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INFLUENCE OF ARGON AND HYDROGEN ENVIRONMENTS ON THE RATE OF DIFFUSION OF COBALT-60 IN NICKEL

H. E. McCoy, Jr.
J. F. Murdock

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ABSTRACT

A series of experiments have been run to determine whether the influence of enviornment on the rate of void growth in nickel and nickel-base alloys during creep may be due to either a change in the concentration of vacancies or in their mobility. The experimental approach used was that of studying the rate of diffusion of dilute quantities of cobalt-60 in nickel. Pairs of specimens were run under duplicate conditions except for environment, which was argon for one specimen and hydrogen for the other. Subsequent sectioning and counting showed that the rate of diffusion of cobalt-60 in nickel is the same whether the environment is argon or hydrogen. This in turn implies that neither the concentration of vacancies nor their mobility is significantly different in the two environments.

INTRODUCTION

The observed reduction of the high-temperature creep strength of nickel-base alloys in a hydrogen environment has prompted studies directed toward defining the mechanism responsible for this reduction in strength. Because of the characteristics of this environmental effect, it was postulated that the role of hydrogen might be that of increasing the concentration of vacancies or of increasing their mobility. The importance of vacancy diffusion in high-temperature

creep has been demonstrated by several experimenters.[1-5] Although the particular mechanisms that have been proposed differ, they all agree that the concentration and mobility of vacancies are important.

The vacancy-atom interchange mechanism (which currently seems the most realistic) for self-diffusion in a pure metal predicts a dependence of the rate of self-diffusion on the energies of formation and transport of vacancies. Hence, studies of self-diffusion in pure nickel should indicate whether the number or mobility of vacancies are increased as a result of the presence of hydrogen in solution. Numerous examples have been reported of an increase in solute atom mobility with concentration of substitutional alloying addition.[6,7] However, the relatively small size of the hydrogen atom makes it seem unlikely that the nickel lattice could be sufficiently distorted by the presence of hydrogen to influence the mobility of the nickel atom. The results of self-diffusion measurements in nickel by MacEwan et al.[8] and Hoffman et al.[9] lend some support to the idea that the rate of self-diffusion may actually be greater in nickel in a vacuum than in hydrogen. The results of MacEwan[8] were obtained by using the nickel-63 isotope and annealing in hydrogen.

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[1]Gunji Shinoda et al., J. Japan Inst. Metals 24, 818–22 (1960).

[2]J. N. Greenwood, D. R. Miller, and J. W. Suiter, Acta Met. 2, 250 (1954).

[3]D. McLean, J. Inst. Metals 85, 468 (1956–57).

[4]E. S. Machlin, Trans. Met. Soc. AIME 206, 106–11 (1956).

[5]R. W. Balluffi and L. L. Seigle, Acta Met. 5, 449 (1957).

[6]A. S. Nowick, Progr. Metal Phys. 4, 43–44 (1953).

[7]A. B. Lidiard, Phil. Mag. [8]5, 1171–80 (1960).

[8]J. R. MacEwan et al., Can. J. Chem. 37, 1623 (1959).

[9]R. E. Hoffman et al., Trans. Met. Soc. AIME 206, 483 (1956).

The results were represented by the equation

$$D = 3.36 \exp\left[- \frac{69,800}{RT} \right] .$$

Hoffman et al.[9] also used nickel-63 but did their annealing in vacuum. Their results are represented by

$$D = 1.27 \exp\left[- \frac{66,800}{RT} \right] .$$

These equations predict a common value of D at 1279°C. At temperatures less than this, a higher value of D is predicted by the latter equation. However, the D values predicted by either of these equations at a given temperature are in relatively good agreement and the point of intersection may not be significant.

Since very little theoretical or experimental evidence supported the postulation that the vacancy concentration is greater in nickel and nickel-base alloys in hydrogen than in an inert environment, a very brief experimental program was initiated to further examine the effects of environment. This program involved a study of the diffusion of cobalt-60 into nickel in both argon and hydrogen environments. This approach was taken because of the experimental ease of counting cobalt-60 as compared with nickel-63 and because the rate of diffusion of dilute quantities of cobalt-60 into nickel should equally well illustrate whether a difference in vacancy concentration does exist. The following report is a summary of the results of this investigation.

