Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Nuclear Materials 329–333 (2004) 1122–1126

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Effects of hydrogen on the mechanical properties of oxide dispersion strengthening steels

J.S. Lee [a,*,1], A. Kimura [a], S. Ukai [b], M. Fujiwara [c]

[a] Institute of Advanced Energy, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan
[b] Japan Nuclear Cycle Development Institute, Tokai 311-1393, Japan
[c] Kobelco, Ltd., Takatsukadai, Nishi-ku, Kobe 651-2271, Japan

---

Abstract

The effects of hydrogen on the mechanical properties of oxide dispersion strengthened (ODS) steels were investigated by means of tensile tests at room temperature. Cathodic hydrogen charging was carried out before and during deformation in a sulfuric acid solution by imposing a constant current density in the range of 100 to −520 A/m^2. With increasing charging current density, the loss of ductility increased accompanied by a change in fracture mode from ductile to intergranular fracture. The critical hydrogen concentration in ODS steels required to transition from ductile to brittle fracture was in the range of 10–12 wppm, which approximately 10 times larger than that of a 9Cr–2W martensitic steel. In addition, the susceptibility to hydrogen embrittlement of ODS steels strongly depended on specimen sampling orientation.

---

1. Introduction

The excellent high temperature strength of oxide dispersion strengthened (ODS) steels has made them for possible application to fusion blanket structural materials. Since a rather high concentration of hydrogen will be generated in the fusion environment, hydrogen effects on the mechanical properties of high strength ODS steels will be one of critical issues for the development of advanced blanket systems. In a fusion environment, besides the external hydrogen sources such as aqueous corrosion, radiolysis of cooling water etc., the hydrogen production rate in first wall steels by (n, p) transmutation reaction is predicted to be about 0.9 wppm/dpa under 14 MeV neutron irradiation [1].

In 9Cr martensitic steels, several wppm of hydrogen could induce considerable reduction in ductility accompanied by a change in the fracture mode from microvoid coalescence type ductile fracture to intergranular or brittle cleavage fracture. It was reported that the fracture mode of F82H and MANET II martensitic steel was changed from ductile rupture to brittle intergranular fracture by the introduction of 1–2 and 3–4 wppm hydrogen, respectively [2]. However, there was no available data for ODS steels.

ODS steel rods manufactured by hot extrusion processing, have anisotropic mechanical properties due to extremely elongated grains parallel to the extruded direction [3]. In addition, since 9Cr martensitic steels often suffer intergranular hydrogen embrittlement, the grain morphology is considered to play an important role in determining the susceptibility to hydrogen embrittlement in ODS steels.

In this work, the effects of hydrogen and microstructural anisotropy on the mechanical properties of ODS steels and a 9Cr–2W steel are investigated.

2. Experimental

The materials used in the present research were three kinds of ODS steels and a 9Cr–2W reduced activation

---

[*] Corresponding author. Tel.: +82-42 869 3854; fax: +82-42 869 3810.

E-mail address: jslee2@kaist.ac.kr (J.S. Lee).

[1] Present address: Department of Nuclear and Quantum Engineering, KAIST, 373-1 Gusong-dong, Yusong-gu, Daejon 305-701, Republic of Korea.

0022-3115/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2004.04.035

martensitic steel (RMS). The ODS steels were produced with variable chromium and aluminum contents with yttria (Y_2O_3) contents of 0.36–0.38 wt%. The chemical compositions are listed in Table 1, where the ODS steels are indexed as K1, K2 and K4. The ODS steel rods were fabricated by hot extrusion, and an austenization heat treatment was performed at 1423 K for 1 h followed by air cooling. Small size tensile specimens (gage length = 5 mm, $1.2^w \times 0.25^t$ mm) were sampled from the extruded rod so that the axis direction is parallel to longitudinal (L) or transverse (T)-direction with respect to the extruded direction. Cathodic hydrogen charging was carried out at room temperature for 30 min and continued during tensile testing in a solution of 1 N H_2SO_4 with an addition of 10 mg/l of As_2O_3. For hydrogen charging, a three electrodes system was used, and a constant current density, I_a, was imposed on the specimen in the range from 100 to −520 A/m^2. Tensile tests were carried out at a strain rate of 9×10^{-5} s^{-1} at room temperature. After pre-charging, hydrogen contents were analyzed by thermal desorption spectroscopy (TDS) with a heating rate of 1 K/s. Fracture surfaces were examined by scanning electron microscope (SEM).

