Hydrogen and Radiation Embrittlement of Cr-Mo-V and Cr-Ni-Mo-V Ferritic RPV Steels

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Abstract

Hydrogen embrittlement of low-alloy steels has been investigated in dependence on hydrogen trapping and release, on the electrolytic hydrogen charging parameters and on irradiation. The interaction of hydrogen with the structure of irradiated and unirradiated steel at higher charging current densities causes structure defects which can lead to a loss of plasticity of the steel even after hydrogen release. The presence and the character of grain boundaries, secondary phases and other defects in the steel structure are of great importance from the viewpoint of hydrogen embrittlement effect.

1. Introduction

In recent years an increasing attention is concentrated on the problem of through-wall failure possibility in corrosion resisting welded cladding and the development of underclad cracks and other types of cracks in the base material of PWR pressure vessels. Crack growth in the presence or in the absence of corroding environment can be affected mostly by hydrogen and radiation embrittlement.

In the present paper the conditions of hydrogen trapping and release were studied in dependence on the presence of structure defects in both irradiated and unirradiated steel. The influence of these parameters was determined from the decreased plastic and strength properties of the steel.

2. Experimental

The experiments were realized on the low-alloy Cr-Mo-V and Cr-Ni-Mo-V steels which are currently used for light water reactor pressure vessels. The material composition of the steels in mass percents was as follows: Cr-Mo-V steel: C 0.15; Cr 2.67; Mo 0.61; V 0.24; Cr-Ni-Mo-V steel: C 0.13; Cr 2.2; Ni 1.26; Mo 0.57; V 0.12.

Tensile tests were conducted at strain rate of $8.3 \cdot 10^{-4} \text{ s}^{-1}$ on cylindrical tensile specimens of the diameter $d = 4 \text{ mm}$ and working section length $l = 20 \text{ mm}$. For constant load test the method of delayed fracture was used with cylindrical 60 deg. V-notched specimens of dimensions $d_1 = 3.5 \text{ mm}$, $d_2 = 5 \text{ mm}$, $l = 17.5 \text{ mm}$ and notch radius 0.05 mm . Both tests were performed at room temperature.

The specimens have been irradiated in an irradiation rig with He environment at temperature of 130, 180 and 290 °C for a fast neutron fluences of $2.6 - 4.9 \cdot 10^{23} \text{ n.m}^{-2}$ ($E > 0.5 \text{ MeV}$).

Unirradiated specimens prior the tensile test were hydrogen charged for 1 h at room temperature in 1 N H_2SO_4 solution (with addition of 30 ppm dm^{-3} of As_2O_3). The delayed fracture test was carried out only on unirradiated notched specimens which had been hydrogen charged under constant load in 1 N H_2SO_4 . The specimens had been stored in liquid nitrogen before tensile test performance or hydrogen content determination. The more detailed data on the steels and experimental conditions are given in Koutský [1,2].

3. Experimental results

3.1. Hydrogen and radiation embrittlement

The mechanical properties of the Cr-Mo-V steel depend on the extent of irradiation-induced defects, on the hydrogen content and on hydrogen charging parameters.

The influence of irradiation becomes evident as radiation strengthening of the steel which raises with the decreasing irradiation temperature in the range 290 to 130 °C. From the data given in Table 1, it is obvious that e.g. for the samples irradiated at 130 °C to the fluence of $9 \cdot 10^{23} \text{ n.m}^{-2}$ the yield strength $R_p 0.2$ raises by 59 % and the tensile strength R_m by 41 %.

The influence of hydrogen is not observed with the contents up to 8–10 ppm after charging at the current densities up to 50 A m^{-2} . On the other hand, the decrease of strength properties of the steel was ascertained with higher hydrogen contents after charging at the current densities over 100 A m^{-2} . For the above-mentioned specimens irradiated at 130 °C the yield strength decreases by 30 % and the tensile strength by 25 % as compared with hydrogen-free specimens.

