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Irradiation embrittlement of $2\frac{1}{4}$Cr–1Mo steel at 400°C and its electrochemical evaluation

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Abstract

The effect of neutron irradiation on mechanical properties of normalized and tempered $2\frac{1}{4}$Cr–1Mo steel was evaluated by conducting postirradiation tensile and Charpy impact tests. The specimens were irradiated at 400°C to a fluence as high as 3×10^{24} n/m^2 ($E > 1$ MeV). Only slight hardening was observed because of the high temperature of irradiation. However, irradiation at 400°C to a fluence larger than 1×10^{24} n/m^2 ($E > 1$ MeV) caused high Charpy shifts accompanied by intergranular fracture. Results of electrochemical tests indicated that a possible element responsible for intergranular fracture was phosphorus.

1. Introduction

Ferritic steels are possible structural materials for the first wall and blanket structure of fusion reactors because of the superior swelling resistance, high heat flux capacity and so on. However, ferritic steels undergo the shift in ductile to brittle transition temperature (DBTT) that is mainly caused by neutron irradiation. The typical alloy compositions of the ferritic steels under investigation are 2.25 Cr, 7–9 Cr and 12 Cr.

A normalized and tempered $2\frac{1}{4}$Cr–1Mo steel is to be used for the pressure vessel material of high temperature engineering test reactor (HTTR) which is the high temperature gas-cooled reactor located in Japan Atomic Energy Research Institute (JAERI) [1]. The pressure vessel will be subjected to a temperature of about 400°C during normal operation. Hence, irradiation embrittlement of the steel exposed to the temperature region in question has been evaluated at JAERI [2,3]. The results obtained by the neutron irradiation experiments at around 400°C up to a fluence of 2×10^{22} n/m^2 ($E > 1$ MeV) have shown that normalized and tempered $2\frac{1}{4}$Cr–1Mo steel has a high toughness value and a comparatively low susceptibility to neutron irradiation embrittlement.

This paper describes the irradiation embrittlement of $2\frac{1}{4}$Cr–1Mo steel at 400°C in terms of hardening and shifts in DBTT, including recent results of postirradiation mechanical tests with higher fluences than previously attained, to provide implications on ferritic steels for fusion application. For the understanding of the above embrittlement, an electrochemical method was applied to the examination of impurity segregation to grain boundaries by neutron irradiation.

2. Experimental procedure

The material used in the present study was a normalized and tempered $2\frac{1}{4}$Cr–1Mo steel plate of 160 mm thickness designated as A387 Gr.22 Cl.2 in accordance with the ASTM Specification for Pressure Vessel Plates, Alloy Steels, Chromium–Molybdenum (ASTM A387/A387 M). Table 1 shows the chemical composition at the quarter thickness position and heat treatment conditions. The microstructure of this steel consists mainly of bainite with a small amount of proeutectoid ferrite. Most of the carbides present at grain boundaries are M_7C_3 type.

The postirradiation mechanical test results reported here are out of a total of 11 capsules. These capsules were irradiated in the Japan Research Reactor-2 and the Japan Material Testing Reactor at JAERI at temperatures ranging from about 250°C to 425°C to neutron fluences from 1×10^{22} to 3×10^{24} n/m^2 ($E > 1$ MeV).

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Table 1
Chemical compositions (wt%) and heat treatments of the steel

C	Si	Mn	P	Ni	Cr	S	Cu	Mo	As	Sn	Fe
0.15	0.05	0.55	0.008	0.11	2.33	0.01	0.07	0.90	0.006	0.008	Balance

Heat treatment (PWHT: post weld heat treatment): 900/930°C–6.5 h, water cooled, 670/690°C–7 h, air cooled, PWHT(680/710°C–20 h).

Electrochemical tests have been performed using coupons with dimensions of 10 mm × 10 mm × 2 mm. Anodic polarization curves were determined in a three-electrode corrosion cell with a platinum and saturated calomel electrode as counter and reference electrodes, respectively. The solution contained 55% $Ca (NO_3)_2$ deaerated beforehand by nitrogen gas and was kept at 30°C during the test. Polarization was initiated at a corrosion potential to transpassive potential at a scanning rate of 0.5 mV/s. More details of experimental conditions were described in Ref. [4]. The height of the secondary peak in the measured anodic polarization curve was earlier identified to be an indicator of phosphorus segregation at grain boundaries [4].

