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Journal of Nuclear Materials 307–311 (2002) 475–478

journal of nuclear materials

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Effect of thermal cycling on impurity grain boundary segregation in maraging steel

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Abstract

The paper presents results of Auger spectroscopy of grain boundary elemental composition of maraging steel 11Cr10Ni2TiMo after typical heat treatment followed by thermal cycling. Specimens in the austenitic condition were subjected to aging at 550 °C and to cyclic heat treatment. Afterwards specimens were doped by hydrogen in an electrolytic cell in order to produce grain boundary brittleness. Fracture was performed by tensile loading in an ultrahigh vacuum chamber of a special Auger spectrometer. A noticeable phosphorus grain boundary segregation was observed after aging at 550 °C. A substantial decrease in grain boundary impurity segregation following thermal cycling has been observed.

1. Introduction

Typical operating parameters for structural materials in fusion reactors include large and time-varying loads. Therefore the study of the influence of cyclically varying temperature on materials properties is very important both from scientific and practical points of view. Under out-of-pile laboratory conditions thermal-cycling processes can in some cases strongly modify material properties. However, under real conditions of a fusion reactor, the combination of cyclic temperature loads with irradiation and the presence of some impurity, may lead to the superposition of several processes with very negative consequences. It seems reasonable to separate the influence of cyclic temperature from the combined effects related to irradiation and the cyclic changes in the operational mode of a reactor.

At present, there is substantial information about metallurgical features of the micro structural and phase transformations accompanying thermal-cycling in high-alloy steels. However, the contribution to segregation at interfaces, in particular, to grain boundaries is largely unexplored [1]. This is especially important for steels with complex chemical compositions and microstructure.

In our work the maraging steel 11Cr10Ni2TiMo was chosen as a representative material, for which substantial improvement in mechanical properties caused by thermal-cycling and aging at 400–550 °C has been observed [1]. It is known that such a thermal history causes problems related to susceptibility to grain boundary fracture and to deterioration of corrosion resistance and impact toughness. These effects have largely been attributed to the influence of phase transformations and microstructural changes.

2. Experimental procedure

The chemical composition (wt%) of commercial 11Cr10Ni2TiMo steel was as follows: Cr 10.8; Ni 9.7; Ti 1.7; Mo 0.9; Si 0.2; C 0.05; N 0.007; S 0.003; P 0.004. The geometry of the specimens used is given in Fig. 1. All specimens were heat treated at 950 °C, 0.5 h, and subsequently aged at 550 °C. In this condition, typical values of relative elongation at room temperature were

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0022-3115/02/$ - see front matter © 2002 Published by Elsevier Science B.V.
PII: S0022-3115(02)01012-7

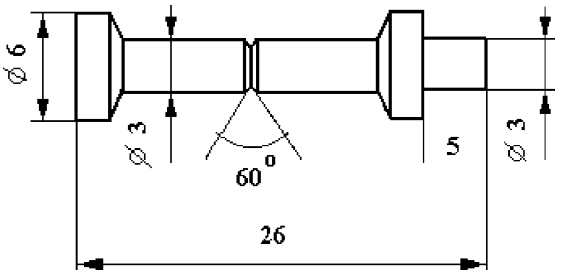

Fig. 1. Specimen geometry (dimensions in millimeters).

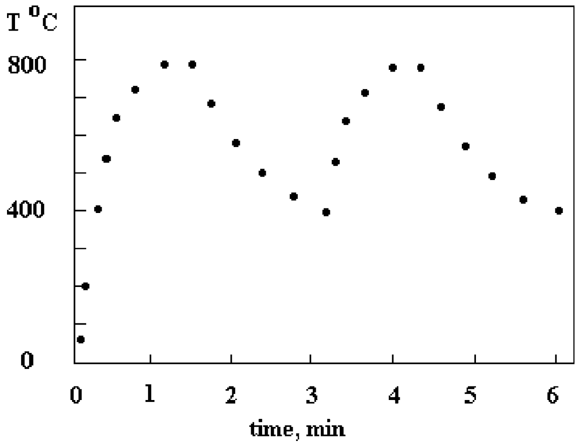

Fig. 2. Typical cyclic temperature–time curve.

near 12–14%. Specimens were then exposed to thermal cycling (2–10 thermocycles) by heating with an electron beam between 400 and 800 °C in a vacuum at about 10^{-5} Pa. Cooling was performed through a metal heat sink. A typical temperature history is shown in Fig. 2.

After thermal-cycling part of the specimens were doped with hydrogen in an electrolytic cell at a current density of 5×10^3 A/m^2. Hydrogen doping was used to promote grain boundary fracture. Specimens were placed into the chamber of a special Auger-electron spectrometer, containing a tensile fracture device. Final fracture was performed in ultrahigh vacuum at 2×10^{-7} Pa, with a slow strain rate of 10^{-4} s^{-1} at room temperature. After that one half-piece of the fractured specimen was positioned with the manipulator for Auger-spectroscopy. For the determination of the average elemental composition on the fracture surface two-to-three samplings were usually performed.

