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Journal of Alloys and Compounds 356–357 (2003) 809–812
Journal of ALLOYS AND COMPOUNDS
www.elsevier.com/locate/jallcom

Positive effects of hydrogen on the plasticity of 2 1/4 Cr–1Mo steel

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Received 10 June 2002; accepted 15 November 2002

Abstract

Steel (2 1/4 Cr–1Mo) and, for comparison, Armco iron were hydrogenated electrochemically in glycerine–phosphoric acid (2:1) electrolyte at 55 °C. The microstructure was studied by optical microscopy and transmission electron microscopy. Compression tests at elevated temperatures of 650 °C showed minor changes in the compressive stress for hydrogenated Armco iron, whereas a tremendous decrease of 50% of the compressive stress in 2 1/4 Cr–1Mo steel after hydrogenation was observed, which would improve the formability during processing. Our investigations indicate that the increase in plasticity of 2 1/4 Cr–1Mo steel strongly depends on the amount of hydrogen, as well as the strain rate, which can be explained by the difference in the mobility of dislocations. The positive effects of hydrogen on the plasticity at higher temperatures and the possible mechanisms which led to the distinct decrease in the compressive stress of 2 1/4 Cr–1Mo steel in comparison to iron are discussed in detail taking into account dynamic recovery as well as recrystallization.

Keywords: 2 1/4 Cr–1Mo steel; Hydrogenation; Dislocations; Softening; Compression test

1. Introduction

The influence of hydrogen on the mechanical properties, especially the yield and flow stress of iron and steels, has been investigated quite extensively. However, there is still controversy as to whether hydrogen causes hardening or softening. Hydrogen was long thought to be detrimental to most engineering materials. As was reviewed in [1], it appears that the yield and flow stress of iron are increased by hydrogen and the hardening considered to be solution hardening due to hydrogen. Softening has been reported only occasionally [2–4]. Kimura, Matsui and co-workers [5,6] investigated extensively the influence of hydrogen in high purity iron and its alloys in a temperature range of 77 K to near room temperature. Their main conclusion was that the softening and/or hardening effect due to hydrogen is strongly dependent on the impurity of the investigated material and the interaction of hydrogen with impurities. Recently Dong and Thompson [7] confirmed these data by measuring thermal activation parameters. However, an increased understanding e.g. of Ti and Ti alloys [8–12] has demonstrated that hydrogen can become also a powerful tool in improving processing and microstructure/mechanical properties.

Hydrogen-induced processing turned out to be very interesting especially for the fabrication of iron and steel. The aim of this paper is to present our recent results on the improved hot formability of high strength 2 1/4 Cr–1Mo steel in comparison with Armco iron after hydrogenation.

2. Experimental

The investigations were performed on commercial Armco iron and 2 1/4 Cr–1Mo steel. Both materials were annealed at 500 °C for 3 h (in the following identified as as-received) before hydrogen charging and compression testing. EDS analysis showed small amounts of trace elements (e.g. Si, S, Cr, Mn, W) for Armco iron and significant amounts of Si, Mn and Ni for 2 1/4 Cr–1Mo steel. The microstructure was studied by optical microscopy (OM) and transmission electron microscopy (TEM: Philips CM200). For optical microscopy polished speci-

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doi:10.1016/S0925-8388(03)00092-6

mens were slightly etched with 2% HNO_3–ethanol. TEM specimens were prepared by electrochemical thinning in a solution of 5% perchloric acid–95% acetic acid at 15 °C.

After grinding Armco iron and 2 1/4 Cr–1Mo steel were charged electrolytically with hydrogen in a glycerine–phosporic acid (2:1) electrolyte at 55 °C and a current density of $I=18$ A/m^2, low enough to avoid charging damage. Since hydrogen diffusion at RT in the investigated Armco iron and 2 1/4 Cr–1Mo steel is very fast and significant desorption of hydrogen after the hydrogenation had to be avoided for the following mechanical testing, all samples were quenched and stored in an acetone–dry ice bath. Chemical and electrochemical coating of the surface with a supersaturated copper sulfate solution and afterwards with a solution consisting of nickel sulfate–boric acid–ammonium chloride (8:1:1) at a current of about 0.5 A turned out to be very effective to retain hydrogen even during compression testing. The hydrogen content was measured by a Leco hydrogen determinator. Compression tests were performed at strain rates of 5%/s and 10%/s at 650 °C using a Gleeble 1500. Since this temperature had to be reached at a very high heating rate in order to reduce hydrogen loss fluctuations of the temperature of ±10 °C as well as of the recorded stress have to be taken into account analyzing the true strain–stress curves.

