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Study of helium embrittlement in boron doped EUROFER97 steels

E. Gaganidze *, C. Petersen, J. Aktaa

Forschungszentrum Karlsruhe, Institut für Materialforschung II, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany

ABSTRACT

To simulate helium effects in Reduced Activation Ferritic/Martensitic steels, experimental heats ADS2, ADS3 and ADS4 with the basic composition of EUROFER97 (9%Cr-WVTa) were doped with different contents of natural boron and separated ^{10}B-isotope (0.008–0.112 wt.%) and irradiated in High Flux Reactor (HFR) Petten up to 16.3 dpa at 250–450 °C and in Bor-60 fast reactor in Dimitrovgrad up to 31.8 dpa at 332–338 °C. The embrittlement and hardening are investigated by instrumented Charpy-V tests with subsize specimens. Complete burn-up of ^{10}B isotope under neutron irradiation in HFR Petten led to generation of 84, 432 and 5580 appm He and partial boron-to-helium transformation in Bor-60 led to generation of 9, 46, 880 appm He in ADS2, ADS3 and ADS4 heats, respectively. At low irradiation temperatures $T_{irr} \leqslant 340$ °C the boron doped steels show progressive embrittlement with increasing helium amount. Irradiation induced DBTT shift of EUROFER97 based heat doped with 1120 wppm separated ^{10}B isotope could not be quantified due to large embrittlement found in the investigated temperature range. At $T_{irr} \leqslant 340$ °C helium induced extra embrittlement is attributed to material hardening induced by helium bubbles and described in terms of phenomenological model.

1. Introduction

Reduced Activation Ferritic/Martensitic (RAFM) steels are reference structural materials for a DEMO Fusion Power Plant (FPP) first-wall and blanket because of their better irradiation resistance and improved radiological properties compared to commercial martensitic steels [1]. The neutron irradiation induced low temperature hardening and embrittlement, thoroughly studied within the former irradiation programmes (MANITU [2], HFR-Ia, HFR-Ib [3]), however, remain the main obstacles for their application in a future FPP. Generation of transmutation product helium in the structural materials to be exposed to 14 MeV neutrons is another important issue that is not fully understood [4]. As materials test reactors do not provide with fusion adequate He/dpa ratios, the role of He is studied in different simulation experiments by using helium ion implantation, nickel- and boron-doping techniques or by replacement of the natural iron in the steel with ^{54}Fe, see e.g. [4] and references therein. An extensive assessment of the helium effects on the hardening and embrittlement of martensitic steels has been performed in [5]. More recently an alternative simulating technique for producing controlled He/dpa ratios under neutron irradiation of NiAl coated TEM discs has been used in [6] for understanding of the evolution of helium bubbles. A clear evidence of the influence of helium on the mechanical properties of steels was identified in [2,3] by comparative studies of RAFM and MANET steels with different contents of constitutive element boron. The ^{10}B isotope (20% of natural boron composition) is a strong absorber of the thermal neutrons and it transforms to helium and lithium at moderate neutron fluences. In order to simulate helium embrittlement and to better control and thus exclude a possible influence of steels' compositions, we studied irradiation performance of experimental heats doped with different contents of natural boron and ^{10}B-isotope in a range of 0.008–0.112 wt%.

2. Experimental

Experimental heats, ADS2, ADS3 and ADS4 with basic composition of EUROFER97 and with different contents of natural boron and separated ^{10}B-isotope, see Table 1, were produced by the materials development group at FZK [7]. In order to control the alloying effect of boron and to exclude significant differences in the microstructure ADS2 and ADS3 were doped with 82 wppm nat. B and 83 wppm separated ^{10}B isotope, respectively. ADS4 was doped with 1120 wppm ^{10}B-isotope. The content of boron in the reference EUROFER97 steel is kept below 0.001 wt%. All three boron doped heats got similar heat treatments of 1040 °C for 0.5 h + 760 °C for 1.5 h. The investigation of the effect of the dopant boron on the microstructure of the selected 9%Cr martensitic steels performed in [7] for boron contents between 5 and 1120 wppm revealed strong degradation of the microstructure in the heat with 1120 wppm boron, characterized by a presence of high density of coarse Fe, Cr and B rich inclusions. The heats with low boron contents (up to 83 wppm) showed however only few amount of small inclusions. Reference EUROFER97 steel was studied under two heat treatment conditions. Part of the specimens (EUROFER97 ANL) was

* Corresponding author. Tel.: +49 7247 82 4083; fax: +49 7247 82 4566.
E-mail address: ermile.gaganidze@imf.fzk.de (E. Gaganidze).