3. Results and discussion

3.1. Auger-spectroscopy data

The histograms in Fig. 3 present Auger spectroscopy data obtained from the steel fracture surfaces. Figs. 4 and 5 show typical Auger-spectra obtained from fracture surfaces after aging. Fig. 6 illustrates a typical brittle intergranular fracture area of a hydrogen-doped specimen after aging, before thermocycling.

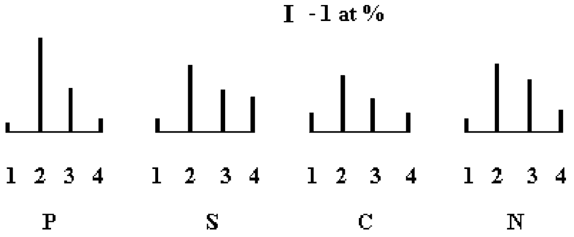

Fig. 3. Elemental composition of the fracture surfaces of 11Cr10Ni2TiMo steel after preliminary treatments and after hydrogen produced brittle fracture: (1) austenization at 950 °C, free of hydrogen (matrix composition); (2) (1) + aging at 550 °C (1 h); (3) (2) + thermocycling (2 cycles); (4) (2) + thermocycling (5 cycles); (2–4) specimens were doped with hydrogen (grain boundary composition).

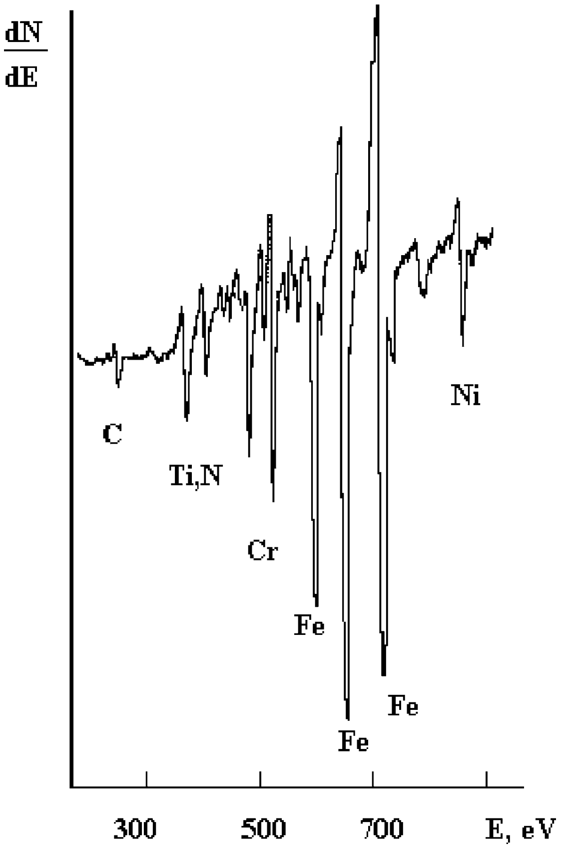

Fig. 4. A typical Auger-spectrum from a dimpled fracture surface of 11Cr10Ni2TiMo steel.

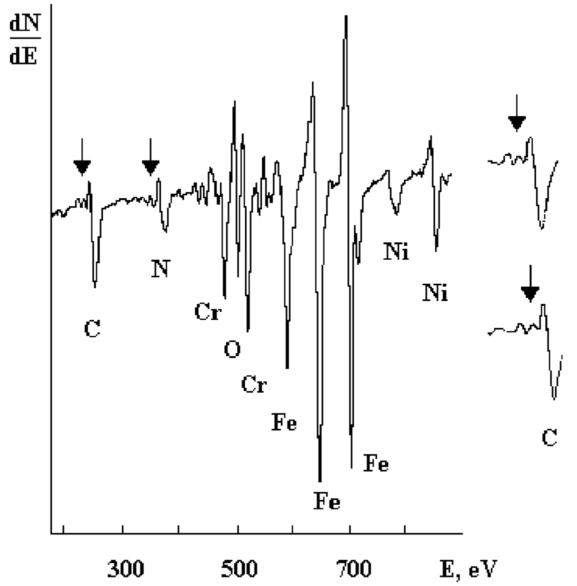

Fig. 5. A typical Auger-spectrum from a grain boundary fracture surface. The absence of Ti at the area is clearly visible. The additional carbon spectra demonstrate a fine structure of carbon, related to carbide phase.

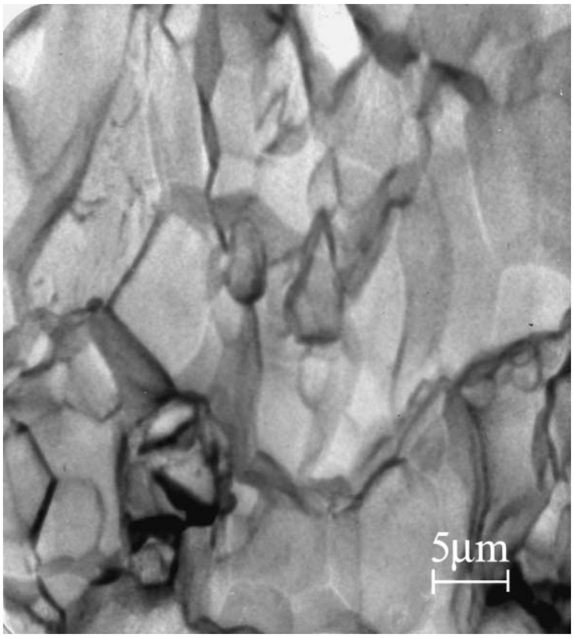

Fig. 6. The typical microphotography of the grain-boundary brittle fracture surface in hydrogen doped state.

