CHANGES IN HYDROGEN DESORPTION PROFILES AND MATERIALS DEGRADATION IN 12%CR ROTOR STEEL

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ABSTRACT

Variation in hydrogen desorption profile with aging was investigated to examine an applicability of hydrogen to microstructure evaluation of advanced high chromium ferritic steels. The 12% chromium rotor steels aged under various conditions were subjected to hydrogen charging by cathodic electrolysis and subsequent thermal desorption spectroscopic (TDS) analyses. Experimental results revealed that a large hydrogen evolution peak appeared at around 100℃ in each hydrogen desorption profile. The peak height decreased markedly with aging. This evolution peak was experimentally decomposed to two hydrogen profiles with different peak temperatures of 80 and 100℃. The hydrogen profile with peak temperature of 100℃ mainly reflected the amount of hydrogen desorbed from dislocations, namely, the dislocation density. There was a good correlation between the amount of hydrogen and the Vickers hardness. Consequently, the present method consisting of hydrogen charging and subsequent TDS analysis was considered to be a useful procedure for evaluating complicated microstructural changes.

1 INTRODUCTION

Recently, attention has been focused on tungsten-added high chromium ferritic steels as candidate materials for boiler headers and heat-exchange tubes of an ultra super critical (USC) boiler. These martensitic steels have improved creep strength by precipitation strengthening attributed to Laves phase in addition to solid-solution strengthening by elements, such as tungsten and molybdenum and dispersion strengthening by MX-type carbonitride particles (e.g. Hasegawa [1]). However, it is not easy to separate the contributions of such strengthening factors to the improved creep strength and quantitatively understand individual contributions and their changes due to aging or service exposure because of extremely complicated microstructure. Therefore, the material degradation mechanism of this kind of steel has not been thoroughly clarified. Needless to say, a nondestructive procedure for damage evaluation, which is required for remaining-life prediction of aged components, has not as yet been established. On the other hand, it is known that diffusible hydrogen in steels is closely associated with delayed fracture (hydrogen embrittlement) of high strength low alloy steels (e.g. Nagumo [2]). This diffusible hydrogen usually trapped by vacancies, dislocations, grain boundaries, precipitates, etc., can be easily desorbed from each trapping site by heating the steels (e.g. Takai [3]). However, temperature of the hydrogen desorption varies according to the trap site, because the binding energy between hydrogen and each trap site is different (Hirth [4]). The energy between hydrogen and precipitates is generally larger than other energies. It seems that this nature of hydrogen can be utilized for evaluating the microstructures of advanced steels, which are too fine and complicated to evaluate quantitatively.

In this study, variation in hydrogen desorption profile with aging was investigated to examine an applicability of hydrogen to the microstructure evaluation of advanced high chromium ferritic steels. The thermally aged 12% chromium rotor steels were subjected to hydrogen charging by cathodic electrolysis and subsequent thermal desorption spectroscopic analyses. A correlation between the changes in hydrogen desorption profiles and mechanical properties, such as Vickers hardness and creep rupture strength, were examined from the viewpoint of change in dislocation density due to aging.

2 EXPERIMENTAL PROCEDURES

The material used in this study was a 12% chromium ferritic steel (C: 0.14C, Si: 0.04, Mn: 0.62, P: 0.007, S: 0.0025, Ni: 0.70, Cr: 10.02, Mo: 0.99, V: 0.19, W: 1.00, N: 0.373 in mass%, and Fe: bal.), which has been recently developed as a steam turbine rotor steel. After a typical heat treatment consisting of normalizing and tempering, the steel was isothermally aged at 630 and 650℃ for 3000 and 10000 h. The steel, which had not been subjected to the thermal aging, was defined as "as-tempered steel". Vickers hardness measurements and creep rupture tests were carried out to investigate changes in mechanical properties with thermal aging. The Vickers hardness was determined under the load level of 9.8 N at room temperature. The creep tests were performed at the temperatures of 600 and 650℃ and stress levels of 245 and 147 MPa using the as-tempered steel and the steels aged at 650℃ for 3000 and 10000 h.

The plate-type specimens with a dimension of 10 x 10 x 0.5 mm were used for a thermal desorption spectroscopic (TDS) analysis of hydrogen. Hydrogen charging into the specimens was conducted by means of cathodic electrolysis in 1 mol/l NaOH aqueous solution under a current density of 5 mA/cm^2 (4 hours). The TDS analyses were carried out at a temperature range from room temperature to 800℃. The heating rate used in this study was 100, 200 and 400℃/h. The desorbed hydrogen carried with high purity argon gas was detected by a gas chromatograph at intervals of 5 minutes. The flow rate of the argon carrier gas was fixed at 1.2 x 10^{-5} m^3/min throughout the analysis. The hydrogen evolution rate was defined as the amount of hydrogen desorbed in one minute per one gram of specimen.