3. Results and discussion

3.1. Irradiation effects on hardening

Fig. 1 shows the increase in the yield and ultimate strengths measured at room temperature as a function of neutron fluence. Irradiation at around 400°C caused slight hardening over a given range of fluence. The irradiation temperature dependence of hardening is shown in Fig. 2. As expected, the increase in the strength is diminished with increasing irradiation temperature.

To characterize the role of irradiation temperature of 400°C in the observed slight hardening, changing the temperature from 290°C to 400°C during neutron exposure were performed to a total fluence of 5.2–7.5×10^{23} n/m^2 ($E > 1$ MeV). Four irradiation conditions using the single capsule were as follows: irradiation at 290°C to a fluence of 2.8×10^{22} n/m^2 (= 28 h) and 3.8×10^{23} n/m^2 (= 265 h) with subsequent 400°C irradiation; continued irradiation at 290°C and 400°C. The total reactor exposure period was 523 h. Fig. 3 shows the total increase in yield strength in the above irradiation conditions. For continued irradiation, hardening becomes small at 400°C irradiation, as also indicated in Fig. 2. The key observation for additional irradiation at 400°C is that the total increase in yield strength in both conditions results in similar values, irrespective of the prior hardening level at 290°C: no additional hardening was observed. Additional irradiation at 400°C contributes only to recovery. Because of the lack of detailed annealing experiments and fine-scale microstructural examination available for the present result, the effect of

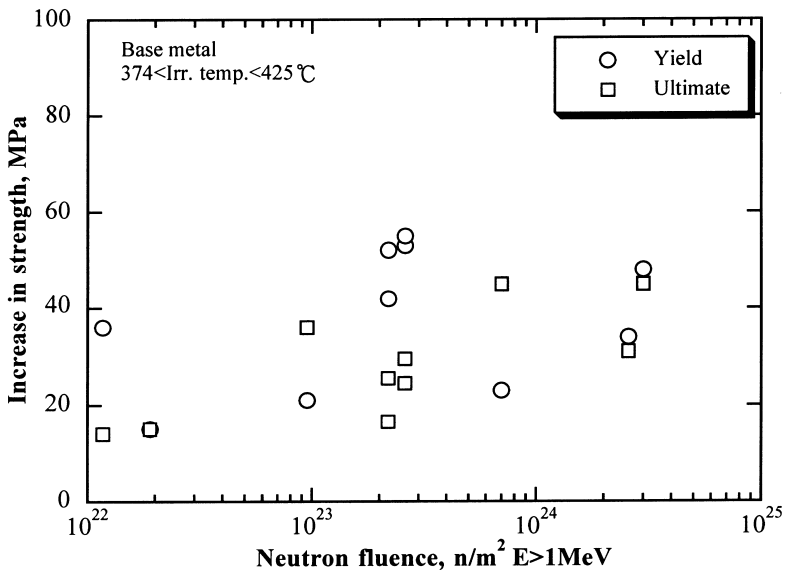

Fig. 1. Effect of neutron fluence on irradiation hardening.

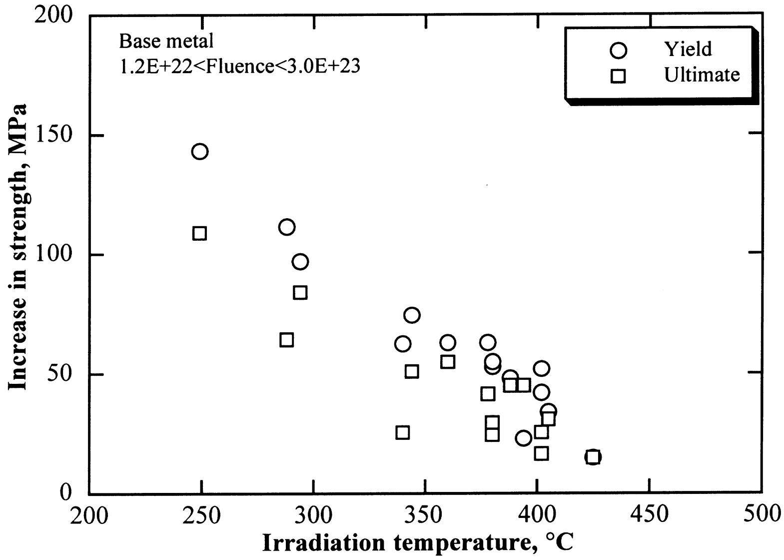

Fig. 2. Effect of irradiation temperature on irradiation hardening.

