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Sulfur segregation on a hydrogen-stimulated nickel surface

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A technique based on combining segregation experiments with a hydrogen permeation technique has been suggested to investigate hydrogen-stimulated segregation of impurities on a metal surface. Using this technique, the influence of hydrogen upon sulfur segregation on a nickel surface was investigated. Sulfur diffusivities in nickel were determined in the temperature range 923–1123 K both with and without hydrogen in the bulk of the nickel sample. Hydrogen was observed to intensify the process of sulfur segregation on the nickel surface. The influence of hydrogen on sulfur diffusivity in nickel was considered in the framework of a model of a solid substitution solution with hydrogen as an interstitial impurity, taking into account different atom configurations in approximation of the nearest neighbors. An equation describing qualitatively the hydrogen bulk concentration dependence of sulfur diffusivity in nickel has been derived.

I. INTRODUCTION

In spite of the importance of the problem concerning hydrogen influence upon impurity segregation in metals, only a few works have been devoted to this phenomenon. Moreover, these works are not recent ones and relate to previous decades. J. Szymerska and M. Lipski[1] observed hydrogen stimulated segregation of sulfur onto a palladium free surface. In their next work,[2] they investigated how hydrogen influences sulfur segregation on free surfaces of platinum, palladium, and copper. When investigating the influence of surface elemental composition upon hydrogen permeability through vanadium, hydrogen was observed to increase the rate of sulfur segregation onto vanadium surface.[3] But these works ascertained an existence of this phenomenon and described some peculiarities of it without considering mechanisms of hydrogen stimulated segregation of the impurities onto metal surfaces.

To perform comprehensive research of this phenomenon, one needs to be provided with the corresponding technique. When investigating the influence of hydrogen being in the bulk of a metal on surface segregation of the impurities in metals, its bulk concentration must be maintained at a constant level while registering kinetic curve of impurity segregation. Hydrogen mobility in metals usually exceeds that of impurities by many orders of magnitude and this fact impedes using the samples previously charged with hydrogen for investigation of hydrogen stimulated segregation.

In the present work, to obtain correct results, the experiments on segregation are suggested to combine with hydrogen permeation technique. At the appropriate size of the specimen and rate of pumping one can continuously control concentration of impurity segregating onto surface of the outlet, in relation to hydrogen, side of the specimen by means of Auger electron spectroscopy (AES) technique. Having constant hydrogen pressure under the surface of inlet side of the sample the concentration of bulk hydrogen can be easily maintained at stationary mode within the total period of time that is necessary to obtain a kinetic curve of surface impurity segregation.

Hydrogen-stimulated segregation of sulfur onto a nickel surface was investigated using the above mentioned technique. The results obtained and possible mechanism of this phenomenon will be discussed further.

II. EXPERIMENT

A. Sample

For research, a disc of polycrystalline nickel (99.2%) with 0.7-mm thickness and 16-mm diameter was used. Concentrations of the main impurities in the sample are represented in Table I.

B. Experimental device

The experimental device used in this work is intended to investigate hydrogen-stimulated segregation of the elements onto research material surface and to determine parameters of hydrogen interaction with materials. It consists of inlet and outlet chambers separated by the sample under research in Fig. 1. The specimen was welded into the diffusion assembly in an argon environment.

Sample heating is carried out indirectly and allows one to investigate surface segregation and hydrogen permeability through material in the temperature range 300–1270 K. The temperature is measured by a thermocouple spot welded to the sample edge. Automation system provides temperature control with the accuracy ± 0.5 K.

The vacuum system is mostly made of stainless steel Cr18Ni10Ti and can be baked out up to 473 K. Inlet and outlet chambers are evacuated with sorption and sputter ion pumps (250 l/s) which provide pressure of residual gases in both chambers 1×10^{-7} Pa, after it's baking out.

Palladium-silver and pure-silver filters are used to admit pure hydrogen and oxygen into the chambers. It allows one to operate with the high-purity gases within the range of pressures from 1×10^{-7} to 1×10^{4} Pa. To admit other gases and its mixtures into vacuum chambers the experimental device is equipped with dosing valve.

Partial pressures of residual gases are analyzed by means of omegatron-type mass spectrometer with the accuracy ±10%.

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TABLE I. Concentrations of the main impurities in the nickel sample according to it's certificate.

Element	S	C	O	P	Si	Al	Ti	Mo	W	Fe
Appm	15	650	160	25	280	900	1500	950	600	950

Surface elemental composition of the outlet side of the specimen is controlled by means of an Auger spectrometer equipped with cylindrical mirror analyzer with energy resolution $\Delta E/E = 0.4\%$ designed by V. Zashkvara.[4]

C. Experimental technique and results obtained

After positioning the specimen (diffusion assembly) into an experimental device, the inlet and outlet chambers were pumped out to the pressure of residual gases 1×10^{-7} Pa. Measurement of partial pressures of residual gases was carried out by omegatron-type mass spectrometer.