3 RESULTS AND DISCUSSION

3.1 Changes in microstructures and mechanical properties with aging

The scanning electron microscope (SEM) observations of the aged steels clearly exhibited that relatively large precipitates predominantly existed on prior austenite grain boundaries. They seemed to be $M_{23}C_6$-type carbide and Laves phase, which have been commonly observed in high chromium ferritic steels. The coarsening and/or disappearance of martensitic lath were not evidently observed by optical microscope.

The Vickers hardness measured on the aged steels is plotted as a function Larson-Miller parameter (LMP) in Fig. 1. The steel shows a loss of hardness as a result of thermal aging both at 630℃ and at 650℃. However, the decrease in hardness due to the aging at 630℃ is slightly more

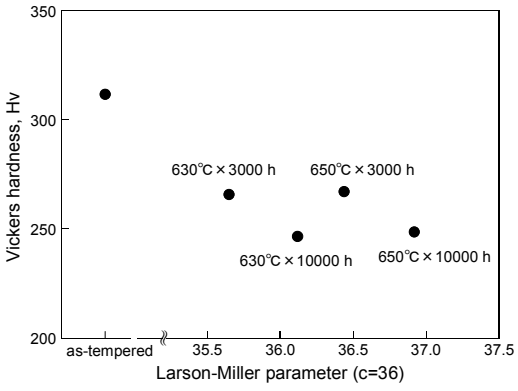

Figure 1: Vickers hardness plotted against LMP.

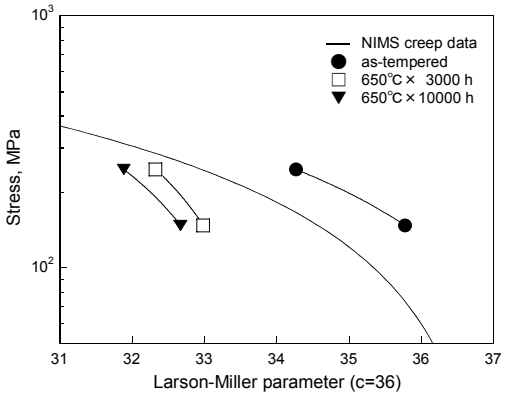

Figure 2: Results of creep rupture tests.

significant than that at 650℃. Figure 2 shows the results of creep rupture tests along with the creep rupture data of 12Cr-1Mo-1W-0.3V steel published by the National Institute of Materials Science (NIMS). The creep rupture strength of the present steel is somewhat superior to that of the NIMS steel. However, the rupture strength decreases significantly after the aging at 650℃, and this reduction in strength is more pronounced with aging time. The above-mentioned microstructural change is likely to cause these degradations of mechanical properties.

3.2 Change in hydrogen desorption characteristics with aging

Figure 3 shows examples of hydrogen evolution curves measured on the as-tempered steel and the steel aged at 650℃ for 10000 h using the heating rate of 100℃/h. The hydrogen evolution rate is plotted against the temperature range from room temperature to 500℃. Two large hydrogen evolution peaks, which were not observed at all in the non-charged specimens, appear at around 100 and 400℃ in both of the profiles. The peak in the lower temperature region is relatively clearer and larger, and its peak height decreases markedly due to aging. The hydrogen profiles of the other aged steels were very similar to that of the steel aged at 650℃ for 10000 h.

In general, the hydrogen evolution peak consists of desorption from various kinds of trap sites with different detrapping activation energies, even if it appears to be a single peak. Thus a single desorption profile can be decomposed to multiple profiles with different peak temperatures. The decomposed profiles with peaks of 80, 100 and 140℃ have been reported to correspond to hydrogen released from prior austenite grain boundaries and packet boundaries, dislocations and precipitates such as a MX-type carbonitride and copper precipitation particle (Yokota [5] and Komazaki [6]), respectively. The present peak in the lower temperature region was also tried to be decomposed to multiple profiles to show quantitatively the variation in hydrogen desorption with aging. In this study, the difference in the hydrogen profiles between the steel aged at 650℃ for 10000 h and the other steels was examined to decompose experimentally the peak profile of the lower temperature region, because the changes in microstructures, such as a recovery of dislocation structures and precipitation and/or coarsening of carbides and TCP phases, were the most pronounced in the steel aged at 650℃ for 10000 h. As a result of decomposition, the single large peak profile was decomposed to two profiles with different peak temperatures. The decomposed profiles of the as-tempered steel are given in Fig. 4, where two different peaks can be clearly seen. These profiles have the peak temperatures of about 80 and 100℃, respectively.

