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V-alloy embrittlement by irradiation in a cooling gas environment

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Abstract

Sub-sized tensile and Charpy specimens of the vanadium-alloy V–4Cr–4Ti have been irradiated in a piggy-back experiment with ferritic–martensitic material in the HFR at Petten at 250–450°C to about 2.5 dpa, and subsequently tested. A complex set of post-irradiation mechanical properties was found. Impact measurements showed severe shifts in ductile–brittle transition temperatures (DBTT) regardless of irradiation temperature and no clear trends of recovery at higher irradiation temperatures. The fracture surfaces always indicated transcrystalline crack propagation. Tensile tests generally revealed irradiation hardening with a maximum around 300°C, accompanied by total elongations which increased with increasing temperature. Extremely small uniform elongations at the lower temperatures suggest high localized plastic deformation under small strain rates. Deviations from expected irradiation effects led to a scrutiny of the atmospheric conditions during irradiation which revealed that the capsule had several times been flushed with He and Ne containing traces of interstitial gases or N_2 for temperature adjustment. A skin was found on the specimens irradiated at the highest temperatures. X-ray diffraction results showed an uptake of nitrogen, whereas microprobe analysis suggested the presence of oxygen in the bulk. The limited data allow only a qualitative discrimination between chemical and irradiation effects.

1. Introduction

Vanadium-alloys play a prominent role in fusion reactor development in the USA which is reflected in a broad data base from US laboratories for the unirradiated material [1]. Moreover there is an ongoing international cooperation on these alloys with regular workshops under the umbrella of an IEA Implementing Agreement [2]. Nevertheless there remain a number of areas of research where data are still insufficient.

In principle, the affinity of vanadium to interstitial gases is well known, but how this translates to the alloys and their mechanical properties is less known. Hydrogen, for example, steadily deteriorates the room temperature tensile properties of V–4Cr–4Ti with increasing concentration until they break down when hydride formation sets in [3]. For the same alloy the role of oxygen depends very much on whether it is precipitated at grain boundaries or homogeneously dispersed. There are also strong indications of synergistic effects between H and O [4]. Increases of tensile strengths and ductile–brittle transition temperatures (DBTT) after nitrogen uptake have also been reported [5].

For irradiated material the data base is still limited. Serious deterioration of mechanical properties has been found for low irradiation temperatures at even small doses [6–8]. The effect of transmutation products, especially He, has also been studied [9]. A concomitant uptake of gases from surrounding media during irradiation has sometimes been contemplated, but not yet explicitly been investigated.

It has been revealed in the course of our work that effects of gas uptake during irradiation could not be excluded. Hence, we consider our results to be some help for an understanding of what may happen in the application of vanadium-alloys for fusion reactor technology.

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2. Experiment

A sheet of the reference alloy V–4Cr–4Ti (heat 832665) with dimensions $100 \times 200 \times 3.75\ \mathrm{mm}^3$ had been provided from Argonne National Laboratory to the Forschungszentrum Karlsruhe on an informal basis in order to cross-check data and techniques in the area of small specimen technology for impact and tensile testing both with unirradiated and irradiated material.

The material condition as delivered was 50% cold worked. Impact test specimens of the KLST type (European sub-size standard, $3 \times 4 \times 27\ \mathrm{mm}^3$, notch depth 1 mm, notch angle 60°, root radius 0.1 mm) were produced and heat-treated for 2 h at 1000°C under the best technically attainable vacuum (2×10^{-4} Pa), with Zr cuts adjacent to the samples to provide gettering of reactive gases. Tensile specimens of 38 mm total length with a gauge section of 3 mm diameter and 18 mm length were machined and then subjected to the same annealing procedure. A number of both Charpy-V and tensile specimens was then used to fill some free space in the irradiation capsule of the HFR Phase 1A (D271-06 and D305-03) experiment as a piggy-back to the investigations on ferritic–martensitic steel.

The irradiation conditions were as follows. The target dose within 281.6 full power days was a nominal 2.4 dpa (according to the HFR-TEDDI post-cycle reports 2.71 dpa were attained for the ferritic–martensitic steel compositions). The nominal irradiation temperatures were 250°C, 300°C, 350°C, 400°C and 450°C within less than 2% of the target values, with maximum deviations of about 3%.

Sufficient specimens were retained to provide the basis for 'irradiated/non-irradiated' comparisons. Moreover the effect of vacuum annealing was established with impact measurements on unirradiated specimens, and was recently reported [10]. The techniques for instrumented impact and for tensile testing as applied in our laboratories are described elsewhere [11,12].

