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REACTION OF NITROGEN WITH NIOBIUM

by

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Reaction rates of niobium with nitrogen were determined gravimetrically from 675 to 975 C with a recording microbalance and volumetrically from 1100 to 1600 C with a modified Sieverts apparatus. Diffusion coefficients and terminal solubilities were determined from 800 to 1600 C by the concentration-gradient technique.

The reaction of nitrogen with niobium follows a parabolic rate law at 675 to 1600 C. The parabolic rate constant can be expressed by

$$K\,[(\mu g/cm^2)^2/sec] = 3.5 \times 10^4 \exp[-(24{,}000 \pm 1{,}000)/RT]$$

at 675 to 975 C, and by

$$K\,[(\mu g/cm^2)^2/sec] = 8.9 \times 10^9 \exp[-(50{,}000 \pm 1{,}800)/RT]$$

at 1100 to 1600 C.

The expression for the diffusion coefficient for nitrogen in niobium at 800 to 1600 C is

$$D\,(cm^2/sec) = 0.061 \exp[-(38{,}800 \pm 700)/RT].$$

The terminal solubility for nitrogen in niobium follows the relationship

$$C\,(a/o\ N) = 180 \exp[-(13{,}700 \pm 200)/RT].$$

INTRODUCTION

The purpose of this work was to investigate the reaction of niobium with nitrogen, and the diffusion and terminal solubilities of nitrogen in the metal. Numerous X-ray studies have been made of the room-temperature structures of the nitrides of niobium.(1-7)* Brauer and Jander(5) reported a hexagonal subnitride having a composition of Nb_2N, and a tetragonal, a face-centered cubic, and two hexagonal nitrides having compositions of $NbN_{0.75}$ to NbN. Their findings are summarized in Table 1. These results are in good agreement with those of other studies. The kinetics of the reaction of nitrogen with niobium have been studied by Gulbransen and Andrew(8) employing a gravimetric technique. They found that the reaction followed a parabolic rate law in the range 400 to 800 C at a nitrogen pressure of 76 mm of mercury. The diffusion of nitrogen in niobium has been studied by Ang(9) and by Powers and Doyle(10) using internal-friction techniques. Also, Ang and Wert(11) have studied the solubility of nitrogen in niobium.

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*References at end.

TABLE 1. SUMMARY OF X-RAY INVESTIGATION OF NITRIDES OF NIOBIUM BY BRAUER AND JANDER(5)

Product	Composition Range, nitrogen/niobium	Structure	Lattice Constants, A		
			a_o	c_o	a_o/c_o
Niobium	0 to 0.02	Body-centered cubic	3.30	--	--
Nb_2N	0.4 to 0.5	Close-packed hexagonal	3.056	4.964	1.624
NbN	0.75 to 0.79	Tetragonal (deformed cubic)	4.385	4.312	0.983
NbN	0.89 to 0.95	Face-centered cubic	4.389	--	--
NbN	0.95 to 1.0	Close-packed hexagonal(a)	2.94	4.46	1.87
NbN	1.0	Hexagonal	2.956	11.275	3.815

(a) Found only in presence of cubic and hexagonal NbN.

MATERIAL

The original niobium bars were cut and fabricated into cylindrical and sheet samples. The samples were vacuum annealed at 1150 C for 1/2 hr. The analysis of the fabricated niobium after annealing is shown in Table 2. The samples had a Vickers hardness of 113.

TABLE 2. ANALYSIS OF THE NIOBIUM FOR REACTION-RATE AND DIFFUSION STUDIES AFTER FABRICATION AND ANNEALING

Element	Analysis, ppm
Tantalum	1500
Iron	200
Tin	200
Molybdenum	50
Silicon	50
Vanadium	50
Chromium	20
Aluminum	20
Titanium	20
Carbon	120
Oxygen	430
Nitrogen	120
Hydrogen	<3(a)

(a) After degassing.

Matheson prepurified nitrogen (99.99^+ per cent pure) was passed through a dry ice-acetone cold trap into the evacuated storage system of the apparatus.

EXPERIMENTAL PROCEDURE

Kinetic data for the reaction of nitrogen with niobium were obtained by volumetric and gravimetric techniques. A modified Sieverts apparatus(12) was employed to obtain reaction rates by the volumetric method at 1100 to 1600 C. Essentially, the apparatus consisted of a reaction tube, gas buret, and a high-vacuum pumping system. Cylindrical specimens approximately 0.8 cm in diameter and 2.5 cm long were dry abraded through 240-, 400-, and 600-grit silicon carbide paper. Each specimen was weighed, measured, and spot welded to a platinum-platinum 10 w/o rhodium thermocouple. After a light final polish with dry 600-grit silicon carbide paper, the sample was hung in the reaction tube and sealed to the Sieverts apparatus. The system was evacuated to less than 0.01 μ of mercury. The sample was then heated by induction to the temperature of the run. The temperature was maintained to ± 10 C.

