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Grain boundary segregation of impurities in neutron irradiated and thermally aged vanadium alloys

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Abstract

A comparison of intergranular impurity segregation induced during neutron irradiation (9.8×10^{24} n/m^2: $E > 0.1$ MeV at 438°C for 2120 h) and thermal ageing has been made in V-20 wt% Ti alloys undoped, P-doped and S-doped all containing residual C and O. Intergranular S segregation in an undoped alloy and S desegregation in a S-doped alloy occurred during neutron irradiation. Thermal ageing produced a large increase in the S segregation in the undoped and S-doped alloys. However, unirradiated, thermally aged and irradiated P-doped alloys showed little S segregation. The P-doped alloy had much smaller P segregation than the S segregation in the undoped and S-doped alloys. The grain boundary enrichment of C, O and Ti was reduced during the irradiation but promoted by the thermal ageing. The defect/impurity interaction affecting the impurity solubility and fluxes is considered to control the intergranular impurity segregation during the irradiation. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Vanadium base alloys have low neutron activation and excellent strength and are therefore considered as candidate materials for fusion nuclear reactors [1]. It has been recognized [2] that the mechanical properties of V alloys are strongly influenced by the amount and type of alloying elements and interstitial impurities. While advanced processing technologies enable one to reduce the level of interstitial impurities in V alloys, intergranular segregation of substitutional impurities like S, that strongly degrades the fracture properties, has been shown to emerge [3–5]. Thus it is important to examine how neutron irradiation influences segregated substitutional impurities to develop better V alloys for the application to fusion nuclear reactor components.

The mechanical properties and grain boundary composition affected by neutron irradiation (9.8×10^{24} n/m^2, $E > 0.1$ MeV at 438°C) have been recently studied in V-20 wt% Ti alloys undoped and doped with P or S [6–8]. In this paper, an attempt is made to compare the intergranular impurities segregation behavior in the irradiated (IRR) and thermal aged vanadium alloys.

2. Experimental procedure

This study employed three V-20 wt% Ti alloys undoped and individually doped with P and S. The undoped (<0.001wt%S–0.0009wt%P–0.012wt%C–0.029wt%O), P-doped (<0.001wt%S–0.03wt%P–0.006wt%C–0.025wt%O) and S-doped (0.0025wt%S–0.002wt%P–0.014wt%C–0.034wt%O) alloys are designated as UND, PD and SD, respectively. These alloys contained residual C and O in an uncontrolled manner. The details of processing and recrystallization treatments of the alloys are described elsewhere [6]. All recrystallized alloys were annealed at 600°C for 2 h. The resulting grain size of the alloys varied from 110 to 160 μm depending on the specimen.

Disk-shaped small punch (SP) specimens were irradiated (IRR) by fast neutrons ($E > 0.1$ MeV) at 438°C for 2120 h using the EBR-II reactor. Stacked SP specimens (about 20 mm long) were subjected to the average neutron fluence of 9.8×10^{24} n/m^2 [6]. Scanning Auger microprobe (SAM) specimens were machined from the

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undamaged part of SP specimens tested [6]. Some unirradiated (UN) specimens were aged in vacuum at 438°C for 2120 h.

SAM specimens were fractured by impact loading below −100°C in an ultra high vacuum SAM chamber of 2×10^{-8} Pa. The V alloy specimens revealed a mixture of intergranular and transgranular fracture. Selected area SAM analyses were carried out on fracture surfaces of the V alloys using Physical Electronics Model 660 with a cylindrical mirror analyzer operated at 5 keV. The first derivative peak height ratio (PHR) of elements such as P_{120}/V_{478}, S_{152}/V_{478}, C_{272}/V_{478}, O_{510}/V_{478} and Ti_{374}/V_{478} was normalized by the relative sensitivity factor to represent the magnitude of impurities and Ti. The average normalized PHR was determined by taking 25–50 data points on individual grain boundary fracture facets.

