EFFECT OF THE SECOND PHASE ON HYDROGEN EMBRITTLEMENT OF IRON ALLOYS

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(Proceedings of 4th Intern. Conference "Hydrogen and Materials", Beijing 9-13 May 1988, eds. P. Azou, N. P. Chen, pp. 311-319)

ABSTRACT

Hydrogen effect on plasticity of high pure iron and that containing iron oxide, aluminium oxide or carbide was studied. Charging with hydrogen prior or during tensile deformation causes higher embrittlement of Fe-carbide and Fe-Al_2O_3 alloys in comparison with pure iron. Negligible effect of hydrogen on plasticity and no effect on fracture mode was observed for Fe-iron oxides material in cold worked and aged conditions. Different susceptibility to HE is attributed to the purity of matrix and the conditions on matrix-particle interface. Resistance of Fe-iron oxide material to HE is due to the absence of carbon atoms in solid solution and to the weak matrix-oxide cohesion.

INTRODUCTION

Hydrogen produces complex effect on mechanical properties of iron alloys and despite the extensive studies there is rather small possibility to predict susceptibility to hydrogen embrittlement (HE) of materials with a complex structure since the interaction of hydrogen with different structural features can manifest itself in different way. In case of high pure iron, the hardening and softening effects of hydrogen have been found and the explanations have been proposed. The next step to understand the hydrogen behaviour in alloys is to study materials consisting of high pure matrix with inclusions of known composition and morphology.

The aim of present work was to measure susceptibility to HE of iron with oxides and carbide and to establish their role in HE.

EXPERIMENTAL

Chemical composition, treatment and mechanical properties of alloys are shown in Table 1.
The wire (0.8 to 1.0 mm dia.) were used for internal friction (IF) measurements and tensile tests.

IF was measured for specimens aged at 600 °C without hydrogen charging at frequency about 1 Hz in temperature range 0 to 400 °C.

Tensile tests were conducted with a strain rate $\dot{\varepsilon}$ = 1.2 x 10^{-5} s^{-1} either under hydrogen charging conditions or in air after precharging for 17 hrs. 1N H_2SO_4 + 5mg/l As_2O_3 solution and current density of 50 mA/cm^2 were used for hydrogen charging.

Amount of hydrogen absorbed during tensile tests as well as during charging of unstressed specimens for different time was measured by vacuum extraction at 300 °C.

Metallographic und fractographic observations were done by optical and SEM microscopy.

RESULTS

In Table 2, the analysis of phase precipitates is shown for studied alloys. No second phases have been found in Fe material.

In Fig. 1, the IF spectrum of studied alloys is shown. The lowest IF background exhibit Fe and FeO materials. IF peak seen at 40 °C for Fe and FeC materials represents Snoek relaxation of carbon atoms in lattice. Similar peak associated with oxygen atoms relaxation appears at 50 °C for FeO material. Peak at 200 °C for FeC and FeO-Al_2O_3 material are associated with Köster type relaxation of interstitials with dislocations surrounded the particles. Peaks at 300 °C for FeO and FeO-Al_2O_3 materials are attributed to the presence of iron oxide particles.

In Fig. 2, the amount of hydrogen absorbed by unstressed specimens for different time of charging is plotted versus the volume fraction of particles found in studied alloys. Almost no effect of very dispersed Al_2O_3 particles on hydrogen absorption is seen. The amount of hydrogen absorbed by specimens hydrogen charged during tensile tests is also marked in Fig. 2.

Change in elongation to fracture for specimen precharged for 17 hrs and specimens charged during tensile tests is shown in Fig. 3. Hydrogen introduced into cold worked FeO alloy either before or during tensile test produces only minor effect on metal plasticity. The highest susceptibility to HE appears for FeC alloy. It is worth to note that in case of FeO alloy, hydrogen introduced during tensile test plays more detrimental role than hydrogen introduced before test. In case of FeO-Al_2O_3 alloy more detrimental effect is produced by hydrogen introduced into the metal before tensile testing, cf. Fig. 3.

All materials tested in air exhibit fully ductile fracture. In hydrogen charged specimens, modified ductile fracture (Fig. 4) as well as fish eyes (Fig. 5) intergranular and transgranular brittle fracture (Fig. 6) have been found. The appearance of specific fracture in differently hydrogen charged alloys is marked in Fig. 3. The cold worked FeO and FeO-Al_2O_3 alloys exhibit ductile fracture for both mode of hydrogen charging.