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Table 1
Selected chemical components of EUROFER97 and boron doped steels in wt%. Last two columns show produced helium amounts due to ^{10}B burn-up in SPICE and ARBOR1 experiment.

Material (heat)	Cr	W	Mn	V	Ta	C	B	He (appm) [SPICE]	He (appm) [ARBOR1]
EUROFER97 (83697)	8.91	1.08	0.48	0.2	0.14	0.12	0.001	10.2	–
ADS2 (806)	9.31	1.27	0.602	0.19	0.055	0.109	0.0082 (nat. B)	83.6	9.2
ADS3 (826)	8.80	1.125	0.395	0.193	0.088	0.095	0.0083 (^{10}B)	432	46
ADS4 (825)	9.0	1.06	0.38	0.197	0.08	0.100	0.112 (^{10}B)	5580	878

produced from 25 mm EUROFER97 plates in the as-delivered state (980 °C for 0.5 h + 760 °C for 1.5 h). Another part of the specimens (EUROFER97 WB) were produced from the plates subjected to a pre-irradiation laboratory heat treatment of 1040 °C for 0.5 h + 760 °C for 1.5 h.

The neutron irradiations of boron doped and reference EUROFER97 steels were performed in irradiation programmes HFR-IIb (SPICE) [8] and ARBOR1 [9]. SPICE experiment was carried out in the High Flux Reactor (HFR), Petten. A volume average damage dose of 16.3 dpa was achieved at neutron fluxes of 1.42 and $3.99 \times 10^{18}\ m^{-2}\ s^{-1}$ for thermal and fast (>0.1 MeV) neutrons, respectively. The irradiation was performed at multiple temperatures of 250/300/350/400/450 °C. ARBOR1 experiment was performed in the BOR-60 experimental fast reactor of SSC RF RIAR. Damage doses between 22.4 and 31.8 dpa were achieved at 332–338 °C in a fast neutron flux of $1.8 \times 10^{19}\ m^{-2}\ s^{-1}$ (>0.1 MeV). Helium amounts produced due to ^{10}B-to-helium transformation under neutron irradiation in HFR and Bor-60 reactors are summarized in Table 1.

Embrittlement and hardening were quantified by sub-sized Charpy-V specimens of KLST type, see e.g. [8] for specimen geometry. The instrumented impact testing of irradiated SPICE specimens was performed at a fusion material laboratory of FZK. The mechanical testing of irradiated ARBOR1 specimens was performed at the material science laboratory of the SSC RF RIAR. The test and evaluation procedures are identical with those employed in previous investigations, see e.g. [9]. The impact energies (E) vs. test temperature (T) curves were analyzed with respect to the upper shelf energy (*USE*) and the ductile-to-brittle transition temperature (*DBTT*) as described in [8]. The dynamic yield stress (σ_{Dy}) was derived from the force vs. deflection curves at the onset of plastic deformation [8].

3. Results and discussion

Fig. 1 shows impact properties of EUROFER97 WB, ADS2 and ADS3 steels in the unirradiated condition and after neutron irradiations at T_{irr} = 250 °C (SPICE) and at 338 °C (ARBOR1). In the unirradiated condition the *DBTT* of ADS2 (−73.5 °C) is only slightly worse compared to reference EUROFER97 WB steel (−90.8 °C), whereas *DBTT* of ADS3 (−99.8 °C) is close to that of reference steel. The both boron doped steels show comparable *USE* of ~9 J, that is only slightly (by ~0.9 J) lower than the *USE* of reference EUROFER97. This indicates only minor chemical effects of boron on the toughness properties. The irradiation in HFR (16.3 dpa/250 °C) leads to embrittlement and reduction of toughness of the steels. The boron doped steels show degraded irradiation resistance compared to reference EUROFER97. The *DBTT* shifts are 149, 271 and 370 °C for EUROFER97 WB, ADS2 and ADS3, respectively. The neutron irradiation in Bor-60 reactor (22.4 dpa/338 °C) lead to less embrittlement of boron doped steels, compared to HFR irradiation. This is because of only partial ^{10}B burn-up in the ARBOR1 specimens due to absence of thermal neutrons in Bor-60 reactor. The *DBTT* shifts for Bor-60 irradiated ADS2 and ADS3 heats are 248 and 274 °C, respectively. There is no clear correlation between produced helium contents in boron doped heats and reduction of the *USE* as can be seen by comparison of the results for 9, 46 and 83 appm He in Fig. 1. The reduction of the *USE* in boron doped heats are considerable larger than that of the base EUROFER97 heat, which indicates modified defect evolution under helium production in boron containing steels. The evolution of the upper shelf impact toughness with damage dose, however, is purely understood and only weakly correlates with the evolution of the *DBTT* even for base RAFM steels. Indeed, the *USE* of EUROFER97 saturates at an early stage of irradiation damage (above ~9 dpa), while the *DBTT* still keeps increasing with increasing irradiation damage (up to 32 dpa) [10]. These observations prevent unambiguous interpretation of the *USE* of the boron doped heats.