3. Results and discussion

3.1. Effect of hydrogen on mechanical stability

The influence of hydrogen on the compressive mechanical properties, especially the yield and the flow stress of Armco iron and 2 1/4 Cr–1Mo steel was investigated at 650 °C for different strain rates of 10%/s (Fig. 1) and 5%/s (Fig. 2). Comparing the stress–strain curves for uncharged Armco iron and 2 1/4 Cr–1Mo steel at 650 °C it can be seen that increasing the strain rate increases the flow stress for both materials.

Figs. 1 and 2 reveal only a small, insignificant increase of the compressive stress for Armco iron after hydrogenation up to 3.2 wt.ppm hydrogen and compression test at 650 °C for strain rates of 10%/s and 5%/s, respectively. In contrast to the results for Armco iron, it was observed that hydrogen has a tremendous influence on the yield and the flow stress of the high strength 2 1/4 Cr–1Mo steel. At a strain rate of 10%/s (Fig. 1) and hydrogenation up to 4.5 wt.ppm 2 1/4 Cr–1Mo steel exhibited a slight decrease in the compressive mechanical properties. However, a smaller strain rate of 5%/s and hydrogen charging up to 4.5 wt.ppm hydrogen (Fig. 2) led to a surprising softening effect down to the values of Armco iron.

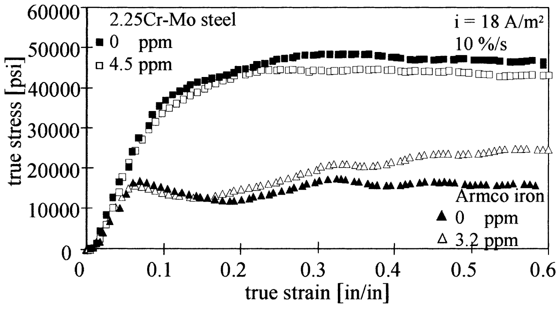

Fig. 1. True strain–stress curves of Armco iron and 2 1/4 Cr–1Mo steel at 650 °C for a strain rate of 10%/s before hydrogen charging and after hydrogen charging.

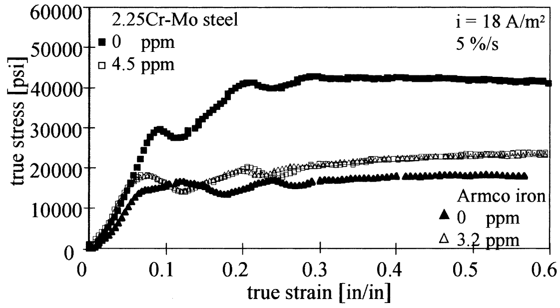

Fig. 2. True strain–stress curves of Armco iron and 2 1/4 Cr–1Mo steel at 650 °C for a strain rate of 5%/s before hydrogen charging and after hydrogen charging.

The influence of the hydrogen content on the true strain–stress curve of 2 1/4 Cr–1Mo steel at 650 °C was investigated at the high strain rate of 10%/s (Fig. 3). The yield and the flow stress decreased by up to 50% with increasing hydrogen content. At a hydrogen content ≥7.8 wt.ppm, similar mechanical properties were observed as for Armco iron.

3.2. Effect of hydrogen on the microstructure

OM of Armco iron and 2 1/4 Cr–1Mo steel in longitudinal direction revealed a ferrite structure for the former and a ferrite–pearlite structure for the latter. Fig. 4 shows the microstructure of uncharged and hydrogenated (7.8 wt.ppm hydrogen) 2 1/4 Cr–1Mo after compression at a

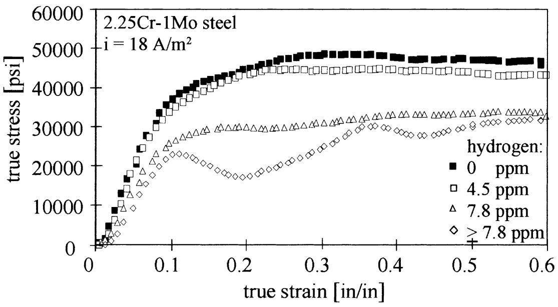

Fig. 3. Influence of the hydrogen content on the true strain–stress curve of 2 1/4 Cr–1Mo steel at 650 °C for a strain rate of 10%/s.