Experimental Materials and Procedures

The nickel used in this work was obtained from the Sanderson Holcomb Works at Syracuse, New York, and was designated as Nivac P. It was obtained in wrought form as a 7/8-in.-diam rod. The vendor's analysis is as follows:

Element	Concentration (wt %)
Carbon	0.007
Manganese	< 0.002
Chromium	< 0.001
Aluminum	0.003, 0.006
Calcium	0.001, 0.01
Cobalt	0.09
Copper	0.003, 0.006
Iron	0.01, 0.05
Magnesium	< 0.001
Oxygen	0.0018

Small specimens having the geometry shown in Fig. 1 were machined from this material. They were annealed 1 hr in vacuum at 1300°C after machining. The large end of the specimen was prepared metallographically to obtain a flat scratch-free surface for plating.

The cobalt-60 was obtained in the form of $Co^{60}Cl_2$ solution. Two millicuries of this solution were diluted with 60 ml H_2O and used as the plating solution. The cathode was platinum and the nickel specimen was the anode. A direct-current potential of 6 v was used which resulted in a current flow of 9 ma. The large end of the specimen was touched to the surface of the plating solution, the circuit was made, and the specimen plated for 1 min. Surface activities of the order of 4000 cps (1.10–1.40 Mev) resulted.

The diffusion anneals were carried out in a tube furnace in which two 1 1/4-in.-OD alumina tubes were placed. These tubes were placed symmetrically inside the 2 1/2-in.-ID furnace tube to ensure the same temperatures within each of the smaller tubes. Argon was passed through one tube and hydrogen through the other. The argon was initially of 99.95% purity and was further purified by passing it over columbium turnings at 800°C. The hydrogen was purified by drying with subsequent diffusion through a Pd–10 wt % Ag thimble. Flow rates of 0.025 cfh (11.8 cc/min) were used for both gases. The temperature was measured with Pt vs Pt–10% Rh thermocouples which were attached to the small-diameter portion of the specimen with nickel wires. All thermocouples

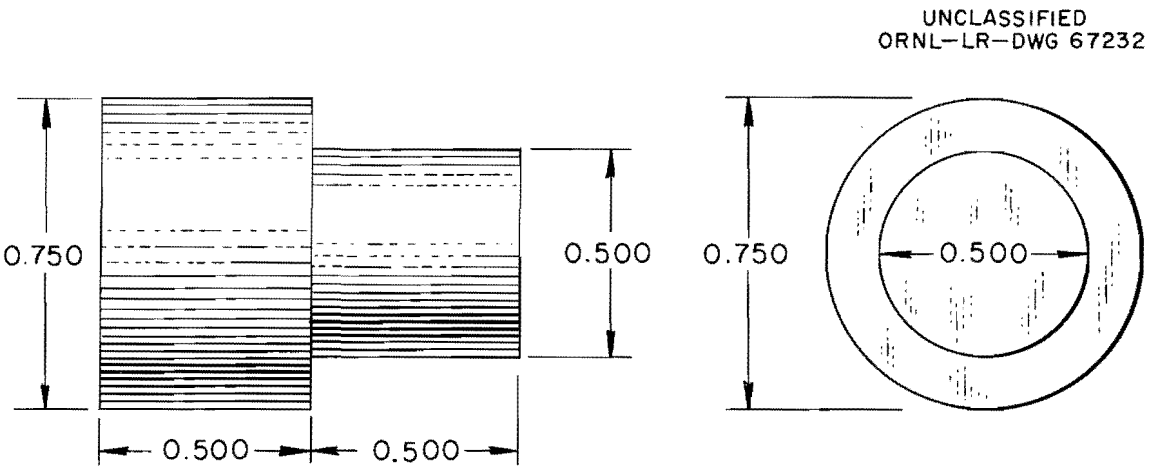

Fig. 1. Geometry of Test Specimen.

were calibrated before use. The furnace temperature was controlled to within ± 1.5°C during the diffusion anneal. The temperatures of the two specimens, one in each tube, always compared to within 1°C. Considerable difficulty was encountered in the use of Pt vs Pt–10% Rh thermocouples in hydrogen. A low-melting phase was formed which caused the effective junction of the thermocouple to progress toward the colder portion of the furnace. Hence, the temperature in the tube containing hydrogen appeared to decrease with time. It was hypothesized that this was due to the formation of Pt-Si compounds which can melt at as low as 830°C.[10] It was felt that the source of silicon was SiO_2 which was present as an impurity in the alumina insulators. The use of silicon-free alumina for thermocouple insulators resulted in satisfactory service.