The reaction was initiated by admitting nitrogen at atmospheric pressure to the reaction tube. The buret was kept balanced at atmospheric pressure at all times. Readings of the buret were taken at convenient time intervals, depending upon the speed of the reaction. The amount of gas reacted with the sample was the difference between the volume added from the buret and the volume remaining in the gas phase in the calibrated dead space of the reaction tube. The original geometrical dimensions of the sample were used to determine the amount of gas reacting per unit surface area.

Since these samples were also to be used in the diffusion studies they were reacted long enough to produce a suitable concentration gradient in the sample. At the end of this time the samples were immediately water quenched to below 500 C in about 1 min.

Reaction rates in the range 675 to 975 C were determined by the gravimetric method using a recording Sartorius Electrona microbalance.(13) Cylindrical specimens, approximately 0.3 cm in diameter and 1 cm long, and sheet specimens, 0.03 cm thick, were dry abraded as in the high-temperature experiments. The specimen was suspended in the reaction tube from the beam of the balance with a platinum wire 0.013 cm in diameter. The reaction tube was evacuated to the order of 0.01 μ of mercury and heated to temperature in a resistance-wound furnace. The temperature was maintained to ±5 C. The reaction was initiated by the addition of nitrogen at atmospheric pressure to the reaction tube.

The concentration-gradient technique(14, 15) was used to determine the diffusion coefficients for nitrogen in niobium. Lengths equal to the radius were cut from the ends of the reacted samples. The remainder of the cylinder was radially machined into layers of equal weight. These layers were then analyzed by the Kjeldahl method. The sensitivity of these analyses was ±10 per cent. Diffusion coefficients were calculated by the graphical method(14) using the average nitrogen concentration and average radius of each layer, and the time of the reaction.

Terminal solubilities of nitrogen in niobium were calculated from the concentration-gradient data. In order to check these solubilities, nitrogen was added to several niobium samples to produce concentrations of 1.7, 2.1, and 2.7 a/o nitrogen. The samples were homogenized at 1500 C or higher. Each sample was heated at three or four temperatures in the range 900 to 1500 C for a time sufficient to establish equilibrium. After each heat treatment, the sample was water quenched and a cross section was examined metallographically to determine the structure.

RESULTS AND DISCUSSION

Kinetics

The kinetics of reaction of niobium with nitrogen at atmospheric pressure were studied in the range 675 to 1600 C. Some representative rate curves are shown in Figure 1, in which the weight gain per unit surface area, μg per cm^2, is plotted against time, t. The initial reaction followed a parabolic rate law, $w^2 = kt$. Rate curves showing the parabolic behavior of the reactions are shown in Figure 2. The experimental rate constants are listed in Table 3. Corresponding constants reported by Gulbransen and Andrew(8) are also given. The variation of the logarithms of the rate constants with reciprocal temperature is shown in Figure 3. It is seen that there is a change in the reaction mechanism between 975 and 1100 C. The equation for the variation of the rate constants with temperature in the range 675 to 975 C is

$$K\,[(\mu g/cm^2)^2/sec] = 3.5 \times 10^4 \exp\,[-(24,400 \pm 1,000)/RT], \qquad (1)$$

as determined by the method of least squares. The activation energy of 24.4 ± 1.0 kcal per mole is in good agreement with the value 25.4 kcal per mole reported by Gulbransen and Andrew(8) for the reaction of nitrogen with niobium at 400 to 800 C. This value is low compared with the activation energies for the reaction below 900 C of nitrogen with the two other elements of Group Vb, tantalum, 39.4 kcal per mole(8), and vanadium, 31.4 kcal per mole(16), or also with zirconium, 39.2 kcal per mole(17), and titanium, 36.3 kcal per mole(18) of Group IVb.

The equation for the reaction-rate constant at 1100 to 1600 C is

$$K\,[(\mu g/cm^2)^2/sec] = 8.9 \times 10^9 \exp\,[-(50,000 \pm 1,800)/RT]. \qquad (2)$$

The activation energy is 50.0 ± 1.8 kcal per mole. This value is close to some values reported for the reaction of nitrogen with zirconium, 48.0 kcal per mole(15) and 52.0 kcal per mole(19) at temperatures above 900 C.

X-ray studies were made on samples reacted with nitrogen at 775 to 1400 C. The experimental conditions for the reactions and the X-ray intensities of the detected products are summarized in Table 4. Both Nb_2N and NbN were produced below 1000 C. Only NbN phases were formed at 1200 C and higher. This difference in surface product accounts for the change in the reaction mechanism between 975 and 1100 C as shown in Figure 3.