Then Auger spectrum of the nickel surface was obtained. The primary beam energy and the primary intensity were 1.6 keV and 10 μA, respectively. The diameter of primary electron beam was 0.5 mm and modulation voltage peak to peak -2 V.

All the Auger spectra were recorded in differential mode dN/dE. Surface atomic concentration of sulfur was obtained from the ratio of S to Ni Auger peak heights. Auger peak 61 eV (L_3VV) of nickel was chosen rather than 848 eV ($M_{23}VV$) as more sensitive to the surface impurity concentration.

When calculating the surface concentration of sulfur, the following argumentation was used. If the bulk concentration of sulfur C_S^b is negligible compared to its surface concentration C_S^S, one can write:

$$C_S^S = K\cdot\frac{I_{S(152\ \mathrm{eV})}}{I_{Ni(61\ \mathrm{eV})}}, \tag{1}$$

where K is the constant value; $I_{S(152\ \mathrm{eV})}$ and $I_{Ni(61\ \mathrm{eV})}$ are the peak to peak heights of sulfur and nickel, respectively. The equilibrium level of sulfur concentration on the nickel surface is known to be $C_S^S \approx 0.45$,[5] in the temperature range 898–1073 K. Having measured values of $I_{S(152\ \mathrm{eV})}$ and $I_{Ni(61\ \mathrm{eV})}$ from the Auger spectrum obtained at the sample temperature 1073 K and after annealing at this temperature for 10 h, K was calculated. Equilibrium in the Ni-S system was experimentally found to be achieved after annealing sample for such period of time at 1073 K.

When heating up the sample, carbon and sulfur segregated onto the nickel surface. To make an interpretation of the experimental results easier, an attempt was made to clean the surface and subsurface region of the sample from carbon. For this purpose, hydrogen was admitted into the inlet chamber up to the pressure 4×10^2 Pa and penetrated into outlet chamber through sample heated up to 1073 K. Hydrocarbons were formed on the sample surface at this temperature and carbon combined with hydrogen was desorbed and pumped out. Duration of a such sample treatment was 30 h.

After carrying out five cycles of treatment at such conditions the surface of outlet side of specimen was free of carbon and its segregation was not observed while performing experiments on sulfur segregation onto a nickel surface.

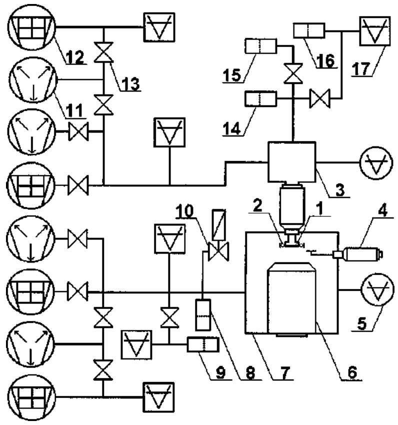

FIG. 1. Experimental device: 1-sample; 2-heater; 3-inlet chamber; 4-manipulator for ignition of glowing discharge; 5-mass-spectrometer; 6-Auger electron energy analyzer; 7-outlet chamber; 8-oxygen diffusion filter; 9-hydrogen diffusion filter; 10-dosing valve; 11-ion sputtering pump, 12-sorption pump; 13-vacuum valve; 14-oxygen diffusion filter; 15-helium leakage; 16-hydrogen diffusion filter; 17-pressure gauge.

To obtain kinetic curve of segregation one needs to have initial surface concentration of sulfur significantly less than its level of equilibrium segregation. Therefore, cleaning of the surface was necessary to be carried out before every segregation experiment. Sulfur removal from the sample surface was implemented using a chemical reaction technique with oxygen as the active gas. For this purpose, the sample was exposed to oxygen at pressure 10^{-1} Pa and sample temperature 873 K for one hour. Then oxygen was pumped out and specimen was annealed at the same temperature in ultrahigh vacuum for three hours. After this treatment sulfur concentration on the surface was less than 5 at. %.

Kinetics of sulfur segregation onto the free surface of nickel were obtained in the temperature range 923–1123 K. Specimen was heated up to the necessary temperature for 2–3 min before taking data and evolution of sulfur coverage was registered. Kinetics of sulfur segregation onto the surface of nickel are represented on Fig. 2.