annealing process cannot be determined here. However, the observed slight hardening in Fig. 1 may be also attributed to this characteristics.

3.2. Irradiation effects on DBTT shift

Fig. 4 shows the shifts in DBTT as a function of neutron fluence. High DBTT shifts which exceed the values expected from the measured yield strength in Fig. 1 are seen at fluences larger than 1×10^{24} n/m^2 ($E > 1$ MeV). The scanning electron micrograph (SEM) on the fracture surface of Charpy specimens irradiated to a fluence of 1.7×10^{24} n/m^2 ($E > 1$ MeV) reveals the occurrence of intergranular fracture (IGF) (Fig. 5) in the lower shelf region. The fraction of IGF was about 25%. Because the data with higher fluence were produced at 400°C in a reactor exposure period of ~3000 h, the thermal aging effects may have to be considered. Our previous study on the temper embrittled $2\frac{1}{4}$Cr–1Mo steel at temperatures ranging from 400°C to 500°C for up to 50 000 h has shown that temper embrittlement is caused by phosphorus segregation to grain boundaries, but, that aging at 400°C for up to 10 000 h caused no DBTT shift and IGF [2]. Therefore, the observed high DBTT

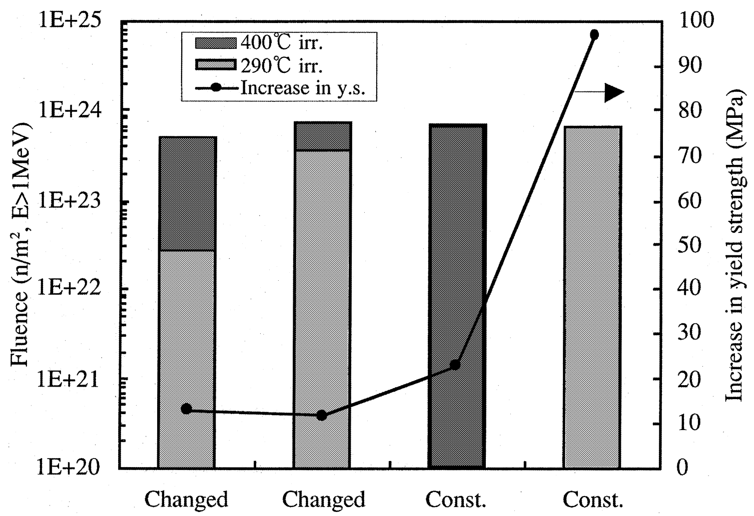

Fig. 3. Hardening due to neutron irradiation with changing temperatures from 290°C to 400°C during irradiation.

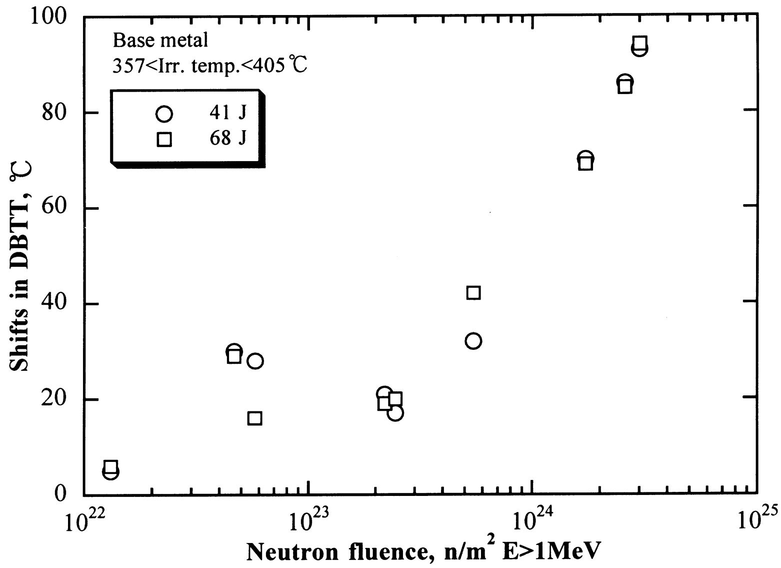

Fig. 4. Effect of neutron fluence on shifts in DBTT.