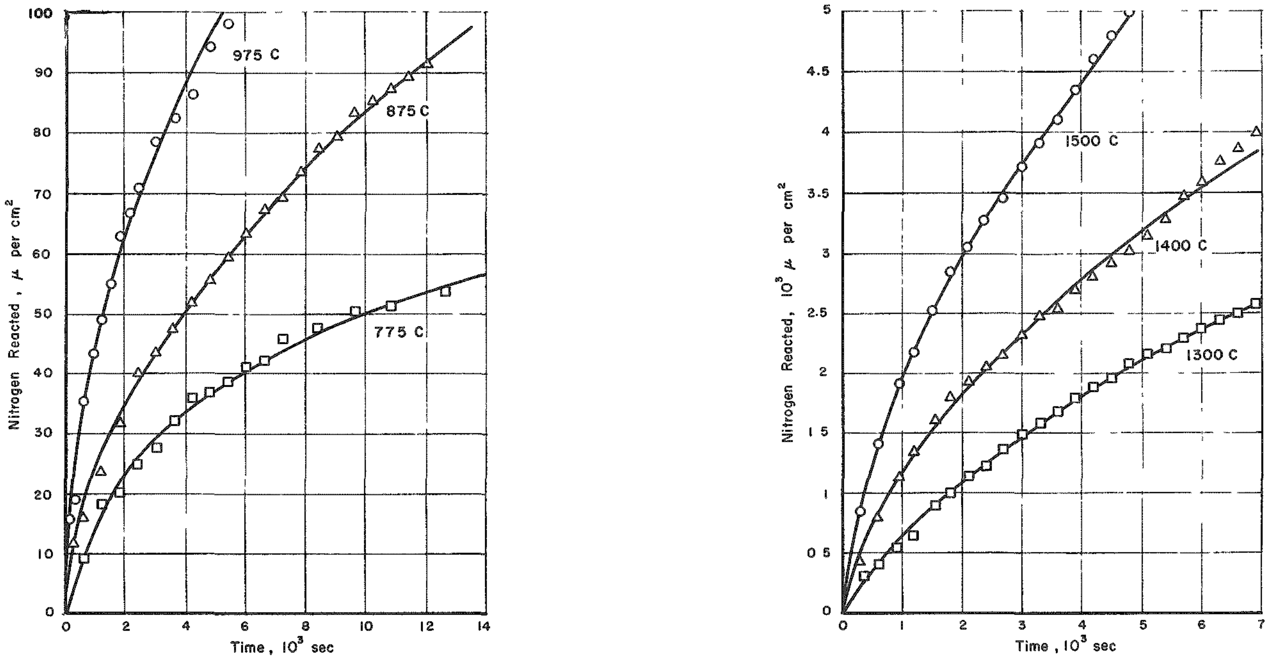


FIGURE 1. REPRESENTATIVE RATE CURVES FOR THE REACTION OF NITROGEN WITH NIOBIUM AT ATMOSPHERIC PRESSURE

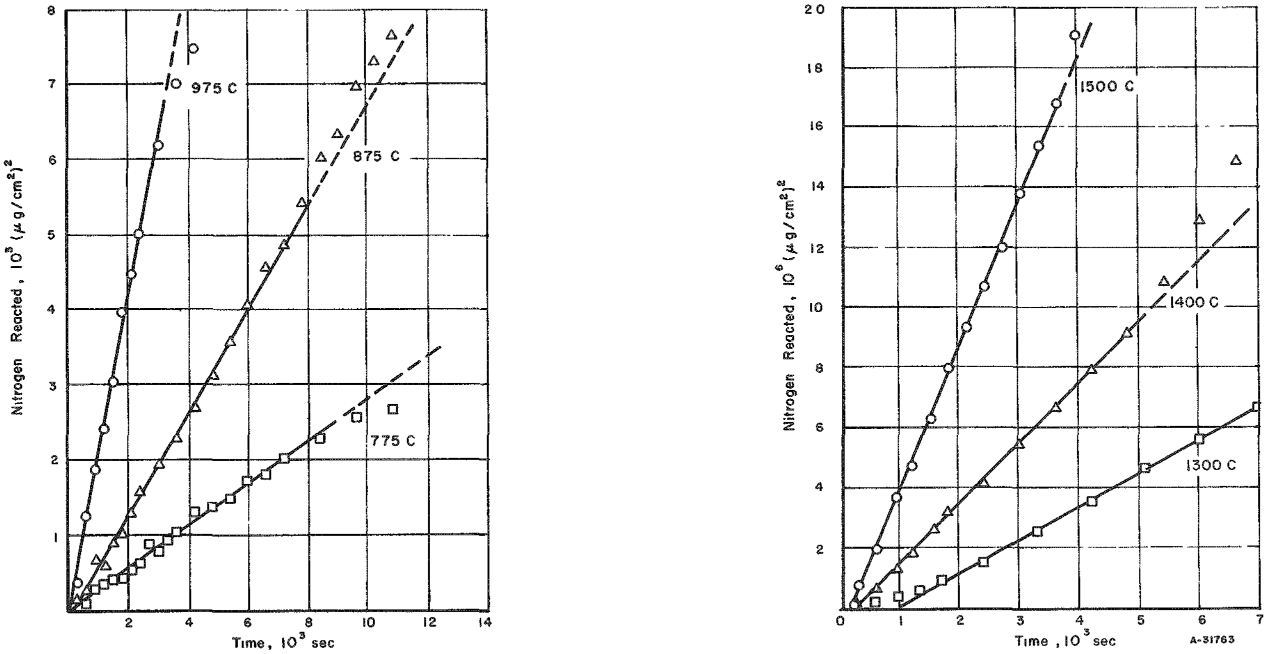


FIGURE 2. PARABOLIC PLOTS FOR THE REACTION OF NITROGEN WITH NIOBIUM AT ATMOSPHERIC PRESSURE

TABLE 3. PARABOLIC RATE CONSTANTS FOR THE REACTION OF NITROGEN WITH NIOBIUM

Temperature, C	Rate Constant, $(\mu g/cm^2)^2/sec$	
	This Study	Gulbransen and Andrew(8)
600	--	2.97×10^{-2}
675	9.4×10^{-2}	--
700	--	1.512×10^{-1}
775	2.8×10^{-1}	--
800	--	5.42×10^{-1}
875	6.9×10^{-1}	--
975	2.1	--
1100	1.0×10^{2}	--
1200	2.9×10^{2}	--
1300	1.1×10^{3}	--
1400	2.0×10^{3}	--
1500	4.9×10^{3}	--
1600	1.6×10^{4}	--

TABLE 4. RESULTS OF X-RAY STUDIES OF THE SURFACE FILMS OF NIOBIUM REACTED WITH NITROGEN

Reaction Temperature, C	Reaction Time, hr	X-Ray Intensities(a) of Indicated Products		
		Nb_2N	Cubic NbN	Hexagonal NbN
775	115.3	S	--	--
800	1669	VS	M	--
875	3.5	M	--	--
975	3	VS	M	MF
1200	13	--	VS	S
1400	2.5	--	VVS	--

(a) V = very, S = strong, M = medium, and F = faint.

Diffusion and Terminal Solubility

The diffusion coefficients and terminal solubilities of nitrogen in niobium were determined from 800 to 1600 C. Figure 4 shows a representative curve for nitrogen concentration distribution determined from samples reacted at 1200 C for 730 min. The vertical dotted lines represent the boundaries of the concentric layers and the points represent the average concentration in each layer. The solid curve through the points shows the theoretical concentration distribution for the sample assuming the relationship

$$Dt/a^2 = 0.035, \tag{3}$$

where

D = diffusion coefficient, cm^2 per sec

t = time, sec

a = radius of the cylinder, cm.

The diffusion coefficients for nitrogen in niobium in the range 800 to 1600 C are given in Table 5. The variation of these coefficients with temperature is shown in Figure 5. A least-squares calculation of the data yields the equation

$$D(cm^2/sec) = 0.061 \exp\left[-(38,800 \pm 700)/RT\right], \tag{4}$$

in which 38.8 kcal per g-atom is the activation energy for the diffusion process. The entropy of diffusion, ΔS, was calculated from D_o, 0.061, and the activation energy by the theory for interstitial diffusion presented by Wert and Zener(20, 21). The equation for a body-centered-cubic lattice is

$$D_o = 1/6\, a_o^2\, \mu \exp(\Delta S/R), \tag{5}$$

where a_o is the lattice constant and μ is the frequency of vibration of a solute atom in an interstitial position. The vibrational frequency is approximated from the expression

