ФИЗИКА КОНДЕНСИРОВАННОГО СОСТОЯНИЯ И ПРОБЛЕМЫ МАТЕРИАЛОВЕДЕНИЯ

GRAIN-BOUNDARY SULPHUR SEGREGATION AND EMBRITTLEMENT OF HIGH-PURITY NICKEL

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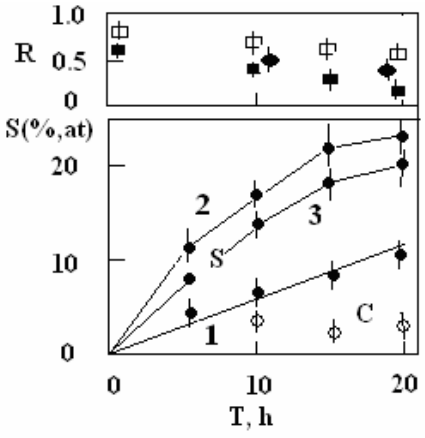
Sulphur grain boundary segregation in vacuum-melted nickel of a special production probe were studied by Auger Electron Spectroscopy. Heat-treated samples of high-purity Ni were electrolytically deuterium doped and fractured by tension and measuring the mechanical characteristics in the ultra-high-vacuum chamber of a special auger-electron spectrometer.

1 Introduction

Nickel and nickel alloys play very important role in modern materials science. Alloying by Ni is used for improving heat-strength and ductility of alloys, to increase the resistivity of steels in different extreme conditions. It is known, however, that under certain conditions nickel and its alloys show the tendency to loss of ductility and up to brittle grain boundary fracture. Embrittlement is often accompanied by impurity segregation on grain boundaries at high-temperature tensile testing of both irradiated and non-irradiated structural materials, especially Fe-Ni-Cr steels and Ni-alloys [1-4]. It should be noticed, that the physical grounds of the effect are not clear up to now. Here the authors make an attempt for getting to better understanding of the aspect of this interesting and practically significant problem.

2 Experimental and Results

Nickel produced by vacuum melting has been investigated [2]. The main impurity contents were as follows: S 0.003, C 0.017, O 0.001, Mn 0.002, Zn 0.004 % wt. Samples in the form of dumbbells with a score in the middle part were subjected to homogenizing annealing at 1050 ^{o}C (2 10^{-3} Pa, 1 h). After that the samples were subjected to heat treatments at different temperatures with the annealing time varied to 20 h. Average grain dimensions obtained were about 190 microns. Deuterium doping was carried out in electrolytical cell at room temperature up to the concentration, providing intergranular fracture by a rate of the axial tension 0.0002 s^{-1}. After that the doped specimens were placed into the chamber of a special Auger spectrometer [4] combining devices for fracture and surface Auger spectroscopy. Specimens tension was performed in a ultra-high-vacuum chamber (P = 1 $\times 10^{-7}$ Pa) at room temperature. A primary electron beam with energy 3000 eV, with diameter about 10 microns, and current 5 $\times$ 10^{-6} A was used for the Auger spectroscopy. Fig.1 presents results of the mechanical testing with fracture of specimens directly inside the Auger spectrometer and data of Auger spectroscopy.



The upper picture: dependence of fracture tension on preliminary heat treatment conditions for deuterium –doped specimens. R = t / t_0 , where t_0 corresponds to untreated deuterium – free specimens. S – the level of S segregation, C – C-levels (% at) measured with AES

Fig.1. T – heat-treatment time (h): 1-500, 2-650 , 3-700 ^{o}C

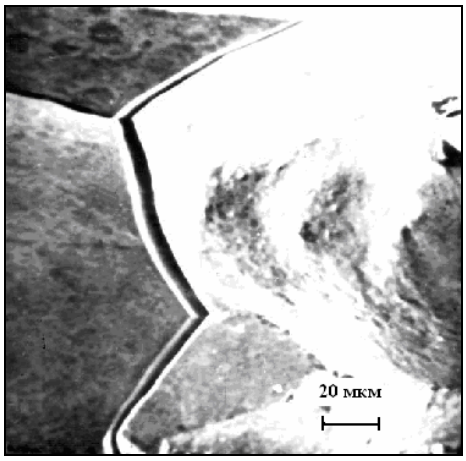


Fig.2. Electron microscopy picture of grain-boundary of Ni after 650^{o} C treatment

Fig.2 presents effect of significant cracking after mechanical testing of the heat- treatment at 650^{o}C.

3 Deuterium – Impurity Interaction

Well known difficulties of "in-situ" observation of deuterium segregation, physical impossibility of its Auger spectrum registration, force investigators to use indirect information including data of fracture type, tension data etc. All that makes more difficult to get insight into physical processes taking place on grain boundaries and restricts the opportunity of their description. In particular, the estimation of the hydrogen concentration on grain boundaries when its chemical content changes, is very difficult. Here we have used an approach [5] which enabled the describing a segregation system with interacting components.