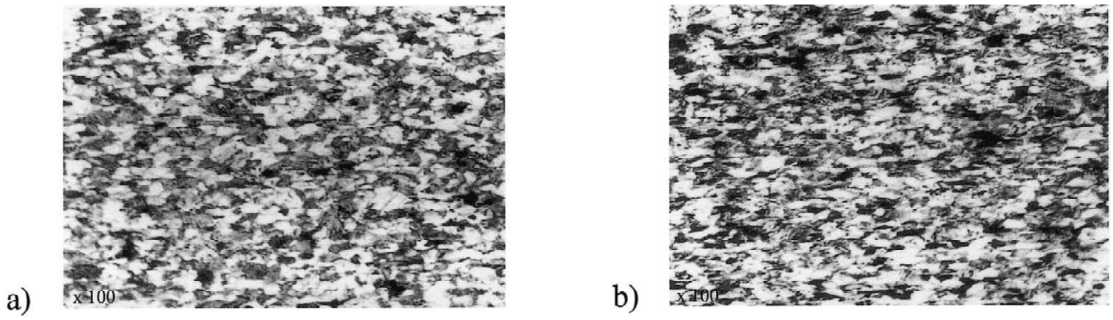

Fig. 4. Optical microscopy of 2 1/4 Cr–1Mo in longitudinal direction: (a) uncharged after compression at a strain rate of 10%/s and (b) hydrogen charged (7.8 ppm hydrogen) after compression at a strain rate of 10%/s.

strain rate of 10%/s. No significant differences between these specimens could be observed by OM. TEM investigations of 2 1/4 Cr–1Mo steel (Fig. 5) give additional information regarding the mechanism during compression before or after hydrogen charging. In comparison to the as-received 2 1/4 Cr–1Mo steel (Fig. 5a) an increase in the dislocation density as well as the formation of a dislocation network, mostly in the ferrite, was observed after compression at 650 °C and a strain rate of 10%/s (Fig. 5b). The observed higher compressive stress of 2 1/4 Cr–1Mo steel might occur due to the formation of dislocations, dislocation networks as well as dislocation pile-ups at the grain boundaries of the ferrite and the very fine lamellar pearlite structure. Hydrogen charging up to 7.8 wt.ppm hydrogen before the compression resulted in well developed cellular dislocation arrangements which are known from dynamic recovery or recrystallization. TEM brightfield images (Fig. 5c) show the formation of small-angle grain boundaries, which are more clearly seen only during tilting of the specimen in the TEM.

The decreasing strain rate in as-received as well as hydrogenated Armco iron and 2 1/4 Cr–1Mo steel permits longer periods for the recovery processes, thus leading to the observed softening effect. The high stacking fault energy which is a prerequisite for the formation of small-angle grain boundaries during recovery of recrystallization, the influence of the high temperature on climbing, cross-slip mechanism of dislocations and a reduced Peierl's potential due to the hydrogen probably increases the mobility of dislocations in 2 1/4 Cr–1Mo steel. This again should accelerate recovery processes leading to softening with increasing hydrogen content in 2 1/4 Cr–1Mo steel. Such an effect is not observed in Armco iron probably due to an already higher mobility of dislocations without

