the fracture surfaces of fully disordered and ordered (Co, Fe) $_3$V display the same brittle intergranular fracture (as shown in Fig. 7(c) and (d)) .

4 DISCUSSION

Nishimura et al[4] suggested that the atomic-size cavities at grain boundaries of strongly ordered alloys serve as hydrogen trapping sites. Therefore hydrogen atoms can segregate extensively at grain boundaries and lower the grain-boundary cohesion. However, if the temperature of the glycerol bath was raised from room temperature to 80 ℃ after outgassing for 48 h, there are no more diffusible hydrogen evolved for both disordered and ordered alloys. And the diffusible hydrogen content of disordered (Co, Fe) $_3$V alloy is comparable to, or higher than that of ordered alloy. It indicates that there may not exist any more strong hydrogen trapping sites at grain boundaries of both disordered and ordered alloys. Therefore, the factor concerning the atomic-size cavities may fail to explain the distinct difference in the susceptibility of the disordered and ordered (Co, Fe) $_3$V alloys to the environmental embrittlement in gaseous hydrogen.

It is well known that it is atomic H which causes severe embrittlement in intermetallics. Our results clearly indicate that either disordered or ordered (Co, Fe) $_3$V alloy is embrittled by an external source of atomic H. The external source of atomic H is introduced by hydrogen charging during testing or by dissociating from H_2 into atomic H by the hot tungsten filament in an ionization gage. When the charging current density is fixed or the ion gage is turned on at the low H_2 pressure, the content of hydrogen on the