3. Results

3.1. Hydrogen effects on stress–strain behavior

The effects of hydrogen charging on the stress–strain curves of K2 ODS steel sampled from L- and T-direction are shown in Fig. 1(a) and (b), respectively. In both cases, hydrogen charging induced a significant reduction in tensile ductility in accordance with the imposed current density (I_a). However, yield and tensile strengths were not significantly affected. It is clear that stress–strain behavior strongly depends on specimen orientation, showing more sever embrittlement in the T-direction. It is considered that the reduction in ductility is due to hydrogen embrittlement since the square root of current density is proportional to the hydrogen concentration in normal interstitial lattice sites (NILS) [4]. In the L-direction, as the cathodic current density increased from 0 to −169.5 A/m^2, the plastic fracture strain was reduced from 0.13 to 0.03, but, a small amount of plasticity was retained even at −519.6 A/m^2.

On the other hand, in case of T-direction, the plasticity completely disappeared when the current density was only −30.4 A/m^2, and approximately 50 percent reduction in fracture strain was observed at 0 A/m^2. It is obvious that even at the zero current density, hydrogen will diffuse into the specimen because zero means the net current between anodic metal dissolution and cathodic hydrogen charging. After hydrogen charging, the yield stress appeared to increase slightly in the L-direction

Table 1
Chemical compositions of ODS steels (K1, K2 and K4) and a 9Cr–2W RMS steel (wt%)

Index	C	Si	Mn	P	S	Cr	W	Al	Ti	Y	O	N	Ar	Y_2O_3
K1	0.05	0.041	0.06	<0.005	0.002	18.37	0.29	< 0.01	0.28	0.29	0.16	0.014	0.005	0.368
K2	0.04	0.033	0.06	<0.005	0.002	13.64	1.65	4.12	0.28	0.30	0.17	0.009	0.005	0.381
K4	0.09	0.039	0.06	<0.005	0.002	18.85	1.83	4.61	0.28	0.29	0.16	0.005	0.005	0.368
RMS	0.10	0.050	0.53	0.002	0.0020	8.98	2.01	0.028	0.018	0.25(V)	0.06(Ta)	0.003(B)	–	–

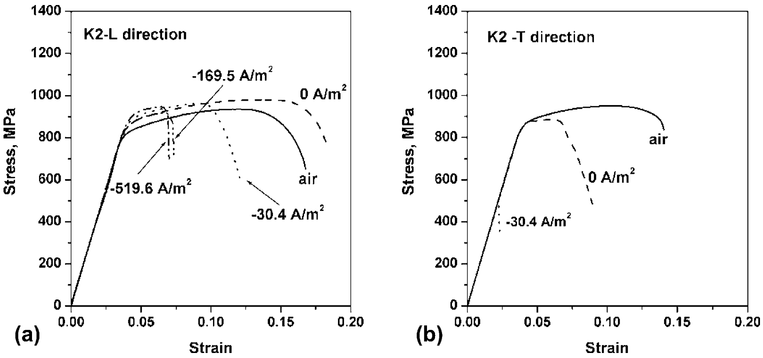

Fig. 1. Effects of hydrogen charging on the stress–strain curves of K2 ODS with (a) L- and (b) T-direction.

specimen, while there was no difference in the T-direction.

The changes in plastic fracture strain (ε_{pf}) of ODS steels and a 9Cr–2W RMS as a function of the square root of applied current density are summarized in Fig. 2(a) and (b). As shown in Fig. 2(a), for the L-direction, the ε_{pf} of ODS steels was about 0.14 in air, and an abrupt reduction occurred with increasing current density. The transition behavior of K2-L and K4-L is very similar. The critical current density where the ε_{pf} becomes 50% of that in air was approximately −42.5 and −23.0 A/m^2, respectively. While the transition behavior of 9Cr–2W RMS was relatively smooth, the plasticity completely disappeared when the current density increased up to −64 A/m^2. An interesting feature of 9Cr–2W is that even at the anodic metal dissolution current, it still showed some amount of reduction in fracture strain. However, the reduction in ductility in the anodic range is not caused by metal dissolution but probably by hydrogen embrittlement, because after a degassing heat treatment of the specimen at 473 K for 2 h the ductility was completely recovered. The critical current density was approximately −4.0 A/m^2.