As we know, that physical situation in complex segregation on the grain boundary is much more complicated than that assumed in [5] oversimplified scheme, a certain number of assumptions were made:

a) deuterium segregates fast towards grain boundary reaching equilibrium with the matrix adjacent to the boundary at room temperature alloying;

b) during the time of equilibrium establishment in the deuterium subsystem the segregation of other elements remains unchanged;

c) the interaction energy of deuterium with the segregation components can be approximated by the values related to hydrides

According to [5], the segregation level P(I) of element I on the matrix surface is defined as

$$P(I) = \frac{X(I)}{X_m(I)} = \frac{X_v(I) \cdot \exp(-G(I)/RT)}{1 + \sum_k X_v(k) \cdot \left[\exp(-G(I)/RT) - 1\right]} \tag{1}$$

Where, $X_m(I)$ is the segregation saturation level , X(I) the segregation level of element I , X_v – the volume concentration of I in solid solution, G(I) – the segregation free energy, R , T – universal gas constant and the temperature, respectively. The peculiarity of the system is that the hydrogen segregation takes place mainly due to diffusion from the outer surface subjected to electrolytical doping directly along the grain boundaries. Formally, we make possible to describe such a situation by the equation for the free energy of H segregation in the following form:

$$G(H^2) = G(H^2, Ni) \cdot \left[1 - X(S) - X(C)\right] + G(H^2, S) \cdot X(S) + G(H^2, C) \cdot X(C), \tag{2}$$

where $G(H^2, Ni) = -4.5 kJ/mol$ [6], $G(H^2, C) = -31.3 kJ/mol$ [6], $G(H^2, S) = -20.1 kJ/mol$ [6] are free energy of hydrogen segregation on nickel grain boundaries and the free energies of H_2S and CH_4 formation respectively.

Equation (2) is based on the assumption that deuterium segregates under conditions when sulphur and carbon segregations are stable.

The results of calculations of the hydrogen equilibrium level on nickel grain boundaries according to (1) using (2) are shown on Fig.3.

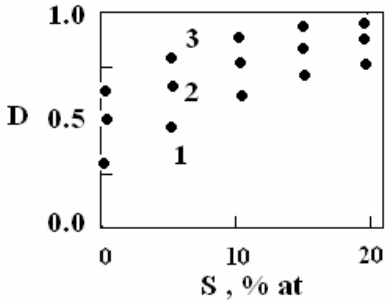


Fig.3. Calculated dependence of deuterium equilibrium level on grain boundaries in monolayer units on sulphur segregation level at different carbon segregation levels:1: free boundary,2: 2 at %, 3: 4 at %

4 Discussion

Results presented in Figures 1 and 3 have shown that fracture strength reduction correlates with increasing sulphur segregation and deuterium level on grain boundaries. One can see, that sulphur segregation level reaches about higher than 20 % atomic. It is also clear, that carbon segregation effectively stimulates the deuterium level growth when the sulphur level at the boundary is relatively small. Experimental data show that carbon rather displaced from the grain boundaries by sulphur segregation. It should be noticed, that for S segregation kinetics plots appeared to be better described by a linear function than by the $\sqrt{t}$ approximate segregation kinetics that according to well known McLean's elementary model [8]. It can be connected with the distortion influence of carbon segregation. As is clear from Fig.1, the maximum sulphur segregation level is observed between temperature interval 650 and 700°C. The equation (1) can be solved with respect to G (S, Ni) in the case of neglecting the carbon segregation at 650°C heat-treatment. As a result the free energy of S segregation on grain boundaries appeared to be equal $G(S, Ni) = (138 \pm 10)$ kJ / mol. The solubility value X(S) was taken equal to 10^{-4} % at., that referred to temperature 630°C. A comparison of the sulphur, carbon, hydrogen energies of segregation -138 < -46 < -4.5 kJ / mol confirmed the correctness of the assumption of a stable segregation structure during deuterium segregation. This thermodynamical approach gives us some additional understanding about quasi-equilibrium processes on grain boundary but unfortunately, it is still not achieved complete understanding in how segregating impurities can change the electronic and mechanical properties of grain boundaries under conditions of embrittlement. We can consider some reasonable possible mechanism, including two main factors: the bonding energies of metal atoms changes through the grain boundary and the surface structure of the boundary changes in the presence of the impurity segregation.

In order to get better understanding about a physical mechanism of what we call as grain boundary embrittlement we performed computer simulation of a typical Ni – S- D cluster configuration.

