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EQUILIBRIUM SOLUTIONS OF NITROGEN IN COLUMBIUM-BASE ALLOYS

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(Prepared under Contract AF 33(657)-10626
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FOREWORD

This report was prepared by the University of Illinois, Department of Mining, Metallurgy and Petroleum Engineering under Contract AF 33(657)-10626. The contract was initiated under Project No. 7351, "Metallic Materials", Task No. 735106, "Behavior of Metals". The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, with Mr. F. G. Ostermann acting as project engineer.

This report covers work conducted from 15 March 1963 to 15 March 1964.

ABSTRACT

Thermodynamic and mechanical properties of columbium-nitrogen and columbium-zirconium-nitrogen alloys were determined. The partial pressure of nitrogen in equilibrium with single-phase and two-phase alloys of various binary and ternary compositions was determined as a function of temperature for temperatures between 1500°C and 2100°C. Heat of solution of nitrogen, heat of formation of Cb_2N, and heat of solution of Cb_2N values were determined for pure columbium and columbium with 0.86 wt % Zr. Internal friction and hardness were measured for several alloys which had been quenched from above 1500°C. For the radiation quench used, solid solutions with 0.075 wt % nitrogen and over could not be retained without precipitation. For the coarse-grained specimens hardness increased from 107 KHN for the pure columbium to 178 KHN for a two-phase alloy containing 0.68 wt % nitrogen.

This technical documentary report has been reviewed and is approved.

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1. Introduction

Interactions of the interstitial atoms with each other and with base metal atoms, other solute atoms or dislocations have been hypothesized to explain certain mechanical, as well as contamination, characteristics of the body-centered cubic (BCC) refractory metals. These interactions are thought to explain not only the effect of the gases which contribute the interstitial atoms, but also the effect of other substitutional alloying elements which modify the distribution of interstitial atoms in solution. The present research was concerned with how the behavior of nitrogen in dilute solution in columbium is affected by a small amount of substitutional alloying elements having a strong affinity for nitrogen.

For assessing the magnitude and kind of nitrogen atom interactions there are two general lines of attack: the physical, and the thermodynamic, both of which were employed in this investigation. The physical methods were the measurement of room temperature hardness of binary and ternary columbium alloys with different compositions and treatments. Measurement of internal friction was used as a means of giving information about the state of the interstitial atoms in the alloys. The thermodynamic method was the determination of the properties of the solid solution by measuring the partial pressures of nitrogen in equilibrium with the binary and ternary alloys at various temperatures above 1600°C. Equilibrium pressure-temperature measurements for a gas-metal system are capable of giving information about the state of the gas in solution, since, in the pressure range of interest, the partial pressure is equal to the thermodynamic activity. Such measurements, suitable for high temperatures, in conjunction with internal friction measurements, suitable for specimens which can be quenched without precipitation, are capable of determining solubilities over a wide range of temperatures.

Much of the work done on refractory metal-gas systems has been done under non-equilibrium conditions so that the observed quantity such as hardness, strength, thickness of contaminated layer, or weight gain was a function of time, specimen geometry, and surface preparation, as well as temperature, pressure, and gas and alloy composition Furthermore,

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many experiments have been carried out under conditions which result in the non-equilibrium formation of a compound or compounds with the metal. While of great practical value, such experiments do not yield a great deal of information about the behavior of the gas atom in equilibirum solutions. Therefore, it seemed desirable to eliminate several of the variables associated with non-equilibrium conditions and to study the gas-metal equilibrium as a function of temperature only.

It was felt that an alloying element from the IVa group (Ti, Zr, Hf, Th) should be chosen to add to columbium. Titanium, however, is too volatile above 1600°C to allow its use, and thorium is only sparingly soluble. Hafnium is soluble and has about the same vapor pressure as columbium, but zirconium, though more volatile than columbium, was chosen because more is known of the mechanical and chemical behavior of Cb-Zr alloys.

This research was performed during the period 15 March 1963 to 15 March 1964 .

