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## Diffusion of Chromium in Nickel

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Diffusion of chromium in pure nickel has been studied by radioactive tracer and residual activity technique. The diffusion coefficient (in units of  $\text{cm}^2/\text{sec}$ ) in the range  $600^\circ\text{--}900^\circ\text{C}$  is given by  $D_{\text{Cr/Ni}} = 0.03 \exp(-40\,800/RT)$  and in the range  $350^\circ\text{--}600^\circ\text{C}$  is given by  $D_{\text{Cr/Ni}} = 5.45 \times 10^{-9} \exp(-13\,700/RT)$ .

The bimodal diffusion behavior has been explained on the basis of solid solubility of chromium in nickel, which falls very rapidly from  $1000^\circ\text{C}$  downwards. The entropy of activation for high-temperature diffusion falls very well on the entropy vs activation energy curve for lattice diffusion in nickel.

### INTRODUCTION

**T**HEORETICALLY, solute diffusion in metal has been related with the size factor<sup>1</sup> and excess valency of solute atom.<sup>2</sup> On the contrary, on the basis of experimental results on diffusion of iron, cobalt, nickel,<sup>3</sup> and chromium<sup>4</sup> in aluminum, and of iron, cobalt, nickel in silver<sup>5</sup> and gold,<sup>6</sup> considerable emphasis has been laid on the solid solubility of the solute in the host metal as one of the controlling factors. The screening theory of Lazarus<sup>2</sup> and its further refinements<sup>7,8</sup> have been of limited application. The consideration that the lattice diffusion will be predominant in case of high solid solubilities at diffusing temperatures is also well reflected in diffusion in nickel of tungsten, titanium, manganese and aluminum,<sup>9</sup> cobalt,<sup>10</sup> iron,<sup>9</sup> and gold,<sup>11</sup> while low activation energies and diffusion frequencies are observed for diffusion of magnesium<sup>12</sup> and zirconium<sup>12</sup> in nickel where solid solubility is quite low.

In view of these, it was considered desirable to undertake the study of diffusion of chromium in nickel where size factor is practically unity and solid solubility is high at elevated temperatures (reported<sup>13</sup> to fall sharply at low temperatures).

The present work was carried out using residual activity technique for different ranges of diffusing temperatures and the results so obtained are in good agreement with those expected when the solid solubility is one of the controlling factors in diffusion.

### EXPERIMENTAL PROCEDURE

Cylindrical disks 0.64 cm in diameter by 0.95 cm thick, of 99.997 wt. % nickel, were annealed in vacuum for several hours to give an average grain size in excess of  $\frac{1}{4}$  cm. End faces were prepared as described before.<sup>14</sup> A layer about  $0.1\,\mu$  thick of chromium containing chromium-51 was electroplated on one end face of each specimen using the electrolyte described earlier.<sup>4</sup> The plated samples had an activity of the order of  $10^4$  counts/min. The electroplated specimens were given short-time hydrogen anneal at  $200^\circ\text{C}$  to homogenize the level of activity over the surface. They were then separately sealed in Vycor tubes under an atmosphere of purified argon at low pressure for diffusion runs. A quartz flat disk was placed in each case inside Vycor tube against the electrodeposited disk of nickel to inhibit evaporation. Diffusion anneal was carried out in the range of  $350^\circ$  to  $900^\circ\text{C}$ . Temperature was controlled to within  $\pm 5^\circ\text{C}$  over a constant zone of several inches.

A 2II geometry NaI (Tl) scintillation counter was used to count the 0.325-MeV  $\gamma$ -radiation of chromium-51 (half-life 27.2 days) after diffusion anneals.

The diffusivity  $D$  was calculated by using the residual activity method based on Gruzins analysis<sup>15</sup>:

$$\mu I_n - (dI_n/dY_n) = \text{const} \exp[-(Y_n^2/4Dt)], \quad (1)$$

where  $\mu$  is the linear absorption coefficient in  $\text{cm}^{-1}$ ,  $I_n$  is the surface activity in counts per unit time after  $n$ th layer has been removed,  $Y_n$  is the thickness of the material removed in cm,  $D$  is the diffusivity in  $\text{cm}^2/\text{sec}$ ,  $t$  is the time of diffusion in sec. The value of  $\mu$  for the absorption of 0.325-MeV  $\gamma$ -radiation of chromium-51 in nickel is  $0.88\,\text{cm}^{-1}$  which<sup>16</sup> is so small that

$$[-(dI_n/dY_n)] \gg (\mu I_n).$$

If  $C$  is the concentration of chromium-51, then  $C(Y_n)$  is proportional to  $[-(dI_n/dY_n)]$  and the latter value can be determined graphically by the  $I_n$  vs  $Y_n$  curves.