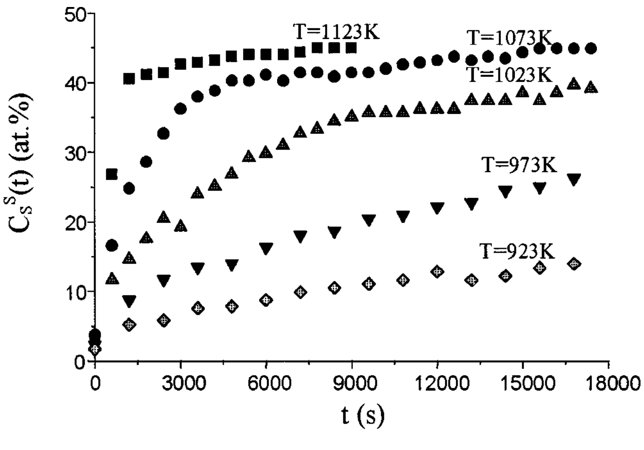

FIG. 2. Kinetics of sulfur segregation on the surface of nickel obtained at different temperatures 923, 973, 1023, 1073, 1123 K (without hydrogen in the bulk).

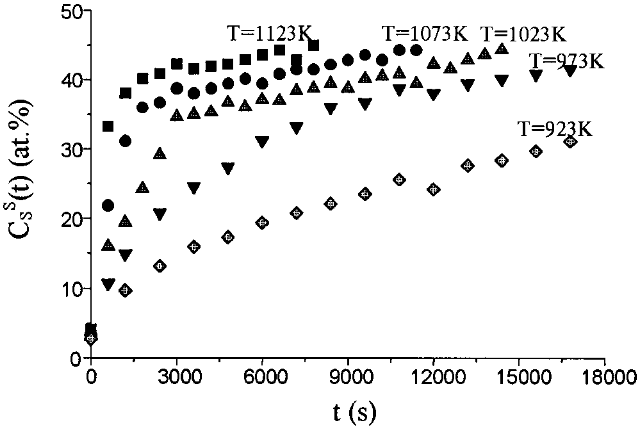

FIG. 3. Kinetics of sulfur segregation on the surface of nickel obtained at different temperatures 923, 973, 1023, 1073, 1123 K and while hydrogen permeating through material. Input pressures of hydrogen were within the range 45–100 Pa.

When investigating hydrogen-stimulated segregation of sulfur, experimental procedure was the same but after achieving the desired temperature hydrogen was admitted into inlet chamber and sulfur segregation kinetics were registered while hydrogen permeating through specimen. Input pressures of hydrogen were taken to provide the same gradient of hydrogen concentration through the nickel sample (at steady-state mode) at different temperatures. To estimate hydrogen concentrations in a subsurface region of the inlet side of the nickel specimen McLellan's and Oates'es data[6] were used. Hydrogen concentration was assumed to depend on pressure according to Sievert's law. Estimated concentration of hydrogen in the subsurface region of outlet side of the sample was ~0.1 appm in the total range of temperatures (923–1123 K) and input H_2 pressures 45–100 Pa. When registering evolution of sulfur coverage, input pressure of hydrogen was maintained at constant level. Kinetics of sulfur segregation on the surface of the nickel specimen with the hydrogen in the bulk are shown in Fig. 3.

Sulfur diffusivities D_S in nickel were calculated from kinetics of segregation in accordance with the following common procedure. Figures 4 and 5 show that kinetics of segregation obtained in the temperature range 923–1123 K can be described in the framework of kinetic model of McLean[7] and Crank.[8] According to this model, the initial stage of segregation can be described by the following equation:

$$\frac{C_S^S(t)-C_S^S(0)}{C_S^S(\infty)-C_S^S(0)}=\frac{2}{\alpha d}\sqrt{D_S t/\pi}, \tag{2}$$

where $C_S^S(0), C_S^S(t), C_S^S(\infty)$-sulfur concentrations on the surface at $t=0$, at the moment of time corresponding to t and equilibrium surface concentration, respectively; $\alpha=C_S^S/C_S^b$ enrichment ratio; D_S-sulfur diffusivity in nickel; d thickness of monolayer.

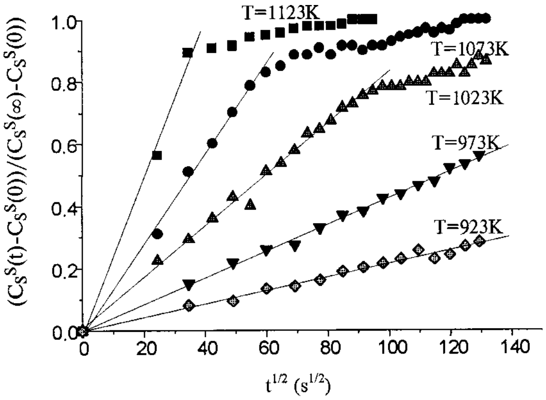

FIG. 4. Kinetics of sulfur segregation on the surface of nickel obtained at different temperatures 923, 973, 1023, 1073, 1123 K and plotted versus $t^{1/2}$ (without hydrogen in the bulk).