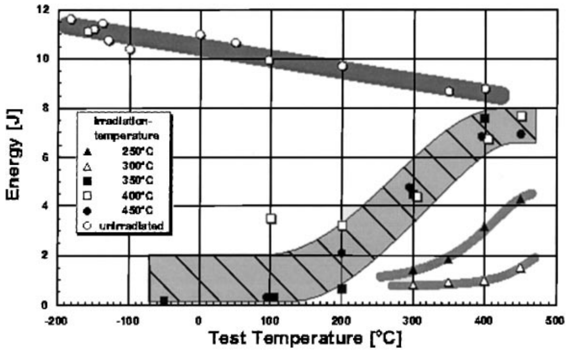

Fig. 1. Impact energy before and after irradiation versus test temperature.

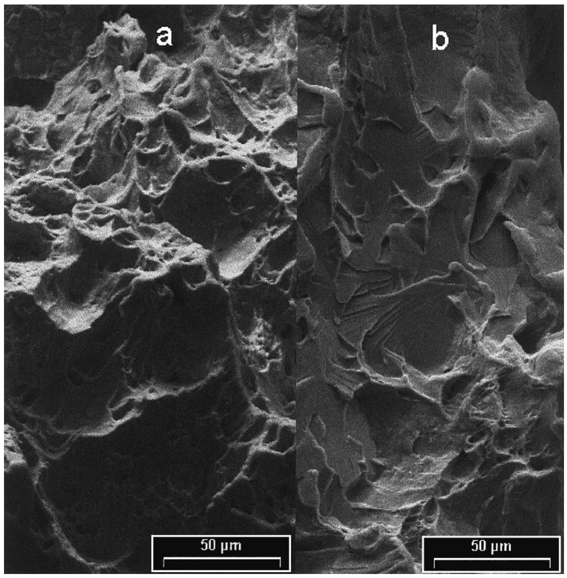

Fig. 2. Transcrystalline ductile (a) or cleavage fracture (b); samples from upper shelf for $T_{\mathrm{irr}} = 450$°C (a) and transition region for $T_{\mathrm{irr}} = 350$°C (b), respectively.

3. Results

3.1. Impact properties after irradiation

In Fig. 1 the results of the impact tests are shown, with the data corresponding to similar irradiation temperatures grouped together. For comparison the curve for the unirradiated, vacuum-annealed material is included. There is obviously a dramatic decrease in impact energy for all irradiated specimens with testing temperatures below 300°C, whereas for the unirradiated vacuum-annealed material upper shelf energies (USE) had been measured down to liquid nitrogen temperature. The characteristic S-shape of the irradiated material curves is not well developed and, for the lower irradiation temperatures, a USE plateau was not found. There is no clear trend in the shift of DBTT towards higher temperatures with decreasing irradiation temperatures. Fracture surface analysis by Scanning electron microscopy (SEM) shows transcrystalline, ductile or brittle fracture (Figs. 2(a) and (b)), on the upper shelf and transition regions, respectively.

3.2. Tensile properties after irradiation

Tensile measurements have been made, according to standard practice, at the same test temperature as the irradiation temperature. The strain rate was 1%/min. The results are shown in Figs. 3 and 4.

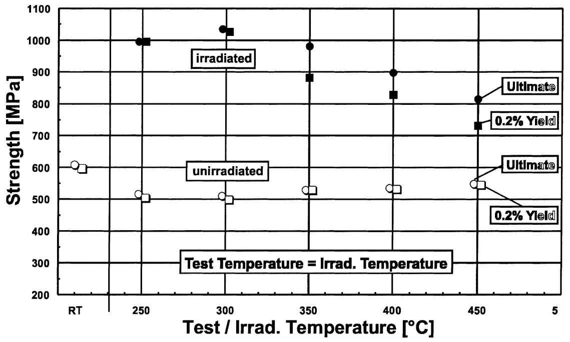

Fig. 3. Engineering strengths as a function of temperature (Section 4).

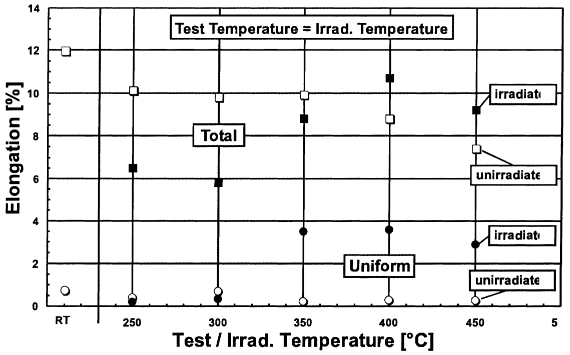

Fig. 4. Elongations as a function of temperature (Section 4).

In Fig. 3 the 0.2% yield and ultimate tensile strengths (engineering stresses) are plotted together along with measurements for the unirradiated material, which are high compared to values reported by other investigators [1,2]. Significant hardening can be observed, especially for the lower irradiation temperatures, where yield and ultimate strength coincide. This is reflected in Fig. 4, where almost no uniform elongation can be found at the low irradiation temperatures suggesting extremely high-localized plastic flow. Necking prior to fracture is still high, but has dropped to about 50% of the initial cross-section as compared to about 90% for the unirradiated material.