2. Materials

The columbium used in this investigation was obtained from the Wah Chang Corporation in the form of 5/16" rod of better than 99.8% purity (Table I).

Its fabrication histroy was as follows:

1. arc melted from electron beam ingot
2. forged 80% at room temperature
3. annealed 1 hour at 1300°C
4. rolled to 1 1/4" rod and swaged to 5/16" rod at room temperature.

Some pure columbium specimens were made by cold swaging to 30 mil wires without intermediate anneals. The zirconium used for alloying was received from the Carborundum Metals Corporation in the form of 40 mil wire and was 97.7% pure.

Alloys of 0.5, 1.0, 1.5, 2.5 and 3.5 nominal weight per cent zirconium were fabricated by electron beam melting at

$<10^{-5}$ torr. To prepare the alloys, zirconium wire of the proper diameter was peened into a slot in the columbium rod and zone melted. After several zone leveling cycles over a 4-6" length the rods were removed from the apparatus and the hardness was measured along their length before swaging into wire. One of the first rods produced in this manner was sectioned for wet chemical and neutron activation analysis over a length which showed uniform hardness readings. The zirconium content was found to vary by 50% of the amount present. It was felt that the lack of large scale uniformity in the zirconium content would not be a serious problem since chemical analysis could be performed after the experiments were performed. A Cb - .86% Zr alloy (Table I) in the form of 45 mil wire was obtained from the Kawecki Chemical Company for comparison with the zone-leveled alloys.

3. Experimental Procedure

The partial pressure of nitrogen in equilibrium with pure columbium and with columbium-zirconium alloys was measured as a function of temperature and nitrogen content in a Sieverts apparatus. This all-glass apparatus consisted of three sections

1. a vycor specimen chamber which was evacuated with a liquid nitrogen-trapped mercury diffusion pump and which could be isolated by means of a stopcock.

2. a McCleod gage which was trapped by liquid nitrogen and which could be isolated by means of a stopcock.

3. a calibrated volume and manometer for introducing known quantities of gas into the system.

Except for the stopcocks and mercury, the specimen chamber and gage could be baked as high as 400°C. in order to minimize subsequent outgassing. It was found that in spite of these precautions outgassing of glass tubing and stopcock grease and release of entrained and dissolved gas in the mercury required several days. The specimens were outgassed at 2000-2200°C for at least 8 hours after which time the dynamic vacuum would reach $<10^{-6}$ torr. as measured on a Phillips gage. After three hours isolation from the pump the pressure would not rise above 5×10^{-6} torr., the low pressure limit of the McCleod gage. The Phillips gage was not used for any of the actual equilibrium measurements due to its tendency to pump.

The 30 mil specimens were heated by the passage of a stabilized alternating current through them. Temperature was measured by an optical pyrometer sighted through a shuttered window. Appreciable temperature gradients existed in the vicinity of the grips, but this was limited to about one-half inch on each end of a 10-12 inch wire. Corrections were applied to allow for absorption in the sight port and emissivity changes as a function of nitrogen content, but it was assumed that the ternary and binary alloys had the same emissivity. Specimen weight loss was measured but was usually small. An experimental run consisted of heating the outgassed specimen to above 1600°C., isolating the system, introducing a small quantity of nitrogen and making pressure readings as a function of time in both a rising and a falling series of temperatures. Additional nitrogen would then be metered into the system and the procedure repeated. At sufficiently high nitrogen contents or low temperatures, reversible nitride precipitation was evidenced by the constancy of pressure as a function of nitrogen content and the change of emissivity due to the precipitate at the surface.

