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Microstructural modifications induced by hydrogen in a heat resistant steel type HP-45 with Nb and Ti additions

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Abstract

Heat resistant stainless steel type HP45 modified by Nb and Ti additions, which is commonly used in chemical and petrochemical industrial plants, was submitted to hydrogen treatment at low and ultra-high pressures. In the low-pressure experiments, 0.1 Pa, hydrogen was supplied in a quartz tube and the material was heat-treated for 100 h at 1200 K. In the high-pressure experiments, 5 GPa, hydrogen was supplied in a NaCl container and the material heat-treated at 873 and 1073 K for 1 h. A coarsening of the $M_{23}C_6$ (M=Fe, Cr, Ni) carbides, was observed in both cases, these being of a sharper shape for the low hydrogen pressure condition, compared with previously aged samples. In the high pressure experiments, where the atomic mobility is higher, a more intense coarsening of the carbides and the cracks associated with them was observed, which is deleterious for mechanical properties. The hydrogen-induced phase coarsening can be understood in terms of the vacancy formation that occurs under such conditions.
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1. Introduction

The study of hydrogen interaction with metals and alloys has been motivated by the embrittlement phenomena that may occur due to the segregation characteristics [1] even if hydrogen is present at low concentrations.

Usually hydrogen embrittlement in stainless steels at low hydrogen pressures is attributed to the nucleation of microcracks or to the phase transformation to the ε-phase, these mechanisms being more common near room temperature [2]. At intermediate temperatures of about 200–500 °C, a chemical reaction between hydrogen and carbides takes place [3]. In this case, methane gas is formed and the precipitates are destroyed by hydrogen forming cavities, which are points for cracks nucleation [4].

At high temperatures and under high pressure, hydrogen promotes fast atomic diffusion in metals [5–7]. This is due to the creation of a superabundant vacancy solution in the metal. This phenomenon can be explained on account of the reduction of the vacancy formation energy by hydrogen trapping, as described by Fukai et al. who observed it in Ni, Pd and Fe alloys [6–8].

Steel parts in chemical and petrochemical industrial plants are usually exposed to conditions where contamination with hydrogen can occur. It is particularly critical to radiant tubes in reformer furnaces operating at temperatures between 1073 and 1373 K, where creep is the main failure mechanism.

It is well recognized that creep rupture in polycrystalline materials at elevated temperatures occurs mainly by the nucleation and growth of cavities at grain boundaries or at interfaces between precipitates and matrix. Coalescence of these cavities leads to the formation of microcracks which link up to precipitate the final fracture of these materials. A considerable amount of work has proposed vacancy formation as the mechanism responsible for cavity growth at high temperatures generating creep [9]. This mechanism can be faster in the presence of hydrogen. The aim of this work is to present a study of the transformation induced by hydrogen in the microstructure of HP 45 steels modified by Nb and Ti additions.

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2. Experimental methods

HP steel modified by additions of Nb and Ti additions was produced in the form of a centrifugally cast tube with external diameter of 111.5 mm and wall thickness of 11.8 mm. The chemical composition of the alloy (in wt%) is: C–0.41; Cr–25.5; Ni–34.9; Mn–1.03; Si–1.91; Nb–0.78; Ti–0.04 and Fe–balance. All samples were aged at 1173 K for 1000 h.

Metallographic characterization was performed in a scanning electron microscope (SEM) using backscattered electrons. Observation was made of unattached samples, using backscattered electrons, which makes it possible to identify different phases as a result of the atomic weight differences.

Two different forms of hydrogen charging were used, low and high pressure ones. Disks of 7 mm diameter and 0.3 mm of thickness were heat treated in a hydrogen atmosphere of 0.1 Pa at 1200 K for 100 h. In the high hydrogen pressure treatments, each sample was encapsulated together with an internal hydrogen source in a NaCl container (7 mm in diameter and 8 mm high) impermeable to hydrogen. The high hydrogen pressure was applied using a belt-type press at 5±0.01 GPa for 1 h for two different temperatures of 873 and 1073 K. The hydrogen source was a pellet of $C_{14}H_{10}$. The sample was separated from the $C_{14}H_{10}$ pellet by a 0.1-mm thick BN disc, which impedes the diffusion of carbon, while permitting hydrogen to diffuse through the BN to form hydride in some alloys, as in the case of Pd analyzed elsewhere [7].

3. Results and discussion

Fig. 1 shows the micrograph of the modified HP 45 steel in the as-cast condition at two different magnifications. The microstructure of this steel can be described as an austenitic matrix surrounded by chromium carbides (dark ones) and niobium titanium carbides (bright ones) in the interdendritic region forming a fragmented network.