$$\mu = (E/2m\,\lambda^2)^{1/2}, \tag{6}$$

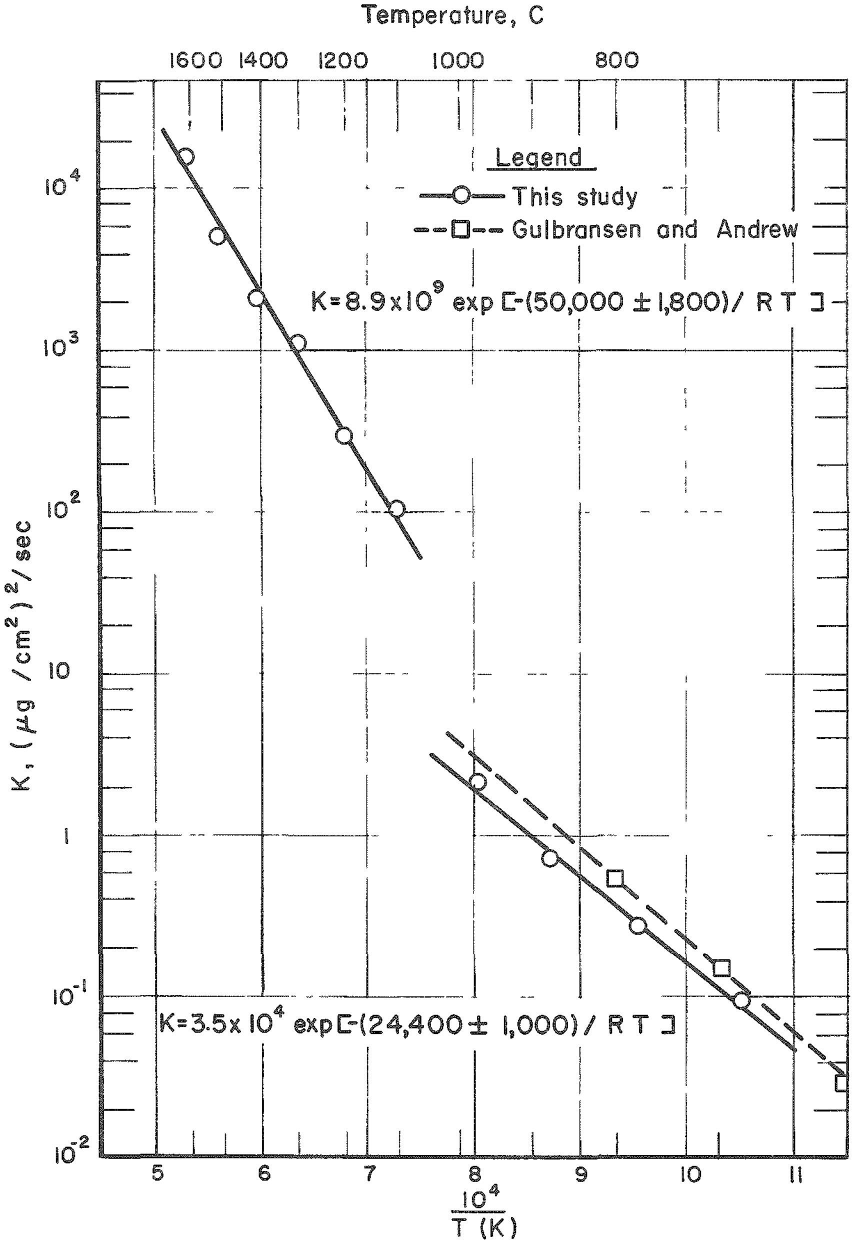
where E is approximately equal to the activation energy in ergs, m is the mass of a gram-atom of nitrogen, and λ is the distance between the interstitial positions ($\lambda = a_o/2$). The ΔS for diffusion of nitrogen in niobium was calculated to be 6.2 cal/(g-atom)(C). According to theory(21), such a low positive value is characteristic of interstitial diffusion as opposed to diffusion through grain boundaries or other short-circuiting paths.

The equation for the variation of the diffusion coefficients with temperature, Equation (4), can be compared with,