4. Discussion

The increase in yield and ultimate tensile strength to the 1000 MPa range after irradiation to about 2.5 dpa is largely in line with literature data [7]. The unusual high tensile strength and low ductility data of the unirradiated V–4Cr–4Ti specimen in Figs. 3 and 4 can most probably be explained by the omitted annealing treatment of 1000°C for 2 h for this specimen series. A recent check of specimen still available after this treatment produced the following tensile data: (an ultimate tensile strength of 420 MPa, a yield strength of 322 MPa, and total and uniform ductiles of 22.8% and 9.7%, respectively). They are well in accordance with data in the literature. Further, mechanical tests and chemical analyses of still available specimens or tested specimens fragments will be necessary to confirm this assumption.

The difficulties of correlations between tensile properties and fracture toughness have been discussed at large in a recent survey paper [13], and a model has been offered that correlates DBTT with the decrease in work hardening. Qualitatively, this model agrees with our measurements. Quantitatively, however, the differences are significant for irradiation temperatures above 350°C (Fig. 1). The impact toughness after the 250°C irradiation was not as degraded as after irradiation at 300°C, although a behaviour like this has also been mentioned in another context in [13].

The deviations in the irradiation temperature dependence of the impact curves from what we would have expected from previous work on ferritic–martensitic steel led us to consider the possibility of an influence during irradiation of the cover gas used to adjust the target temperatures. The procedure uses a variable mixture of inert gases with different thermal conductivity to adjust the temperature. This gas enters the capsule at the bottom and leaves it at the top. Our suspicion was that, except for hydrogen, the impurities in the gas mixture might have been gettered by the high temperature-specimens as a result of increasing diffusity with rising temperature. A very rough estimate suggested that the quantities should have been sufficient to provoke effects. The reactor logbook revealed that the capsule had repeatedly been flushed with nitrogen instead of fully inert gases. In principle an uptake of nitrogen has a similar effect as oxygen, but its diffusion coefficient in the temperature of interest is smaller by a factor of roughly 50 [5]. Because of the high partial pressure during N_2 flushing it was not possible to decide beforehand whether or which of the interstitial gases would prevail in the matrix. The appearance of fracture surfaces of specimens from the 450°C irradiation showing a brittle skin on specimen external surface (Figs. 5(a) and (b)), however, hinted at the presence of V-nitride, which is reported to be the intermediate step in nitrogen uptake [5].

For further clarification, the cross-section of a specimen from the 450°C irradiation was investigated with a microprobe, and a more or less uniform oxygen content of about 1.7% by weight was found, which is distinctly above the as-received level of between 300 and 400 wppm [4]. Also nitrogen was increased above its normal level in the alloy (Fig. 6). The approximately 100 μm thick skin clearly shows up in the cross-section as a different phase, but attempts to identify it by microprobe

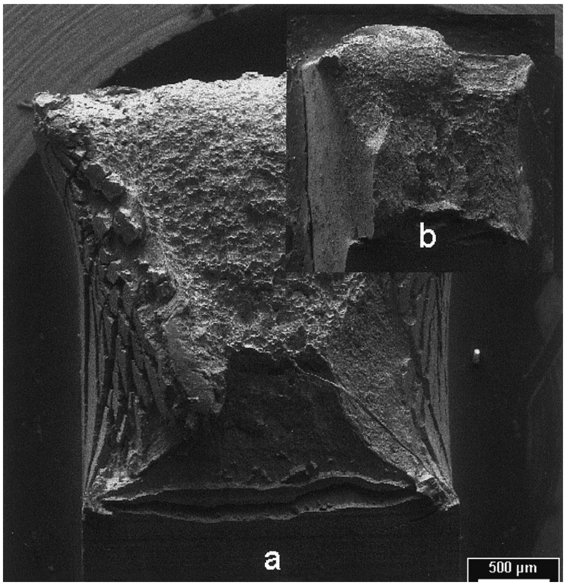

Fig. 5. Fracture surfaces of samples from high (a) and low (b) temperature irradiation.

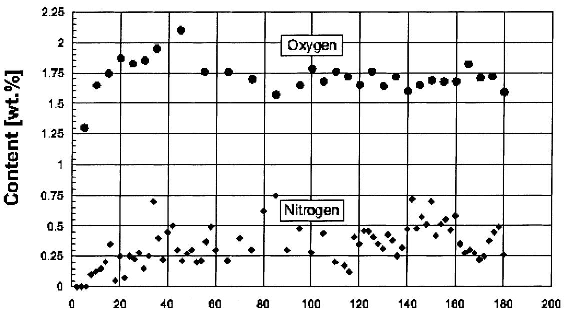

Fig. 6. Oxygen and nitrogen profile in a specimen irradiated at 450°C.

failed. Therefore X-ray diffraction measurements were made on this specimen and a reference sample. As demonstrated by Fig. 7, the skin can was clearly identified as V_2N.