Fig. 2 shows the microstructure of the steel after aging at 1173 K for 1000 h. A fine chromium carbide precipitation can be observed in addition to the primary phase coarsening. This secondary precipitation, observed at the resolution limit of the SEM, shows particles with cubic and needle-shaped forms.

Fig. 3 shows the microstructure of the aged HP 45 steel, after treatments with low hydrogen pressure. It can be observed that the heat treatment promoted a coarsening of the secondary $M_{23}C_6$ precipitation and an additional precipitation in the interdendritic region. The microstructural modifications induced by hydrogen can be seen more clearly in Fig. 4, where the sample was submitted to high hydrogen pressure, 5 GPa at 1073 K. In this case, a dramatic microstructural coarsening in both primary and secondary carbides can be observed. This microstructural modification, characterized by the Cr carbides coarsening, occurs without a concomitant growth of the Nb-rich phase. This behavior can be explained considering the higher stability of Ti carbides in the presence of hydrogen [1]. On the other hand, it can also be considered that all Nb and Ti are forming carbides and as a consequence there are no

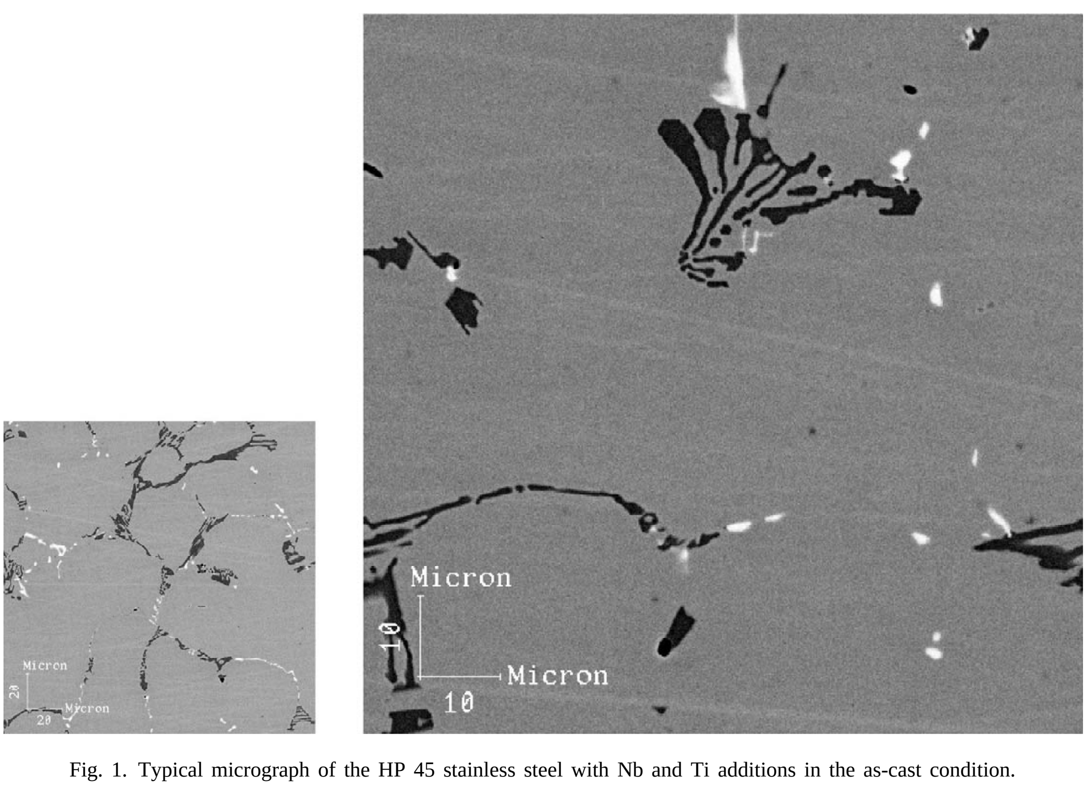

Fig. 1. Typical micrograph of the HP 45 stainless steel with Nb and Ti additions in the as-cast condition.