Sectioning and Counting Procedure

After the diffusion anneals, each specimen was aligned in a lathe so the surface on which the cobalt-60 was originally plated was normal to the lathe axis. The diameter of each specimen was then reduced by machining from 0.750 in. to 0.500 in. to remove effects of possible surface diffusion. The diameters of each Ar-H_2 pair were machined to the same measurement.

Uniform layers 0.002 in. thick were then machined from the original interface. The chips were collected in a plastic box which enclosed the specimen and lathe collet. The section thicknesses were calculated from the weights of the chips as determined by a semimicrobalance.

The cobalt-60 activity of each section was determined using a 3 x 3 in. NaI(Tl) scintillation crystal enclosed in a 3-in.-thick lead chamber and a single-channel analyzer. The cobalt-60 decays to metastable nickel-60 giving a 1.17 Mev gamma; the metastable nickel-60 decays by isomeric transition to stable nickel-60 giving a 1.33 Mev gamma. The activity was determined between 1.10 and 1.40 Mev which included both the 1.17 and 1.33 Mev gamma peaks associated with the cobalt-60 decay. The specific activity for each section was determined by dividing the activity by the section weight.

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[10] M. Hanson, Constitution of Binary Alloys, p 1140, McGraw-Hill, New York, 1958.

RESULTS

The results which were obtained in this study are shown graphically in Figs. 2 and 3 and are tabulated in Tables 1–4 in the Appendix. The slopes of log activity vs depth-squared plots are proportional to the diffusion coefficient since the paired specimens were machined to the same diameter. These results show that the rate of diffusion of cobalt-60 into nickel is not influenced by whether the specimen environment is argon or hydrogen. For the purpose of this work, it was not necessary to compute actual D values. However, values were computed to compare with the results of other investigators. This comparison is made in Table 5 in the Appendix. The good agreement is indeed gratifying.

An additional pair of diffusion couples was run. The annealing temperature varied from 1190 to 1166°C and the couple in argon was badly oxidized. The results of these diffusion couples indicated that the rate of diffusion was about 10% greater with a hydrogen environment than with an argon environment. However, in light of the surface oxidation which occurred, these results are not felt to be significant.

DISCUSSION OF RESULTS AND CONCLUSIONS

It is felt that the experimental accuracy realized with the four specimens is sufficient to warrant the conclusion that the rate of diffusion of cobalt-60 into nickel is not different when the environment is argon or hydrogen. Because of the similarity of the atomic sizes of cobalt and nickel, these results also imply that the rate of self-diffusion of nickel is not different in argon and hydrogen environments. This in turn means that neither the concentration of vacancies nor their mobility is significantly different.

These results invalidate the proposal that the influence of environment on the rate of void growth in nickel and nickel-base alloys during creep may be due to either a change in the concentration of vacancies or in their mobility. However, this does not imply that environmental influences on creep properties cannot be manifested through an alteration of the rates of void nucleation or growth. The surface energy of these voids as influenced by the presence or absence of an environmental media may be a very important factor.

