

# Surface diffusivity of atomic deuterium on $\text{Ni}_3(\text{Al}, \text{Ti})$ (110) surface with and without boron<sup>①</sup>

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**[Abstract]** The electron-stimulated desorption was used to measure the surface diffusivity of atomic deuterium on clean and boron-modified  $\text{Ni}_3(\text{Al}, \text{Ti})$  (110) surfaces. Boron dosing was performed using a solid-state boron ion source. Earlier studies showed that boron dissociates water readily at temperatures as low as 130 K and that the resulting atomic hydrogen is bound to the surface strongly. The surface diffusion coefficient of atomic D on 0.05 monolayer boron-modified surface was measured to be about 10 times smaller than that on the clean surface. This slower diffusion of atomic hydrogen may explain why boron improves the ductility of polycrystalline  $\text{Ni}_3\text{Al}$  in moist environments.

**[Key words]** surface diffusion; deuterium; hydrogen;  $\text{Ni}_3\text{Al}$

**[CLC number]** TG 146.1

**[Document code]** A

## 1 INTRODUCTION

It is well accepted that moisture-induced embrittlement is the major cause of the low ductility and intergranular failure of  $\text{Ni}_3\text{Al}$  and other intermetallic alloys<sup>[1]</sup>. During tensile deformation, cracks are generally formed along grain boundaries. Water vapor may react with fresh reactive surfaces (cracks) to produce atomic hydrogen, which then diffuses into crack tips and causes embrittlement. The authors studied the interaction of water with different  $\text{Ni}_3(\text{Al}, \text{Ti})$  single crystal surfaces. These studies revealed that water dissociates on clean  $\text{Ni}_3(\text{Al}, \text{Ti})$  (100) and (110) surfaces, resulting in hydrogen desorption at about 350 and 400 K respectively, while the (111) surface is inactive to water dissociation<sup>[2, 3]</sup>.

In 1979, Aoki and Izumi found that the ductility of  $\text{Ni}_3\text{Al}$  is dramatically improved by microalloying with boron, which occupies interstitial sites. Tensile ductility as high as 50% at room temperature has been achieved in  $\text{Ni}_3\text{Al}$ -based alloys by doping with only 0.1% boron (mass fraction). Many subsequent investigations were carried out to explore the beneficial effect of boron on the ductility of  $\text{Ni}_3\text{Al}$ . Liu et al.<sup>[4-6]</sup> found that boron exhibits a strong tendency to segregate to grain boundaries of  $\text{Ni}_3\text{Al}$ , although the extent of segregation appears to vary from boundary to boundary and depend on the alloy composition. It was proposed later that boron segregation might serve two functions: enhancing grain-boundary cohesion and suppressing the environmental effect<sup>[7, 8]</sup>. Another model<sup>[9-11]</sup> to explain the boron effect is based on the localized composition disorder induced by boron segregation to grain boundaries. This may facilitate

slip transfer across grain boundaries, thereby resulting in less stress concentration and reduced crack nucleation at grain boundaries. King and Yoo<sup>[12]</sup> showed theoretically that slip transmission across a disordered grain boundary is indeed easier.

Recently, The authors used a negative boron ion source to introduce controlled surface coverage of boron<sup>[13]</sup>. This source works by extracting cesium ions ( $\text{Cs}^+$ ) from a solid electrolyte to bombard a boron target. These cesium ions eject boron by sputtering, while deposition of cesium reduces the work function of the surface so that  $\text{B}^-$  emission becomes favorable. This process provides a clean source of low-energy boron ions with adjustable energy and flux. Using this source, a boron-modified  $\text{Ni}_3(\text{Al}, \text{Ti})$  (110) surface readily dissociates water to produce atomic hydrogen, which is bound very strongly to the surface<sup>[13]</sup>. Since the  $\text{B}-\text{H}$  bond dissociation energy (340 kJ/mol) is significantly greater than that for  $\text{Ni}-\text{H}$  (252 kJ/mol), atomic hydrogen might prefer to sit on boron sites. In this case, atomic hydrogen may be less mobile, which should result in lower concentration of atomic hydrogen at the crack tip, thus suppressing hydrogen-induced embrittlement. The primary purpose of this work is to determine the surface diffusivity of hydrogen on boron-free and boron-modified  $\text{Ni}_3(\text{Al}, \text{Ti})$  surfaces, using the technique of electron-stimulated desorption (ESD).

