

## Environments and Hydrogen Uptake

## Hydrogen entry into steel by atmospheric corrosion

T.KUSHIDA

Structural Steels with higher strength are recently required. Therefore, environmental degradation by hydrogen, delayed fracture, should be afraid. Absorbed hydrogen contents in structural steels have been investigated by thermal hydrogen analysis. Hydrogen entry into steel has been directly measured by electrochemical hydrogen permeation technique. Hydrogen entry into steel occurs immediately after weathering by atmospheric corrosion. The maximum absorbed hydrogen content is observed at half a year. Hydrogen entry into steel is not affected by area location, weathering conditions, air born salts and so on. Hydrogen entry is due to the pH drop of hydrolysis of  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  with initial rust formation.

(cf. *ISIJ Int.*, 43 (2003), 470)

## Effect of applied cathodic potential on susceptibility to hydrogen embrittlement in high strength low alloy steel

S.KOMAZAKI *et al.*

In order to investigate the effects of applied cathodic potential and chemical hydrogen absorption promoter (thiourea) on the susceptibility to hydrogen embrittlement of the high strength low alloy (HSLA) steel, slow strain rate tensile (SSRT) tests were conducted in various buffer aqueous solutions of pH 10.0. During SSRT tests, the specimens were cathodically polarized under potentiostatic control. Polarization levels were varied from the corrosion potential ( $E_{\text{corr}}$ ) to hydrogen gas evolution potential ( $E_{\text{H}_2\text{gas}}$ ), including the adsorbed hydrogen potential ( $E_{\text{Hads}}$ ) determined by cyclic voltammetry (CV). Additionally, thermal desorption spectroscopic (TDS) analyses were applied to the specimens fractured by SSRT test and the dependence of hydrogen absorption characteristic on applied potential was also examined for understanding the SSRT test results. Experimental results revealed that the hydrogen embrittlement behavior was strongly dependent on the applied cathodic potential. In the  $E_{\text{Hads}}$  region, the susceptibility to hydrogen embrittlement increased with increasing cathodic overpotential. On the other hand, in the  $E_{\text{H}_2\text{gas}}$  region, the susceptibility was independent of the applied potential. Moreover, by adding thiourea to the solution, the susceptibility to hydrogen embrittlement increased slightly in the  $E_{\text{H}_2\text{gas}}$  region compared with that in the solution without thiourea. There was a relatively good correlation between the amount of hydrogen absorption per unit time ( $C_{\text{H}}/t_{\text{f}}$ ) and the time to failure ( $t_{\text{f}}$ ), namely, the susceptibility to hydrogen embrittlement has a tendency to increase monotonically with increasing  $C_{\text{H}}/t_{\text{f}}$ . As a consequence, the potential dependence of hydrogen embrittlement was closely associated with the variation in hydrogen absorption rate under applied potential.

(cf. *ISIJ Int.*, 43 (2003), 475)

## Development of scanning laser-enhanced electrochemical microscopy for visualizing hydrogen distribution on a steel

T.HARUNA *et al.*

A Scanning Laser-Enhanced Electrochemical Microscope for Hydrogen detection (H-SLEEM) has been developed in order to *in-situ* visualize the distribution of hydrogen localized on a steel surface. Introduction and detection of hydrogen for the steel sheet was conducted by hydrogen permeation technique with a pair of electrochemical cells. When the hydrogen detection side under hydrogen permeation is irradiated with focused Ar laser, anodic current relating to hydrogen oxidation reaction is thermally enhanced at the irradiation spot and then anodic current increment corresponding to the hydrogen permeation rate at the spot is expected to be determined. In the case that whole the hydrogen detection side was irradiated with diffused laser, the anodic current increased and the current increment increased with an increase in the hydrogen permeation current. The use of focused laser also permitted the measurement of the anodic current increment depending on the hydrogen permeation current. The modulated laser provided more stable and reproducible current increment. When the specimen whose hydrogen entry side was masked except for a small exposed area in center was employed and the modulated laser was raster-scanned under hydrogen permeation, a very clear image of the two-dimensional distribution in the current increment corresponding to local hydrogen permeation rate on the detection side was obtained. It is concluded that the H-SLEEM can successfully visualize the localized hydrogen distribution on the steel surface.