On the fracture surfaces with dimpled patterns, a heterogeneous distribution of Ti, Cr, N, C predominated. A typical Auger spectrum in the energy interval 270–850 eV, from an area containing a second phase particle, is given in Fig. 4. Here the carbon Auger-peaks in spectra from the fracture surfaces show a fine structure deriving from the contribution of carbides. (Figs. 4 and 5). It suggests that in this kind of steels the microvoid nucleation occurred at titanium carbo-nitride particles. Fig. 5 presents an Auger spectrum in the energy interval 270–850 eV from a grain boundary facet. It is similar to that presented in Fig. 4, except for the absence of a titanium peak. This spectrum more clearly illustrates the fine structure of the carbon Auger peak. These peculiarities are shown by arrows above the carbon peak within the spectrum as well as above additional peaks written at the right side in Fig. 5, which have been obtained with a lower sweep. A similar fine structure was registered near nitrogen peak (380 eV) and this feature likely originates from a nitride phase. The data demonstrate that phosphorus, nitrogen and carbon segregated at grain-boundaries during aging at 550 °C.

Data obtained in Fig. 3 show that impurity levels decreased on grain boundaries following thermal cycling after aging at 550 °C. The levels of grain boundary impurity segregation were reduced significantly after only a few cycles. We could not obtain data from samples after 6 thermal cycles due to the poor susceptibility to H-induced embrittlement at grain boundaries. Recently, it was demonstrated for some steels [2,3] that grain boundary segregation substantially increased under isothermal conditions and constant stress.

Improvement of the fracture behavior may be related to an increase in defect density – particularly, dislocations and to a corresponding depletion in grain boundary impurity segregation. While a decrease in grain size might also contribute, no noticeable reduction of the grain size was observed.

3.2. Cycling stress state close to a particle–matrix interface

One of the possible mechanisms which can be suggested for impurity redistribution relates to the development of thermomechanical stresses as a result of relatively fast thermal cycling.

To obtain quantitative estimates based on an elastic approach [4] we shall consider a model system – a particle in the form of a rotation ellipsoid with axes R_1 and R_2, introduced into a matrix, of dissimilar material. Let α_1 and α_2 be coefficients of linear expansion of the matrix and inclusion, respectively. If the forms of particles are close to spherical and if it is possible to neglect overlapping stress fields from the nearest neighboring particles, the radial and tangential stresses created by the inclusion in a matrix may be written:

$$\sigma_r = \frac{-P(R_1 + R_2)^3}{8r^3}, \quad \sigma_\tau = \frac{P(R_1 + R_2)^3}{8r^3}. \tag{1}$$

Here P is a pressure on the boundary and r is the a distance from the center of the particle. The value of the pressure may be estimated by:

$$P = (\alpha_1 - \alpha_2)\Delta T \frac{2E_1E_2}{(1+\nu_1)E_2 + (1+\nu_2)E_1}. \quad (2)$$

Here ΔT is the cyclic temperature interval, and $\nu_{1,2}$ and $E_{1,2}$ are, respectively, the Poisson ratio and Young's modulus for the matrix and the particle. It is possible to estimate the value of the contact pressure P, by using values for the Cr–Ti–Mo system in the temperature interval ΔT from 400 up to 800 °C. The calculated contact pressure on the particle boundary due to thermal cycling can be equal to $P = 1500$ MPa, which is close to the strength of the steel. Further, we shall estimate from (1) and (2) the characteristic distance over which the inner stress falls to a plastic limit fluidity value ($\approx$1000 MPa). If the precipitate size is of the order $R = \frac{1}{2}(R_1 + R_2) = 500 \times 10^{-10}$ m the average radius of the high stress region would be about 600×10^{-10} m. In a real matrix pressure created at an interface will substantially relax due to plastic deformation. This produces a high density of dislocations near the interface. These dislocations are potential sinks for impurity atoms moving to/or from an interface. They provide favorable sites and may promote a decrease in segregation. H-induced grain-boundary embrittlement of steel after a typical heat treatment is therefore reduced.

4. Conclusions

The composition of fracture surfaces of 11Cr10Ni2-TiMo steel after heat treatments followed by hydrogen doping was investigated. The formation of grain boundary phosphorus and nitrogen segregation after 550 °C aging was shown.

It was shown that thermocycling in an interval 400–800 °C provided a substantial decrease in grain boundary impurity segregation. It is proposed, that this phenomenon originates from interface stress fields near small particles, which influence the local boundary dislocation density. Thermomechanical stresses at matrix/particle interfaces and at grain boundaries have been estimated based on linear elasticity.

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