In case of aged materials, hydrogen changes the fracture mode: few fish eyes in FeO and IG and TG fracture in FeO-Al_2O_3 alloys have been observed. Fully IG fracture occurs in FeC alloy after both mode of hydrogen charging.

DISCUSSION

Mechanical testing and fractographic examinations show that iron containing iron oxide particles exhibits a very high resistance to the action of hydrogen of high fugacity. In case of cold worked FeO alloy strength of which is close to that of structural steels, the ductile fracture and only small decrease in plasticity occur despite the alloy absorbs ten times more hydrogen than that caused the brittle fracture of Fe and FeC alloys, cf. Figs 2 and 3.

The reason for the different behaviour of studied alloys and for the high resistance of iron-iron oxid alloy to HE might be the difference in metal matrix purity as well as different stress state on metal-particle interface of materials.

As follows from IF measurements, the purity of Fe material is enough to exhibit the hydrogen induced softening (low Snoek peak and no Köster peak). However, that effect is observed only in the easy glide region, and in case of complex dislocation movement, the hindering of dislocations occurs leading to the crack nucleation in sites of plastic incompatibility as has been found for Fe material.

In multiphase materials, the easy glide occurs within a very small region, so the high resistance of FeO material to HE might be attributed to the presence of iron oxides.

The difference of thermal expansion coefficient (α) of matrix and inclusion affects the state on matrix-particle interface causing the formation of either local stress concentration (if α value for particle is lower than that for matrix) or voids at inclusions (if α value for particle is higher than that for matrix). In Table 3 the values of α for different phases and state on the interface of studied inclusions and α-Fe matrix are shown.

The voids or at least the weak cohesion of iron oxides with α-Fe matrix is expected for FeO-alloy. In case of hydrogen charging, those interfaces serve as traps where hydrogen accumulates without causing material damage, as illustrates the increase in hydrogen absorption with increase in volume fraction of iron oxides, cf. Fig. 2. Prestraining of that material causes the expansion of voids, i.e. enlargement of hydrogen traps and despite the metal strengthening the susceptibility to HE decreases due to prestraining.

In case of hydrogen charging of iron-iron oxide material during straining, hydrogen is swept out from the matrix to the voids which expand due to plastic deformation, so material can absorb high amount of hydrogen without cracking, cf. Figs 2 and 3. Straining of precharged iron-iron oxide material causes redissolution of hydrogen within the slip bands and the formation of fish eyes can occur as found in case of aged FeO, cf. Fig. 3. As follows from the IF measurement, some amount of oxygen is present in FeO material matrix, however, its effect seems not to be so detrimental as that of carbon.

As seen in Table 3, around Al_2O_3 and Fe_3C particles in α-Fe, the local stress and complex dislocation structure can exist. This is supported by the IF measurement showing the appearance of Köster peaks, in those materials, cf. Fig. 1.

In case of FeC material, hydrogen diffuses to the sites of high stress concentration (Fe_3C – α-Fe interface) causing crack formation and IG fracture of metal absorbed very low hydrogen content, cf. Figs 2 and 3.

In FeO-Al_2O_3 material, the competition between iron oxide and Al_2O_3 particle effects takes place. Iron oxide serves as void nucleation sites whereas the very small Al_2O_3 particles (less than 100 Å) affect the dislocation motion and plastic deformation processes in a hydrogen free matrix. In case of hydrogen charging of FeO-Al_2O_3 material during deformation, the effect of iron oxides (especially in prestrained material) is more pronounced, so the low susceptibility to HE takes place.

In case of precharging, the interaction of hydrogen with complex dislocation structure promoted by the presence of Al_2O_3 prevails, leading to the hydrogen embrittlement of materials.

CONCLUSIONS

High resistance of iron-iron oxid material to HE is attributed to the absence of carbon atoms in solid solution and to the weak matrix-ironoxide cohesion.

REFERENCES

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[2] Kubaschewski O, Hopkins B. E: “Oxidation of Metals and Alloys”, Butterworths, 1962

(see also: Lunarska; E.; Mikeladze, A.: Effect of second phase particles on hydrogen embrittlement of iron alloys. International Journal of Hydrogen Energy, 22 [1997] 131-139)

Table 1
Chemical composition, treatment and mechanical properties of used alloys

alloy	chemical composition	H_2 ppm	treatment	ε_f	σ_{UTS} MPa
Fe	5.6 ppm C+N	0.1	aging 600 °C	0.38	102
FeO	0.18 wt % O	0.7	cold work aging 600 °C	0.075 0.47	980 470
FeO+ Al_2O_3	as above + 4 wt % Al_2O_3	0.2	cold work aging 600 °C	0.084 0.275	804 230
FeC	0.68 wt % C+ 0.008 wt % N		aging 600 °C	0.242	580