<sup>14</sup> K. Hirano, R. P. Agarwala, B. L. Averbach, and M. Cohen. *J. Appl. Phys.* **33**, 3049 (1962).

<sup>15</sup> P. L. Gruzins, Problems of Metallography and Physics of Metals, Fourth Symposium, Moscow AEC-tr 2924, 329 (1955).

<sup>16</sup> E. Bleuler and G. J. Goldsmith, *Experimental Nucleonics* (Rinehart and Company, New York 1952).

<sup>1</sup> R. A. Swalin, *Acta Met.* **5**, 443 (1957).

<sup>2</sup> D. Lazarus, *Phys. Rev.* **93**, 973 (1954).

<sup>3</sup> K. Hirano, R. P. Agarwala, and M. Cohen, *Acta Met.* **10**, 857 (1962).

<sup>4</sup> R. P. Agarwala, S. P. Murarka, and M. S. Anand, Atomic Energy Establishment Trombay/C.D./15, (1963).

<sup>5</sup> K. Hirano, M. Cohen, and B. L. Averbach, *Acta Met.* **11**, 463 (1963).

<sup>6</sup> D. N. Duhl, K. Hirano, and M. Cohen, *Acta Met.* **11**, 1 (1963).

<sup>7</sup> F. Blatt, *Phys. Rev.* **99**, 600 (1955).

<sup>8</sup> A. D. LeClaire, *Phil. Mag.* **7**, 141 (1962).

<sup>9</sup> R. A. Swalin, University Microfilms Publication No. 10043, Ann Arbor, Michigan.

<sup>10</sup> R. C. Ruder and C. E. Birchenall, *J. Metals* **3**, 142 (1951).

<sup>11</sup> J. E. Reynolds, B. L. Averbach, M. Cohen, and J. E. Hilliard, *Acta Met.* **5**, 29 (1957).

<sup>12</sup> H. W. Allison and H. Samelson, *J. Appl. Phys.* **30**, 1419 (1959).

<sup>13</sup> A. Taylor and R. W. Floyd, *J. Inst. Metals* **80**, 577 (1951–1952).

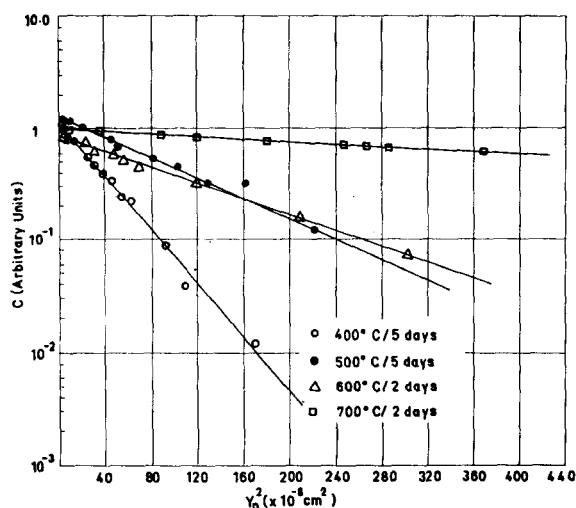
FIG. 1.  $\ln C$  vs  $V_n^2$  plots for diffusion of Cr in Ni.

Figure 1 shows the plots of  $\ln C$  vs  $V_n^2$  for diffusion of chromium at different temperatures. They obey Eq. (1) very well.

It is seen from the graph of  $\ln D$  vs  $1/T$  (Fig. 2) that all the points do not fall on a straight line but on two distinct straight lines with a break at 600°C, suggesting a bimodal diffusion behavior. The diffusion coefficients calculated by least-square method along with the corresponding diffusion temperatures and time of diffusion anneal are listed in Table I. The activation energy and frequency factors were also calculated by least-square method and obey the equations

$$D = 0.03 \exp(-40\,800/RT) \text{ for high temperatures}$$

and

$$D = 5.45 \times 10^{-9} \exp(-13\,700/RT) \text{ for low temperatures.}$$

### DISCUSSION

It has been mentioned above that the plot of  $\ln D$  vs  $1/T$  (Fig. 2) shows a break in the straight line at 600°C leading to a different branch. It is seen that diffusivity at low temperature is much higher than one would expect from the higher temperature values, thus suggesting a bimodal diffusion for different temperature ranges.