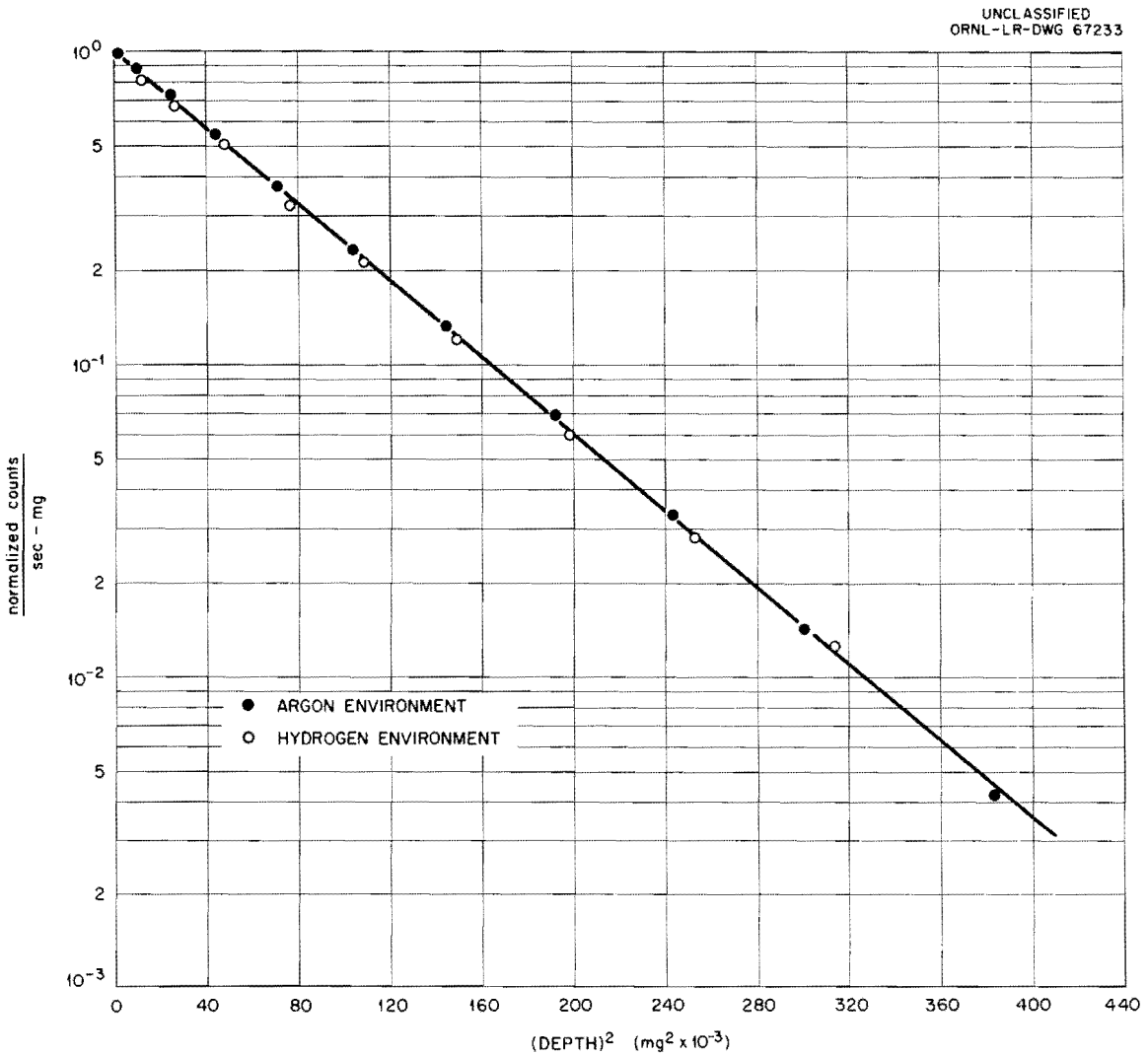

Fig. 2. Penetration Plot of the Diffusion of Cobalt-60 into Nickel After 1171 hr at 1095°C.