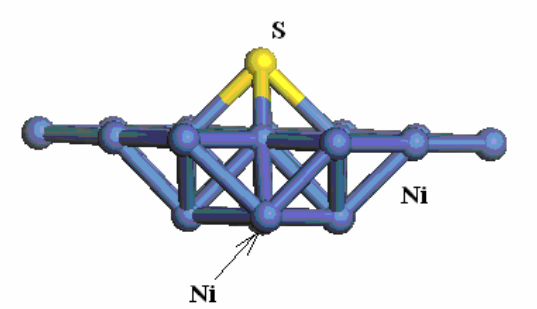


Fig. 4. Simulation of a Ni_{22}-S - cluster for MO-LCAO calculations

At first we considered a configuration of a Ni – S cluster , which is presented in Fig.4. The equilibrium position of S atom over surface was found out with using calculations of binding energy in different points along the 4^{th} order normal (Fig.5). The binding energy has maximum equal to -1.6 eV by a distance equal to 1.5 Å to the Ni -surface.

Further we calculated the binding energy between Ni-atoms in fragment for two cases: for pure Ni and for Ni – S system. Results of calculations show that presence of sulphur atom on the surface affects a binding energy of atoms from a low layer (it is displayed by an arrow). Effects of calculation of a total energy were converted on one atom of nickel to avoid dimensional effect. For pure nickel binding energy E_b^0 = -1,5 eV for nickel with atom of sulphur E_b^s = - 0,8 eV has been gained.

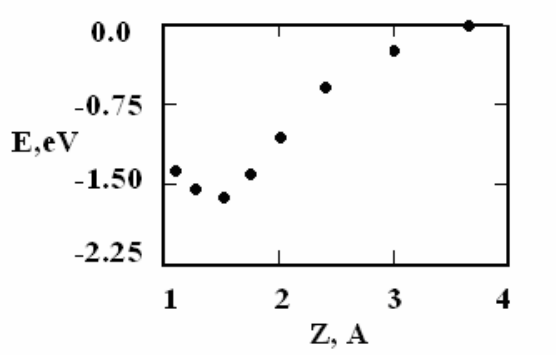


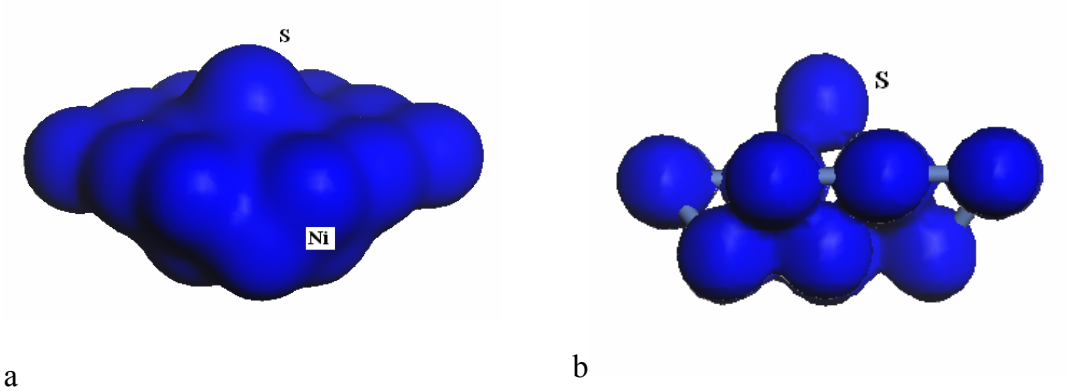
Fig.5. Dependence of S-atom binding energy on Z distance from the Ni-surface. The S-atom was placed in a position with symmetry of 4^{th} order (Fig.4)

From the results obtained one can see, that in the case of S-segregation there is an overflowing of electronic charge from the lower layer to the upper one. For checking this supposition the distribution of electron density on a cluster has been calculated and the binding energy between the top and bottom atomic layers was estimated.

Comparison of figures 6 a) and b) displays also essential weakening of an electron charge cloud between atoms of nickel and between atomic layers at magnification of a density of charge to an appropriate covalent linkage.

The binding energy of layers for pure nickel was obtained as large as 163 κJ / mol, and for nickel with sulphur adsorbed it was noticeably less: 131 κJ /mol.