The internal friction of the outgassed specimens was measured prior to doping, and after doping (for low nitrogen contents only) to monitor the level of nitrogen and oxygen in solution. The specimens were radiation quenched and took several minutes to reach room temperature. A torsion pendulum operating at the natural frequency of approximately one cycle per second was used in a vacuum of about 10^{-3} torr to prevent contamination. The data of Powers and Doyle(1) for nitrogen and Powers and Doyle(2) for oxygen was used to convert from peak internal friction to interstitial content. Microhardness readings were taken on the lateral surface of the wires using a Knoop indenter with a 1000 gram load. Where this method was found unsatisfactory due to surface roughness, bent wires, and brittle behavior, segments of the specimen were mounted in bakelite and ground flat and hardness readings were taken on the longitudinal section. The wires were examined metallographically after the thermodynamic measurements to determine the extent of precipitation during the cooling of the wires from the reaction temperatures.

4. Experimental Results

The ease of atmospheric contamination of refractory metals is illustrated for pure columbium in Figure 1 which compares internal friction curves for as-swaged, annealed at

1100°C. at 10^{-6} torr for one hour, and properly outgassed specimens. By comparing curves A and B it may be inferred that the large oxygen damping peak at about 150°C. is due to the fact that the 1100°C. treatment was sufficiently high to allow the solution of the oxide film in the metal resulting in a much higher oxygen content than the starting material. Curve C for a specimen outgassed as described under "experimental procedure" has internal friction peaks at 150°C. and 250°C. whose heights indicate less than 50 wt ppm of oxygen and 25 wt ppm of atomic nitrogen in solution. A Cb-.86% Zr specimen showed somewhat lower oxygen and nitrogen peaks after proper outgassing. This level of interstitial content is considered acceptable for these experiments, since it gives rise to an equilibrium nitrogen pressure below the sensitive measurement range of the McCleod gage. The lowest intentional nitrogen addition is more than a factor of ten greater than this residual nitrogen content. Curve D for a specimen doped with 750 wt ppm of nitrogen has a peak which indicates only about two-thirds this amount in solution. Metallographic examination revealed a substantial amount of precipitate, indicating that such a nitrogen solid solution is too concentrated to be successfully retained in the radiation quench employed for the specimen. A 1500 wt ppm specimen showed an internal friction peak even smaller than for the 750 wt ppm specimen, indicative of even more extensive nitride precipitation, undoubtedly due to the higher saturation temperature.

Knoop microhardness readings were made on the above two specimens and also on an outgassed specimen and the specimen for which the thermodynamic data had been determined, which contained 0.68 wt % (4.32 at %) nitrogen. The averaged readings for the ground and polished longitudinal sections were 107 KHN, 163 KHN, 142 KHN, and 178 KHN, for 0.004 wt %, 0.075 wt %, 0.15 wt %, and 0.68 % respectively. The specimens all had a bamboo structure with a grain size much larger than the size of the indentations. The somewhat lower hardness in the 0.15 wt % alloy is believed to result from the lower amount of interstitial nitrogen resulting from the larger amount of precipitation. The additional amount of precipitate did not compensate for the decrease as it did for the 0.68 wt % specimen.

Figure 2 presents a comparison of the thermodynamic data obtained in the present work with that obtained by Cost and

Wert$^{(3)}$ for slightly different columbium stock (Table 1). Table 2 contains a tabulation of the heat of solution of nitrogen gas in columbium, ΔH_N, which is calculated from the slope of the log p vs. 1/T curves. The values tend to increase slightly with nitrogen content, in contrast with the values of Cost and Wert which varied about an average value of -45.4 Kcal/gm atom of N. The latter value is somewhat lower than -46.0 reported by Cost and Wert since they disregarded the value for the lowest concentration of nitrogen. They justified this on the assumption that the readings were taken rapidly with a cold cathode ionization gage to minimize the pumping effect of the gage. They thus felt that equilibrium was not obtained for these measurements. The present results also exhibit a low value for the low concentration of nitrogen, however in this case all pressures were measured with a McCleod gage. On the other hand, this value would be expected to be somewhat low, because it is derived from the lowest pressure data where the gage would be less sensitive and outgassing of the system walls would be a more serious problem. The agreement in heat of solution average values for the two investigations is considered quite reasonable, assessing the uncertainty as plus or minus two or three Kcal/gm atom. A comparison of the curves for 1.3 at % N is made in Figure 2, illustrating that the data are in close agreement at this composition. At lower nitrogen contents their lines are somewhat below and at higher nitrogen contents are somewhat above the present data.

