475 ℃ Embrittlement in High Chromium Oxide Dispersion Strengthened Steels

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1. Introduction

High Cr oxide dispersion strengthened (ODS) steels whose Cr concentration were in the range of 13 to 22 wt. % were recently developed and showed high resistance to corrosion in SCPW [1] and also to the hydrogen embrittlement such that critical hydrogen concentration required for brittle cracking was about one order higher value than that of 9Cr reduced activation martensitic steels [2].

Since ODS steels have been developed for the use of high temperature applications in the range from ~400 to 700℃, they will inevitably experience thermal aging related problems as service time prolonged. Particularly, it is well known that high Cr ferritic steels can result in the precipitation of coherent particles of ά (Cr-rich ferrite) with an associated reduction in ductility [3] when serviced at temperatures between 400 and 550℃. However, limited data were available for the microstructural and mechanical property changes of high Cr ODS steels by thermal aging treatments.

In this work, the effects of thermal aging treatment on the microstructural stability and mechanical property changes of ODS steels were investigated by using TEM, microhardness and small punch (SP) tests.

2. Experimental

The materials used were five kinds of ODS steels (K1~K5) produced by varying Cr from 13 to 22 wt. % content but keeping yittria contents within 0.36~0.38 wt. %. Main chemical compositions of K1, K2, K3, K4 and K5 are 19Cr, 13Cr-4Al, 16Cr-4Al, 19Cr-4Al and 22Cr-4Al, respectively. Disk type SP specimens ($3\varphi \times 0.28^t$ mm) were sampled from the extruded rod so that the axis direction is parallel to transverse (T)-direction with respect to the extruded direction. Specimens were thermally aged at temperatures from 420 to 475℃ up to 1000 hours. Thin foils for transmission electron microscopy (TEM) were fabricated by twin jet electropolisher in a solution of 10% perchloric acid + 90% ethanol at -30 °C. SP tests were performed at a cross-head speed of 0.2 mm/min. at room temperature. Vickers micro-hardness test was carried out with a 500 g load at room temperature.

3. Results

3.1. Microstructural characteristics by thermal aging

Our previous works showed that after thermal aging treatment at 420 ℃ for 322 hours, any discernable precipitation could not be found in the ODS steels even though they experienced significant embrittlement accompanied by hardening [4]. However, when thermal aging temperature increased up to 475 ℃, gradual microstructure changes were identified depending on the aging time, showing the phase separation of ferrite matrix (Figure 1). Based on the EDS line scanning profiles (Figure 2), we could know that it was resulted from the formation of Cr-rich and Fe-rich zone either by

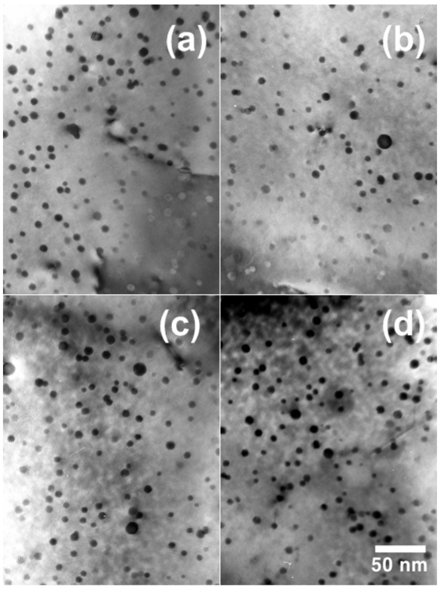

Figure 1. Typical transmission electron micrographs, showing as thermally aged K5 ODS steel at 748 K up to (a) 5, (b) 50, (c) 505 and (d) 1000 hr, respectively (bright field images).

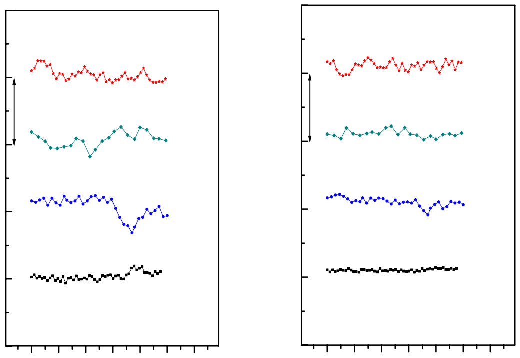

Figure 2. Concentration fluctuations of Fe and Cr in thermally aged K5 ODS steel at 748 K.