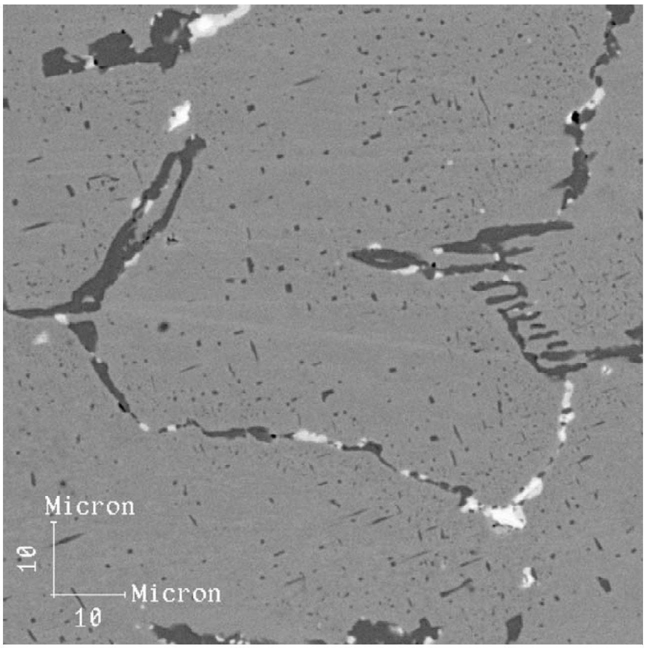

Fig. 2. Typical micrograph of HP 45 stainless steel after aging for 1000 h at 1173 K.

more elements in the matrix for the (Nb,Ti)C coarsening. A remarkable feature, which can be also observed in Fig. 4, is the presence of well-defined cracks crossing several chromium carbides.

Fig. 5 shows the microstructural modifications in a sample that was submitted to high-hydrogen pressure, 5 GPa at 873 K. In this case, chromium carbides coarsening can also be observed on a reduced scale. The presence of

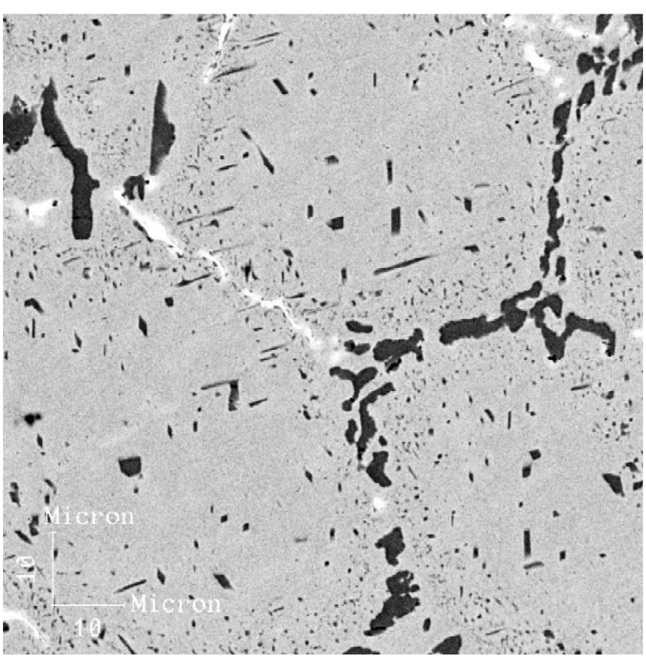

Fig. 3. Microstructure of the HP 45 stainless steel after treatment with a low hydrogen pressure of 0.1 Pa for 100 h at 1200 K.

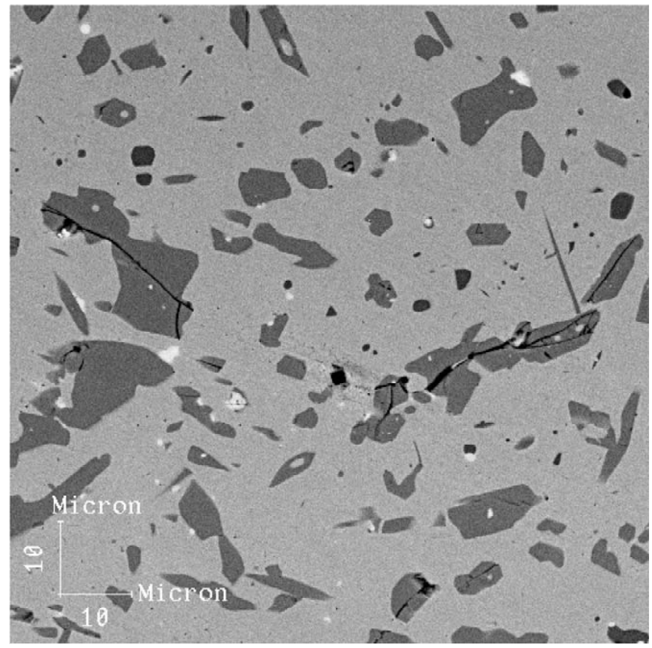

Fig. 4. Microstructure of the HP 45 stainless steel after treatment with a high hydrogen pressure of 5 GPa for 1 h at 1073 K.

cracks crossing the chromium carbides and in the interface between Nb-rich phase or chromium carbides with the matrix are also defined and can also be observed. These cracks were formed during the hydrogen treatment due to the elevated stress state.