The limit of solid solubility represents the point at which the nitride Cb_2N starts to precipitate, which is detected as the point on the curves at which the pressure becomes dependent only on temperature and not on nitrogen content. The locus of these points is the line of smaller negative slope in the upper right of Figure 2. The heat of formation of Cb_2N is calculated from the slope of this curve. The magnitude of the solubility determined by Cost and Wert is in good agreement with the present work, but their value for the heat of formation of Cb_2N (-67.± 2 Kcal/mole) is higher than that found here (-57.4 Kcal/mole). In consideration of the different columbium stock, different McCleod gage and slightly different experimental apparatus and procedure, it is felt that the agreement between these values is reasonably good. It may be noted here that Mah$^{(4)}$ has reported a value of

-61.± 1.0 Kcal/mole for the heat of formation of Cb_2N at 298° K., as determined by bomb calorimetry.

The simple formulation of Sieverts' law requires that at a given temperature the equilibrium nitrogen pressure is proportional to the concentration squared. Thus a log p vs. log $x_{\underline{N}}$ plot should be linear and ideally would have a slope of 2. Isothermal pressure-composition values taken from the curves of Figure 2 are plotted in Figure 3, along with a line of slope 2. It may be seen that Sieverts' law is not followed precisely since the slope is a function of composition. It may be noted that the concentrations involved extend outside the range for which the simple theory, which assumes random distribution and regular solution behavior, would be expected to hold. The data of Cost and Wert taken at constant temperature are in better agreement with Sieverts' law, however the slope does vary with temperature.

The heat of solution of the nitride in the solid solution may be determined from the data in two ways. For this reaction

$$Cb_2N \rightarrow 2Cb + \underline{N}$$

$$\Delta F^\circ = -RT \ln a_{\underline{N}} \approx -RT \ln x$$

$$\frac{\delta\left(\frac{\Delta F^\circ}{T}\right)}{\delta\ 1/T} = \Delta H^\circ = -R\frac{\delta \ln x}{\delta\ 1/T}$$

where x is the at % nitrogen in equilibrium with Cb_2N; i.e. at the solubility limit. From the slope of the plot of ln x vs. 1/T this heat of solution was determined to be 19.7 Kcal/mole. The other way of determining this quantity is by combining the two previously determined heats as follows:

$$\begin{array}{ll}
1/2\ N_2(g) \rightleftharpoons \underline{N} & \Delta H = -\ 40.4\ \text{Kcal.} \\
Cb_2N \rightleftharpoons 2Cb + 1/2\ N_2(g) & \Delta H = +\ 57.4\ \text{Kcal.} \\
\hline
Cb_2N \rightleftharpoons 2Cb + \underline{N} & \Delta H = +\ 17.\ \text{Kcal.}
\end{array}$$

The agreement between the values is as well as may be expected considering that neither method of determining it is as accurate as for the other heats. Cost and Wert reported a graphical heat of solution of 20. Kcal and the one calculated by difference as 21. ± 2 Kcal. The data of Albrecht and Goode(5) and Elliot and Komjathy(6) yield values of 13. Kcal. and 12. Kcal. respectively.

Figure 4 presents the p-T-x data for the Cb-.86% Zr alloy (Table 2). For any composition inside the solubility limits of the single-phase region log p is linear with 1/T, the slopes giving the heat of solution of nitrogen in the Cb-.86% Zr alloy, ΔH_N (.86 Zr). These values, listed in Table 2, are consistently lower in magnitude than those for the pure material, averaging 38. vs 40. Kcal. for the pure columbium stock used in this investigation. Interpretation of this small difference will depend on future work with the other alloys containing varying amounts of zirconium. The most outstanding difference in behavior of the ternary alloys and that of the binary alloys is found at low nitrogen concentrations. Here the ternary alloy curves fall significantly below those for the pure columbium. In other words, the presence of zirconium allows the nitrogen to be held in solution at a lower equilibrium pressure i.e. activity, at least at low nitrogen contents. At a particular high nitrogen content, however, the log p vs. 1/T curve for the ternary alloy would be closer to that for the binary alloy, except that its slope would be lower. The Sieverts' law plot for the ternary alloy, Figure 5, has a slope very close to the ideal value of 2.