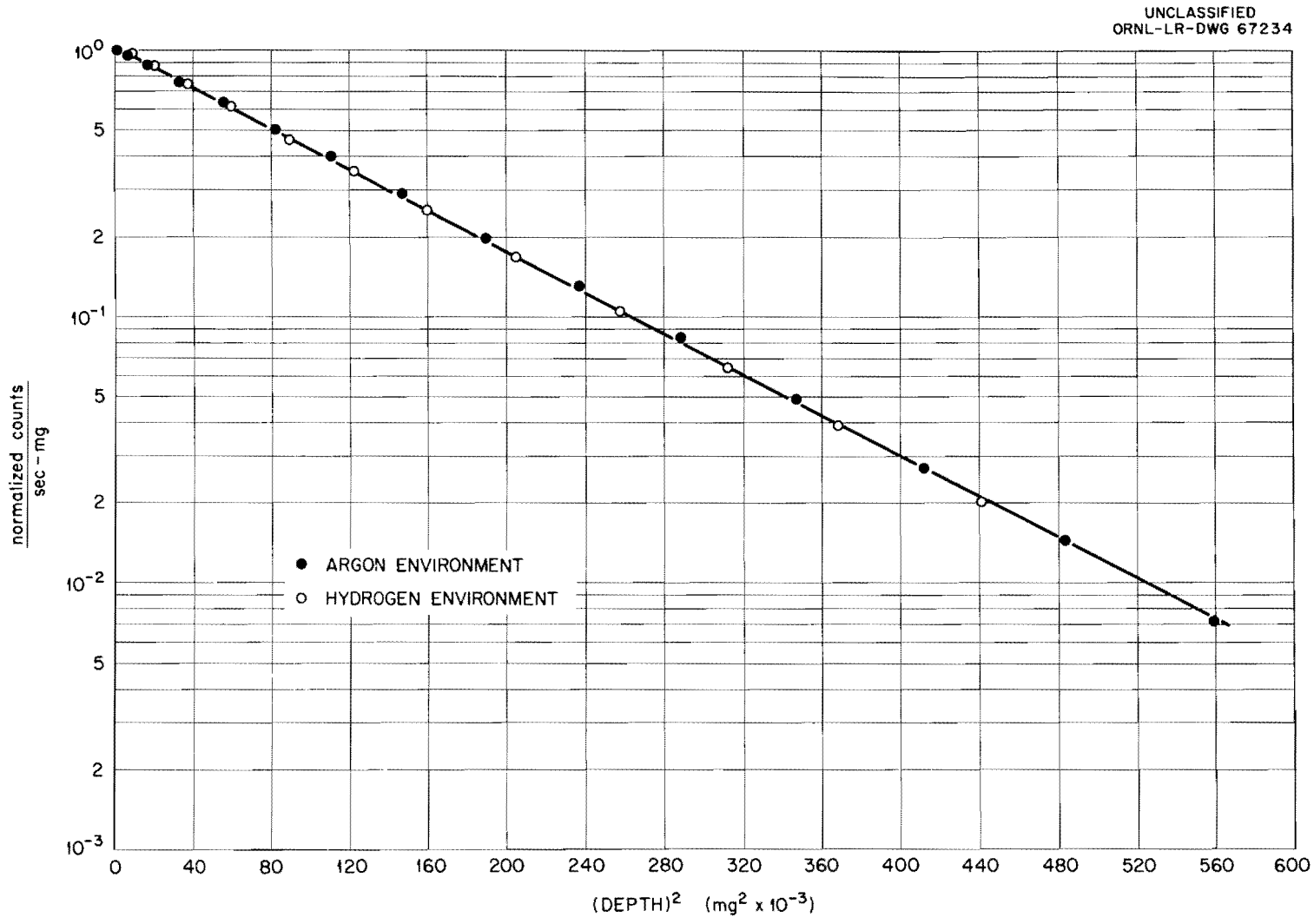

Fig. 3. Penetration Plot of the Diffusion of Cobalt-60 into Nickel After 446.2 hr at 1193°C.

APPENDIX

Table 1. Diffusion of Cobalt-60 into Nickel — Sectioning Data
Specimen Annealed 446.2 hr at 1193°C in Hydrogen

Section No.	Weight (mg)	Depth (mg)	Depth Squared ($mg^2 \times 10^{-3}$)	Activity (counts/sec)	Specific Activity (counts/mg·sec)	Normalized Specific Activity (counts/mg·sec)
1	66.44	33.22	1.103	259.598	3.9073	1.0000
2	48.17	90.52	8.194	182.678	3.792	0.97049
3	55.18	142.20	20.221	188.576	3.417	0.87452
4	46.46	193.02	37.257	136.209	2.932	0.75039
5	54.07	243.28	59.185	129.669	2.398	0.61372
6	57.89	299.26	89.556	104.407	1.8035	0.46157
7	43.75	350.08	122.556	60.915	1.392	0.35626
8	55.81	399.86	159.888	54.739	0.9808	0.25102
9	50.83	453.18	205.372	33.540	0.6598	0.16886
10	58.24	507.72	257.779	24.257	0.4165	0.10660
11	43.23	558.45	311.866	11.002	0.2545	0.065134
12	53.93	607.03	368.485	8.289	0.1537	0.039337
13	59.52	663.76	440.577	4.718	0.07926	0.020285

Table 2. Diffusion of Cobalt-60 into Nickel — Sectioning Data
Specimen Annealed 446.2 hr at 1193°C in Argon