Table 2
Second phase analysis of alloys

Alloy	Volume fraction	mean dia. µm	composition estimated by EDS
FeO	0.064	4.6	Fe(Cr) oxides
FeO cold worked	0.04	5.0	Fe(Cr) oxides
FeO-Al_2O_3	0.016	4.6 0.1	Fe(Cr) oxides Al_2O_3
FeO-Al_2O_3 cold worked	0.017	4.4 0.1	Fe(Cr) oxides Al_2O_3
FeC	0.21	1.8	Fe_3C globular

Table 3
Elastic properties of phases

	α-Fe	FeO	Fe_2O_3	Al_2O_3	Fe_3C
thermal expansion coeffizient $\alpha*10^6$	11.46	14.2	12.2	8.0	6.3
state of matrix-particle interface	–	void	void	stress	stress
Ref.	[1]	[2]	[2]	[1]	[1]

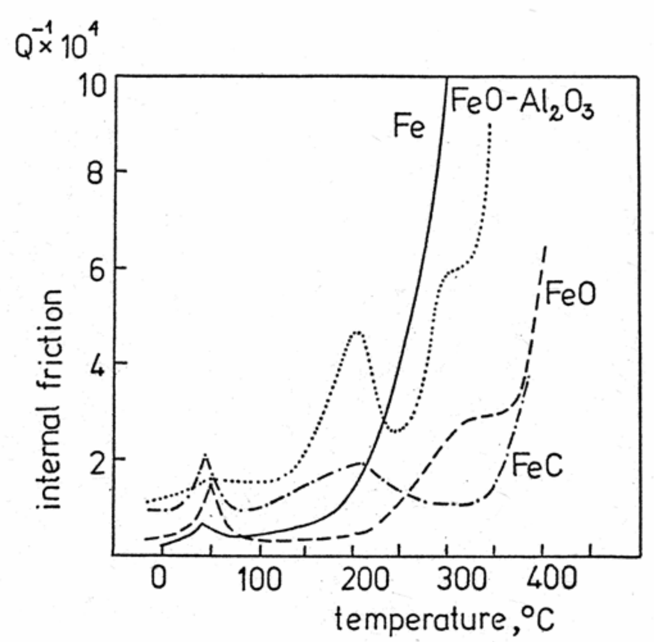

Fig. 1. Internal friction spectrum for studied alloys aged at 600 °C

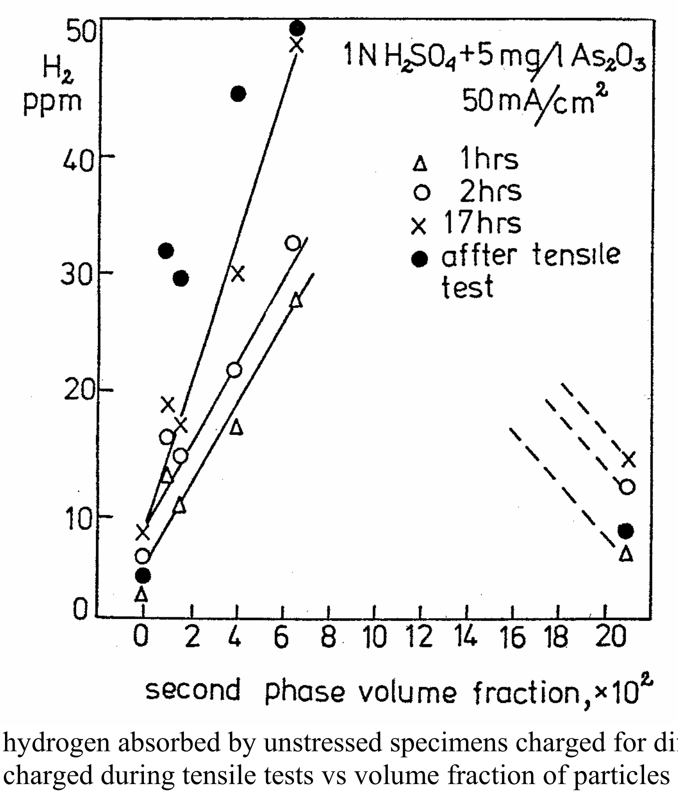

Fig. 2. Amount of hydrogen absorbed by unstressed specimens charged for different time and by specimens charged during tensile tests vs volume fraction of particles