Spinodal decomposition or by nucleation and growth mechanism. But, current aging conditions did not give any changes of number density and size of oxide particles.

3.2 Hardening behaviors

Hardening behaviors of ODS steels as a function of aging parameter, P, were shown in Figure 3. From the figure, increase in micro-Vickers hardness (ΔHv) in each ODS steel revealed linear relationship with aging parameter. Furthermore, as Cr content increased from 13 (K2 ODS) to 22 w/o (K5 ODS), the amount of hardening also increased linearly as well. As the results, we could obtain the generalized hardening formula as a function of Cr, aging temperature and time as follows.

$$\Delta Hv = (2.37Cr-3.02)xT(20+\log t)x10^{-3} - (34.8Cr-31.5)$$

Where, T is temperature [K] ($703 \leq T \leq 748$), t is aging time [hour] ($5 \leq t \leq 1000$) and Cr is weight percent ($13 \leq Cr \leq 22$). In addition, yield stress and SP energy of the given ODS steels also correlated successfully with the ΔHv.

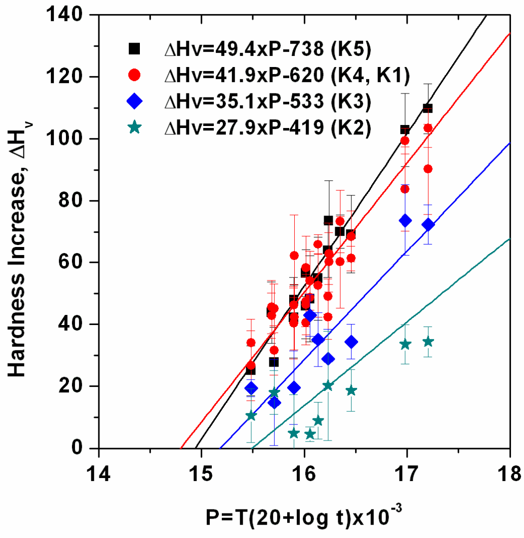

Figure 3. Increase in micro-Vickers hardness (ΔHv) as a function of aging parameter P.

3.3 Hardening mechanism

Figure 4 presents that the activation energy determined by micro-hardness is in the range of 214 ~ 240 kJ/mol that is very similar to the diffusion activation energy of Cr and Fe in Fe-26Cr steel [5]. Therefore, the formation of Cr-rich ά-phase must be due to the inter-diffusion of Cr and Fe in the ferrite matrix, and it resulted in the increase in internal stress caused by atomic misfit and different modulus between the phases [6]. Finally, the presence of ά retards the motion of dislocations and hardens the materials which results in the loss of toughness and ductile to brittle transition temperature shift.

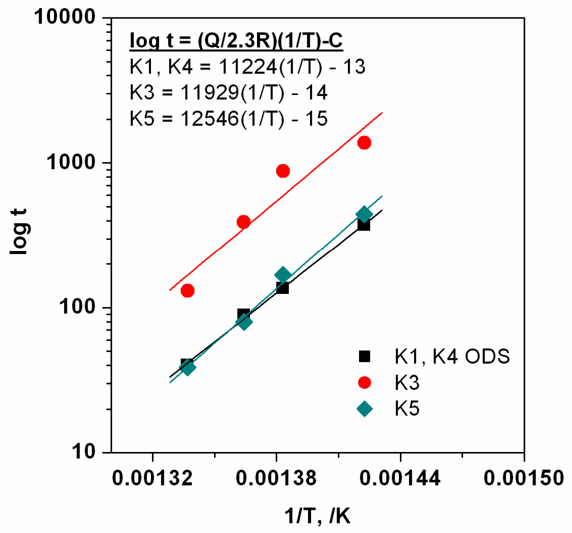

Figure 4. The activation energy of each ODS steel determined by micro-hardness tests.

4. Summary

Main cause of embrittlement in thermally aged high Cr ODS steels at temperatures from 420 to 475 C is the formation of Cr-rich coherent ferrite phase, α' phase. The activation energy of α' phase is measured in the range of 214~240 kJ/mol, which is similar to the diffusion activation energy of Fe and Cr in alpha iron. The hardening relationship at current test conditions can be obtained successfully as a function of Cr content and aging time.

Acknowledgment

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