In the T-direction, as shown in Fig. 2(b), the fracture strain of K1-T, K2-T and K4-T ODS steels was about 0.10, 0.097 and 0.03 in air, respectively, but resulted in zero plasticity after applying a small amount of cathodic current. The critical current density was 0 A/m^2, irrespective of the materials. Such a high susceptibility of T-direction specimens suggests a role of the microstructural inhomogeneity caused by elongated grains.

3.2. Fracture surface observation

The loss of ductility in hydrogen charged specimens was accompanied by a change in the fracture mode from ductile shear rupture to brittle fracture. Fig. 3(a)–(c) shows the typical ductile fracture surface of K2-L, K2-T and 9Cr–2W steel, respectively. When hydrogen was introduced into the specimen, however, the fracture mode changed to a brittle type, and there appeared to be different cracking appearances between ODS and

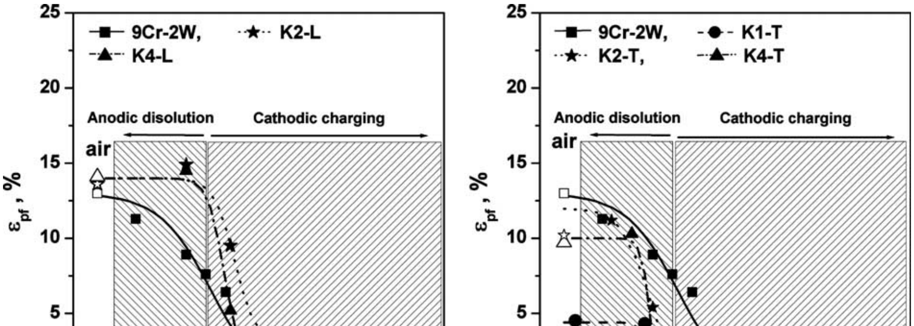

Fig. 2. The dependence of plastic fracture strain (ε_{pf}) on the hydrogen charging current density in (a) L- and (b) T-direction.

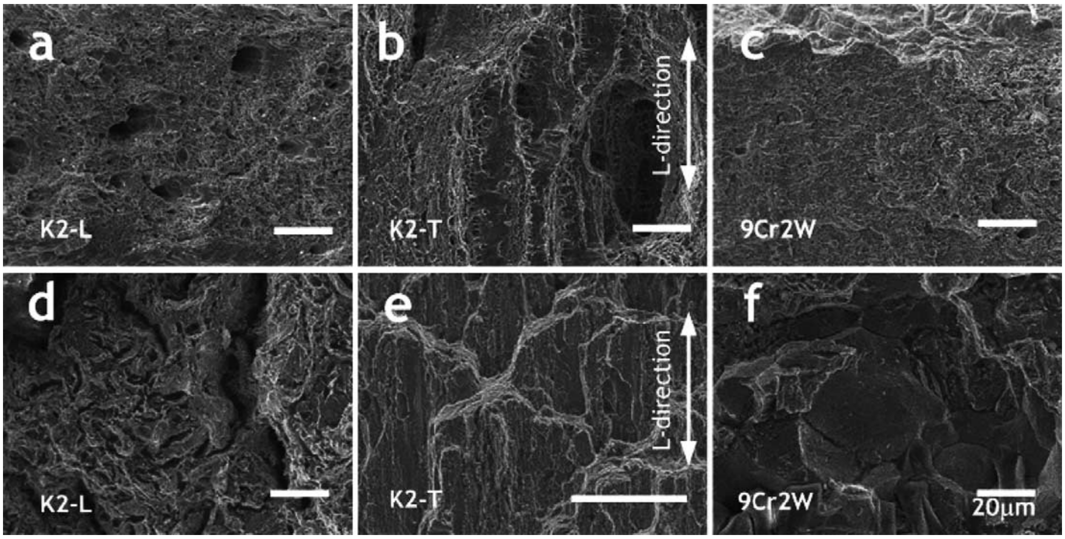

Fig. 3. Changes in fracture mode by hydrogen charging. (a)–(c) is uncharged, and (d)–(f) is hydrogen charged at the current density of −519, −30 and −514 A/m^2 on the K2-L, K2-T and 9Cr–2W, respectively.