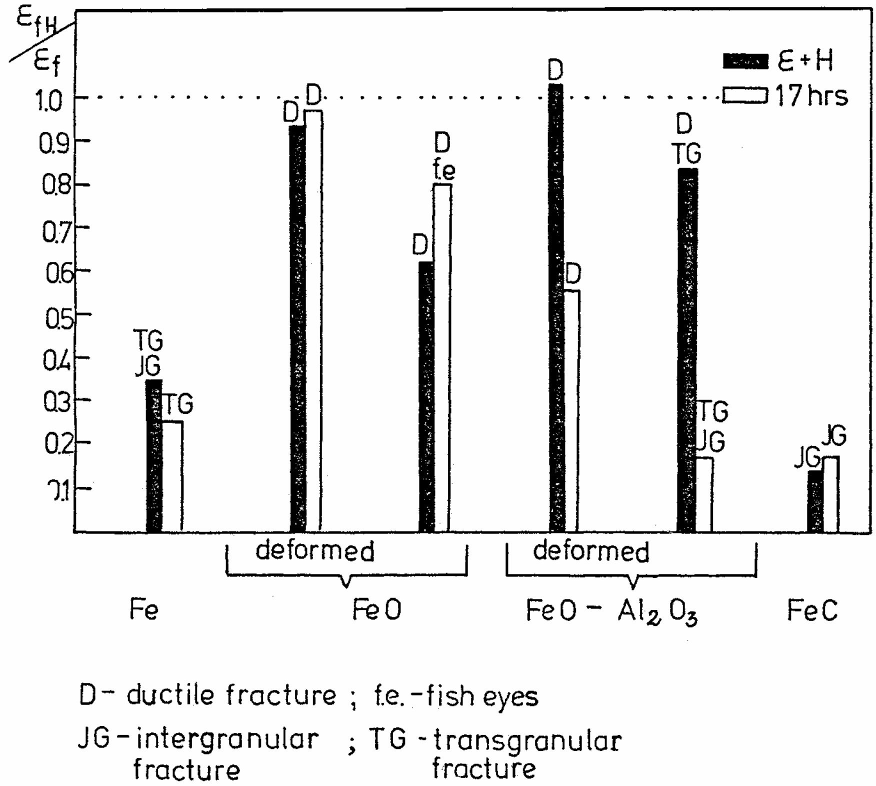

Fig. 3. Effect of precharging (for 17 hrs) and charging during tensile test on elongation to fracture of alloys

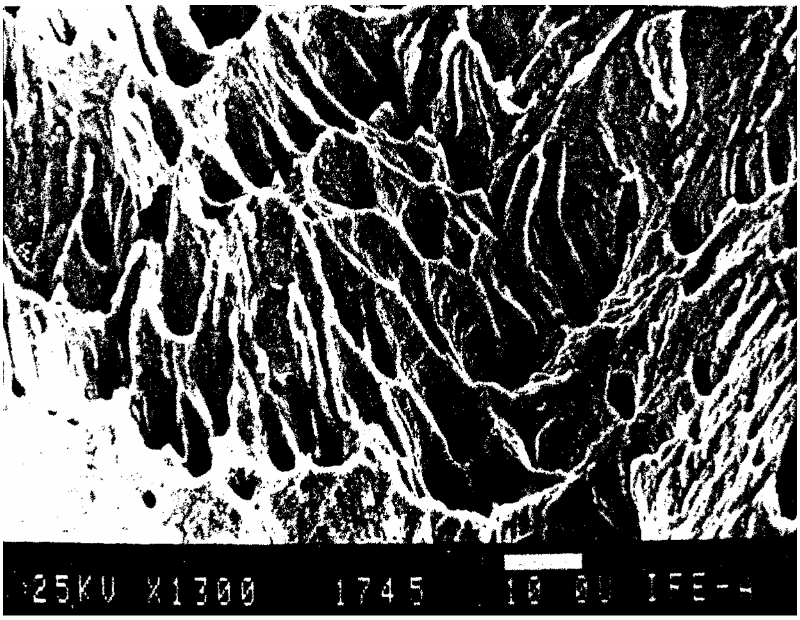

Fig. 4. Modified ductile fracture of cold worked $FeO-Al_2O_3$ specimen hydrogen charged during tensile test