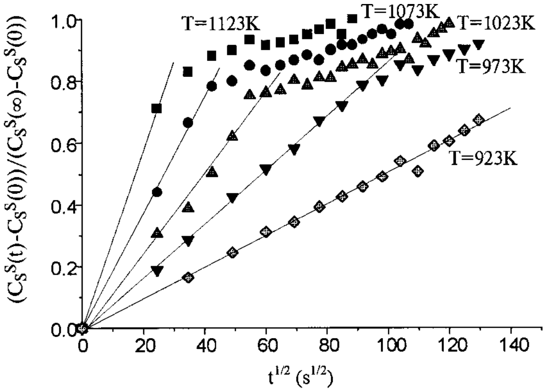

FIG. 5. Kinetics of sulfur segregation on the free surface of nickel obtained at different temperatures 923, 973, 1023, 1073, 1123 K in the process of hydrogen permeation through material and plotted versus $t^{1/2}$. Input pressures of hydrogen were within the range 45–100 Pa.

Taking the values $C_S^b=1.5\times10^{-3}$ at. %, $C_S^S(\infty)\approx45$ at.%, $d=2\times10^{-8}$ cm diffusion coefficients of sulfur in nickel D_S, D_S^H were extracted in the absence and in the presence of hydrogen in the bulk of nickel, respectively.

Obtained temperature dependencies of sulfur diffusivities in nickel together with the data published by Vladimirov[9] and Wang-Grabke[10] are represented in Fig. 6.

One can see that obtained results on sulfur diffusivity in nickel without hydrogen in the bulk are in a good agreement with the data of other authors. Hydrogen inserting into the specimen increases diffusion coefficient of sulfur in nickel.

Temperature dependencies of sulfur diffusivities in nickel can be written in the form of Arrenius equations

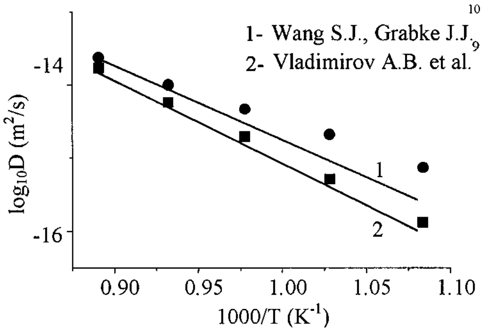

FIG. 6. Temperature dependencies of sulfur diffusivities in nickel; straight lines-data of Vladimirov (Ref. 9) and Wang-Grabke (Ref. 10), symbols-results of present work: ■-without hydrogen, ●-with hydrogen.

$$D_{\mathrm{S}}=9.8\times 10^{-5}\exp\left(-\frac{209.7\dfrac{kJ}{\text{mole}}}{\text{RT}}\right),m^2s^{-1},$$

$$D_{\mathrm{S}}^{\mathrm{H}}=1.6\times 10^{-7}\exp\left(-\frac{146.9\dfrac{kJ}{\text{mole}}}{\text{RT}}\right),m^2s^{-1}. \tag{3}$$

It is appropriate to mention here that there is some incorrectness in determination of sulfur diffusivity using approach described above. In calculations of diffusivities the value of bulk sulfur concentration taken from specimen's certificate was used. But when operating with the single specimen, in the course of experimental procedure the sample surface was cleaned up several times and this treatment had to decrease bulk sulfur concentration in the subsurface region of the sample. Obviously, this fact should introduce some incorrectness in the values of sulfur diffusivities obtained. Nevertheless, performed experiments clearly show an acceleration of sulfur segregation on the nickel surface caused by hydrogen. Assumed mechanism of this phenomenon is suggested in theoretical section of this work.

III. THEORY AND DISCUSSION OF THE RESULTS OBTAINED

The problem concerned with the influence of interstitial impurity on coefficient of selfdiffusion of metal was analyzed for Fe-C system.[11] In the present paper, using the same approach, we attack a more complicated problem that is formulated as: the change of diffusivity of substitution impurity in a regular solution when an interstitial impurity is inserted in that.

It can be easily shown that diffusion coefficient of sulfur in nickel is able to be written as

$$D_{\mathrm{S}}=f\frac{a^2}{4}C_V\omega, \tag{4}$$

where a-lattice parameter; C_V-relative concentration of vacancies in metal; ω-probability of transition of sulfur atom into a neighboring vacancy per unit time; f-correlation coefficient.