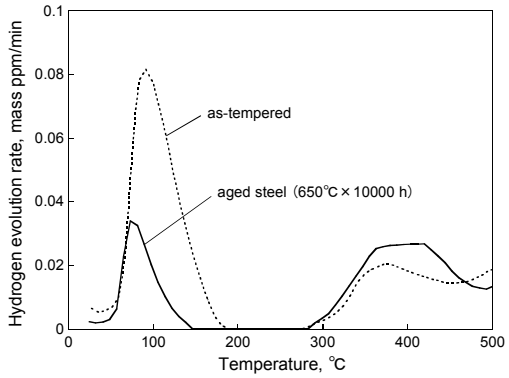

Figure 3: Hydrogen evolution curves measured on as-tempered and aged steels.

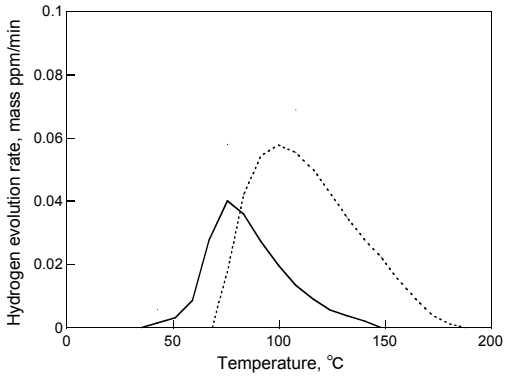

Figure 4: Decomposed hydrogen profiles obtained from as-tempered steel.

According to the reports mentioned above, they are considered to be attributed to hydrogen released from grain boundaries and dislocations, respectively. Hydrogen evolution peaks commonly contain hydrogen desorption from precipitates, such as a MX-type carbonitride. As can be seen in Fig. 4 where there is no distinct hydrogen profile with peak temperature of 140℃, the hydrogen desorption from MX-type carbonitrides could not be separated by the present experimental way. This profile is considered to be included in the above-decomposed profile with peak temperature of 100℃, because large asymmetric hydrogen desorption is observed at around 140℃ in the decomposed profile.

The apparent detrapping activation energy of hydrogen was estimated from the dependence of the peak temperature on heating rate to confirm that the hydrogen desorption with peak temperature of 100℃ results from the hydrogen released from dislocations. The apparent activation energy, E_a, was determined by using equ (1) (Choo [7]).

$$-\frac{E_a}{R} = \frac{\partial \ln(\phi / T_p{}^2)}{\partial(1/T_p)} \tag{1}$$

Where T_p, ϕ, R are the peak temperature, the heating rate and the gas constant, respectively. Figure 5 shows the result obtained from the as-tempered steel, where the $\ln(\phi/T_p{}^2)$ is plotted against the $1/T_p$. From the slope, the apparent activation energy was estimated to be 31.7 kJ/mol. This value is in relatively good agreement with the detrapping activation energy of hydrogen from dislocations (Hirth [4]). This result indicates that the hydrogen profile with peak temperature of 100℃ principally reflects the amount of hydrogen trapped by dislocations, namely, the dislocation density. The amount of hydrogen trapped by dislocations was estimated by calculating the area of the decomposed profile with peak temperature of 140℃. The result obtained is plotted as a function of Larson-Miller parameter in Fig. 6. The amount of hydrogen decreases abruptly as a result of the aging at 630℃ for 3000 h. However, it shows almost no variation with additional aging. This change is very similar to that in Vickers hardness.

3.3 Relationship between mechanical properties and hydrogen desorption characteristics

Figure 7 shows the amount of hydrogen which had been trapped by dislocations plotted against the Vickers hardness. A good correlation can be obviously seen in this figure. This result seems to come from the fact that both of the values are strongly dependent on dislocation structures. The

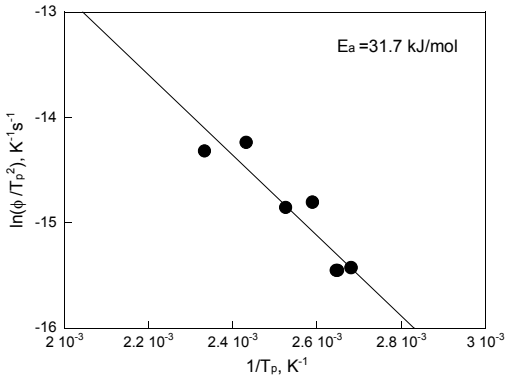

Figure 5: Dependence of peak temperature on heating rate.