Fig. 6 shows the microstructure of the same sample shown in Fig. 5 at a higher magnification after heat

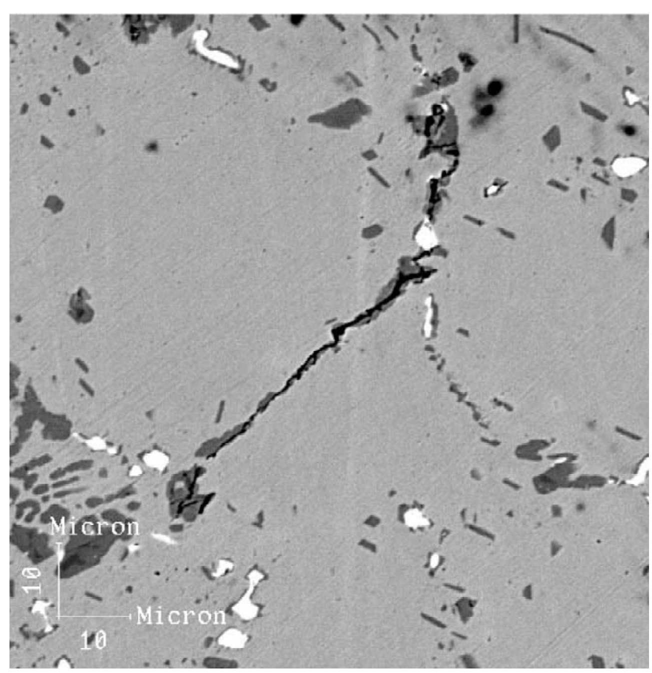

Fig. 5. Microstructure of the HP 45 stainless steel after treatment with a high-hydrogen pressure of 5 GPa for 1 h at 873 K.

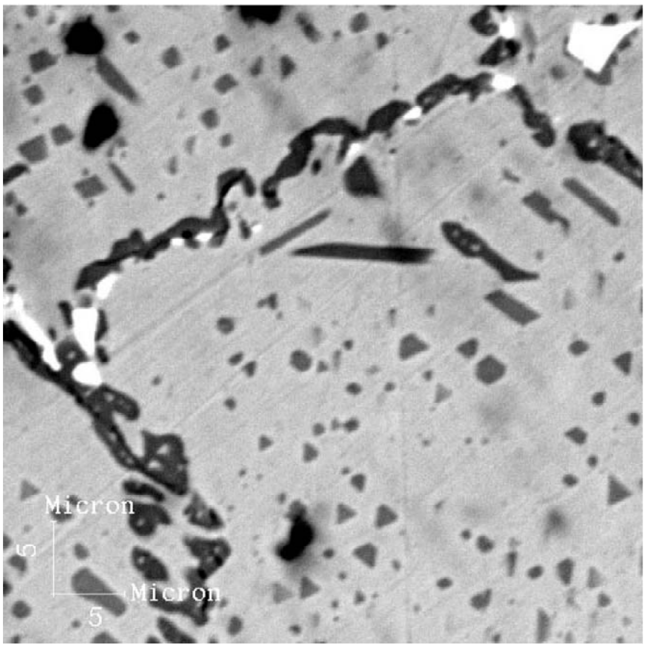

Fig. 6. Higher magnification of microstructure of the HP 45 stainless steel, shown in Fig. 5 after heat treatment for 1 h at 873 K.

treatment at 1073 K for 1 h. This treatment was done to promote the diffusion of defects generated during the hydrogen treatment to the surface. The formation of defects with a triangular shape can be observed. This suggests the condensation of the vacancies as tetrahedral stacking faults [10,11].

The coarsening mechanism of the carbides, induced by hydrogen, can be understood based on the formation of vacancies. This phenomenon is supported by the recent results of Fukai et al. [12] who have observed a formation of 19 at% of vacancies in pure Fe using 4.7 GPa at 1053 K. If in this case superabundant vacancies are produced in the alloys, it is probable that a great number of these vacancies are used to promote fast diffusion in the alloy since this is the main auto-diffusion mechanism in metals [8,13].

4. Conclusions

Hydrogen treatment of HP 45 stainless steels induces coarsening of the chromium carbides, this being more pronounced at high hydrogen pressures. This is due to hydrogen inducing lattice migration, which is attributed to the generation of superabundant vacancies. The same behavior of carbides coarsening cannot be observed in case of (Nb,Ti)C which demonstrate a higher stability of these carbides in the presence of hydrogen. Cracks crossing the chromium carbides and propagating in the interface of (Nb,Ti)C with the matrix and with the chromium carbides was also observed.

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