

## AUGER SPECTROSCOPY OF IMPURITY GRAIN BOUNDARY SEGREGATION IN A STAINLESS Ni-Cr-Ti-Mo STEEL

The paper presents results of Auger spectroscopy of grain boundary elemental composition of 11Cr10Ni2TiMo stainless steel after typical heat treatment followed by thermal cycling. Specimens in initial austenitic condition were subjected to aging at 550 °C and to cyclic heat treatment. Afterwards they were doped by deuterium in an electrolytic cell in order to facilitate the grain boundary brittle fracture, which was performed by tensile loading directly in an ultrahigh vacuum chamber of a special Auger spectrometer. A noticeable phosphorus grain boundary segregation was observed after aging at 550 °C, but after the applied thermal cycling a substantial decrease in impurity segregation has been proved.

**1. Introduction.** The effect of impurities on the properties of structural materials is a long standing issue, especially for nuclear reactor materials exposed to extreme service conditions. It is known well that grain boundary segregation processes under equilibrium conditions in low-alloyed steels and austenitic stainless steels can dramatically change their mechanical properties [1]. It has been shown previously that segregations induced by irradiation reflected the main features found in unirradiated state but in many cases displayed greater intensity and more unfavorable effect on mechanical properties [2–4]. It is known well, that typical operating parameters for structural materials in nuclear fission and 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. Recently, the effects of a stressed state and temperatures on the segregation processes in some structural steels have been demonstrated [5–11].

At present, there is substantial information about metallurgical features of the micro structural and phase transformations accompanying thermal-cycling in high-alloy steels, but some aspects of the problem left as a subject of discussion. This is especially important for steels with complex chemical compositions and microstructure.

In our work the stainless 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. 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.

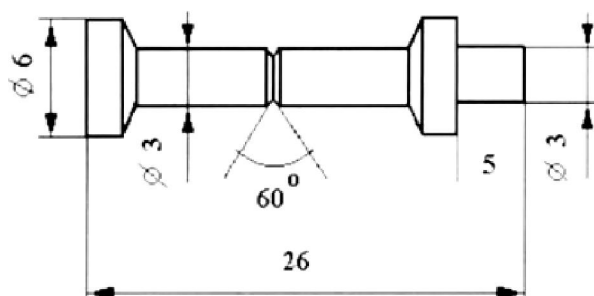


Fig. 1. Specimen geometry (dimensions in millimeters)

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 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.

After thermal-cycling part of the specimens were doped with deuterium in an electrolytic cell at a current density of  $5 \cdot 10^3$  A/m<sup>2</sup>. Deuterium doping was used to promote grain boundary fracture because of hydrogen brittleness. After this procedure 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  $2 \cdot 10^{-7}$  Pa, with a slow strain rate of  $10^{-4}$  s<sup>-1</sup> 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. 2 present Auger spectroscopy data obtained from the steel fracture surfaces.

Figs. 3 and 4 show typical Auger-spectra obtained from fracture surfaces after aging.

On the fracture surfaces with dimpled patterns, a heterogeneous distribution of Ti, Cr, N, C predomi-

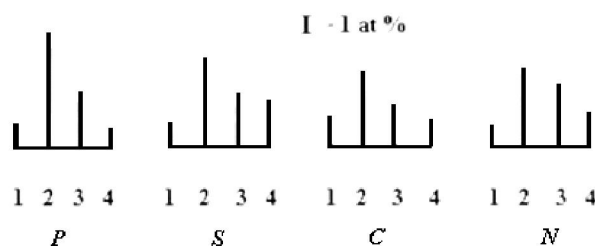


Fig. 2. Elemental composition of the fracture surfaces of 11Cr10Ni2TiMo steel after preliminary treatments and after hydrogen produced brittle fracture:

- (1) austenization at 950 °C, free of hydrogen (matrix composition);
- (2) (1)+aging at 550 °C (1h);
- (3) (2)+ thermocycling (2 cycles);
- (4) (2)+thermocycling (5 cycles); (2–4) specimens were doped with hydrogen (grain boundary composition)