## 2 EXPERIMENTAL

All experiments were carried out in a bakeable stainless steel ultrahigh vacuum chamber with a base pressure of  $(1.5 \sim 3.0) \times 10^{-8}$  Pa equipped with

① [Received date] 2001- 10- 08

sputtering, gas handling, Auger electron spectroscopy, X-ray photoelectron spectroscopy (XPS), residual gas analysis (RGA), and low energy negative boron ion source capabilities. Surface cleaning was done with several cycles of Ar<sup>+</sup> ion bombardment at 2 kV, 45° angle of incidence, followed by annealing at about 1 000 K for 30 min. In this study, D<sub>2</sub>O was used to minimize unwanted H<sub>2</sub>O and H<sub>2</sub> contributions from the background. The gas was purified by multiple freeze-pump-thaw cycles. D<sub>2</sub>O was admitted into the chamber through a needle doser placed about 1 cm from the sample. To achieve different gas exposures, a constant uncorrected pressure of  $1.33 \times 10^{-5}$  Pa was maintained for different lengths of time. Deuterium and hydrogen are taken as equivalent in the following discussion.

A SKION negative ion beam source (Model: NMIBS-CS02) was used to dose the sample with boron ions at 50~150 eV. The surface coverage of boron ( $\theta_B$ ) was determined separately by Auger calibration. One boron monolayer is defined as  $1.1 \times 10^{15}$  atoms/cm<sup>2</sup> (same as the atomic density of the Ni<sub>3</sub>Al (110) plane).

Temperatures were measured by a K-type (chromel-alumel) thermocouple spot-welded to the sample. The sample can be heated to about 1 000 K using a tungsten wire radiation heater mounted behind the sample or cooled to about 90 K via a copper contact with a liquid-nitrogen reservoir. A glass envelope was mounted in front of the RGA ionizer. During thermal desorption, the sample was placed in front of this envelope to minimize detection of background desorption.

Electron-stimulated desorption was used to measure surface diffusion coefficients of atomic deuterium on D<sub>2</sub>O-dosed surfaces. The surface was prepared in the usual way as described above, followed by D<sub>2</sub>O exposure to produce atomic deuterium. An electron beam was then allowed to impinge on this surface (which was kept at a fixed temperature), desorbing the atomic deuterium through electronic excitation (an athermal process). The beam energy was 1.5 keV to ensure excitation of the Ni 2s level. We let the desorption continue until all adsorbed deuterium was removed (as monitored by the RGA). At this point, the electron beam was turned off. A small spot of the surface was then free of deuterium. Due to the surface concentration gradient, surrounding deuterium atoms diffuse inwards to fill the void. Therefore, after some delay time, more deuterium can be desorbed by the electron beam impinging the same spot. The variation of the deuterium desorption signal as a function of delay time is directly related to the surface diffusivity.

Single crystals of Ni<sub>3</sub>(Al, Ti) with 75% Ni-20% Al-5% Ti (mole fraction) were used in this study. 5%

Ti was added to Ni<sub>3</sub>Al to facilitate single crystal growth. After obtaining the required orientation using the back-reflection Laue method, single crystal samples were wire-cut to about 10 mm in diameter and 2 mm thick. Each wafer was mechanically polished using standard metallographic techniques, with the final step using 0.05  $\mu$ m Al<sub>2</sub>O<sub>3</sub>, and then electropolished in a solution of 90% methanol, 10% sulfuric acid at 12 V, 273 K. The (110) orientation was used for the present study.

### 3 RESULTS AND DISCUSSION

Strong B—H bonding may reduce the diffusivity of atomic hydrogen. Since the diffusion of atomic hydrogen to the crack tip plays a fundamental role in moisture-induced embrittlement, it is important to study the extent to which boron may affect the surface diffusion of atomic hydrogen on Ni<sub>3</sub>(Al, Ti) surfaces. After 50 L D<sub>2</sub>O dosing at about 130 K on clean and boron-modified Ni<sub>3</sub>(Al, Ti) surfaces, the sample was slowly warmed up to about 270 K, at which the ESD experiment was performed as discussed in the experimental section.