(cf. *ISIJ Int.*, 43 (2003), 482)

## Tensile properties of TiAl based alloy in a gaseous hydrogen atmosphere in a temperature range from room temperature to 973 K

M.NAKAMURA *et al.*

Ti-48Al-2Cr-2Nb (at%) with a  $\gamma$  phase structure was tensile-tested in a high purity hydrogen gas in a temperature range of room temperature to 973 K. The reduction of elongation was observed in hydrogen gas in the entire temperature range, although the fracture surface changed mainly from cleavage to grain boundary facets both in vacuum and in hydrogen gas as the temperature increases. From transmission electron microscopy, fractography, the content of hydrogen introduced during tensile testing, and consideration of the diffusion rate of hydrogen, the hydrogen environmental embrittlement of the TiAl based alloy is suggested to result not from the formation of hydrides but from local accumulation of solute hydrogen introduced by dislocations from the test environment during testing. The hydrogen introduced during tensile deformation mainly decreases not grain boundary strength but cleavage strength, and then the reduction of elongation in hydrogen gas is caused by the decrease of the transgranular strength in the wide temperature range, although the grain boundary strength may also decrease with increasing temperature.

(cf. *ISIJ Int.*, 43 (2003), 489)

## Hydrogen Characterization and States

## Recent development in hydrogen microprint technique and its application to hydrogen embrittlement (Review)

K.ICHITANI *et al.*

A hydrogen microprint technique was overviewed. Its optimal fixing process was discussed to improve the reproducibility and the spatial resolution of this technique. The examples of its application to the examination of hydrogen transport and hydrogen distribution in steels were introduced. Finally, its detection efficiency was quantitatively discussed.

(cf. *ISIJ Int.*, 43 (2003), 496)

## The state of hydrogen in Nb-based Nb-Mo alloys by the channelling method

E.YAGI

In order to locate hydrogen dissolved in metals a channelling method utilizing a nuclear reaction  $^1\text{H}(^{11}\text{B}, \alpha)\alpha$  with a  $^{11}\text{B}$  beam has been developed. This method has been applied to study the effect of metallic solutes on the state of hydrogen in metals. The lattice location of hydrogen in Nb-based Nb-Mo alloys with different concentrations ( $C_{\text{Mo}}$ ) of undersized Mo atoms of 3, 10, 20 and 26 at% has hitherto been investigated. These results are summarized in this paper and the interaction of hydrogen with metal solutes is discussed. At low Mo concentrations less than 10 at% hydrogen is trapped by Mo atoms at room temperature due to attractive interaction to be located at sites displaced from tetrahedral ( $T$ ) sites by about  $0.6 \text{ \AA}$  toward the nearest neighbour Mo atom. In the case of  $C_{\text{Mo}}=3 \text{ at\%}$ , hydrogen is detrapped at 373 K and enter a  $T$  site. The number of H atoms trapped by one Mo atom is limited. It is 0.7-1.0 for  $C_{\text{Mo}}=3 \text{ at\%}$  and decreases with increasing  $C_{\text{Mo}}$ . The excess H atoms are located at  $T$  sites. For  $C_{\text{Mo}}=20 \text{ at\%}$  such trapped site occupancy is not observed, and 70-80% of the H atoms are located at  $T$  sites and the rest are at octahedral ( $O$ ) sites at low H concentrations. For  $C_{\text{Mo}}=26 \text{ at\%}$ , most of the H atoms are located at  $T$  sites.

(cf. *ISIJ Int.*, 43 (2003), 505)

## Simulation of hydrogen thermal desorption under reversible trapping by lattice defects

T.YAMAGUCHI *et al.*

The hydrogen thermal desorption of a martensitic steel has been simulated assuming lattice hydrogen diffusion under a local equilibrium with reversibly trapped hydrogen as the rate-determining process. The calculated desorption curves reproduced the observed shift of the peak temperature associated with the specimen thickness and the heating rate. The calculation method involves a combination of a defect density and a hydrogen/defect binding energy as parameters. The dependence of the peak temperature on the defect density and the binding energy has been quantitatively shown. Assignment of the lattice defect relevant to the desorption curves is discussed. A calculation that took into account the increase in the defect density yielded results consistent with the observed change in the desorption

curves associated with plastic strain.