$$D\ (cm^2/sec) = 0.098 \exp\left[-38,600/RT\right], \tag{7}$$

reported by Ang(9) and with

$$D\ (cm^2/sec) = 0.0072 \exp\left[-34,800/RT\right], \tag{8}$$



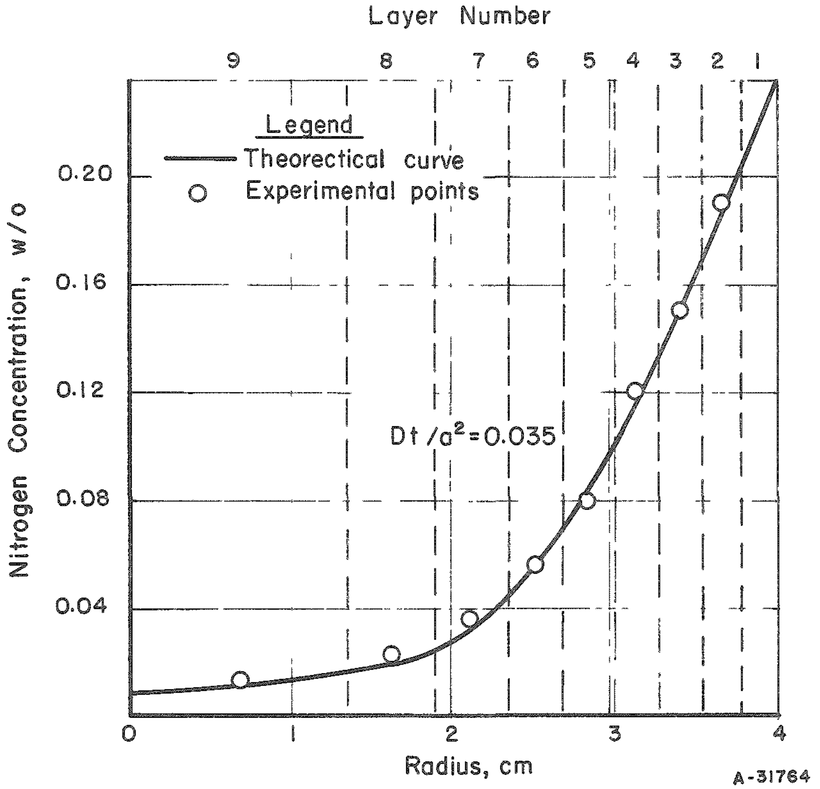


FIGURE 4. CONCENTRATION-DISTRIBUTION CURVE FOR NIOBIUM CYLINDER REACTED WITH NITROGEN AT 1200 C FOR 730 MIN

FIGURE 3 (Left). VARIATION OF PARABOLIC RATE CONSTANT WITH TEMPERATURE FOR REACTION OF NITROGEN WITH NIOBIUM reported by Powers and Doyle(10). Both equations were developed from internal-friction studies. Diffusion coefficients calculated from Equations (7) and (8) are presented in Table 5. These values are also plotted in Figure 5. It is seen that the data for the present study fall between the other sets of data.

TABLE 5. DIFFUSION COEFFICIENTS FOR NITROGEN IN NIOBIUM

Temperature, C	Diffusion Coefficient, 10^{-7} cm^2 per sec This Study	From Equation (7)(9)	From Equation (8)(10)
800	0.0068	0.014	0.0059
1100	0.41	0.71	0.21
1200	1.3	1.8	0.50
1300	3.1	4.3	1.1
1400	5.5	8.9	2.1
1500	8.8	18	3.7
1600	15	31	6.3

The terminal solubility of nitrogen in a metal is its concentration in the metal at the interface of the metal and a surface film of the metal nitride. The values of C_o determined in the gradient study are, therefore, the terminal solubilities for nitrogen in niobium. The values obtained for 800 to 1600 C are given in Table 6. Their variation with temperature is shown in Figure 6. A least-squares calculation yielded the relationship,

$$C\ (a/o\ N) = 180 \exp\left[-(13,700 \pm 200)/RT\right]. \qquad (9)$$

TABLE 6. TERMINAL SOLUBILITIES FOR NITROGEN IN NIOBIUM

Temperature, C	Terminal Nitrogen Solubility, a/o This Study	From Equation (10)(11)
800	0.28	0.20
1100	1.2	0.32
1200	1.6	0.35
1300	2.3	0.39
1400	2.8	0.43
1500	3.4	0.46
1600	4.7	0.49