The possibility of grain boundary diffusion at lower temperatures is eliminated since the grain size developed before diffusion anneal was quite large. In the presence of a very thin radioactive deposit (of the order of nearly  $0.1 \mu$ ) the formation of intermetallic compounds in concentration to affect the diffusion rate could easily be ruled out; at the same time the possibility of Kirkendall effect does not arise. The chances of formation of oxide layer immediately below the radioactive layer are minimized since the samples of nickel were annealed in an atmosphere of purified

TABLE I. Temperature dependence of diffusivities.

Temperature (°C)	Time (10 <sup>5</sup> sec)	Diffusion coefficients $D$ (cm <sup>2</sup> /sec)
350	8.640	$8.90 \times 10^{-14}$
350	8.640	$8.59 \times 10^{-14}$
400	4.100	$2.14 \times 10^{-13}$
400	4.320	$1.93 \times 10^{-13}$
450	4.320	$3.79 \times 10^{-13}$
450	4.320	$3.95 \times 10^{-13}$
500	2.556	$0.87 \times 10^{-12}$
500	4.320	$0.92 \times 10^{-12}$
550	3.456	$1.20 \times 10^{-12}$
600	1.728	$1.85 \times 10^{-12}$
650	1.728	$6.70 \times 10^{-12}$
650	0.864	$6.29 \times 10^{-12}$
700	1.734	$1.25 \times 10^{-11}$
800	0.864	$1.26 \times 10^{-10}$
800	0.864	$1.35 \times 10^{-10}$
900	0.864	$7.89 \times 10^{-10}$

argon and polished, followed by very light etching just before electrodeposition.

The values of activation energy and diffusion frequency in the range of 600° to 900°C correspond to lattice diffusion giving positive entropy of activation (Table II) calculated on the basis of Zener's equation<sup>17</sup>  $\Delta S/R = \ln(D_0/a^2\nu)$ , where  $a$  and  $\nu$  are the lattice parameter and vibration frequency of the host lattice.

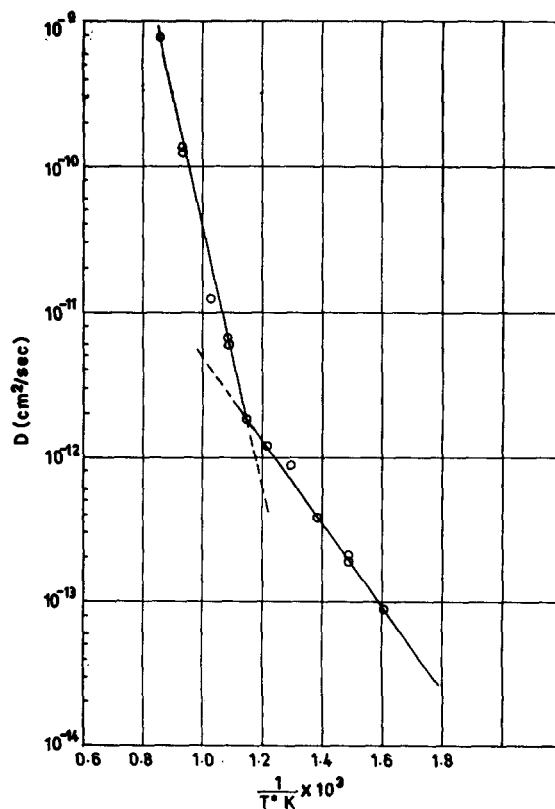


FIG. 2. Temperature dependence of diffusion coefficients.

<sup>17</sup> C. Zener, J. Appl. Phys. 22, 372 (1951).

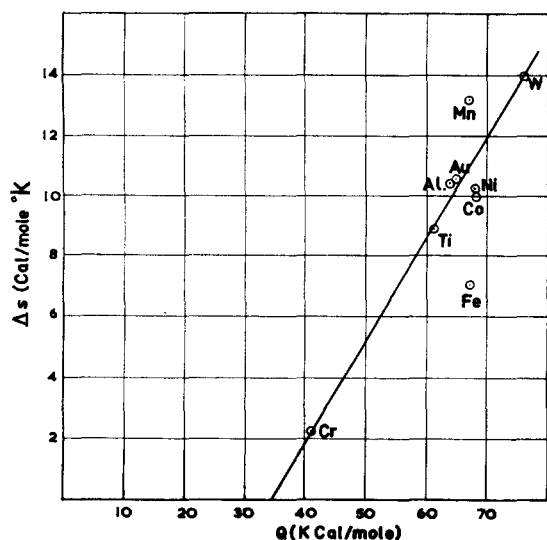


FIG. 3. Activation entropy vs activation energy for diffusion of impurity atoms in Ni.