Hydrogen and radiation embrittlement impair plasticity of the steel. A substantial decrease of the total elongation and reduction of area of both irradiated and unirradiated specimens is observed with hydrogen content over 2.5 ppm. For the specimens irradiated at the temperature 130 and 180 °C the increased hydrogen content above 8–10 ppm (current densities $> 100 \text{ A m}^{-2}$) leads to a full loss of the plasticity, like Koutský [1,2].

Radiation embrittlement causes the decrease of the uniform elongation which for both hydrogen charged and hydrogen-free specimens (in the range up to 50 A m^{-2}) reaches approximately the same value and decreases with the dropping irradiation temperature (Fig. 1). On the contrary, for the specimens irradiated at 290 °C the uniform elongation after hydrogen charging increases in comparison with the unirradiated specimens. The local necking elongation is determined with the hydrogen contents over 2.5 ppm (Fig. 2). A considerable decrease of the local necking elongation is observed from the values 10 A m^{-2} and the obtained dependences have the straight line character in semilogarithmic coordinates.

The effect of the initial stress R on the time to fracture up to 167 hrs was investigated for both steels charged at the same time. From the plotted curves the lower threshold stress was obtained and the dependence R_i on the charging current density was determined (Fig. 3). The value of the limit threshold stress R_{it} can be determined below which the specimens are no failure even at higher current densities. For the Cr-Mo-V steel and for the Cr-Ni-Mo-V steel R_{it} equals 210 MPa and 410 MPa, respectively. A fractographic investigation proved that the controlling mechanism of fracture was intercrystalline separation the relative area of which on the fracture face is inversely proportional to the initial stress, like Axamit [3].

3.2. Interaction of hydrogen with steel structure

Hydrogen trapping is affected by the presence and the activity of structural defects. Up to the hydrogen content of 2.0 ppm the hydrogen distribution on the cross section can be assumed to be uniform. The further increase of hydrogen content is observed mostly on traps, i.e. on the initial austenitic grain boundaries, on the inclusions, and on the interface boundaries. Reaching of local critical hydrogen concentration can then lead to the crack formation even in non-deformed specimens (Fig. 4). The importance of grains is remarkable above all after hydrogen charging of the specimens irradiated at lower temperature and in the delayed fracture; in these cases the influence of inclusions is suppressed. The failure is initiated by intercrystalline fracture on the surface it focuses either in the local area or in the coherent layer under the whole surface of specimens (Fig. 5).

3.3. Hydrogen trapping and release

The effect of traps for hydrogen embrittlement was evaluated from the course of hydrogen charging and hydrogen release in both the unirradiated specimens and those irradiated at 290 °C to the fluences $3.4 \cdot 10^{23} \text{ n.m}^{-2}$ (Figs 6,7). The influence of hydrogen charging time in the range of 1–48 hrs on the change of the total elongation is not significant.

The current density of hydrogen charging proves to have the decisive effect on interaction of hydrogen with traps. By increasing current density from 20 to 300 A m⁻² the total elongation is decreasing and its values are lower for irradiated specimens practically in the whole range of hydrogen charging time (Fig. 7). The decrease of the total elongation is inversely proportional to the hydrogen content (Fig. 6).

The hydrogen release during 48 hrs degassing time at room temperature results in recovery of plasticity. For the specimens charged at 20 A m⁻² and those unirradiated and charged at 300 A m⁻² (for 1 - 24 hrs) the total elongation and the total hydrogen content reached nearly the initial values. For the irradiated specimens and an unirradiated specimen hydrogen charged for 48 hrs we can assume that the interaction of hydrogen with structural defects with charging at 300 A m⁻² results in stable defects which do not make possible the plasticity recovery even when the hydrogen content reaches the same values as those of unirradiated specimens, like Hrubý [4].

4. Conclusions

The Cr-Mo-V steel both in unirradiated and irradiated state is sensitive to hydrogen embrittlement at hydrogen contents above 2.5 ppm, like Brinkman [5], Takaku [6] after charging at current densities 10 - 50 A m⁻². Radiation embrittlement decreases the uniform elongation, hydrogen embrittlement affects the decrease of local necking elongation.