Section No.	Weight (mg)	Depth (mg)	Depth Squared ($mg^2 \times 10^{-3}$)	Activity (counts/sec)	Specific Activity (counts/mg·sec)	Normalized Specific Activity (counts/mg·sec)
1	54.01	27.01	0.7295	214.106	3.9642	1.00000
2	49.08	78.55	6.1701	186.129	3.7923	0.95664
3	53.07	129.62	16.412	184.660	3.4796	0.87776
4	49.03	180.70	32.652	148.177	3.0191	0.76159
5	60.32	235.40	55.413	152.275	2.5244	0.63799
6	41.51	286.31	81.973	83.374	2.0085	0.50666
7	50.75	332.44	110.516	80.524	1.5867	0.40026
8	51.34	383.49	147.064	59.056	1.1503	0.29017
9	53.03	435.67	189.808	41.830	0.7888	0.19898
10	49.76	487.07	237.237	25.970	0.5219	0.13165
11	50.10	537.00	288.369	16.846	0.3362	0.084809
12	53.95	589.02	346.944	10.564	0.1958	0.049392
13	51.68	641.84	411.958	5.606	0.1085	0.027370
14	55.10	695.23	483.344	3.144	0.05705	0.014391
15	50.06	747.81	559.219	1.432	0.02860	0.007215

Table 3. Diffusion of Cobalt-60 into Nickel — Sectioning Data
Specimen Annealed 1171 hr at 1095°C in Hydrogen

Section No.	Weight (mg)	Depth (mg)	Depth Squared ($mg^2 \times 10^{-3}$)	Activity (counts/sec)	Specific Activity (counts/mg·sec)	Normalized Specific Activity (counts/mg·sec)
1	86.63	43.31	1.875	314.500	3.625	1.0000
2	47.25	110.25	12.155	140.400	2.961	0.81683
3	56.78	162.27	26.332	130.250	2.443	0.67393
4	57.30	219.31	48.097	105.430	1.831	0.50510
5	56.60	276.26	76.319	67.274	1.180	0.32552
6	49.38	329.25	108.406	38.431	0.7680	0.21186
7	63.98	385.93	148.942	28.652	0.4399	0.12135
8	55.41	445.62	198.577	12.583	0.2179	0.060110
9	58.62	502.64	252.647	6.496	0.1021	0.028166
10	56.20	560.05	313.656	3.110	0.04628	0.012767
11	61.17	618.73	382.827	1.447	0.01533	0.004229

Table 4. Diffusion of Cobalt-60 into Nickel — Sectioning Data
Specimen Annealed 1171 hr at 1095°C in Argon

Section No.	Weight (mg)	Depth (mg)	Depth Squared ($mg^2 \times 10^{-3}$)	Activity (counts/sec)	Specific Activity (counts/mg·sec)	Normalized Specific Activity (counts/mg·sec)
1	67.78	33.89	1.148	198.891	2.934	1.0000
2	61.89	98.72	9.746	162.091	2.619	0.89264
3	51.67	155.50	24.180	111.079	2.150	0.73279
4	57.71	210.19	44.180	93.991	1.629	0.55521
5	54.06	266.08	70.799	59.011	1.092	0.37219
6	56.99	321.60	103.427	39.473	0.6926	0.23606
7	60.00	380.10	144.476	23.427	0.3904	0.13306
8	56.04	438.12	191.949	11.399	0.2034	0.069325
9	55.10	493.69	243.730	5.366	0.09738	0.033190
10	53.80	548.14	300.457	2.253	0.04188	0.014274

Table 5. Comparison of Results with Those of Other Investigators

	D (cm/sec^2)			ΔH (kcal/mole)		
Temp (°C)	This Investigation	MacEwan[a] (calculated)	Hoffman[b] (calculated)	This Investigation	MacEwan[a]	Hoffman[b]
1193	1.71×10^{-10}	1.32×10^{-10}	1.40×10^{-10}	66.3	69.8	66.8
1095	3.42×10^{-11}	2.43×10^{-11}	2.71×10^{-11}			

[a]J. R. MacEwan et al., Can. J. Chem. 37, 1623 (1959).

[b]R. E. Hoffman et al., Trans. Met. Soc. AIME 206, 483 (1956).

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