9Cr–2W, although those were basically grain boundary cracking. As shown in Fig. 3(d)–(f), with increasing current density up to −519, −30 and −514 A/m^2 for the K2-L, K2-T and 9Cr–2W, respectively, the fracture mode changed to brittle intergranular. In the case of K2-L, as shown in Fig. 3(d), the formation of many secondary cracks into the L-direction was identified, which is considered to be cracking of longitudinally elongated grain boundary. Small amounts of microvoids were also observed. The fracture mode of K2-T in Fig. 3(e) is also considered to be intergranular, although it appears to be quasi-cleavage fracture. Fig. 3(f) clearly shows the intergranular type cracking of 9Cr–2W steel.

4. Discussion

4.1. Critical hydrogen concentration for ODS steels

The hydrogen concentration as a function of cathodic current density in K2 ODS and 9Cr–2W steel measured by TDS analysis were shown in Fig. 4. According to previous research, the critical hydrogen concentration required to induce cracking of steel matrix in martensitic steels is reported as a several wppm [2], and our analysis results in 9Cr–2W RMS reveal that the critical concentration, which corresponds to the current density of −4 A/m^2, is also in the range of 1–2 wppm. On the contrary, hydrogen concentration in K2 ODS steel is much higher than that of the RMS steel at the same charging condition, and critical hydrogen concentration for the K2-L ODS is in the range of 10–12 wppm that is almost 10 times higher concentration than the RMS steels. It is considered that the high concentration of hydrogen in ODS steel is attributed to the high density of hydrogen trapping sites such as grain boundary and oxide/matrix

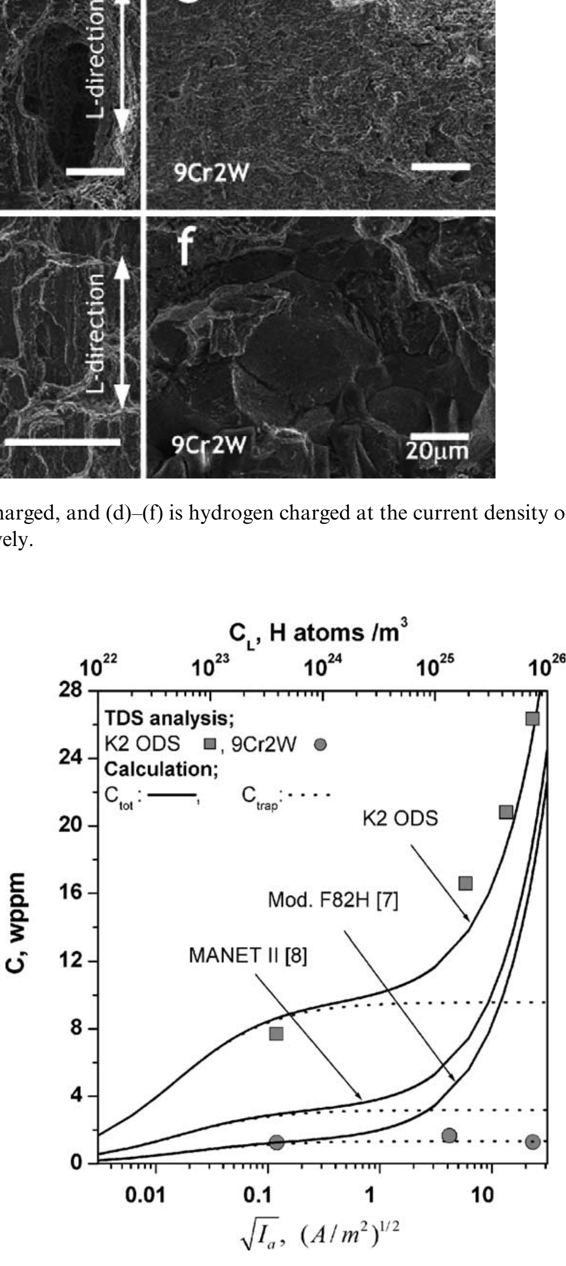

Fig. 4. Experimental and calculated hydrogen contents in K2 ODS and martensitic steels as a function of current density. The calculation used the trap densities (N_t) and binding energy (E_b) of 6.3×10^{24} sites/m^3 and 39.0 kJ/mol for Mod. F82H and 1.5×10^{25} sites/m^3 and 39.5 kJ/mol for MANET II, respectively [7,8].

interface, because the ODS steel has a very fine grain size and a high number density of yttria particles [5].