The determination of the solubility curve in the ternary alloys is not as accurate as for the binary alloys since it is necessary to obtain equilibrium with respect to zirconium content as well as with respect to nitrogen content. Thus for a given nitrogen content, when the nitride solubility limit is approached, the nitride which forms is probably in equilibrium with respect to the nitrogen content of the solid solution, but not with respect to the zirconium content. As the zirconium slowly diffuses to reach equilibrium, the nitrogen also must be continually redistributing itself. Even if equilibrium were maintained at all times, in a two-phase region of a ternary, the equilibrium nitrogen pressure would vary with nitrogen content at constant temperature. This is due to the fact that the tie lines in the $\alpha + Cb_2N$ phase field would not necessarily be parallel to the line along which the nitrogen content is being changed (i.e. the line at 0.86% Zr). Thus, as nitrogen is added in the two-phase region, tie lines are being crossed and the equilibrium compositions continually change.

The curves of constant composition in Figure 4 do not all merge into the nitride solubility curve as in the binary, but merely show a change in slope indicative of the formation of the first, non-equilibrium precipitate. From the locus of points at which precipitation begins a heat of formation of Cb_2N of -45.Kcal/mole has been determined. This would give a value of 45. -38. = 7 Kcal/mole for the heat of solution of this nitride in the solid solution. This value, though inaccurate, is less than one-half the heat of solution found for the binary Cb-N alloys. It is in closer agreement with the low temperature heat of solution value of 5.Kcal/mole determined by Cost and Wert and Ang and Wert(7) from internal friction data. Further research involving more extensive data on more zirconium ternary alloys is needed to complete the interpretation of these results.

5. Recommendations for Future Work

The present findings demonstrate that the investigation of other ternary alloys might be fruitfully pursued using the same technique for obtaining the thermodynamic data. Several possibilities would have both practical and theoretical value. The Cb-Zr-O system should be explored, and the choice of a different substitutional element would logically be made from the refractory transition elements. Other properties and characteristics of the alloys herein studied should be investigated. In particular, the aging behavior should be determined and the identification of the stable and metastable nitrides should be made. The mechanical properties of the alloys need to be determined with a thought to the identification of the role which zirconium plays in affecting the distribution of nitrogen in solution. The ternary alloys may aid in interpreting and understanding the many effects which interstitial elements have on mechanical behavior of B.C.C. elements.

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Table 1. Chemical Analysis

	Form	Source	A			
			O	N	H	C
Cb	Rod	Wah Chang	.0093	.0048	.0003	.0043
Zr	Rod	Carborundum Metals		.0059		.03
Cb-.86 Zr	Wire	Kawecki	.0313	.0033		.0041
N_2	Encapsulated	Union Carbide		>99.99		
Cb	Ingot	Wah Chang-Temscal	estimated to be about .015 wt % total			

sis of Materials

Analysis (wt %)								BHN
	W	Ta	Zr	Ti	Hf	Fe	Others	
43	.021	.058	.027	.004	.008	.005	<.096	155
	<.002		<97.7	.0035	2.	.13	<.17	143
11	<.05	.11	.86	.0242		.0022		
	<.03	<.1						