On the other hand, at the lower temperatures (350°–600°C), both activation energy and diffusion frequency are quite low, resulting in a negative entropy of activation (Table II). A comparison of the latter values with those of the diffusion of iron, nickel, cobalt, and chromium in aluminum<sup>3,4</sup> and iron, cobalt, nickel in silver<sup>5</sup> suggest that the diffusion is controlled through dislocation short circuiting paths. At higher temperatures one may assume that the diffusion is governed by a much larger number of slower elementary atomic jumps through the lattice as compared to a limited number of faster atomic jumps along the dislocations and hence the diffusion through the lattice predominates, result-

ing in a high value of activation energy and diffusion frequency.

In recent investigations, solid solubility and size factor have been stressed as controlling factors for impurity diffusion. A comparison of activation energies and diffusion frequencies for magnesium and zirconium in nickel,<sup>12</sup> iron, cobalt, nickel, and chromium in aluminum<sup>3,4</sup> iron, cobalt, nickel in silver<sup>5</sup> confirms the view that in case of low solid solubility of the diffusing species in the host lattice (Table II), diffusion is controlled through short circuiting dislocation paths. Taylor and Floyd<sup>13</sup> have reported that the solid solubility of chromium in nickel decreases sharply from 1000°C downwards being 46 at.% at 1000°C and 36 at.% at 700°C. It is, therefore, expected that lattice diffusion will be predominant as indeed it has been observed for diffusion of chromium in nickel at these temperatures. Other cases where diffusion is controlled by flux through lattice are of iron, cobalt, nickel in gold<sup>6</sup> and of aluminum, titanium, tungsten, manganese,<sup>9</sup> iron,<sup>9</sup> gold,<sup>11</sup> and cobalt<sup>10</sup> in nickel. In the absence of solid solubility data of chromium in nickel for lower temperatures, the diffusion coefficients at low temperatures where diffusion would appear to occur through short circuiting dislocation paths remains to be explained.

Swalin<sup>1</sup> has shown the effect of size factor for impurity diffusion in nickel and silver. Present results do not fall in line with his theory. Neither is it possible to apply the screening theory of Lazarus due to the difficulty in assuming the exact charge on chromium.

Swalin<sup>9</sup> has also plotted  $\Delta s$  vs  $Q$ , for diffusion of aluminum, manganese, titanium, and tungsten in nickel. A plot of  $\Delta S$  vs  $Q$  for diffusion of iron, cobalt, nickel, manganese, aluminum, titanium, gold, chromium, and tungsten in nickel has been redone (Fig. 3) and chromium very well falls on this line, where slope is  $3.36 \times 10^{-4}/^\circ\text{K}$  which is close to theoretical slope  $2.65 \times 10^{-4}/^\circ\text{K}$  calculated by Swalin<sup>9</sup> on the basis of elastic constants. This is also in quite good agreement with the value  $5.78 \times 10^{-4}/^\circ\text{K}$  obtained by Dienes<sup>18</sup> from the empirical relation  $\Delta S = Q/Tm + \text{Constant}$  ( $Tm$  = melting point in  $^\circ\text{K}$ ).

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TABLE II. Activation entropies for diffusion in nickel.

Diffusing atom	Diffusion frequency $D_0$ (cm <sup>2</sup> /sec)	Activation energy $Q$ (Cal/mole)	Activation entropy $\Delta S$ (Cal/mole, $^\circ\text{K}$ )	Ref.
Nickel	1.70	68 100	+10.252	14
Aluminum	1.87	64 000	+10.442	9
Titanium	0.86	61 400	+ 8.898	9
Tungsten	11.10	76 000	+13.981	9
Manganese	7.50	67 100	+13.202	9
Iron	0.34	67 500	+ 7.054	9
Magnesium	$2.30 \times 10^{-6}$	31 300	-12.027	12
Zirconium	$1.00 \times 10^{-5}$	26 700	-13.683	12
Cobalt	1.46	68 300	+ 9.950	10
Gold	1.98	65 000	+10.556	11
Chromium	0.03	40 800	+ 2.229	Present work
	$5.45 \times 10^{-9a}$	13 700	-28.620	

<sup>a</sup> From low-temperature values.

<sup>18</sup> G. J. Dienes, J. Appl. Phys. **21**, 1189 (1950).