Even if its effect on mechanical behaviour may not be significant, its existence is a clear indication of the presence of nitrogen in the bulk. On the other hand, additional oxygen with concentrations as low as about 200 wppm already has a deteriorating influence on room temperature tensile properties as discussed in [4], so that in our case we must assume synergistic effects of both elements on the mechanical properties.

If the uptake of interstitial gases is responsible for some of the reduction in impact energies as implied here, the smallest chemical, but highest radiation effect would be expected for the lower irradiation temperatures;

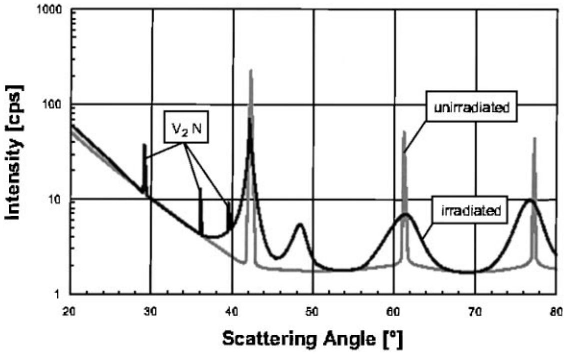

Fig. 7. Diffraction spectrum of specimen with ('irradiated') and without skin ('unirradiated').

whereas the highest chemical, but lowest irradiation effect (if one assumes the occurrence of damage annealing) might be expected for the higher irradiation temperatures. In this sense the 350°C curve still reveals 'normal' irradiation behaviour; whereas for the two higher irradiation temperatures, the annealing effect might be increasingly counteracted by interstitial embrittlement. The DBTT shifts measured can thus be considered as being in the range between 'pessimistic' for the higher temperatures, and 'realistic' for the lower temperatures. Even the 'pessimistic' may be 'realistic' if impurity contamination cannot be avoided.

5. Summary

Tensile and Charpy specimens of V–4Cr–4Ti have been irradiated in a material test reactor under conditions in which contamination by oxygen and nitrogen occurred. The test results qualitatively exhibited some of the same features that have been reported and discussed elsewhere for irradiations without contamination. In a quantitative sense the results differed for irradiation temperatures above 350°C.

An attempt has been made to attribute a fraction of the DBTT shift for the samples irradiated at these higher irradiation temperatures to a deterioration of impact properties due to uptake of nitrogen and oxygen. An 'irradiation-only' effect may be assumed to dominate for the low irradiation temperature samples for which the uptake of both interstitial gases was probably too slow. This more or less pure dpa effect would, however, still be disturbingly high for fusion reactor applications of this material.

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References

[1] D.L. Smith, H.M. Chung, B.A. Loomis, H.C. Tsai, J. Nucl. Mater. 233–237 (1996) 356.
[2] Proceedings of the IEA-Workshop on V-Alloy Development, Sendai, 1st November, 1997, p. 892.
[3] H.D. Röhrig, J.R. DiStefano, L.D. Chitwood, J. Nucl. Mater. 258–263 (1998) 1356.
[4] J.R. DiStefano, J.H. De Van, H.D. Röhrig, L.D. Chitwood, J. Nucl. Mater. 273 (1999) 102.
[5] E. Fromm, E. Gebhardt, Gase und Kohlenstoff in Metallen, Springer, Berlin, 1976, p. 444.
[6] H.M. Chung, D.L. Smith, J. Nucl. Mater. 258–263 (1998) 1442.
[7] E.V. van Osch, M.I. de Vries, J. Nucl. Mater. 271&272 (1999) 162.
[8] P.M. Rice, S.J. Zinkle, J. Nucl. Mater. 258–263 (1998) 1414.
[9] H. Matsui, M. Tanaka, M. Yamamoto, M. Tada, J. Nucl. Mater. 191–194 (1992) 919.
[10] H.D. Röhrig, M. Rieth, in: Proceedings of the IEA-Workshop on V-Alloy Development, Petten, 20–22 May 1996.
[11] M. Rieth, B. Dafferner, H.D. Röhrig, C. Wassilew, Fus. Eng. Design 29 (1995) 365.
[12] E. Materna-Morris, M. Rieth, K. Ehrlich, in: Proceedings ASTM-19th Symposium of Effects on Radiation Materials, Seattle, WA, USA, 1998.
[13] S.J. Zinkle, H. Matsui, D.L. Smith, A.F. Rowcliffe, E. van Osch, K. Abe, V.A. Kazakov, J. Nucl. Mater. 258–263 (1998) 205.