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Determination of Self-diffusion Coefficient of Nickel in Nickel Sulfide

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Synopsis. The self-diffusion coefficient of nickel in nonstoichiometric nickel sulfide, $Ni_{1-\delta}S$, was measured as a function of δ, using ^{63}Ni in the temperature range of 550—750 °C. At $\delta=0.028$, the self-diffusion coefficient, D^*_{Ni}, was expressed by the following equation:

$$D^*_{Ni} = 3.3 \times 10^{-7} \exp\left(-\frac{73.2\pm9.2/\text{kJ mol}^{-1}}{RT}\right) \text{m}^2\,\text{s}^{-1}.$$

At 550 °C and 650 °C, D^*_{Ni} increased with an increase in δ from 0 to 0.04 and tended to reach the saturation point above $\delta=0.04$.

Generally, the self-diffusion in inorganic crystals takes place *via* point defects, so it is necessary to know the relation between the self-diffusion coefficient and the defect concentration in order to elucidate the diffusion mechanism. There have, however, been only a few studies which have determined the self-diffusion coefficient as a function of the defect concentration. $Ni_{1-\delta}S$ has a wide nonstoichiometric region, δ.[1-3] The purpose of the present study is to determine the self-diffusion coefficient of nickel in $Ni_{1-\delta}S$ as a function of δ at 550—750 °C.

Experimental

Specimen. The nickel sulfide was prepared by sulfidizing electrolytic nickel powder (99.99% purity) with sulfur purified by distillation *in vacuo*.

They were reacted in a Vycor reaction tube, first at 400 °C for a week and then at 900 °C for 4 days to complete the sulfidization. A single crystal of nickel sulfide, 5 mm in diameter and 50 mm long, was grown by the Bridgeman method. The crystal orientation was determined by the Laue method. Disks, 2 mm in thickness, were cut perpendicular to the c-axis from the single crystal by means of a crystal cutter and polished with polishing paper.

Controlling of δ. A sulfide specimen and sulfur were sealed in an evacuated Vycor tube and placed in an electric furnace which had two different temperature zones. The specimen was set in the high-temperature zone (700 °C), while the sulfur was placed in the low-temperature zone. The specimen was then annealed for 4 days in sulfur vapor, whose vapor pressure was controlled by the lowest temperature of the tube. The δ was determined using the relation between the sulfur pressure and δ,[2] and doubly checked by means of the lattice constant using Laffitte's results.[3]

Diffusion Annealing. About 10 µCi of ^{63}Ni was applied to one end of the disk specimen, after which the specimen was placed in a Vycor tube, evacuated, and sealed. Then the tube was placed in an electric furnace kept at a desired temperature for diffusion annealing. In order to avoid any change in composition resulting from the decomposition of sulfide, the volume of the reaction tube was minimized to about 3 cm³.

Measurement of the Self-diffusion Coefficient. After the diffusion-annealing the specimen was taken out and sectioned by successive grinding by means of a grinding machine which has been described elsewhere.[5] The thickness of each layer was 5—10 µm, as determined from the weight decrease in the specimen after grinding.

The radioactivity of ^{63}Ni on the polishing paper was counted by the liquid-scintillator-method, since β-rays from ^{63}Ni are too weak for the radioactivity to be measured by the use of a Geiger-Muller counter, especially at low radioactivity. Polishing paper smeared with sulfide powder was immersed in the liquid scintillator, and photons activated by β-rays were measured by means of a photomultiplier.

Results and Discussion

Figure 1 shows the Arrhenius plot for the self-diffusion coefficient, D^*_{Ni}, in $Ni_{1-\delta}S$ at $\delta=0.028$. The D^*_{Ni} value obtained by Klotsman at $\delta=0.03$ is also shown in the same figure for the sake of comparison. There is a good agreement between the two results. The present result at $\delta=0.028$ can be expressed by the following equation:

$$D^*_{Ni} = 3.3 \times 10^{-7} \exp\left(-\frac{73.2\pm9.2/\text{kJ mol}^{-1}}{RT}\right) \text{m}^2\,\text{s}^{-1}$$

Since δ is constant, the activation energy, 73.2 kJ mol⁻¹, indicates the enthalpy of activation for the migration of nickel in $Ni_{1-\delta}S$.

Figure 2 shows the relation between D^*_{Ni} and δ at 550 °C and 650 °C. D^*_{Ni} increases with an increase in δ from 0 to 0.04 at both temperatures. However,

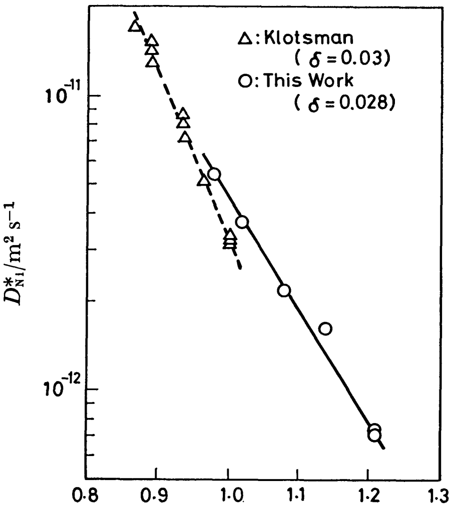

Fig. 1. Arrhenius plot of D^*_{Ni} in $Ni_{1-\delta}S$.

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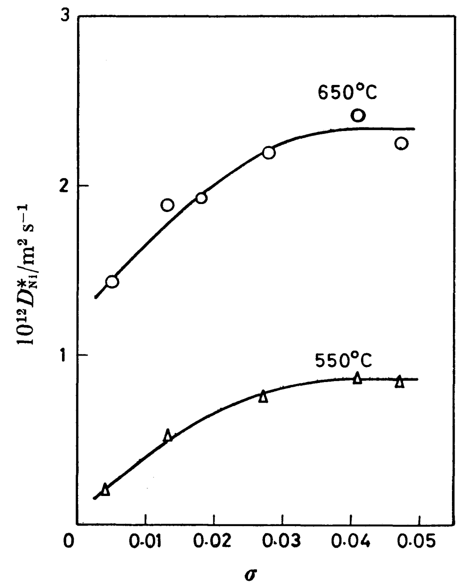

Fig. 2. Relation between D^*_{Ni} and δ in $\mathrm{Ni}_{1-\delta}\mathrm{S}$.

D^*_{Ni} is not linearly related to δ and tends to reach the saturation point above $\delta=0.04$. A simple defect model would thus appear to be inappropriate for $\mathrm{Ni}_{1-\delta}\mathrm{S}$.

The same tendencies for the D^*_{Fe} in $\mathrm{Fe}_{1-\delta}\mathrm{S}$, which has the same Ni–As type of crystal structure,⁶⁾ and also for D^*_{Fe} in $\mathrm{Fe}_{1-\delta}\mathrm{O}$⁷⁾ have been reported. The dependence of the D^*_{Fe} in $\mathrm{Fe}_{1-\delta}\mathrm{O}$ on δ was explained by the formation of clusters of iron vacancies.⁷⁾ If the defect clusters are formed in $\mathrm{Ni}_{1-\delta}\mathrm{S}$, the concentration of free vacancies that are responsible for the diffusion process would not be expected to be linearly related to the deviation from stoichiometry. To ascertain the defect structure of $\mathrm{Ni}_{1-\delta}\mathrm{S}$, detailed studies, for example, neutron and X-ray diffraction studies, are necessary.

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