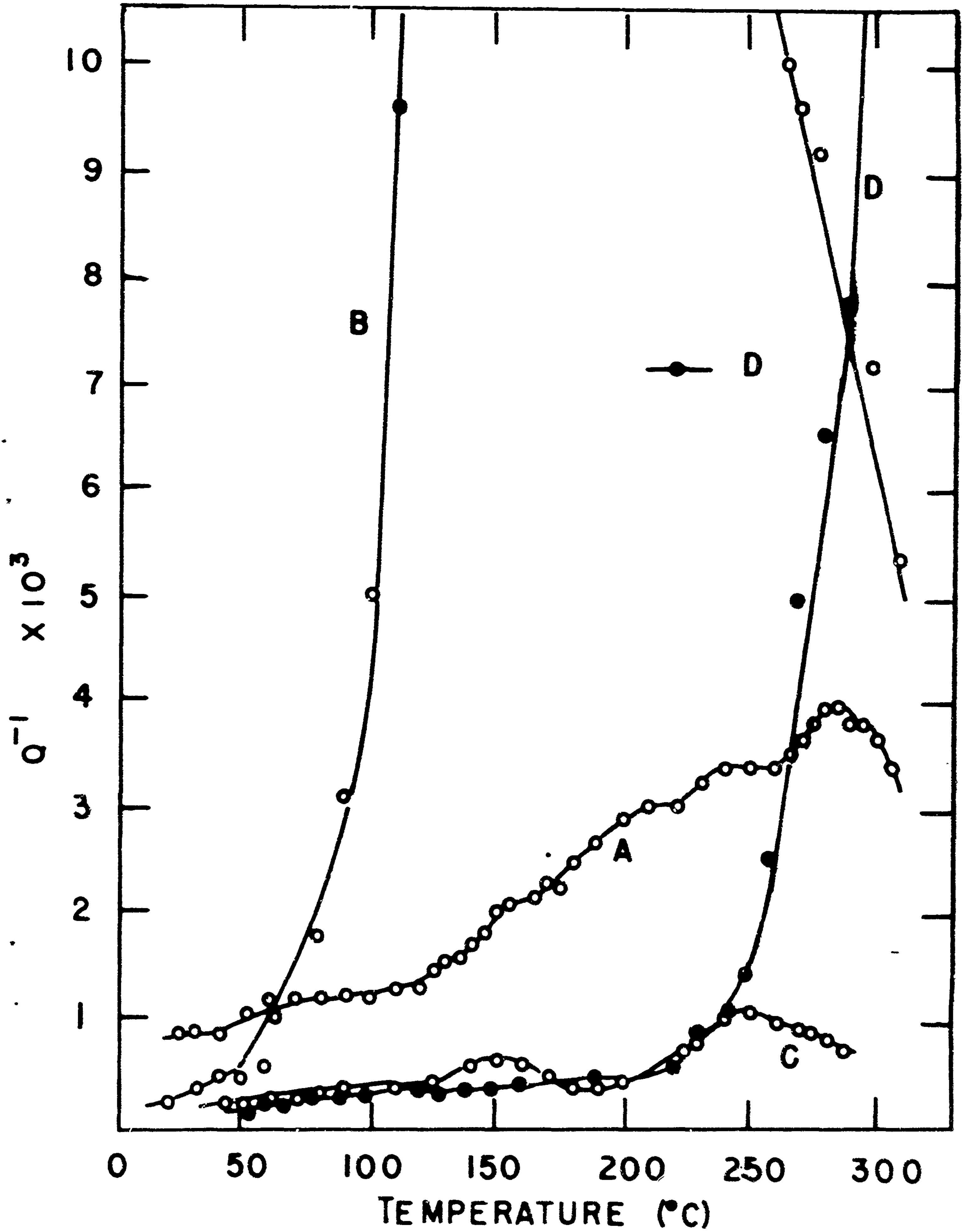

Fig. 1 Internal friction vs. temperature for various treatments of columbium. A. as-swaged. B. annealed 1 hour at 1100°C. at 10^{-6} torr. C. annealed 10 hours at 2000°C. at 10^{-6} torr. D. doped with 750 wt ppm of nitrogen after treatment C.