3. Results

S and P were found to be segregated at grain boundaries in the form of monolayer coverage in variously treated V alloys [6]. Figs. 1 and 2 indicate the comparisons of intergranular S and P segregation in UN, thermally aged (TA) and IRR alloys. The standard deviations are indicated on the top of bars. It is evident that the standard deviation and average values had similar magnitudes. This means that the S and P segregation heterogeneously occurred depending on the grain boundary structure. As shown in Fig. 1, an UN SD alloy showed higher S segregation than an UN UND alloy. Thermal ageing resulted in a large increase in the S segregation in the UND and SD alloys. However, the irradiation led to an increase in the S segregation in the UND alloy and a decrease in the S segregation in the SD alloy. Negligible S segregation was observed in UN, TA and IRR PD alloys. The PD alloy exhibited much smaller amounts of segregated P, compared to the S segregation in the UND and SD alloys (Figs. 1 and 2). Both the irradiation and thermal ageing promoted the intergranular P segregation. The irradiation induced a little higher P segregation than the thermal ageing in the impurity-doped alloys but inverse effects were observed in the UND alloy. The PD and SD alloys had coarse titanium rich phosphides and sulfides, respectively, that appeared in a similar density [6].

Grain boundaries were enriched with C, O and Ti in the vanadium alloys. The results for C and Ti are indicated in Figs. 3 and 4. All the alloys were found to have smaller contents of O at grain boundaries than C [6]. Note that the grain boundary content of Ti depended on the type of the alloys and alloy treatments despite the same bulk content. The thermal ageing increased the grain boundary content of C and Ti in all the alloys and that of O in the SD alloy. The neutron irradiation

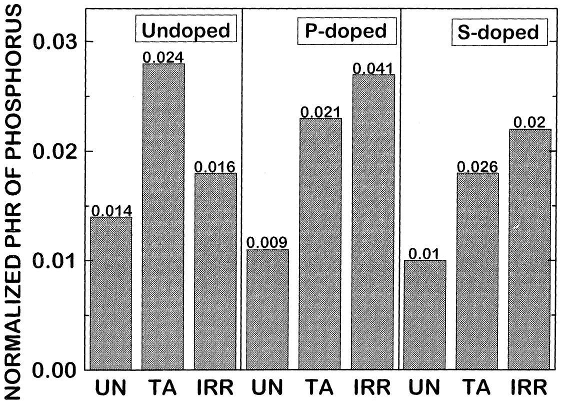

Fig. 2. Comparison of average normalized PHR of phosphorus in various UN, TA and IRR alloys. The standard deviation is indicated on the top of bars.

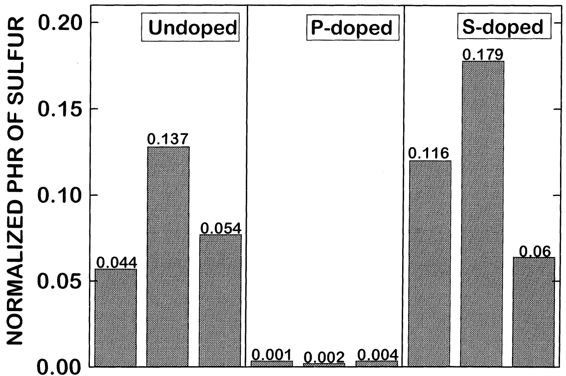

Fig. 1. Comparison of average normalized PHR of sulfur in various UN, TA and IRR alloys. The standard deviation is indicated on the top of bars.

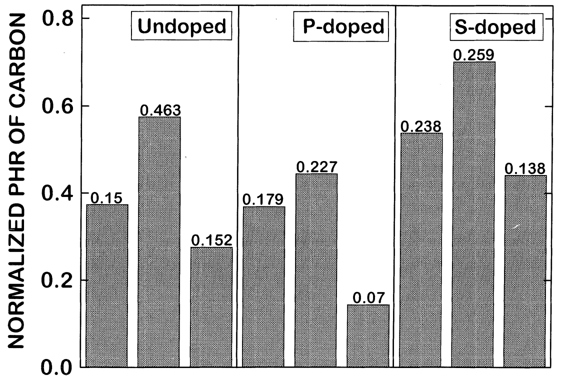

Fig. 3. Comparison of average normalized PHR of carbon in various UN, TA and IRR alloys. The standard deviation is indicated on the top of bars.