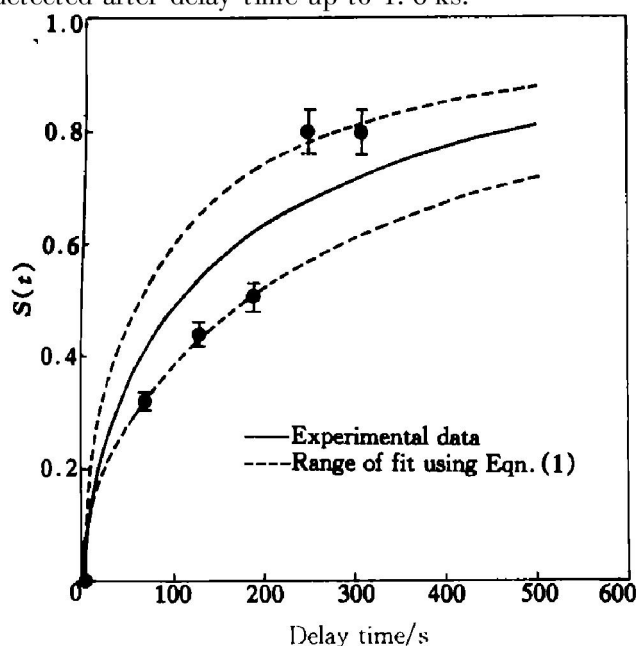
After a circular area under the electron beam was cleared of atomic deuterium, and the electron beam was turned off, diffusion of D from the surrounding to fill this area occurred. Fick's second law has been solved for this situation by Rideal and Tadayon<sup>[14]</sup>. For a uniform surface D concentration outside the circular area at  $t = 0$  diffusing into the circular area at zero coverage, one can show that,

$$S(t) = 1 - 2 \int_0^\infty \frac{J_1^2(ur)}{u} \exp(-Dtu^2) du \quad (1)$$

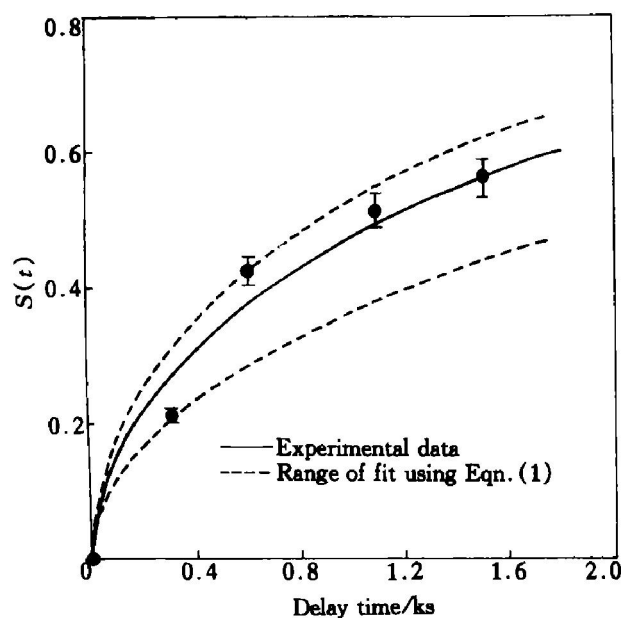
where  $S(t)$  is the total amount of deuterium within this circular area after delay time  $t$ , normalized by the initial amount of deuterium;  $J_1$  is the Bessel function of the first kind of order one;  $D$  is the surface diffusion coefficient of deuterium;  $r$  is the radius of the circular area. Under our experimental conditions,  $r = 108 \pm 6 \mu\text{m}$ .

Fig. 1 shows the normalized D<sup>+</sup> desorption signal versus delay time at 270 K on water-dosed boron-free Ni<sub>3</sub>(Al, Ti) (110). Fitting Eqn. (1) to the data shown in Fig. 1 gives a deuterium surface diffusion coefficient of  $(2.4 \pm 1.1) \times 10^{-7} \text{ cm}^2/\text{s}$  at 270 K. Fig. 2 shows the corresponding data for 0.05 monolayer boron-modified Ni<sub>3</sub>(Al, Ti) (110). The same fitting procedure gives a deuterium surface diffusion coefficient of  $(2.3 \pm 0.5) \times 10^{-8} \text{ cm}^2/\text{s}$  at 270 K. The above data show that the surface diffusion of atomic deuterium is significantly suppressed by only 0.05 monolayer boron on the Ni<sub>3</sub>(Al, Ti) (110) surface. To ensure that the above desorption signal at  $m/e = 2$  is not due to adsorption of background H<sub>2</sub>, the authors performed the same electron-stimulated

desorption on a clean  $\text{Ni}_3(\text{Al}, \text{Ti})$  surface at 270 K without any dosing. No observable electron-stimulated desorption signal above noise level at  $m/e = 2$  was detected after delay time up to 1.6 ks.



