Sulphur Precipitation in Annealed Sulphur-Doped Nickel Studied by Fluorescent X-ray Emission

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The results of measurements of S L_{2,3} ultra-soft X-ray emission spectra excited by synchrotron radiation at $h\nu = 163\text{--}165$ eV for samples with 240 ppm S in Ni after annealing at 400–700°C are presented. It is found that S L_{2,3} X-ray emission spectra of S-impurity atoms in Ni show fine structure which can be simulated by a superposition of spectra of nickel sulphide and pure sulphur providing evidence that sulphur atoms are present after annealing both in solid solution and in clusters where they form S–S bonds. The variation of temperature and time of annealing (at $T = 400^\circ\text{C}$ for 1 h and at $T = 700^\circ\text{C}$ for 2 h) leads to some redistribution of intensity of S L_{2,3} X-ray emission valence spectra which can be attributed to changes in the number of S–Ni and S–S bonds in accordance with the limit of sulphur solubility at these temperatures.

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I. Introduction

Sulphur is a widespread impurity element in transition metals and alloys. The precipitation of impurity sulphur atoms on the grain boundaries is considered as one of the main factors for the embrittlement of these materials⁽¹⁾. Usually the segregation takes place during a heat treatment of S-containing metals and alloys at comparatively high temperatures⁽²⁾⁽³⁾. The appearance of sulphur on the grain boundaries dramatically influences their mechanical properties⁽⁴⁾. Therefore, it is very important to obtain the direct evidence of sulphur segregation in transition metals and alloys that have been heat treated.

According to the Ni–S phase diagram⁽⁵⁾, the solid solubility of sulphur in solid nickel is very small: only 350 appm of sulphur dissolves in nickel at 900°C and the temperature dependence of the solubility is unknown. When the sulphur concentration in the solid solution exceeds the solubility limit, decomposition of the Ni–S solid solution may occur during aging heat treatment. Aging processes in materials are commonly studied using residual resistance measurements, small-angle X-ray scattering, electron microscopy and other techniques. Unfortunately, the direct methods, such as transmission electron microscopy are not efficient in this case because of the extremely small amount of precipitate in the sample. This is especially acute in the early stages of the solid solution decomposition.

Recent developments of third generation synchrotron

radiation sources provides an opportunity to overcome the difficulty to measure the low intensity of S L_{2,3} fluorescent X-ray emission spectra of S-impurity atoms in metals due to the low L-fluorescent yield of light elements and the small concentration of emitting atoms⁽⁶⁾⁽⁷⁾. X-ray emission spectroscopy (XES) has some advantages for study of sulphur precipitation in metals on grain boundaries with respect to surface sensitive spectroscopic technique (as Auger spectroscopy and XPS) because it probes mainly bulk of material.

In the present paper we present the results of a study of S L_{2,3} X-ray emission spectra (XES) of S-impurity atoms in Ni (240 ppm S) excited by synchrotron radiation and provide direct spectroscopic evidence of sulphur segregation in heat treated Ni.

II. Experimental

All samples were diffusion doped with gaseous phase sulphur at 1050°C in a quartz tube under clean vacuum conditions. After doping the samples were cooled at a rate of 200–400 K/min. The total concentration of sulphur in Ni was about 240 ppm. The sulphur concentration was determined from resistivity measurements, assuming the sulphur contribution to the residual resistivity of nickel to be $r = 0.0068$ nΩm/appm⁽⁸⁾. After cooling about 80% of sulphur was in solid solution and the remaining sulphur precipitated from the solid solution and formed clusters of sulphur atoms. After annealing at 400°C for 1 h (sample 1) the solid solution attained an

equilibrium concentration of 40 ppm sulphur. After annealing at 700°C for 2 h (sample 2) the amount of sulphur in solid solution was equal to the solubility limit at this temperature (over 70 ppm). This concentration of sulphur was achieved because the samples were cooled at a rate of over 100 K/s after annealing. The sulphur precipitates at this temperature and coalesces into clusters containing tens of atoms as inferred from the work of Arbuzov *et al.*⁽⁸⁾⁽⁹⁾.

All samples under investigation were diffusion doped in conditions of oxygen free high vacuum. Residual resistivity measurements without a sulphur atmosphere indicate level of oxygen to be less than 10^{-5} at%. All the samples have been annealed in a helium atmosphere purified by means of a titanium getter so that the partial pressure of oxygen less than 10^{-8} Pa.

High-energy resolved S $L_{2,3}$ X-ray emission spectra (valence $3s3d \rightarrow 2p$ transition) were measured on the Advanced Light Source (ALS) Beamline 8.0, a 5.0 cm period undulator beamline with a spherical grating monochromator operating between 70 eV and 1200 eV ($1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$). The energy resolution of the monochromator was set to be about 0.3 eV during these measurements. The soft X-ray endstation includes a Rowland circle grating spectrometer coupled to a photon-counting area detector⁽¹⁰⁾. All soft X-ray emission spectra reported in this work were recorded with a 100 μm entrance slit for the spectrometer and a 1500 lines/mm, 5 m radius grating. At the S $L_{2,3}$ region, the energy resolution of the spectrometer was approximately 0.4 eV. The time of measurements of spectra was about 1.5 h and it was sufficient to accumulate spectra with maximal intensity about 700–800 counts.