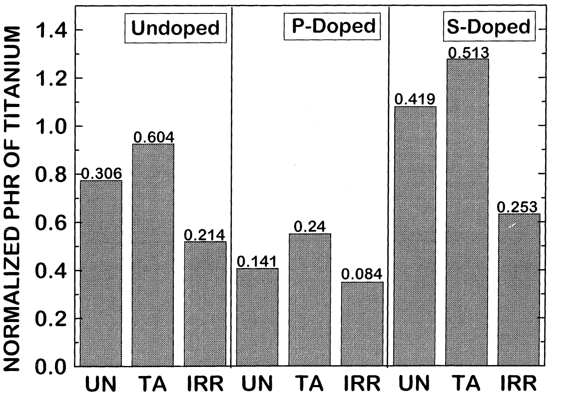

Fig. 4. Comparison of average normalized PHR of titanium in various UN, TA and IRR alloys. The standard deviation is indicated on the top of bars.

conversely reduced the grain boundary amount of C, O and Ti. The IRR PD alloy exhibited the lowest content of C, O and Ti. It has been shown [6] that the enrichment of C, O and Ti at gain boundaries is ascribed not only to the segregation but also to the precipitation (carbides and oxides). In addition, IRR SD alloys were found to have variations in the irradiation effect on the grain boundary content of C and O that influenced the ductility [6].

4. Discussion

The defect/impurity interaction affecting the impurity flux and the grain boundary capacity of segregated impurities is considered to control the grain boundary composition during neutron irradiation. The dynamic interaction between defect and impurity fluxes gives rise to a change in the grain boundary composition in IRR alloys [9–12]. Intergranular segregation of undersized solute is enhanced by forming mobile interstitial-solute pairs. On the contrary, oversized or substitutional solute at grain boundaries is depleted by the vacancy/solute exchange mechanism (inverse Kirkendall effect). Impurity diffusion is also driven by the impurity concentration gradient during irradiation as well as thermal ageing [13]. S and P are regarded as undersized substitutional solute in the vanadium alloy so that they would interact with interstitials and vacancies [14]. Therefore, the segregating and desegregating fluxes of S and P would emerge during the neutron irradiation depending on the relative strength of impurity fluxes via interstitials, concentration gradients and vacancies near grain boundaries [15].

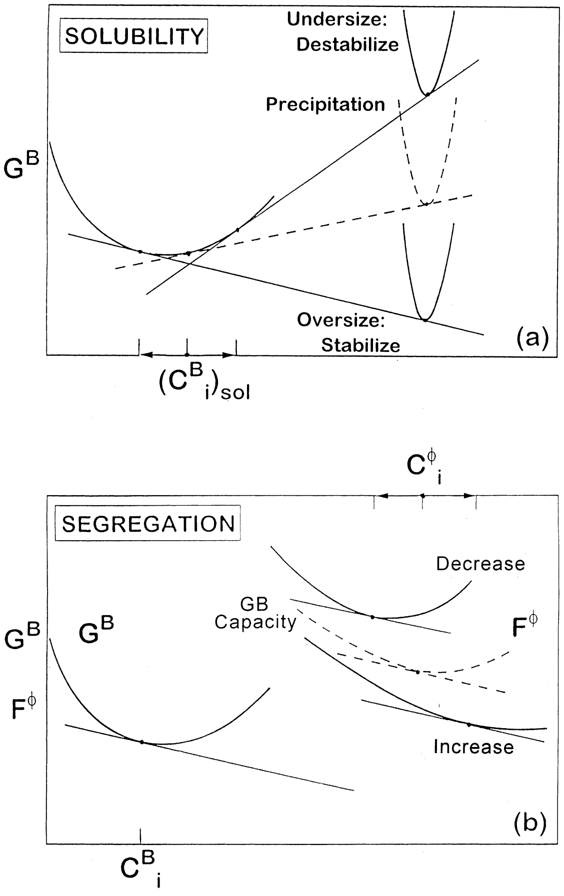

Fig. 5. Influence of stability of bulk precipitation and segregated boundary relative to that of matrix on (a) the solubility and (b) intergranular segregation of impurities. G^B is Gibbs free energy in the bulk and F^ϕ is Hermholz free energy of segregated boundary.