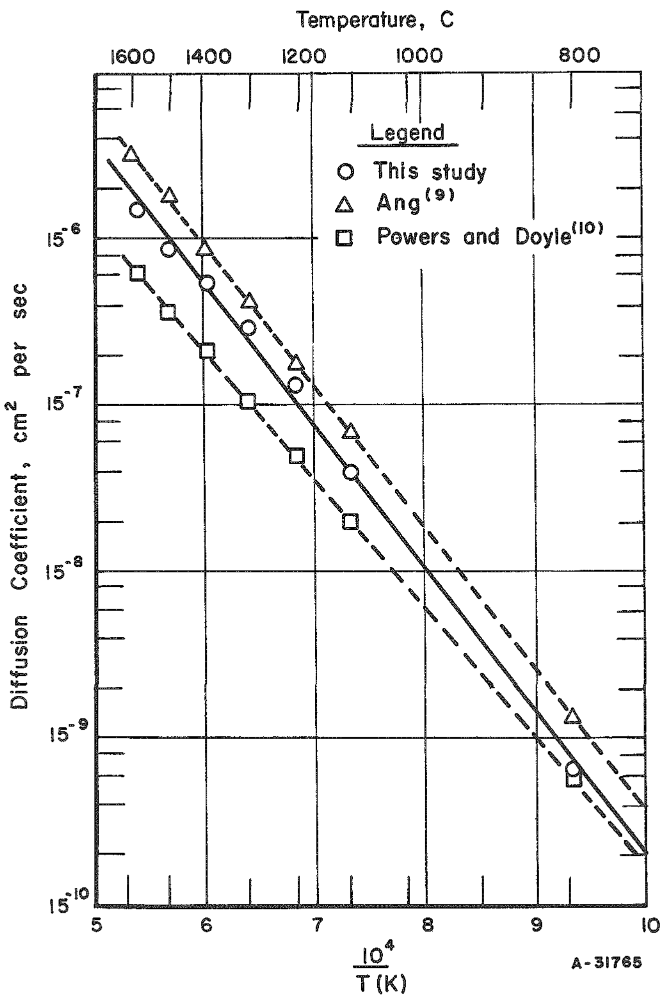


FIGURE 5. VARIATION OF DIFFUSION COEFFICIENTS WITH TEMPERATURE FOR NITROGEN IN NIOBIUM

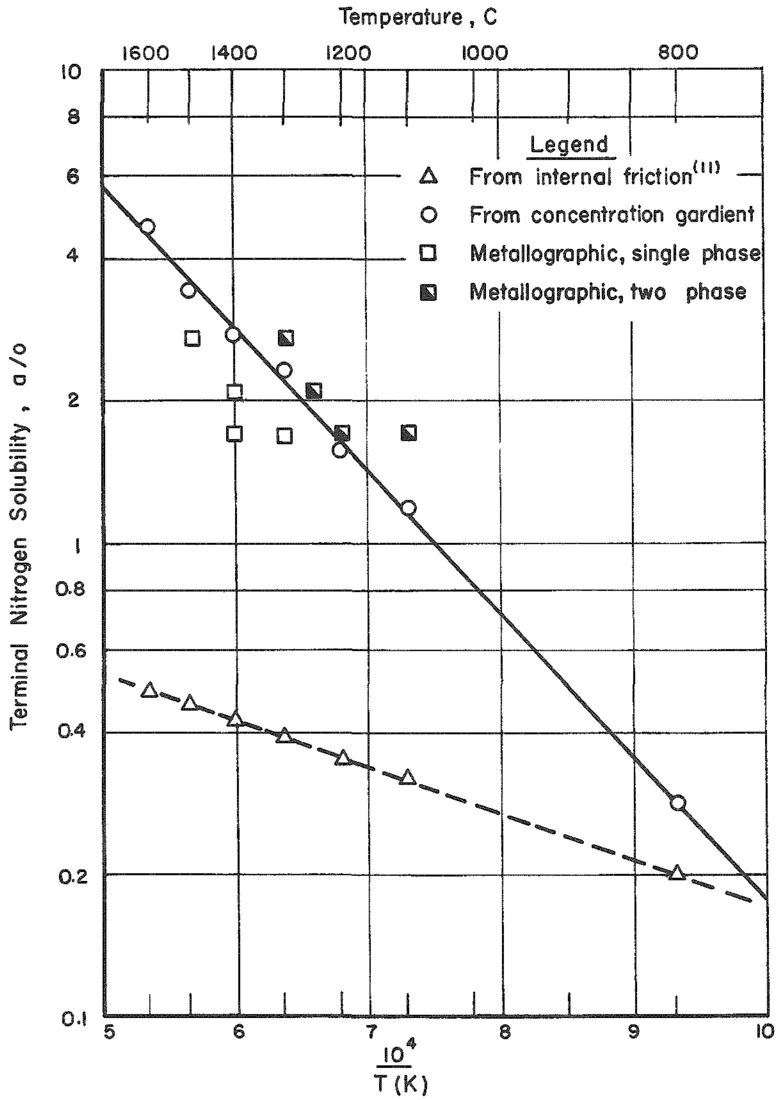


FIGURE 6. VARIATION OF THE THERMINAL SOLUBILITY OF NITROGEN IN NIOBIUM WITH TEMPERATURE

Ang and Wert(11) report the equation

$$C\ (a/o\ N) = 1.7 \exp\left[-4,600/RT\right], \qquad (10)$$

determined by internal-friction studies. Values for the terminal solubilities for nitrogen in niobium at 800 to 1600 C calculated from Equation (10) are given in Table 6 and are shown in Figure 6. The results of metallographic examination of niobium samples having concentrations of 1.7 to 2.7 a/o nitrogen also are shown in Figure 6. It can be seen that the phase structure of the samples is in good agreement with the terminal solubilities obtained from the diffusion study. It can be seen that the published solubilities are considerably less than those obtained in this work.