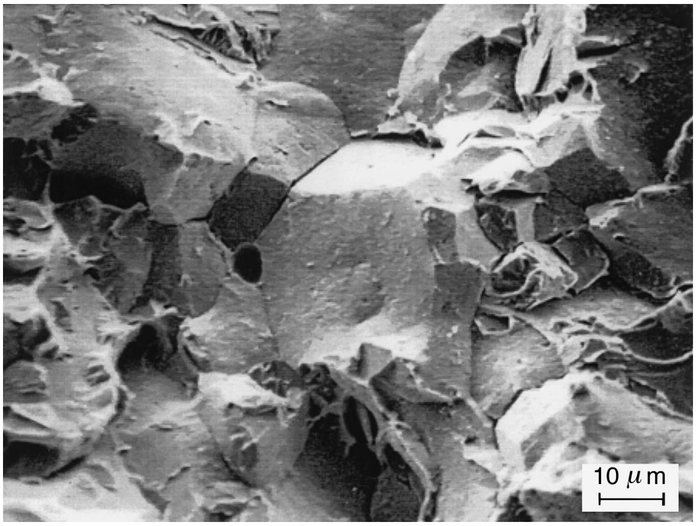

Fig. 5. SEM micrograph of the surface of the Charpy specimen irradiated at 400°C to a fluence of 1.7×10^{24} n/m^2 ($E > 1$ MeV).

shifts is attributed to irradiation-induced impurity segregation to grain boundaries. Even at such relatively low neutron fluence, Kameda et al. [5] also reported an example of irradiation-induced impurity segregation to grain boundaries through the mechanisms of the inverse Kirkendall effect and the formation of mobile defect-solute complexes.

To summarize, the high DBTT shifts which exceed the values expected from the measured yield strength at 400°C irradiation in the $2\frac{1}{4}$Cr–1Mo steel is caused by non-hardening embrittlement by the occurrence of intergranular fracture.

3.3. Electrochemical evaluation

It is known that intergranular segregation of Group IV–VI metalloid impurities weakens cohesion to grain boundaries in ferritic alloys. A possibility of phosphorus segregation is examined by electrochemical method. This method makes use of the preferential dissolution of specific microstructures due to the presence of carbides or segregated impurity atoms. The secondary peak in the anodic polarization curve measured in calcium nitrate solution was found to be an indicator on intergranular segregation of phosphorus in our previous

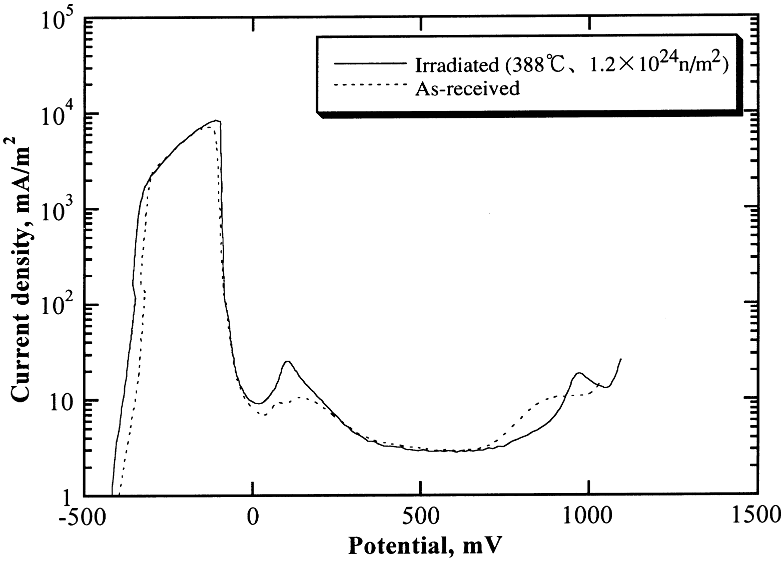

Fig. 6. Anodic polarization curves in calcium nitrate solution.