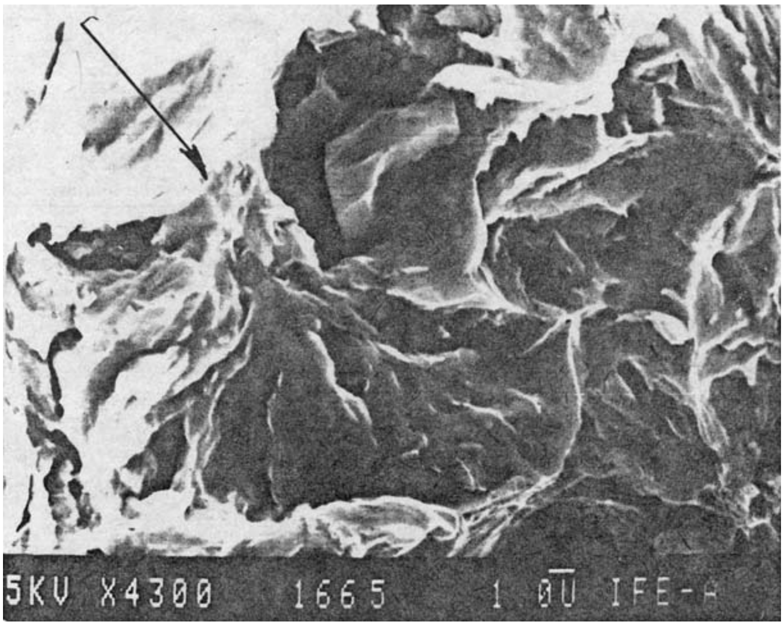

Fig. 5. Fish eyes seen on surface of aged and precharged FeO specimen

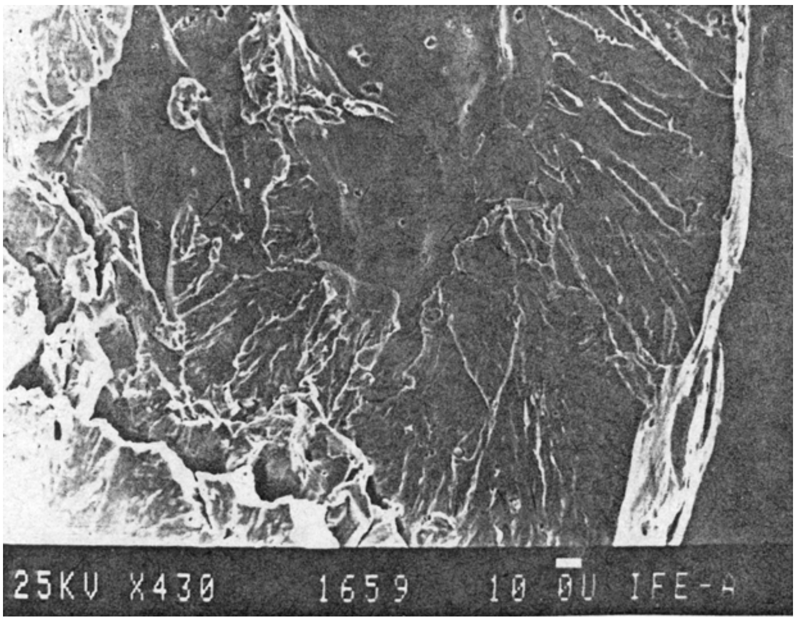

Fig. 6. Intergranular and transgranular fracture surface of aged and precharged FeO-Al_2O_3 specimen

POSTLECTURE

Q: M. HABASHI

The great difference between dilatation coefficients, matrix/oxides, I think, is not the only factor to H.E. importance; form and distribution of these oxides may also act to achieve H.E.

A: E. LUNARSKA

Undoubtedly, the shape and distribution of the second phase particles strongly affect the susceptibility to H.E. However, all studied materials contain globular (nonelongated) particles, homogenously distributed in bulk, so in that case the difference in HE could be determined by the interphase cohesion.

Q: C. ALTSTETTER

As I understand your explanation, one effect of particles is that they allow voids to be created, and these voids act as harmless sinks for H_2. Would you agree that small islands of γ, as in dual phase steels, may have the same beneficial effect?

A: E. LUNARSKA

It is quite possible; since the higher hydrogen solubility in γ than in α phase, the islands in dual steel may serve as nonharmful hydrogen sinks.

Q: F. MOUSSY

Do you produce any void around second phase particles during hot and cold deformation of your basic material?

A: E. LUNARSKA

The voids (or at least weak interphase cohesion) around iron oxide particles in iron are formed during any treatment consisting of heating and cooling of material: solidification, sintering, forging, heat treatment. The cold rolling in case of pure iron matrix may even enlarge the voids as was seen in present case.

Q: M. HABASHI

How did you measure hydrogen quantities in your materials? Is it at melting point?

A: The vacuum extraction at 300^{o}C was used to measure the content of hydrogen in charged specimens.