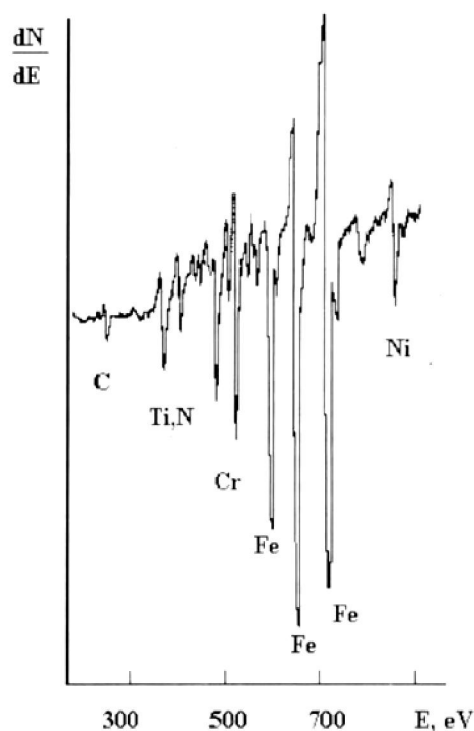


Fig. 3. A typical Auger-spectrum from a dimpled fracture surface of 11Cr10Ni2TiMo steel

nated. A typical Auger spectrum in the energy interval 270–850 eV, from an area containing a second phase particle, is given in Fig. 3. Here the carbon Auger-peaks in spectra from the fracture surfaces show a fine structure deriving from the contribution of carbides. (Figs. 3 and 4). It suggests that in this kind of steels the micro-void nucleation occurred at titanium carbo-nitride particles. Fig. 4 presents an Auger spectrum in the energy interval 270–850 eV from a grain boundary facet. It is similar to that presented

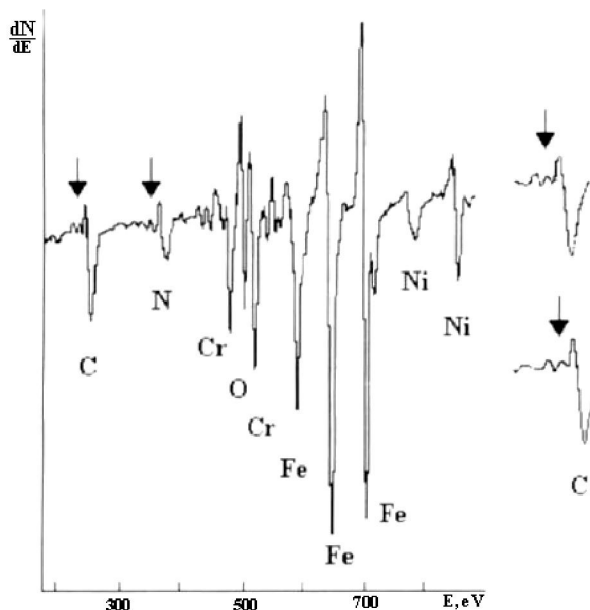


Fig. 4. A typical Auger-spectrum from a grain boundary-fracture surface. The absence of Ti at the area is clearly visible. The additional carbon spectra demonstrate a fine structure of carbon, related to carbide phase

in Fig. 3, 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. 4, 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 presented in Fig. 2 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 [5–7] 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 [12] 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  $\delta_1$  and  $\delta_2$  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:

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

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  $\Delta T$  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  $\Delta T$  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  $R = (R_1 + R_2)/2 = 500 \cdot 10^{-10}$  m the average radius of the high stress region would be about  $600 \cdot 10^{-10}$  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/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.

**Conclusions.** The composition of fracture surfaces of 11Cr10Ni2TiMo 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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## Резюме

Оже-спектроскопия әдісімен 11Cr10Ni2TiMo тот баспайтын болаттың үлгілері түйірлерінің шекарасындағы химиялық құрамының зерттеу нәтижелері көрсетілген. Үлгілер термоөңдеуден және одан кейінгі термоциклдеуден өткізілді. Дәлірек айтқанда бастапқы аустениттік күйден 550 °C-та ескірітіліп, термоөңдеуден өткізілді. Одан кейін, морт қирау үшін оларға электролиттік ваннада дейтерий енгізілді. Одан кейін үлгі арнайы Оже-спектрометрдің өте жоғары вакуумдық камерасының ішінде қирағанға дейін созылды. Түйір шекараларында 550 °C-та ескіртуден кейін фосфор қоспаларының сегрегациясы байқалды. Термоциклдеуден кейін түйірлер шекараларында қоспалар сегрегациясы едәуір азайды.

## Резюме

Представлены результаты исследований с помощью Оже-спектроскопии элементного состава границ зерен образцов из нержавеющей стали 11Cr10Ni2TiMo после типичной термообработки с последующим термоциклированием. Образцы для испытания из первоначального аустенитного состояния были подвергнуты старению при 550 °C с последующей термообработкой. Далее они были легированы дейтерием в электролитической ванне, для ускорения хрупкого разрушения по границам зерен, которое было выполнено растяжением внутри сверхвысокой вакуумной камеры специального Оже-спектрометра. Наблюдалась сегрегация примеси фосфора на границах зерен после старения в 550 °C, но после применения термоциклирования сегрегации примеси на границах зерен существенно уменьшались.

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