And accordingly, for diffusion coefficient of sulfur in nickel in the presence of hydrogen in interstitial positions

$$D_{\mathrm{S}}^{\mathrm{H}}=f\frac{a^2}{4}C_V^H\omega_H, \tag{5}$$

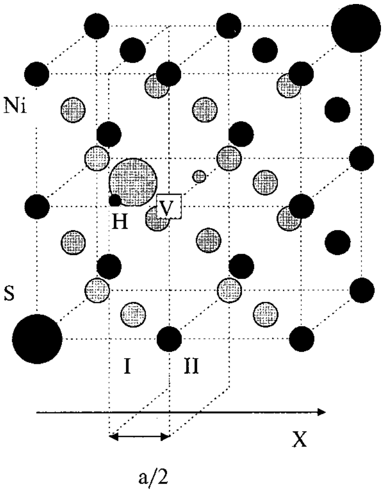

FIG. 7. Ni-(S-H) system.

where $D_{\mathrm{S}}^{\mathrm{H}}$ is the sulfur diffusivity in nickel in the presence of hydrogen in interstitial positions; C_V^{H} is the equilibrium concentration of vacancies in the system Ni-S-H; ω_{H} is the probability of transition of sulfur atom into a neighboring vacancy per unit time in the presence of hydrogen atoms in interstitial positions. Having written this equation, we assume that hydrogen has no influence on the correlation coefficient. Thus, to solve the problem one needs to determine C_V^{H} and ω_{H}.

Let us investigate problem in the framework of approximation of the nearest neighbors. Sulfur atoms on the plane I (see Fig. 7) that are the closest to the vacancy in plane II can be positioned in four places. Taking into account l nearest vacancy atoms of hydrogen, $0\leqslant l\leqslant 6$, one can see that for any of four positions of sulfur atoms there are only two the nearest places for hydrogen to influence on energy being necessary for transition of sulfur into neighboring vacancy.

The probability of the appearance of such a configuration when l atoms of hydrogen $(0\leqslant l\leqslant 6)$ are adjacent to the vacancy given that there are m such atoms $(0\leqslant m\leqslant 2)$ in two interstitial positions neighboring to sulfur is

$$\Omega_{m,l}=\frac{\dfrac{2!}{m!(2-m)!}\cdot\dfrac{4!}{(l-m)![4-(l-m)]!}}{\dfrac{6!}{l!(6-l)!}}. \tag{6}$$

Then, probability of transition of sulfur atom into neighboring vacancy per unit of time under hydrogen influence can be written as

$$\omega_H=\frac{1}{\tau_0}\sum_{l=0}^{6}\sum_{m=0}^{2}\exp\left(\frac{-\Delta V_{\mathrm{S}}+mq}{kT}\right)\frac{\dfrac{2!}{m!(2-m)!}\cdot\dfrac{4!}{(l-m)![4-(l-m)]!}}{\dfrac{6!}{l!(6-l)!}}, \tag{7}$$

where τ_0^{-1} is a constant having the order of magnitude of average vibration frequency of the lattice $\sim 10^{13}\,\mathrm{s}^{-1}$; ΔV_{S} is the activation energy of sulfur diffusivity in nickel in the absence of hydrogen; q is the difference of interaction energies between hydrogen and sulfur at the distances $a/2$ and $a\sqrt{2}/4$; k is the Boltzmann constant; T is the temperature of the system. Value of a is considered to be equal to the lattice parameter of pure nickel neglecting lattice deformation caused by inserted atoms of sulfur and hydrogen.

These equations for probabilities were written down in for Fe-C system[11] and used with some argumentation in the present paper to show its applicability for our case.

To determine the equilibrium concentration of vacancies in the Ni-S-H system, let us consider regular substitution solution of sulfur in nickel with hydrogen inserted in interstitial positions. Let N_{S}, N_{Ni}, and N_{H} be the numbers of atoms of sulfur, nickel, and hydrogen, respectively. At temperatures above absolute zero there are always vacancies in a crystal. These vacancies can be surrounded with different numbers of neighboring atoms of sulfur, nickel, and hydrogen. Let there be $l\,(0\leqslant l\leqslant 6)$ the nearest to vacancy atoms of hydrogen located in interstitial positions in the center of it. Let N_V^l be the number of vacancies surrounded with l atoms of hydrogen.

Now, we shall try to write down, in approximation of the nearest neighbors, the equation for energy of solution E of sulfur and hydrogen in nickel having the vacancies surrounded with the different numbers of nickel, sulfur, and hydrogen atoms.