The effect of hydrogen on the time to fracture depends on the charging current density and appears in the Cr-Mo-V steel with hydrogen contents above 3 ppm. The lower threshold stress R_{Ht} of the Cr-Ni-Mo-V steel is two times higher than that of the Cr-Mo-V steels. The higher resistivity of the Cr-Ni-Mo-V steel can be explained by a higher micropurity, causing a higher cohesion strength of the grain boundaries and therefore a higher resistivity against intercrystalline failure.

The critical development of initial defects proves to be located on the grain boundaries. It is evident that the quantity of hydrogen trapped on the defects both inside grains and on the grain boundaries as well as the quantity of necessary additional hydrogen on the potential failures is increasing with the increasing current density.

Under these conditions the leading role can be set down to the interaction of hydrogen with steel structure. At lower charging current densities hydrogen trapping on structural defects does not lead to stable defects, after hydrogen release from the specimens plasticity reaches the initial values. The increased current densities of hydrogen charging and radiation damage of the steel result in irreversible hydrogen embrittlement. When the critical hydrogen content is exceeded, trap sites are being formed. The given defects remain in the steel structure even after hydrogen release and they are effective for the initiation and the course of specimen failure.

In operating conditions with the corrosion effect of the coolant, the influence of hydrogen on the crack propagation process is determined mostly by hydrogen overpotential (in modelling conditions it is dependent on the current density of hydrogen charging) and by the degree of hydrogen trapping in stainless cladding and in the base material of the pressure vessel of PWRs. For the specimens of the cladding material which were irradiated for a long time in overheated water under operating conditions of PWRs, the hydrogen content of 3 - 4 ppm was determined. Assuming establishing of concentration equilibrium on the cladding-base material interface, hydrogen content could reach the values significant from the viewpoint of the hydrogen embrittlement for low-alloy steels.

References

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Table 1. Strength properties of Cr-Mo-V steel

	Unirrad.		$t_{ir} = 290\text{ }^{\circ}\text{C}$ $2.4 \cdot 10^{23}\text{ nm}^{-2}$		$t_{ir} = 180\text{ }^{\circ}\text{C}$ $2.6 \cdot 10^{23}\text{ nm}^{-2}$		$t_{ir} = 130\text{ }^{\circ}\text{C}$ $4.6 \cdot 10^{23}\text{ nm}^{-2}$		$t_{ir} = 130\text{ }^{\circ}\text{C}$ $9.0 \cdot 10^{23}\text{ nm}^{-2}$	
	$R_p\text{ }0.2$	R_m	$R_p\text{ }0.2$	R_m	$R_p\text{ }0.2$	R_m	$R_p\text{ }0.2$	R_m	$R_p\text{ }0.2$	R_m
	/MPa/	/MPa/	/MPa/	/MPa/	/MPa/	/MPa/	/MPa/	/MPa/	/MPa/	/MPa/
initial state	560	628	600	668	698	734	860	865	888	888
H charged 5 - 20 A m ⁻²	560	625	619	693	689	728	863	842	882	883
H charged 100 - 200 A m ⁻²	563	635	639	689	656	657	796	795	725	725

Fig. 1. Effect of charging current density on the uniform elongation A_m of Cr-Mo-V steel, charging time 1 h.

Fig. 2. Effect of charging current density on the local necking elongation A_5-A_m of Cr-Mo-V steel, charging time 1 h.

Fig. 3. Lower threshold stress R_i as a function of charging current density for unirradiated notched specimens.

Fig. 4. Hydrogen-induced cracks in the structure of unirradiated Cr-Mo-V steel

- on grain boundaries
- at non-metallic inclusion

Fig. 5. Intergranular fracture of notched specimens, delayed fracture test

- crack initiation near the surface
- local region on the surface

Fig. 6. Hydrogen content as a function of charging time for specimens in H charged condition and for specimens in H charged and H released (48 hrs, 25°C) condition

Fig. 7. Total elongation A_5 as a function of charging time for specimens in H charged condition and for specimens in H charged and H released (48 hrs, 25°C) condition