(cf. *ISIJ Int.*, **43** (2003), 514)

### Hydrogen in trapping states innocuous to environmental degradation of high-strength steels

*K.TAKAI et al.*

Hydrogen in trapping states innocuous to environmental degradation of the mechanical properties of high-strength steels has been separated and extracted using thermal desorption analysis (TDA) and slow strain rate test (SSRT). The high-strength steel occluding only hydrogen desorbed at low temperature (peak 1), as determined by TDA, decreases in maximum stress and plastic elongation with increasing occlusion time of peak 1 hydrogen. Thus the trapping state of peak 1 hydrogen is directly associated with environmental degradation. The trap activation energy for peak 1 hydrogen is 23.4 kJ/mol, so the peak 1 hydrogen corresponds to weaker binding states and diffusible states at room temperature. In contrast, the high-strength steel occluding only hydrogen desorbed at high temperature (peak 2), by TDA, maintains the maximum stress and plastic elongation in spite of an increasing content of peak 2 hydrogen. This result indicates that the peak 2 hydrogen trapping state is innocuous to environmental degradation, even though the steel occludes a large amount of peak 2 hydrogen. The trap activation energy for peak 2 hydrogen is 65.0 kJ/mol, which indicates a stronger binding state and nondiffusibility at room temperature. The trap activation energy for peak 2 hydrogen suggests that the driving force energy required for stress-induced diffusion during elastic and plastic deformation, and the energy required for hydrogen dragging by dislocation mobility during plastic deformation are lower than the binding energy between hydrogen and trapping sites. The peak 2 hydrogen, therefore, is believed to not accumulate in front of the crack tip and to not cause environmental degradation in spite of being present in amounts as high as 2.9 mass ppm.

(cf. *ISIJ Int.*, **43** (2003), 520)

### Effects of Microstructure and Deformation

#### Hydrogen trapping behavior in vanadium-added steel

*H.ASAHI et al.*

Hydrogen trapping and de-trapping behavior was investigated for steels with and without V. The de-trapping of hydrogen is very slow while the trapping presumably proceeds rapidly for steels containing VC precipitates. The activation energy for de-trapping is in the range of 33 to 35 kJ/mol. The trapped-hydrogen content and diffusible-hydrogen content in the steady state increase with increasing hydrogen entry rate into the steel. The density of hydrogen trapping sites decides the maximum trapped-hydrogen content; 9 ppm for 1% V steel tempered at peak secondary hardening temperature. Analysis of hydrogen embrittlement cracking tests in terms of hydrogen contents such as the critical hydrogen content should be performed on the specimens with uniform hydrogen distribution and must consider the nature of hydrogen whether it is trapped or

diffusible.

(cf. *ISIJ Int.*, **43** (2003), 527)

### Evaluation of hydrogen content trapped by vanadium precipitates in a steel

*T.YOKOTA et al.*

Hydrogen content trapped by vanadium precipitates was evaluated using vanadium bearing martensitic steels which show single TDA desorption peak. The peak consists of desorption from various sorts of trap site with different detrapping activation energy, even if it appears to be a single peak. Experimentally obtained single desorption profile taken from vanadium bearing martensitic steels was decomposed to multiple profiles with different peak temperature. Form of each desorption profile was approximated to Gaussian function. Area surrounded by each Gaussian function was calculated by integrating the functions to obtain decomposed hydrogen contents related to each peak temperature. It was revealed that decomposed profile with 140°C peak was caused by vanadium precipitates trapping, by comparing an amount of vanadium precipitates with decomposed hydrogen contents. Most of hydrogen in vanadium bearing tempered martensitic steel was revealed to be trapped by vanadium precipitates.