Let C_{Ni}, C_{H}, and C_{S} be the relative concentrations of atoms of nickel, hydrogen, and sulfur, respectively. We assume atoms of nickel and sulfur to be located only in the lattice positions while hydrogen only in interstitial ones so $C_{\mathrm{Ni}}+C_{\mathrm{S}}=1$ and $C_{\mathrm{H}}=N_{\mathrm{H}}/(N_{\mathrm{Ni}}+N_{\mathrm{S}})$ if the number of lattice positions is approximately equal to the number of interstitial positions. If $E_{\mathrm{Ni}}(C_{\mathrm{Ni}},C_{\mathrm{H}})$ is the energy of interaction between a nickel atom and all the nearest atoms, one can write down an equation for $E_{\mathrm{Ni}}(C_{\mathrm{Ni}},C_{\mathrm{H}})$ taking into account that in each of the 12 nearest-lattice sites an atom of nickel can occur with the a priori probability C_{Ni} or an atom of sulfur with a priori probability C_{S}, and in every interstitial position an atom of hydrogen can occur with a priori probability C_{H}.

Thus,

$$E_{\mathrm{Ni}}(C_{\mathrm{Ni}},C_{\mathrm{H}})=12(C_{\mathrm{Ni}}\Phi_{\mathrm{Ni-Ni}}+C_{\mathrm{S}}\Phi_{\mathrm{Ni-S}})+6C_{\mathrm{H}}\Phi_{\mathrm{Ni-H}}, \tag{8}$$

and similar to that for $E_{\mathrm{S}}(C_{\mathrm{S}},C_{\mathrm{H}})$, the interaction energy of a sulfur atom with all its nearest neighbors

$$E_{\mathrm{S}}(C_{\mathrm{S}},C_{\mathrm{H}})=12(C_{\mathrm{S}}\Phi_{\mathrm{S-S}}+C_{\mathrm{Ni}}\Phi_{\mathrm{Ni-S}})+6C_{\mathrm{H}}\Phi_{\mathrm{S-H}}, \tag{9}$$

where $\Phi_{\text{Ni-Ni}},\Phi_{\text{Ni-S}},\Phi_{\text{Ni-H}},\Phi_{\text{S-S}},\Phi_{\text{S-H}}$ are potential energies of binding between corresponding atoms. Then, if E_V is the difference of potential energy when removing either a nickel atom from lattice position, which could be located there with *a priori* probability C_{Ni}, or a sulfur atom, which could be located there with *a priori* probability C_{S}, one can write:

$$E_V=-\eta[C_{\mathrm{Ni}}E_{\mathrm{Ni}}(C_{\mathrm{Ni}},C_{\mathrm{H}})+C_{\mathrm{S}}E_{\mathrm{S}}(C_{\mathrm{S}},C_{\mathrm{H}})], \tag{10}$$

where η is a constant value indicating that not the all bindings are broken while a vacancy is forming but approximately half of that and therefore $\eta\approx 0.5$. Minus in this equation shows that according to its physical sense $E_V>0$ while the potential energies of binding have negative values.

Equation for E, the energy of solution of hydrogen and sulfur in nickel in the presence of vacancies surrounded with different numbers of nickel, sulfur, hydrogen atoms and in the approximation of the nearest neighbors, can be written as follows:

$$\begin{aligned}E&=E_0+E_V\sum_{l=0}^{6}N_V^l=E_0-[6(C_{\mathrm{Ni}}^2\Phi_{\mathrm{Ni-Ni}}+2C_{\mathrm{Ni}}C_{\mathrm{S}}\Phi_{\mathrm{Ni-S}}\\&\quad+C_{\mathrm{S}}^2\Phi_{\mathrm{S-S}})+3(C_{\mathrm{H}}C_{\mathrm{Ni}}\Phi_{\mathrm{H-Ni}}+C_{\mathrm{S}}C_{\mathrm{H}}\Phi_{\mathrm{S-H}})]\cdot\sum_{l=0}^{6}N_V^l,\end{aligned} \tag{11}$$

where E_0-energy of solution without vacancies.

Then, one can be easily convinced that W different arrangements of N_{Ni} nickel atoms, N_{S} sulfur atoms, N_V^l, vacancies in the lattice positions and N_{H} hydrogen atoms in the interstitial positions for the all N_V^l, assuming number of lattice positions to be equal to that of interstitial positions, can be written down as

$$W=\frac{\left(N_{\mathrm{Ni}}+N_{\mathrm{S}}+\sum_{l=0}^{6}N_V^l\right)!}{N_{\mathrm{Ni}}!\,N_{\mathrm{S}}!\prod_{l=0}^{6}N_V^l!}\;\frac{\left(N_{\mathrm{Ni}}+N_{\mathrm{S}}-5\sum_{l=0}^{6}N_V^l\right)!\prod_{l=0}^{6}\left[\frac{6!}{l!(6-l)!}\right]^{N_v^l}}{\left(N_{\mathrm{H}}-\sum_{l=0}^{6}lN_V^l\right)!\left(N_{\mathrm{Ni}}+N_{\mathrm{S}}-5\sum_{l=0}^{6}N_V^l-N_{\mathrm{H}}+\sum_{l=0}^{6}lN_V^l\right)!}. \tag{12}$$