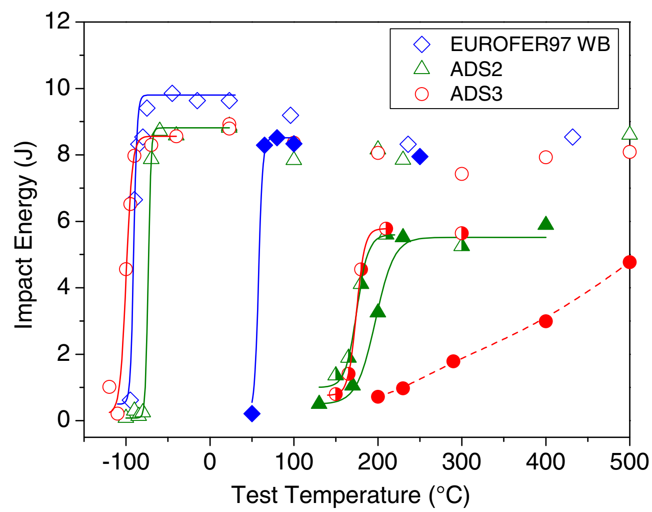

Fig. 1. Charpy impact energy vs. test temperature for EUROFER97 WB, ADS2 and ADS3 in the unirradiated condition (open symbols) and after neutron irradiations in HFR (16.3 dpa/250 °C, full symbols) and Bor-60 reactor (22.4 dpa/338 °C, semi-full symbols).

Fig. 2 shows impact properties of ADS4 in the unirradiated condition and after neutron irradiation at T_{irr} = 300 °C (SPICE) and 332 °C (ARBOR1). ADS4 showed degraded impact properties already in the unirradiated condition indicating substantial chemical effects of boron. The *DBTT* of SPICE (16.3 dpa/300 °C) and ARBOR1 (32.3 dpa/332 °C) irradiated ADS4 could not be quantified due to large embrittlement found at investigated temperatures. Such a large embrittlement is partly due to largely degraded microstructure of the unirradiated heat, characterized by relatively high concentrations of Fe, Cr and B rich inclusions [7].

Fig. 3 shows extra, helium induced embrittlement (defined as *DBTT* shift in boron doped heat after subtraction the corresponding *DBTT* shift in reference EUROFER97) vs. extra helium amount produced in boron doped steels. For assessment of helium embrittlement for ARBOR1 experiment, the *DBTT* shift of reference EUROFER97 was estimated at 22.4 dpa by interpolating the results from SPICE [8] and ARBOR1 [9] experiments. That way we obtained

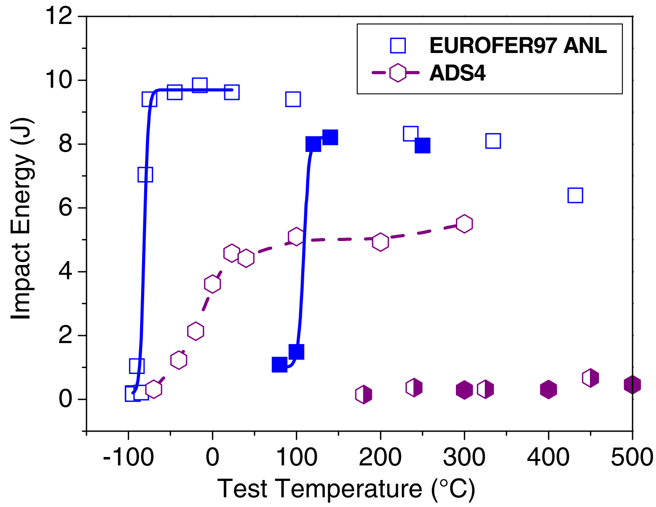

Fig. 2. Charpy impact energy vs. test temperature for EUROFER97 ANL and ADS4 in the unirradiated condition (open symbols) and after neutron irradiations in HFR (16.3 dpa/300 °C, full symbols) and Bor-60 reactor (32.3 dpa/332 °C, semi-full symbols).