As the next step we have performed calculation of the system Ni - S - D (Fig.7).



a b

Fig.6. Distribution of the electron charge at density equal to a) 0.03 and b) 0.3

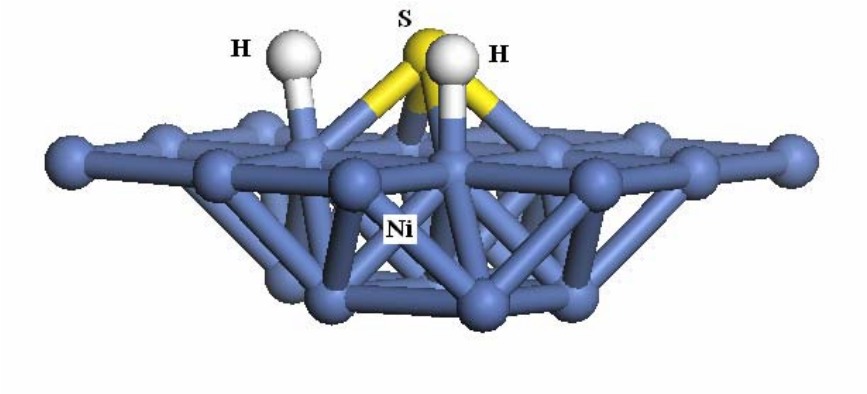


Fig.7. Atomic structure of the cluster $Ni_{22} – S – H_2$

Deuterium atoms were arranged approximately nearly to their location in the $S-H_2$ molecule, but randomly on the Ni –surface.

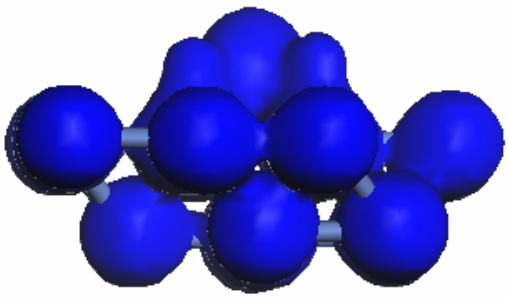


Fig. 8. Electron charge distribution on the cluster Ni_{22} - S - H_2 at a density equal to 0.25 el / $Å^3$

Fig.8 shows, that the effect of decreasing the electron charge density between the atomic layers is obviously large. It is in a good agreement with results of calculation of a binding energy between layers for this system(95 кJ /mol).

So, we can resume results of MO-LCAO calculations of binding energy between atomic layers for these systems:

95 кJ/mol (Ni-S-H) < 131 кJ/mol (Ni-S) < 163 кJ/mol (Ni)

References

1. Votinov S.N., Prokhorov V.I., Balashov V.D., Shamardin V.K. Role of irradiation in high temperature embrittlement of steels. // Radiation physics of solids and nuclear reactor materials science. – M., 1970. p.82.

2. A.M.Ilyin and S.N.Votinov. Using Auger Electron Spectroscopy for Examining Sensitising of Nickel and Stainless Steel to Intergranular Failure in Doping with Deuterium //Journal of Advanced Materials. 1994.V.1.N3.269-272.

3. Ilyin A.M., Volkova T.V., Melikhov V.D. and Votinov S.N. The Deuterium – Impurity Interaction and the Grain Boundary Embrittlement in Nickel. // Phys. Stat. Sol. (a) 148 (1995) 89.

4. А.М.Ильин,Б.А.Борисов, Т.В.Волкова. Проявления химического взаимодействия в зернограничных сегрегациях примесей и водорода в никеле // "Вопросы атомной науки и техники. Сер. Физика радиационных повреждений и радиационное материаловедение".1995, т.1(60), 93-96.

5. A.M.Ilyin, V.N.Golovanov. Auger Spectroscopy Study of the Stress Enhanced Impurity Segregation in a Cr-Mo-V Steel. “ J. Nucl.Mater.” 1996. 233-237. 233-235.

6. M.Guttman. Equilibrium Segregation in a Ternary Solution: a Model for Temper Embrittlement. // Surf. Sci. 53 (1975) 213.

ЖОҒАРЫ ТАЗАЛЫҚ НИКЕЛЬ ДӘНДЕРІНІҢ ШЕКАРАСЫНДА КҮКІРТІҢ СЕГРЕГАЦИЯСЫ ЖӘНЕ ОНЫҢ СЫҢҒАҚТЫҒЫ

А. М. Ильин, В.А. Борисов

Вакуумдық балқуымен алынған никельдегі дәндердің шекарасында күкіртің сегрегациясы Оже - спектрометрдің камерасында зерттелді. Электролиттік астауда өте таза никельдің үлгілеріне дейтериймен легирлеу өткізілді және арнайы Оже - спектрометрдің жоғары вакуумдық камерасында күйзелтуі және механикалық қасиеттерінің өлшеуі жүргізілді.

СЕГРЕГАЦИЯ СЕРЫ НА ГРАНИЦЕ ЗЕРНА НИКЕЛЯ ВЫСОКОЙ ЧИСТОТЫ И ЕГО ОХРУПЧИВАНИЕ

А.М. Ильин, Б.А.Борисов

Сегрегация серы на границе зерна в никеле, полученной вакуумной плавкой, была изучена в камере Оже - спектрометра. С образцами очень чистого никеля в электролитической ванне проводилось легирование дейтерием с последующим разрушением и измерением механических свойств в высоковакуумной камере специального Оже - спектрометра.