study on temper embrittled $2\frac{1}{4}$Cr–1Mo steel [4]. From the SEM observations of the surface and section of tested samples, the preferential dissolution of phosphorus segregated grain boundaries was observed only for the temper embrittled material showing the increase in the secondary peak in the passive potential region. This is because intergranular segregation of phosphorus prevents the formation of passive layer at grain boundaries. Its increase was found to be correlated with shifts in DBTT. We applied this method to irradiated and de-embrittled (575°C × 1 h) $2\frac{1}{4}$Cr–1Mo steel using a remote handled corrosion cell. It was also verified that the de-embrittling treatment lowered DBTT shifts to the initial level.

Fig. 6 shows typical anodic polarization curves for as-received and irradiated material. A secondary peak, which is higher for the irradiated material than for the as-received material, is recognized in the passive potential region. To clarify the fluence dependence of this observation, Fig. 7 is shown to illustrate the change in secondary peak values. The secondary peak is clearly increased with neutron irradiation to a fluence of 2.4×10^{24} n/m^2 ($E > 1$MeV) as compared to the lower fluence result, while the secondary peak due to

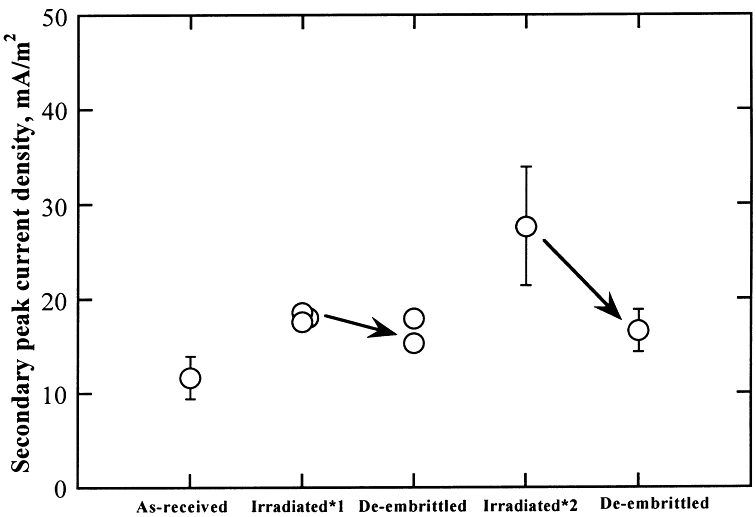

Fig. 7. Change of the secondary peak due to neutron irradiation (*1: 2.4×10^{23} n/m^2 at 410°C, *2: 1.2×10^{24} n/m^2 at 388°C) and de-embrittling treatment (575°C × 1 h).

de-embrittlement treatment is not completely reversible. The observed increase in secondary peak is consistent with intergranular fracture and high DBTT shifts observed above a fluence of 1×10^{24} n/m^2 ($E > 1$MeV) in Fig. 3. It can be concluded that a possible element responsible for IGF and high DBTT shifts is phosphorus.

4. Conclusions

Normalized and tempered $2\frac{1}{4}$Cr-1Mo steel was irradiated at 400°C to a fluence of 3×10^{24} n/m^2 ($E > 1$MeV) to characterize irradiation hardening and shifts in DBTT, and results obtained were as follows:

1. Irradiation hardening was slight at 400°C at neutron fluences ranging from 1×10^{22} to 3×10^{24} n/m^2 (E>1MeV).
2. Additional neutron irradiation with changing the temperature from 290°C to 400°C during irradiation induced substantial recovery of prior hardening at 290°C, irrespective of the prior hardening level.
3. Irradiation at 400°C to a fluence larger than 1×10^{24} n/m^2 (E>1MeV) caused intergranular fracture and high DBTT shifts.
4. The results of electrochemical test suggested that a possible element responsible for intergranular fracture was phosphorus.

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