Theoretical calculations of the relation between hydrogen concentration and cathodic current density are also shown in Fig. 4. Solid and broken lines represent total (C_{tot}) and trapped (C_{trap}) hydrogen concentration, respectively. In this calculation, the empirical relationship between hydrogen concentration in NILS (C_{L}) in iron and the cathodic current density was used [4]. In addition, local equilibrium between hydrogen atoms in NILS and those in trapping sites, proposed by McNabb and Foster [6], was assumed. For the martensitic steels Mod. F82H and MANET II, the critical hydrogen concentration has been reported as 1–2 and 3–4 wppm, respectively [2], which correspond to the saturated concentration of trapped hydrogen when trap densities (N_{t}) and binding energy (E_{b}) were 6.3×10^{24} sites/m^3 and 39.0 kJ/mol for Mod. F82H and 1.5×10^{25} sites/m^3 and 39.5 kJ/mol for MANET II, respectively [7,8]. The variation of hydrogen concentration for 9Cr–2W RMS and K2 ODS steel is also well described by the assumption of trap densities of 6.3×10^{24} and 4.5×10^{25} sites/m^3, respectively, with a binding energy of 39.0 kJ/mol. Based on the above analysis, the critical hydrogen concentration is considered to be related to the saturated hydrogen concentration in trap sites.

4.2. Embrittlement mechanism

Hydrogen-induced intergranular fracture is responsible for the considerable reduction in ductility in ODS steels and 9Cr–2W RMS steel. Based on the above analysis [6], most of hydrogen transported into the specimen by lattice diffusion will be trapped at various kinds of trap sites such as vacancy, grain boundary, carbide and oxide/matrix interface, lath boundaries, dislocations etc.; and after filling up the trap sites, the hydrogen will be able to occupy NILS. In this situation, mobile dislocations could sweep the hydrogen atoms presented at NILS or dislocations to the grain boundaries during plastic deformation, resulting in sufficient hydrogen accumulation to weaken grain boundaries and enhanced brittle intergranular fracture.

5. Summary

1. Cathodic hydrogen charging considerably reduced the tensile ductility of ODS steels and a 9Cr–2W RMS. The reduction in ductility was attributed to the change in fracture mode from ductile shear rupture to brittle intergranular fracture. The hydrogen embrittlement of ODS steels was strongly affected by specimen sampling orientation, showing significant embrittlement in the T-direction. This comes from the microstructural anisotropy caused by elongated grains of ODS steels in L-direction.
2. The ODS steels contained a higher concentration of hydrogen than 9Cr–2W RMS at the same cathodic charging condition, and the critical hydrogen concentration required to induce intergranular cracking in ODS steels and 9Cr–2W RMS is in the range of 10–12 and 1–2 wppm, respectively. The high concentration of hydrogen in ODS steels may be interpreted in terms of a high capacity of hydrogen trapping caused by very fine grain size and introduction of yttria in the steel matrix. The critical hydrogen concentration is considered to be related to the saturated concentration of hydrogen at trap sites for martensitic steels.

References

[1] M.L. Grossbeck, K. Ehrlich, C. Wassilew, J. Nucl. Mater. 174 (1990) 264.

[2] M. Beghini, G. Benamati, L. Bertini, R. Valentini, J. Nucl. Mater. 258–263 (1998) 1295.

[3] H. Okada, S. Ukai, M. Inoue, J. Nucl. Sci. Technol. 33 (1996) 936.

[4] J.L. Lee, J.Y. Lee, Scr. Metall. 19 (1985) 341.

[5] S. Ukai, T. Okuda, M. Fujiwara, T. Kobayashi, S. Mizuta, H. Nakashima, J. Nucl. Sci. Technol. 39 (8) (2002) 872.

[6] A. McNabb, P.K. Poster, Trans. TMS-AIME 245 (1969) 618.

[7] G. Benamati, Complier, Hydrogen Permeation and Embrittlement Studies, ENEA Fusion Division Report ERF FUS ISP MAT 62, January, 1996.

[8] R. Valentini, A. Solina, L. Tonelli, S. Lanza, G. Benamati, A. Donato, J. Nucl. Mater. 233–237 (1996) 1123.