**Fig. 1** Normalized electron-stimulated desorption signal of  $\text{D}^+$  ( $m/e = 2$ ) versus delay time at 270 K after 50 L  $\text{D}_2\text{O}$  exposure to clean  $\text{Ni}_3(\text{Al}, \text{Ti})$  (110) surface at 130 K



**Fig. 2** Normalized electron-stimulated desorption signal of  $\text{D}^+$  ( $m/e = 2$ ) versus delay time at 270 K after 50 L  $\text{D}_2\text{O}$  exposure to 0.05 monolayer boron-modified  $\text{Ni}_3(\text{Al}, \text{Ti})$  (110) surface at 130 K

Wan et al.<sup>[15]</sup> studied hydrogen diffusion along grain boundaries in  $\text{Ni}_3\text{Al}$  doped with boron by examination of grain boundary fracture after cathodic charging of hydrogen. The depth of intergranular fracture as measured from the fracture surface was taken as the apparent diffusion distance. They found that the apparent hydrogen diffusivity in  $\text{Ni-23Al-}$

0.012B was about  $2.0 \times 10^{-10} \text{ cm}^2/\text{s}$ , while that in  $\text{Ni-21Al-0.1 B}$  was about  $1 \times 10^{-11} \text{ cm}^2/\text{s}$ . The difference between these results and the authors' is probably due to two reasons: 1) grain boundary diffusivity is generally lower than surface diffusivity; 2) the underestimate of diffusivity by using the depth of the intergranular fracture as the diffusion distance. The depth at which there is sufficient hydrogen concentration to cause intergranular fracture is likely to be much less than the actual diffusion distance. In addition, the diffusion path along grain boundaries is generally tortuous.

Lee et al.<sup>[16]</sup> measured the Auger intensities of oxygen on intergranular fracture surfaces of undoped and boron-doped  $\text{Ni}_3\text{Al}$  after water exposure, indicating less oxygen on the fracture surface of boron-doped sample. Assuming that boron segregation is not primarily associated with a reduction in grain boundary transport of atomic hydrogen, they reached a conclusion that boron may reduce the kinetics of water dissociation. The authors' work indicates that boron does affect the surface diffusion of atomic hydrogen, which means the above assumption is not appropriate. Due to the lower mobility of atomic hydrogen on the boron-modified surface, less atomic hydrogen diffuses from the grain boundaries to the crack tip. Therefore, less atomic sites are available for the subsequent adsorption of water, which explains the lower oxygen Auger intensity on the boron-modified surface.

Based on above results, a consistent picture of how boron suppresses the environmental effect begins to emerge. During room temperature tensile testing of boron-doped  $\text{Ni}_3\text{Al}$  in moist air, water vapor in air interacts with boron or Al on fresh crack surfaces, producing atomic hydrogen. Due to strong B-H bonding and hence smaller surface diffusivity, atomic hydrogen is much less mobile than that on the crack surfaces of boron-free  $\text{Ni}_3\text{Al}$ . This leads to lower concentration of atomic hydrogen at the crack tip, thus suppressing hydrogen-induced embrittlement. The authors believe this is an important mechanism explaining why boron improves the ductility of polycrystalline  $\text{Ni}_3\text{Al}$  in moist air.

## 4 CONCLUSIONS

1) Earlier X-ray photoemission studies demonstrated that water dissociates on boron-modified  $\text{Ni}_3(\text{Al}, \text{Ti})$  (110) at about 130 K. The resulting atomic hydrogen species are strongly bound to the surface.

2) The surface diffusion of atomic hydrogen adsorbed on  $\text{Ni}_3(\text{Al}, \text{Ti})$  (110) is strongly suppressed by 0.05 monolayer of boron on the surface.

3) The slower hydrogen diffusion may explain the suppression of moisture-induced embrittlement of

Ni<sub>3</sub>Al and related alloys by boron.

# ACKNOWLEDGMENT

This work is supported by the National Science Foundation of USA, grant No. DMR 9713052.

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( Edited by YANG Bing )