Free energy of solution is

$$\Psi=E-kT\cdot\ln W. \tag{13}$$

Taking equations for E and W, one can find the energy of our system. To obtain the equilibrium concentration of vacancies in the lattice positions surrounded with l hydrogen atoms, we can use the condition of equilibrium

$$\frac{\partial\Psi}{\partial N_V^l}=0, \tag{14}$$

for all l.

Using Stirling's formula for large N $(\ln N!=N\ln N-N)$ and having carried out differentiation we have

$$-6(C_{\mathrm{Ni}}{}^{2}\Phi_{\mathrm{Ni-Ni}}+2C_{\mathrm{Ni}}C_{\mathrm{S}}\Phi_{\mathrm{Ni-S}}+C_{\mathrm{S}}{}^{2}\Phi_{\mathrm{S-S}})+3(C_{\mathrm{H}}C_{\mathrm{Ni}}\Phi_{\mathrm{H-Ni}}+C_{\mathrm{H}}C_{\mathrm{S}}\Phi_{\mathrm{H-S}})$$

$$=kT\ln\left[\frac{(N_{\mathrm{Ni}}+N_{\mathrm{S}}+\sum_{l=0}^{6}N_V^l)(N_{\mathrm{Ni}}+N_{\mathrm{S}}-5\sum_{l=0}^{6}N_V^l)^{-5}\dfrac{6!}{l!(6-l)!}}{N_V^l(N_{\mathrm{H}}-\sum_{l=0}^{6}lN_V^l)^{-l}(N_{\mathrm{Ni}}+N_{\mathrm{s}}-5\sum_{l=0}^{6}N_V^l-N_{\mathrm{H}}+\sum_{l=0}^{6}lN_V^l)^{l-5}}\right]. \tag{15}$$

Taking into account that number of vacancies is small and performing the summation for all l, the equation for equilibrium concentration of vacancies in the Ni-S-H system is written down as

$$C_V^{\mathrm{H}}=\frac{1}{(1-C_{\mathrm{H}})}\exp\left[\frac{3(C_{\mathrm{H}}C_{\mathrm{Ni}}\Phi_{\mathrm{H-Ni}}+C_{\mathrm{H}}C_{\mathrm{S}}\Phi_{\mathrm{H-S}})}{kT}\right]\times\exp\left[\frac{6(C_{\mathrm{Ni}}{}^{2}\Phi_{\mathrm{Ni-Ni}}+2C_{\mathrm{Ni}}C_{\mathrm{S}}\Phi_{\mathrm{Ni-S}}+C_{\mathrm{S}}{}^{2}\Phi_{\mathrm{S-S}})}{kT}\right]. \tag{16}$$

Finally, substituting for C_V^H and ω_H in Eq. (5) for $D_{\mathrm{S}}^{\mathrm{H}}$ gives

$$D_{\mathrm{S}}^{\mathrm{H}}=f\frac{a^2}{4\tau_0}\cdot C_V^{\mathrm{H}}\cdot\exp\left(-\frac{\Delta V_{\mathrm{S}}}{kT}\right)\left\{1+C_{\mathrm{H}}\left[\exp\left(\frac{q}{kT}\right)-1\right]\right\}^2. \tag{17}$$

Accordingly, the change of sulfur diffusivity in nickel when inserting hydrogen in metal is

$$\frac{D_{\mathrm{S}}^{\mathrm{H}}}{D_{\mathrm{S}}}=\exp\left[\frac{3(C_{\mathrm{H}}C_{\mathrm{Ni}}\Phi_{\mathrm{H-Ni}}+C_{\mathrm{H}}C_{\mathrm{S}}\Phi_{\mathrm{H-S}})}{kT}\right]\times\frac{1}{(1-C_{\mathrm{H}})}\left\{1+C_{\mathrm{H}}\left[\exp\left(\frac{q}{kT}\right)-1\right]\right\}^2. \tag{18}$$

As a first approximation, let us determine q as a work for transition of sulfur atom charged $-2e$ in the field of hydrogen atom charged $+e$, from the point located at the distance $a/2$ to a point at the distance $a\sqrt{2}/4$ in relation to hydrogen adjusted to vacancy. An atom of sulfur in nickel lattice is assumed to be charged negatively while hydrogen positively.

$$q=\frac{4e^2}{a}\left[\frac{2}{\sqrt{2}}\exp\left(-\frac{a\sqrt{2}}{4\rho}\right)-\exp\left(-\frac{a}{2\rho}\right)\right]=1.3\,\mathrm{eV}, \tag{19}$$

where $\rho=4.8\times10^{-9}$ cm is the radius of screening in nickel; $a=3.5\times10^{-8}$ cm is the lattice parameter of nickel.