The capacity of grain boundaries to absorb impurities would change during irradiation. It is known that the grain boundary enrichment of impurities is inversely related to the impurity solubility [16]. Guttmann and McLean [17] have suggested that the impurity precipitation and segregation would be analogous and simultaneous processes. In an effort to account for the stability of precipitates and segregated boundaries, the free energy diagrams are schematically illustrated in Fig. 5(a) and (b). Increasing the free energy of bulk precipitates enhances the impurity solubility while increasing the free energy of segregated boundaries reduces the impurity segregation and vice versa. The analogy of precipitation and segregation in the equilibrium state would be applied to the kinetic process under irradiation provided the local equilibrium condition is maintained at precipitates and segregated boundaries. Maydet and Russel [18] have studied the stability of precipitates in IRR materials by estimating a potential energy change of precipitates. Their analysis has shown that irradiation would destabilize undersized precipitates by increasing the effective free energy and conversely stabilize oversized ones. The effective free energies of precipitates and segregated boundaries under irradiation are likely to change in a similar trend due to the interaction of defects with precipitates and segregants. In this way, it is possible that the grain boundary ability to accommodate undersized impurities is reduced during the irradiation.

This study has shown that the IRR UND and SD alloys contained much lower amount of segregated S, compared to the TA ones which maintained the equilibrium segregation (Fig. 1). Two reasons for this finding are to be considered. First, the solubility of S, forming undersized sulfides, increases during the irradiation, thereby reducing the capacity of grain boundaries to absorb S. Second, the desegregation flux of S assisted by annihilating vacancies compete and overwhelm the segregation flux via interstitials and/or concentration gradients, respectively, in the UND and SD alloys. The PD alloy had negligible S segregation. This is probably ascribed to an increase in the S solubility resulting from doping P.

The P segregation occurred in the PD alloy to much smaller extents than the S segregation in the UND and SD alloys (Figs. 1 and 2). Since the PD and SD alloys with different bulk contents of S and P had similar densities of coarse phosphides and sulfides [6], the vanadium alloy is expected to have higher solubility of P than that of S. Thus the grain boundary would not accommodate P segregation in the PD alloy. The irradiation would not affect the solubility of P as much as that of S probably because of smaller volume misfit of phosphides.

The neutron irradiation led to a decrease in the grain boundary content of C, O and Ti in all the alloys in contrast to the thermal ageing effect (Figs. 3 and 4). Increasing the free energy of undersized titanium carbides or oxides in the IRR matrix would result in an increase in the solubility of interstitial impurities (Fig. 5(a)). Hence, segregated C and O and precipitates at grain boundaries are dissolved into the grain matrix during the neutron irradiation. Moreover, the solubility of C and O heterogeneously might change in the IRR SD alloy with higher bulk contents of C and O due to possible large variations in the precipitation morphology induced by the irradiation.

Finally, the irradiation effect on the fracture properties in the V alloys is summarized [6]. Based on the result of ferritic alloys [19,20], it is postulated in the V alloys that the S and P segregation produce an embrittling effect while the C segregation gives rise to grain boundary toughening. Thus the irradiation produced complex effects on the fracture behavior. Grain boundary microcracks more heterogeneously formed in the IRR UND alloy due to the broad distribution of segregated S over many grain boundaries. The IRR UND alloy showed ductility loss to smaller extents than expected from the easy microcrack formation due to the mixture of intergranular and transgranular cracking. The irradiation effect on the ductility varied in the SD alloy because of the S desegregation and the wide variation in the C desegregation. Conversely, in the PD alloy, the irradiation suppressed intergranular microcracking and improved low temperature ductility. The IRR PD alloy showed little S segregation and the smallest content of C and O at grain boundaries. Thus crack nucleation along grain boundaries would become more difficult in the IRR PD alloy, thereby increasing the low temperature ductility.

5. Conclusions

Neutron irradiation (9.8×10^{24} n/m^2 :$E > 0.1$ MeV at 438°C) and thermal ageing exerted different effects on intergranular impurity segregation in three V-20 wt% Ti alloys undoped and doped with P or S. Intergranular S segregation in an undoped alloy and S desegregation in an IRR S-doped alloy were observed during irradiation. A large increase in the S segregation occurred in TA undoped and S-doped alloys. Grain boundaries contained negligible S segregation in all conditions of a P-doped alloy. The irradiation and ageing enhanced the amount of segregated P in all the alloys. However, the amount of segregated P was much smaller than that of segregated S in the undoped and S doped alloys. The irradiation reduced the grain boundary content of C, O and Ti while the ageing increased it. It is pointed out that not only the coupling of defect/impurity fluxes but also the impurity solubility play a role in changing the grain boundary composition during the irradiation.

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