(cf. *ISIJ Int.*, **43** (2003), 534)

### Hydrogen trapping in quenched and tempered 0.42C-0.30Ti steel containing bimodally dispersed TiC particles

*F.-G.WEI et al.*

The effect of tempering on hydrogen trapping in 0.42C-0.30Ti steel was studied by means of a microhardness test, hydrogen thermal desorption spectrometry and high resolution transmission electron microscopy. In addition to the coarse undissolved TiC particles, fine TiC particles with a volume fraction up to 0.22% precipitated tempering at temperatures above 500°C. Coherent TiC square platelets with a diagonal length of about 2 nm and a thickness of less than 1 nm precipitated at 550 and 600°C, which act as reversible hydrogen traps. Tempering at 700°C caused the fine TiC particles to lose their coherency with the matrix, resulting in a very limited increase in reversibly trapped hydrogen content compared to the samples tempered below 500°C without TiC precipitation. On the other hand, the coarse undissolved TiC particles with an average diameter of 2 μm, acting as irreversible traps, greatly enhanced the irreversibly trapped hydrogen content when tempered at 500°C and were accompanied by a decrease in hydrogen desorption rate peak temperature. Comparison of both types of TiC particles with the same volume fraction indicated that the fine coherent TiC platelets were more effective in trapping hydrogen than the coarse incoherent undissolved TiC particles.

(cf. *ISIJ Int.*, **43** (2003), 539)

### Effect of mechanical deformation on permeation of hydrogen in iron

*Y.HUANG et al.*

Rate of hydrogen permeation was measured under

static as well as dynamic mechanical deformation conditions. Cylindrical tensile test specimens were used for the study and hydrogen permeation was measured electrochemically. It was observed that the hydrogen diffusivity decreased as plastic deformation increased for the static deformation experiments while elastic deformation had no significant effect on diffusivity but increased the steady state permeation flux. For the dynamic loading experiment, an elastic deformation increased the hydrogen permeation rate almost linearly. Onset of plastic deformation led a sudden decrease of permeation rate and the reduced rate was rapidly recovered when the plastic deformation ceased. These rapid changes in the permeation rates were explained that the absorbed hydrogen was trapped by dislocations and creation rate and density of dislocations changed drastically when plastic deformation started and stopped.

(cf. *ISIJ Int.*, **43** (2003), 548)

### Strain rate dependence of tensile behavior and environmental effect in zirconia ceramics

*M.MATSUZAWA et al.*

The tensile strength of four kinds of zirconia ceramics (two kinds of Y-TZP with different grain sizes, Mg-PSZ and Ce-TZP) has been investigated for a wide range of strain rates ( $3 \times 10^{-9}$ – $1.0 \times 10^{-12}$ –1) in both air and vacuum. The obviously unique strain rate dependence was observed in Y-TZPs and Mg-PSZ, which have anelastic properties. On the other hand, such strain rate dependence was not observed over the whole range of strain rates for Ce-TZP, which does not exhibit anelasticity. For all of the samples investigated, there was no significant difference between both values of tensile fracture strength in air and vacuum. It was found that a decrease in strength with decreasing strain rate should not be associated with the static fatigue growth of microcracks nucleated during loading. It was concluded that the extent of the occurrence and the exhaustion of anelasticity predominantly controls the tensile strength of zirconia ceramics.

(cf. *ISIJ Int.*, **43** (2003), 555)

### Kinetics and Control of Hydrogen Embrittlement

#### Effect of microstructure on moisture-induced embrittlement of L1<sub>2</sub> intermetallic compounds (Review)

*T.TAKASUGI*

The effects of grain size and second phase on moisture-induced embrittlement of L1<sub>2</sub>-type Co<sub>3</sub>Ti and Ni<sub>3</sub>(Si, Ti) alloys were investigated by tensile test in air and vacuum as functions of strain rate and temperature, in combination with microstructural and fractographic observation. In both the intermetallic alloys, brittle-ductile transition (BDT) strain rate defined from an elongation vs. strain rate curve decreased with decreasing grain size, meaning that fine-grained microstructure has the effect of reducing the moisture-induced embrittlement. Also, it was found that dispersion of Co solid solution phase and Nb-containing second phase has the effect of re-

ducing moisture-induced embrittlement of the  $\text{Co}_3\text{Ti}$  and the  $\text{Ni}_3(\text{Si}, \text{Ti})\text{-Nb}$  alloys, respectively, when their second phases are incoherent with the  $\text{L1}_2$  matrix. Contrarily, finely precipitated Co solid solution phase that is coherent with the  $\text{L1}_2$  matrix has the effect of enhancing moisture-induced embrittlement of the  $\text{Co}_3\text{Ti}$  alloys. Mechanisms responsible for the microstructural effect on the moisture-induced embrittlement of the  $\text{L1}_2$  intermetallic alloys were presented and discussed.