CONCLUSIONS

The reaction of nitrogen with niobium in the range 675 to 1600 C was found to follow a parabolic rate law. A change in the reaction mechanism is indicated between 1000 and 1100 C. The activation energies are 24.4 ± 1.0 kcal per mole at 675 to 975 C and 50.0 ± 1.8 kcal per mole at 1100 to 1600 C. X-ray studies indicate that there is a change in the surface product of the reaction between 1000 and 1200 C. It is thought that the change in the reaction mechanism is associated with this change in the surface product of the reaction.

The diffusion coefficients and terminal solubilities for nitrogen in niobium were determined in the range 800 to 1600 C. The diffusion coefficients were found to follow the relationship

$$D\ (cm^2/sec) = 0.061 \exp\left[-38,800/RT\right],$$

where the activation energy is 38.8 ± 0.7 kcal per g-atom. The ΔS for diffusion was calculated to be 6.2 cal/(g-atom)(C), which is consistent with the theory for interstitial diffusion.

The terminal solubilities for nitrogen in niobium expressed in a/o nitrogen were found to have the relationship

$$C\ (a/o\ N) = 180 \exp\left[-13,700 \pm 200/RT\right].$$

These solubilities were checked by metallographic examination of heat-treated niobium samples containing known concentrations of nitrogen.

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REFERENCES

(1) Becker, K., and Ebert, P., Z. Physik, 31, 268 (1925).

(2) Umanski, Y. S., J. Phys. Chem. (U.S.S.R.), 14, 332 (1940).

(3) Aschermann, G., Friederich, E., Justi, E., and Kramer, J., Physik Z., 42, 349 (1941).

(4) Horn, F. H., and Ziegler, W. T., "Superconductivity and Structure of Hydrides and Nitrides of Tantalum and Columbium", JACS, 69, 2762 (1947).

(5) Brauer, G., and Jander, J., Z. anorg. u. allgem. Chem., 270, 160 (1952).

(6) Brauer, G., Jander, J., and Rogener, H., Z. Physik, 134, 432 (1953).

(7) Schonberg, N., Acta Chem. Scand., 8, 208 (1954).

(8) Gulbransen, E. A., and Andrew, K. F., "Kinetics of the Reaction of Columbium and Tantalum with Oxygen, Nitrogen, and Hydrogen", Trans. AIME, 188, 586 (1950).

(9) Ang, C. Y., "Activation Energies and Diffusion Coefficients of Oxygen and Nitrogen in Niobium and Tantalum", Acta Met. 1, 123 (1953).

(10) Powers, R. W., and Doyle, M. V., "Internal Friction Studies in Niobium", Trans. AIME, 209, 1285 (1957).

(11) Ang, C. Y., and Wert, C., "Some Properties of Niobium Containing Nitrogen", Trans. AIME, 197, 1032 (1953).

(12) Albrecht, W. M., and Mallett, M. W., "Reaction of Hydrogen with Uranium", J. Electrochem. Soc., 103, 404 (1956).

(13) Mallett, M. W., Albrecht, W. M., and Bennett, R. E., "Reaction of Zirconium with Water Vapor at Subatmospheric Pressures", J. Electrochem. Soc., 104, 349 (1957).

(14) Mallett, M. W., Baroody, E. M., Nelson, H. R., and Papp, C. A., "The Diffusion and Solubility of Nitrogen in Beta Zirconium", J. Electrochem. Soc., 100, 103 (1953).

(15) Mallett, M. W., Belle, J., and Cleland, B. B., "The Reaction of Nitrogen with and the Diffusion of Nitrogen in Beta Zirconium", J. Electrochem. Soc., 101, 1 (1954).

(16) Gulbransen, E. A., and Andrew, K. F., "Kinetics of the Reactions of Vanadium with Oxygen and Nitrogen", J. Electrochem. Soc., 97, 396 (1950).

(17) Gulbransen, E. A., and Andrew, K. F., "Kinetics of the Reactions of Zirconium with Oxygen, Nitrogen, and Hydrogen", Trans. AIME, 185, 515 (1949).

(18) Gulbransen, E. A., and Andrew, K. F., "Kinetics of the Reactions of Titanium with Oxygen, Nitrogen, and Hydrogen", Trans. AIME, 185, 741 (1949).

(19) Dravnieks, A., "The Kinetics of the Zirconium-Nitrogen Reactions at High Temperatures", JACS, 72, 3568 (1950).

(20) Wert, C., and Zener, C., "Interstitial Atomic Diffusion Coefficients", Phys. Rev., 76, 1169 (1949).

(21) Zener, C., "Theory of D_o for Atomic Diffusion in Metals", J. Appl. Phys., 22, 272 (1951).

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