When using such an approach for estimation of the q value, it is assumed that within the term of sulfur atom transition from the lattice site into vacancy, hydrogen does not change its position. Moreover, we have used the value of nickel lattice parameter at $T=300$ K neglecting both its temperature dependence and deformation caused by sulfur and hydrogen atoms. These points should introduce some incorrectness in the estimate.

Experimental results together with the theoretical curves calculated at different hydrogen concentrations C_{H} and $C_{\mathrm{S}}=1.5\times10^{-5}$, $q=1.3$ eV, $\Phi_{\mathrm{Ni-H}}=-0.057$ eV, $\Phi_{\mathrm{S-H}}=-0.35$ eV are shown in Fig. 8.

The theoretical curves describing the change of sulfur diffusivity in nickel in dependence of hydrogen concentration in specimen and calculated for the same values of q, $\Phi_{\mathrm{Ni-H}}, \Phi_{\mathrm{S-H}}$ are represented in Fig. 9.

Figure 8 shows a good agreement between theory and experimental data obtained in the temperature range 923–1123 K. But at $T=300$ K theoretical change of sulfur diffusivity in nickel at minor bulk concentration of hydrogen is an absurdly large value, which is in contradiction with literature data. There is a well-known technique[12] of charging steel samples with hydrogen at 473 K to stimulate its brittleness which is necessary to have for investigation of grain boundary impurity segregation. After such a procedure, the authors did not observe redistribution of impurities between bulk of grains and its boundaries.

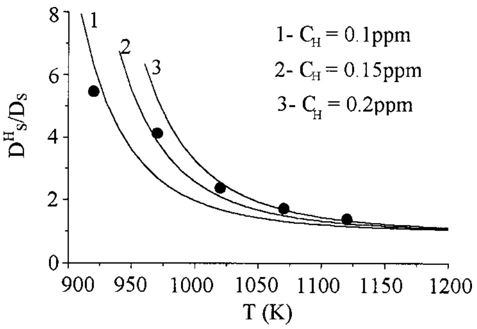

FIG. 8. Temperature dependence of the change of sulfur diffusivity in nickel caused by hydrogen in the bulk; ● is the experimental data; solid lines are the theoretical curves calculated at different hydrogen concentrations: $C_{\mathrm{H}}=0.1$, 0.2, 0.15 ppm, and $q=1.3$ eV, $\Phi_{\mathrm{Ni-H}}=-0.057$ eV, $\Phi_{\mathrm{S-H}}=-0.35$ eV, $C_s=15$ ppm.

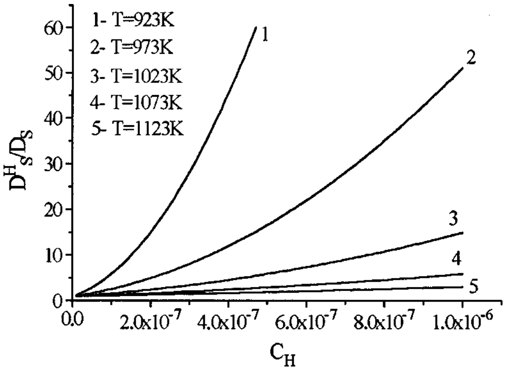

FIG. 9. Theoretical curves indicating the change of sulfur diffusivity in nickel as a function of hydrogen concentration in the bulk calculated for different temperatures and $q=1.3$ eV, $\Phi_{\mathrm{Ni-H}}=-0.057$ eV, $\Phi_{\mathrm{S-H}}=-0.35$ eV, $C_{\mathrm{S}}=1.5\times10^{-5}$.

Therefore, we intuitively assume value of q to be decreased with the temperature decreasing. Moreover, at some values of q and T sulfur diffusivity in nickel can decrease with the hydrogen bulk concentration increasing, because equilibrium concentration of vacancies decreases with the increase of hydrogen bulk concentration in solution. Thus, the model suggested in present work, more likely, can be applied only in the investigated range of temperatures but is useful for qualitative understanding of the phenomenon observed.

It is interesting to note that all the argumentation mentioned above can be applied to the change of self-diffusion coefficient of nickel having sulfur as substitution impurity with concentration C_{S} and hydrogen in interstitial positions with the concentration C_{H}. The only difference is q value, which has to define interaction between nickel and hydrogen in this case.

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