(cf. *ISIJ Int.*, **43** (2003), 564)

#### Atomic-scale effects of hydrogen in iron toward hydrogen embrittlement: *Ab-initio* study

Y. TATEYAMA *et al.*

We have investigated atomic-scale effects of hydrogen atoms in  $\alpha\text{-Fe}$  by means of *ab-initio* calculations and examined microscopic mechanism of hydrogen embrittlement in Fe-based materials. Our calculations indicate that accumulation of interstitial hydrogen in a tensile-stress-concentrated region ahead of a crack tip is estimated to be hundredfold increase of the concentration at most, which is much lower than the assumption of the representative models for hydrogen embrittlement. On the contrary, we quantitatively demonstrate that hydrogen significantly facilitates vacancy formation in  $\alpha\text{-Fe}$  and the resultant vacancies trapping hydrogen incline to the anisotropic clusterization. These results suggest considerable contribution of vacancy-related processes to hydrogen embrittlement in those materials, rather than support interstitial hydrogen effects on which the existent models mainly based.

(cf. *ISIJ Int.*, **43** (2003), 573)

#### *In situ* AFM imaging system for the environmentally induced damage under dynamic loads in a controlled environment

K. MINOSHIMA *et al.*

The atomic force microscope (AFM) based system has been developed for *in situ* topographic imaging of the environmentally induced damage such as a stress corrosion crack under a dynamic loading condition. The system consists of an atomic force microscope (AFM), a mechanical testing machine, an X-Y-Z positioning stage, an environment chamber, and their controllers. To reduce disturbing vibration, the system is equipped with isolators. A dynamic load can be applied to a sample by using an electromagnetic actuator: it provides various loading waveforms including sinusoidal, triangular, and other arbitrary programmable ones, and has a maximum load capacity of  $\pm 100\text{ N}$ . Nanoscopic *in situ* AFM observation can be conducted in a controlled gaseous environment or in an aqueous solution. By using the developed system, *in situ* AFM observation of the following growing crack was successfully performed in a high-strength stainless steel: a fatigue crack in dry air and a stress corrosion crack under high-frequency vibratory stresses superimposed on a sustained load (dynamic stress corrosion cracking), and under a low-frequency varying load (cyclic stress corrosion cracking): the nanoscopic crack tips can be clearly visualized. The crack tip of the stress corrosion crack under dynamic loads is sharp compared with a fatigue crack in dry air, with a larger scatter of the crack tip opening displacement than those of the fatigue crack in dry air.

(cf. *ISIJ Int.*, **43** (2003), 579)

#### Direct observations of cracks and voids in structural materials by X-ray imaging using ultra-bright synchrotron radiation

T. NAKAYAMA *et al.*

Refraction contrast X-ray imaging experiments were conducted on acrylic resin with an artificial cylindrical hole, A7075 aluminum alloy, A6063 aluminum castings, mild steel with cracks or voids, and low alloy steel with inclusions, using a ultra-bright synchrotron radiation X-ray beam in BL24XU hutch C of SPring-8. Conventional absorption contrast X-ray imaging experiments were also done for the comparison. The X-ray beam was controlled to be monochromatic by Si double-crystals and collimated by a slit. The distance between the sample and the detector was changed from 0 to 3 m, and the X-ray energy was 15 to 25 keV. Photographs were taken by X-ray film and/or X-ray CCD camera. As a result, the refraction imaging method gave a much more distinct image of the artificial cylindrical hole in acrylic resin as compared with the absorption method. The fatigue cracks in aluminum alloy and mild steel were also distinctly observed. The X-ray imaging revealed the presence of MnS nonmetallic inclusions in low alloy steel. Void defects in aluminum castings were clearly detected by the imaging. In addition, *in-situ* observation of tensile fracture of aluminum alloys using a high resolution X-ray CCD camera system was successfully conducted. The observations by use of asymmetric reflection technique for X-ray imaging experiment were also well performed. From above, the X-ray imaging method using ultra-bright synchrotron radiation is concluded to be very useful for fracture research of materials.

(cf. *ISIJ Int.*, **43** (2003), 589)