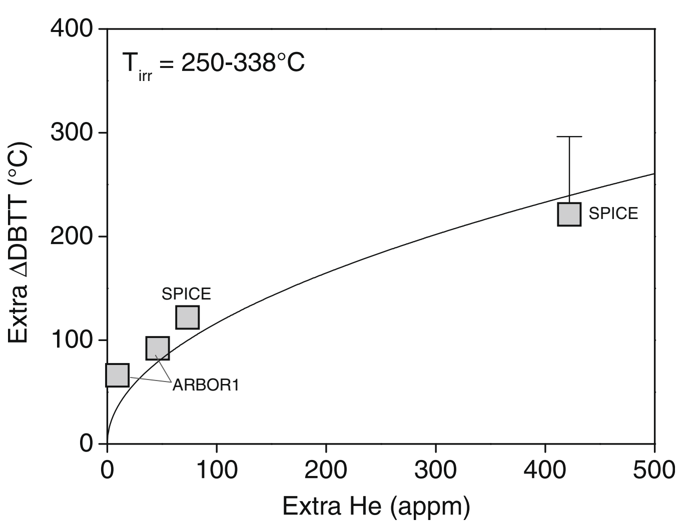

Fig. 3. Helium induced extra embrittlement vs. extra helium amount for irradiated boron doped steels. Extra $\Delta DBTT = \Delta DBTT_{EUROFER+B} - \Delta DBTT_{EUROFER}$. Extra He = helium amount produced in boron doped heat after subtraction of helium amount produced in EUROFER97. The line is a $A\sqrt{p_{He}}$ – type least square fit to the data, with A as fitting parameter.

Extra ΔDBTT of 66 and 92 °C for ADS2 and ADS3 heats in ARBOR1 experiment, respectively. A progressive material embrittlement with produced helium amount is seen for both SPICE and ARBOR1 experiments.

The analysis of the hardening vs. embrittlement behaviour of SPICE specimens at $T_{irr} \leqslant 350$ °C in [11] revealed hardening nature of the embrittlement for helium contents up to 84 appm and indicated the possible existence of additional non-hardening embrittlement mechanisms beyond the helium induced hardening at helium contents of 432 appm.

Material hardening as a result of decreased dislocation mobility due to impeding obstacles can be evaluated according to the standard dispersed barrier hardening model [12]

$$\Delta\sigma = M\alpha\mu b\sqrt{Nd} \quad (1)$$

with M being the Taylor factor, α *is* an average obstacle strength, μ *is* the shear modulus of the steel, b is the Burgers vector of the moving dislocation, N is the number density of the obstacles and d is their average diameter. Helium amount p_{He} produced in boron doped steels is a measure for volume fraction of the helium bubbles, i.e. $p_{He} \propto N_{He}d_{He}^3$ with N_{He} being the bubble number density and d_{He} the bubble average diameter. Therefore, for the case of hardening dominated embrittlement, where irradiation induced embrittlement strongly correlates to irradiation induced hardening, as identified for low helium contents at low irradiation temperatures in [8,10], the helium induced embrittlement can be phenomenologically described with a function of type $\propto (N_{He}d_{He})^{1/2} \propto (p_{He})^{1/2}$ (under assumption of d_{He} = const). The corresponding line shown in Fig. 3 describes qualitatively the embrittlement up to helium contents of 432 appm. The observed deviation from the model line from the experimental points is possibly related to simplification of the model that neglects distribution of helium bubble diameters and barrier strengths. Evolution of microstructure can also be different between SPICE and ARBOR1 experiments due to different helium production rates in *mixed spectrum* HFR and *fast* Bor-60 reactor. In addition, there is no distinct information about the distribution of the boron in the steel matrix. Possible non-uniform distribution of boron, e.g. preferentially on dislocations or prior-austenite grain boundaries may over-predict helium effects. The production of the transmutation product lithium is another disadvantage for the boron doping technique. Remarkably, the effect of lithium on irradiation hardening and embrittlement was argued to be very small by comparative fracture mechanical studies of ^{10}B doped and He implanted martensitic steels in [13]. For low helium contents (<400 appm), however, a close correlation of the irradiation induced hardening and embrittlement as well as good agreement of the hardening vs. embrittlement ratio with the corresponding ratios from alternative simulating experiments producing more homogeneous helium distribution, e.g. Spallation Proton irradiation [5], provide credit to boron doping technique for the study of the helium effects.

4. Conclusion

In conclusion we evaluated the role of helium in the embrittlement of RAFM steels by studying irradiation performance of boron doped experimental heats. Boron doped steels show progressive embrittlement and reduction of toughness with increasing produced helium amount. Helium induced extra embrittlement was quantified and qualitatively described in terms of phenomenological model. Planned microstructural investigations for quantification of size, density and cites of produced helium bubbles will shed more light on the helium effects.

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