III. Results and Discussion

S $L_{2,3}$ X-ray emission spectra (XES) correspond to $3s$ or $3d \rightarrow 2p$ transitions when the vacancy in the $2p$ core level created by photon excitation is filled by electrons having $3s$ or $3d$ symmetry from the valence band. Therefore S $L_{2,3}$ XES probes the S $3s(3d)$ density of states (DOS) distribution in the valence band of S-containing materials. Furthermore S $L_{2,3}$ XES is sensitive to the chemical bonding of sulphur and thus the energy distribution and fine structure of the spectra are different for elemental sulphur⁽¹¹⁾⁽¹²⁾, chemical compounds containing sulphur⁽¹²⁾⁽¹³⁾ and transition metal sulphides^{(14)–(17)}. In addition, the X-ray transition is localized within the limits of the first coordination sphere of the emitting atom and S $L_{2,3}$ XES is therefore sensitive to short order (coordination number, bond length, etc.). All these factors make it possible to use XES to distinguish the changes in the nearest surrounding and local chemical bonding of the emitting atom induced by heat treatment. It provides the basis to study the segregation of dissolved impurities in transition metals induced by heat treatment.

In Fig. 1 the results of measurements of S $L_{2,3}$ XES of S-impurities (240 ppm S) in Ni are shown after heat treating the sample at 400°C for 1 h (solid dots) and another sample at 700°C for 2 h (open circles). The intensity distribution of S $L_{2,3}$ XES from the different samples are noticeably different as a result of the heat treatment. The spectra were normalized at the maximum of intensity and it is seen that intensity of high-energy structure located at $E = 153\text{--}159 \text{ eV}$ is decreased for the sample one given a heat treatment of 400°C with respect to the sample two given a heat treatment at 700°C. For interpretation of these data the S $L_{2,3}$ XES of sample two is compared with

Fig. 1 S $L_{2,3}$ XES of sample 1 (240 ppm S in Ni, annealed at 400°C for 1 h) and sample 2 (240 ppm S in Ni, annealed at 700°C for 2 h) excited at $E = 163\text{--}165 \text{ eV}$.

Fig. 2 Comparison of S $L_{2,3}$ XES of sample 2 with spectra of reference samples: BaNiS_2 and pure sulphur⁽¹¹⁾.

Fig. 3 Comparison of S $L_{2,3}$ and Ni L_3 XES of BaNiS_2 in the scale of binding energy.

the spectra of reference samples: BaNiS_2 ⁽¹⁸⁾ and pure sulphur⁽¹¹⁾. A comparison of the S $L_{2,3}$ from these compounds in Fig. 2 shows that the main intensity maximum (b) of S $L_{2,3}$ XES of sample two coincides with that of BaNiS_2 and NiS_2 ⁽¹⁷⁾ (not plotted) and the less intensive high-energy maximum (c) at $E=150$ eV corresponds closely to pure sulphur. In Fig. 3 we compare the S $L_{2,3}$ and Ni L_3 valence emission spectra in BaNiS_2 adjusted to the same energy scale using XPS binding energy data⁽¹⁸⁾. The Ni L_3 emission spectrum is a map of valence states having 3d symmetry and has a maximum about 2 eV below the Fermi level. This maximum corresponds closely in energy to the maximum e of S $L_{2,3}$ XES in Fig. 2 and strongly suggests that S 3s(3d)–Ni 3d hybridization takes place and the maximum e is a measure of Ni–S bonds. The maximum intensity of the S $L_{2,3}$ XES of pure sulphur

coincides with shoulder c in Fig. 2. Sugiura⁽¹⁹⁾ suggests that the broadening in the S $L_{2,3}$ XES of pure sulphur in the α -molecular crystalline state⁽²⁰⁾⁽²¹⁾ is due to the short range order induced by the formation of molecular bonding orbitals from the S 3s electrons. From this information we conclude that the S $L_{2,3}$ intensity distribution obtained from sample two can be reproduced by a superposition of spectra from nickel sulphide (BaNiS_2) and pure sulphur.

Therefore, our results show strong evidence that S–Ni and S–S bonds form after annealing. We also have direct spectroscopic evidence that heat treatment of Ni containing S impurities induce the precipitation of S. Furthermore, the intensity of S $L_{2,3}$ XES due to transitions of electrons having Ni–S bonds (the transitions associated with feature e in Fig. 2) decreases as the annealing temperature and time decrease as a result of the lower solubility of sulphur in nickel at reduced annealing temperature⁽⁸⁾⁽⁹⁾.

IV. Conclusion

In summary we have made S $L_{2,3}$ XES measurements on sulphur doped nickel sample annealed at 400 and 700°C, and compared these spectra with those of elemental sulphur and nickel sulphide (BaNiS_2). The results of the comparison provided strong evidence that after annealing, sulphur precipitates from solid solution forming both S–Ni and S–S bonds. The S $L_{2,3}$ spectra from the two samples annealed at different temperatures (at $T=400^\circ\text{C}$ for 1 h and at $T=700^\circ\text{C}$ for 2 h) show a redistribution of intensity which can be attributed to changes in the numbers of S–Ni and S–S bonds in accordance with the sulphur solubility limit at these temperatures.

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