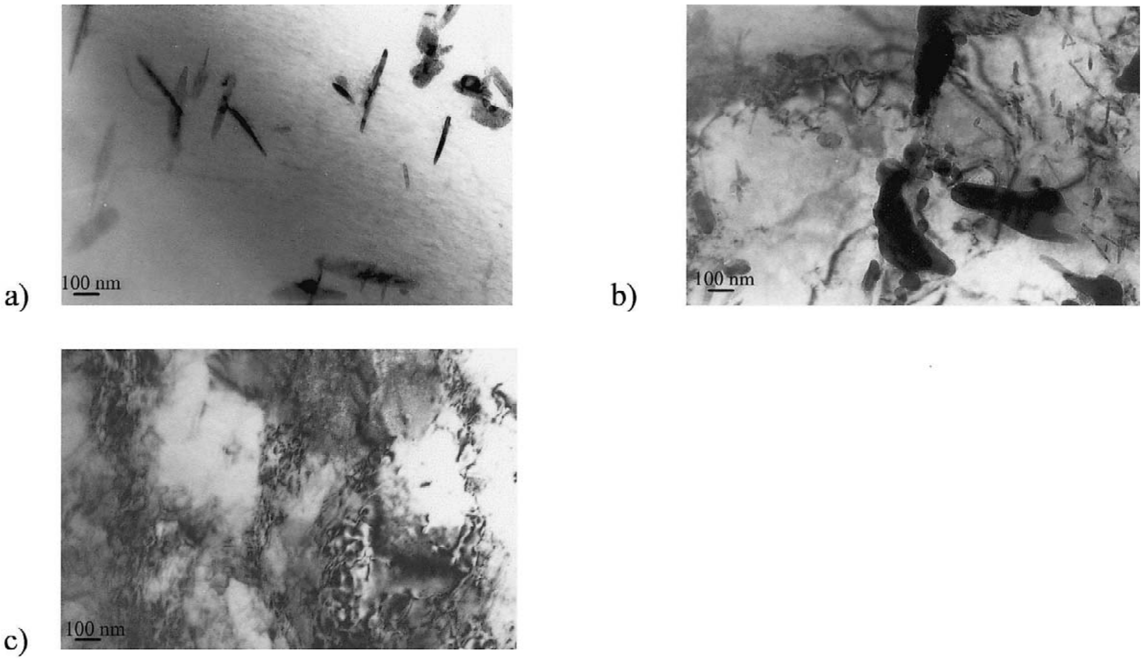

Fig. 5. TEM of 2 1/4 Cr–1Mo steel (cross section): (a) as-received, (b) uncharged after compression at a strain rate of 10%/s and (c) hydrogen charged (7.8 ppm hydrogen) after compression at a strain rate of 10%/s.

hydrogen. Further studies at lower temperatures are underway in order to verify these assumptions.

4. Conclusions

The studies of Armco iron and 2 1/4 Cr–1Mo steel showed a strong influence of hydrogen on compressive mechanical properties, e.g. yield and flow stress, of the high strength 2 1/4 Cr–1Mo steel. It was observed that compression at 650 °C resulted in minor changes in the compressive stress for hydrogenated Armco iron, whereas a tremendous decrease of the compressive stress occurred in hydrogenated 2 1/4 Cr–1Mo steel.

Microstructural studies indicated that the observed softening effect of 2 1/4 Cr–1Mo steel strongly depends on the amount of hydrogen, which can be explained by the difference in the mobility of dislocations, as manifested in the formation of dislocation networks.

It was shown that the positive influence of hydrogen on the mechanical properties at higher temperatures and the mechanism which led to the distinct decrease in compressive stress of 2 1/4 Cr–1Mo steel can improve the formability during processing.

Acknowledgements

The authors acknowledge and appreciate the support of the US Army Research Office.

References

[1] E. Lunarska, in: R.A. Oriani, J.P. Hirth, M. Smialowski (Eds.), Hydrogen Degradation of Ferrous Alloys, Noyes, Park Ridge, NJ, 1985, p. 321.
[2] C.D. Beachem, Met. Trans. 3 (1972) 437.
[3] I.M. Bernstein, Script. Met. 8 (1974) 343.
[4] H. Matsui, S. Moriya, H. Kimura, in: Proc. 4th Int. Conf. Strength of Metals and Alloys, Nancy, France, 1976, p. 291.
[5] H. Kimura, H. Matsui, A. Kimura, T. Kimura, K. Oguri, in: I.M. Bernstein, A.W. Thompson (Eds.), Proc. 3rd Int. Conf. on Effects of Hydrogen on Behavior of Materials 1980, The Metallurgical Society of AIME, 1981, p. 191.
[6] H. Matsui, S. Moriya, H. Kimura, Mat. Sci. Eng. 40 (1979) 207.
[7] H. Dong, A.W. Thompson, Mat. Sci. Eng. A188 (1994) 43.
[8] U. Zwicker, et al., US Patent No. 2892742, June 1959.
[9] W.R. Kerr, P.R. Smith, M.E. Rosenblum, F.J. Gurney, Y.R. Mahajan, L.R. Bidwell, in: H. Kimura, O. Izumi (Eds.), Proc. 4th Int. Conf. Titanium, Kyoto, Japan, AIME, Warrendale, PA, 1980, p. 2477.
[10] F.H. Froes, D. Eliezer, H.G. Nelson, The Minerals, Metals and Materials Society/AIME (1996) 719.
[11] D. Zander, D.L. Olson, D. Eliezer, Metal. Mat. Trans., in press.
[12] D. Zander, B. Kofmann, D. Eliezer, E.Y. Gutmanas, E. Abramov, D. Olson, in: N.R. Moody, A.W. Thompson (Eds.), Hydrogen Effect on Material Behavior, TMS, Warrendale, 2002, in press.