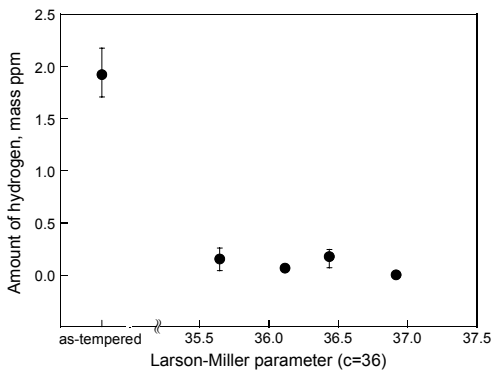

Figure 6: Amount of hydrogen plotted as a function of LMP.

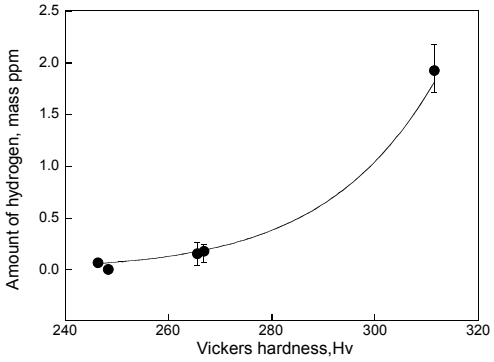

Figure 7: Relationship between amount of hydrogen and Vickers hardness.

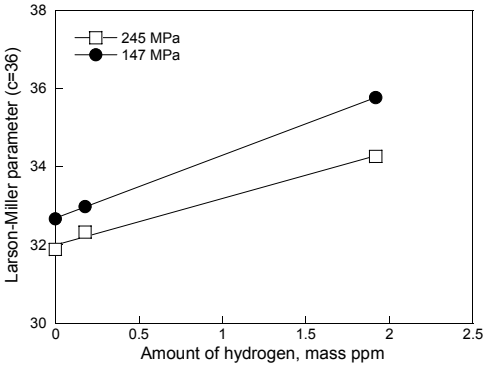

Figure 8: Relationship between amount of hydrogen and creep rupture test result.

reduction in dislocation density is the most effective factor of softening, and it also leads to the decrease in the number of hydrogen trap sites. Figure 8 shows the relationship between the amount of hydrogen and the result of creep rupture test. The rupture strength decreases monotonously as the amount decreases. From these results, it may be concluded that the change in dislocation density, which influences considerably the mechanical properties represented by the creep rupture strength, can be evaluated by measuring hydrogen desorption profiles.

In this study, the attention was focused on the decomposed profile with peak temperature of 100℃, and the variation in hydrogen desorption profile due to aging was examined from the viewpoint of the change in dislocation density alone. As described above, the hydrogen evolution peak consists of desorption from not only dislocations but also grain boundaries inclusive of packet boundaries, block boundaries and lath boundaries and precipitates such as a carbide and TCP phase. Furthermore, hydrogen is also likely to accumulate at defects such as a creep cavity and microcrack. If other decomposed profiles could be obtained and assigned to these microstructures and defects, the present method consisting of hydrogen charging into steel and subsequent it's desorption by heating would be a useful nondestructive procedure for evaluating microstructure changes of the advanced high chromium ferritic steels and, in turn, their materials degradation during service operations.

4 CONCLUSIONS

Variations in hydrogen desorption profile with aging were investigated to examine an applicability of hydrogen to the microstructure evaluation of advanced high chromium ferritic steels. The thermally aged 12% chromium rotor steels were subjected to hydrogen charging by cathodic electrolysis and subsequent thermal desorption spectroscopic (TDS) analyses. A correlation between the changes in hydrogen desorption profiles and mechanical properties, such as Vickers hardness and creep rupture strength, were examined from the viewpoint of change in dislocation density. From the present investigation, the following conclusions can be drawn.

(1) Two large hydrogen evolution peaks appear at around 100 and 400℃ in the hydrogen desorption profiles. The peak in the lower temperature region is relatively clearer and larger, and its peak height decreases markedly with thermal aging of the steel.

(2) The above hydrogen evolution peak in the lower temperature region is decomposed to two hydrogen profiles with different peak temperatures of 80 and 100℃. The hydrogen profile with peak temperature of 100℃ mainly reflects the amount of hydrogen trapped by dislocations,

namely, the dislocation density. The apparent detrapping activation energy of hydrogen from dislocations is estimated to be 31.7 kJ/mol.
(3) There is a good correlation between the amount of hydrogen trapped by dislocations and the Vickers hardness and time to rupture of which both are strongly dependent on dislocation density. The present method consisting of hydrogen charging into steels and subsequent it's desorption by heating is considered to be a useful procedure for evaluating microstructural changes of the advanced high chromium ferritic steels.

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