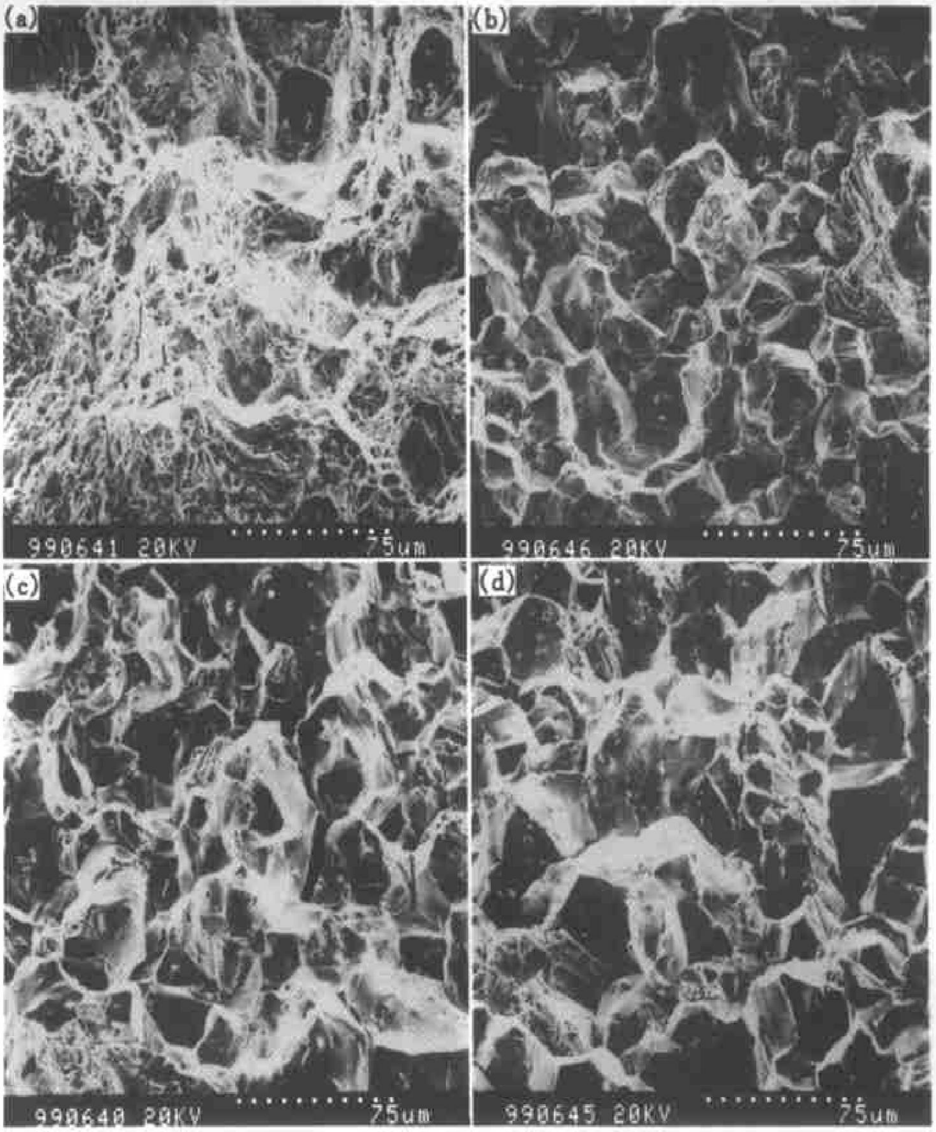

Fig. 7 Fracture surface morphologies of (Co, Fe)$_3$V alloy tensile tested at hydrogen pressure of 5×10^3 Pa
(a) —Fully disordered with gage turned off; (b) —Fully ordered with gage turned off;
(c) —Fully disordered with gage turned on; (d) —Fully ordered with gage turned on

surface of (Co, Fe)$_3$V is fixed. Therefore the sensitivity of the disordered or ordered alloys to hydrogen embrittlement is similar. However, the critical H_2 pressure to cause the reduction of ultimate tensile strength and ductility is much more higher in disordered (Co, Fe)$_3$V alloy than in ordered (Co, Fe)$_3$V alloy. The hydrogen gas-induced environmental embrittlement is believed to result from the following catalytic dissociation reaction of hydrogen gas under stress on the surface of transition metals, such as Fe, Co, Ni, etc[7~10]:

$$H_2 \longrightarrow H + H$$

The atomic H penetrates into metal and segregates at the grain boundaries, and then embrittles the metal. The mechanism is thought to be the promotion of electrons from the partially filled d —band of the transition metal to the anti-bonding s-orbital of the H_2 molecule, thereby destabilizing the H —H bond[16]. Therefore, the catalytic dissociation reaction is strongly influenced by transition metal activation and H_2 adsorption, which is under the control of the outer electron scatterance per atom[17]. Zhu et al suggested that the outer electron of Ni_3Fe partially transferred from Ni atom to Fe atom in ordering process of Ni_3Fe and Ni, and Fe atoms in ordered Ni_3Fe both are beneficial for adsorption of H_2 and promote catalytic reaction. Therefore the different critical pressure of disordered and ordered (Co, Fe)$_3$V alloys may result from the atomic ordering which may accelerate the kinetics of the catalytic reaction for the dissociation of molecular hydrogen into atomic hydrogen.

Without doubt, the ordered alloy is highly susceptible to the embrittlement in atomic hydrogen or hydrogen gas than disordered alloy. Therefore, it can not be roled out the view that atomic ordering can promote hydrogen atoms to segregate at grain boundaries and lower the grain boundary cohesion through the intense planar slip and restricted cross-slip at the grain boundaries of the superlattice dislocation. However, the repulsive forces determining the interatomic distance of transition metals such as iron, cobalt, nickel, etc. are due to the overlapping of their d —

bands[18]. The electrons of the hydrogen atoms in solution in a transition metal will enter the d-bands of the metallic cores. If the outer electron scatterance per atom near the grain boundaries changed in the process of ordering, the electron concentration of these bands changed correspondently even introducing the same contents of hydrogen atom at the grain boundaries. Therefore, atomic ordering may increase the repulsive forces between the metallic cores or decrease the cohesive strength of the grain boundary after introducing hydrogen atom.

5 CONCLUSIONS

1) Atomic ordering can not promote hydrogen penetration in the (Co, Fe)$_3$V alloys.

2) With fixed diffusible hydrogen content, the ultimate tensile strength and elongation of disordered alloy are higher than those of ordered one.

3) (Co, Fe)$_3$V alloy with ordered structure is highly susceptible to the embrittlement in hydrogen gas.

4) The factor which may affect the susceptibility of (Co, Fe)$_3$V alloy to the embrittlement in hydrogen gas is mainly due to that the atomic ordering may accelerate the kinetics of the catalytic reaction for the dissociation of molecular hydrogen into atomic hydrogen.

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