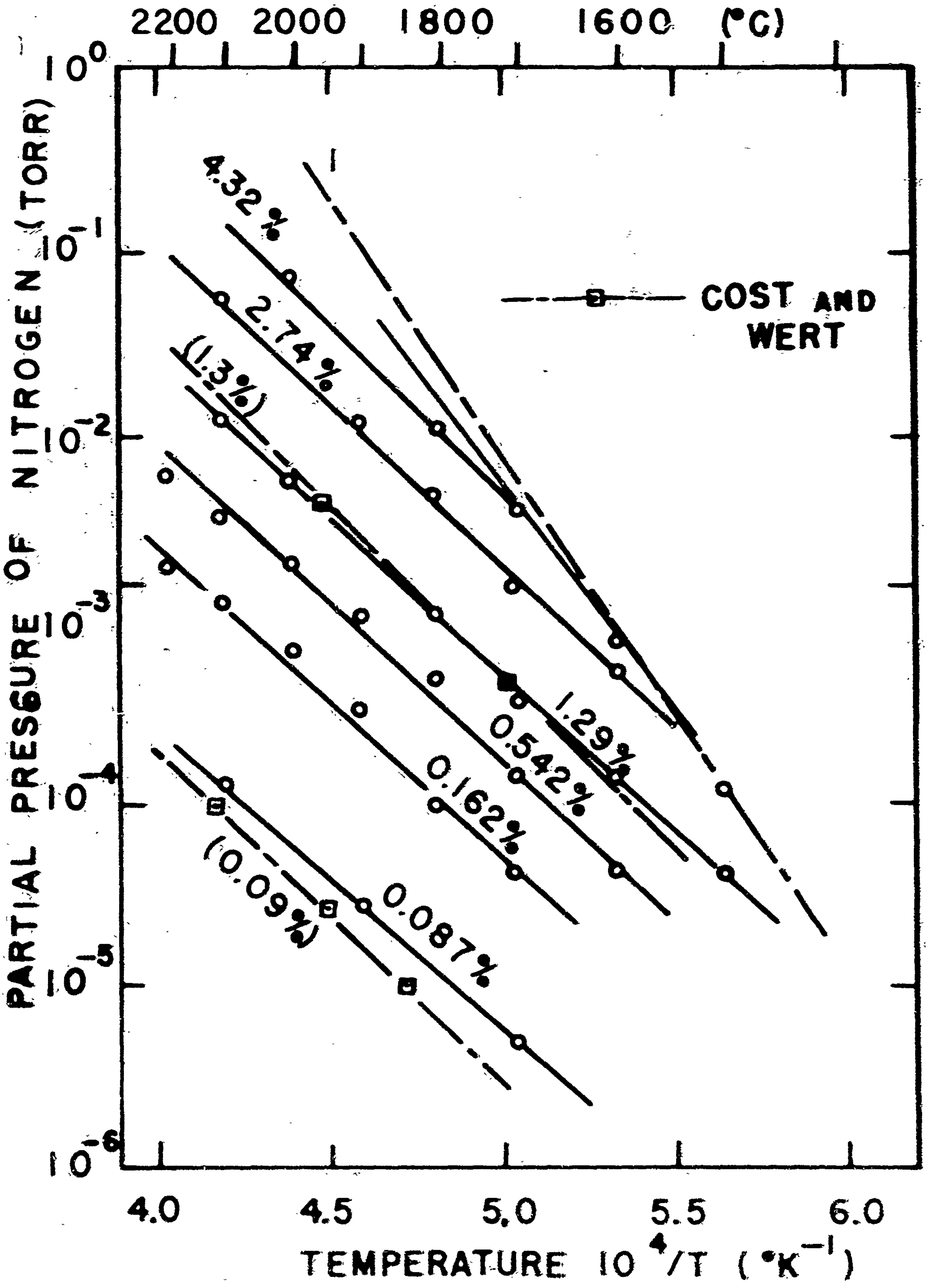

Fig. 2 Equilibrium nitrogen pressure vs. reciprocal temperature for columbium doped with various at % nitrogen

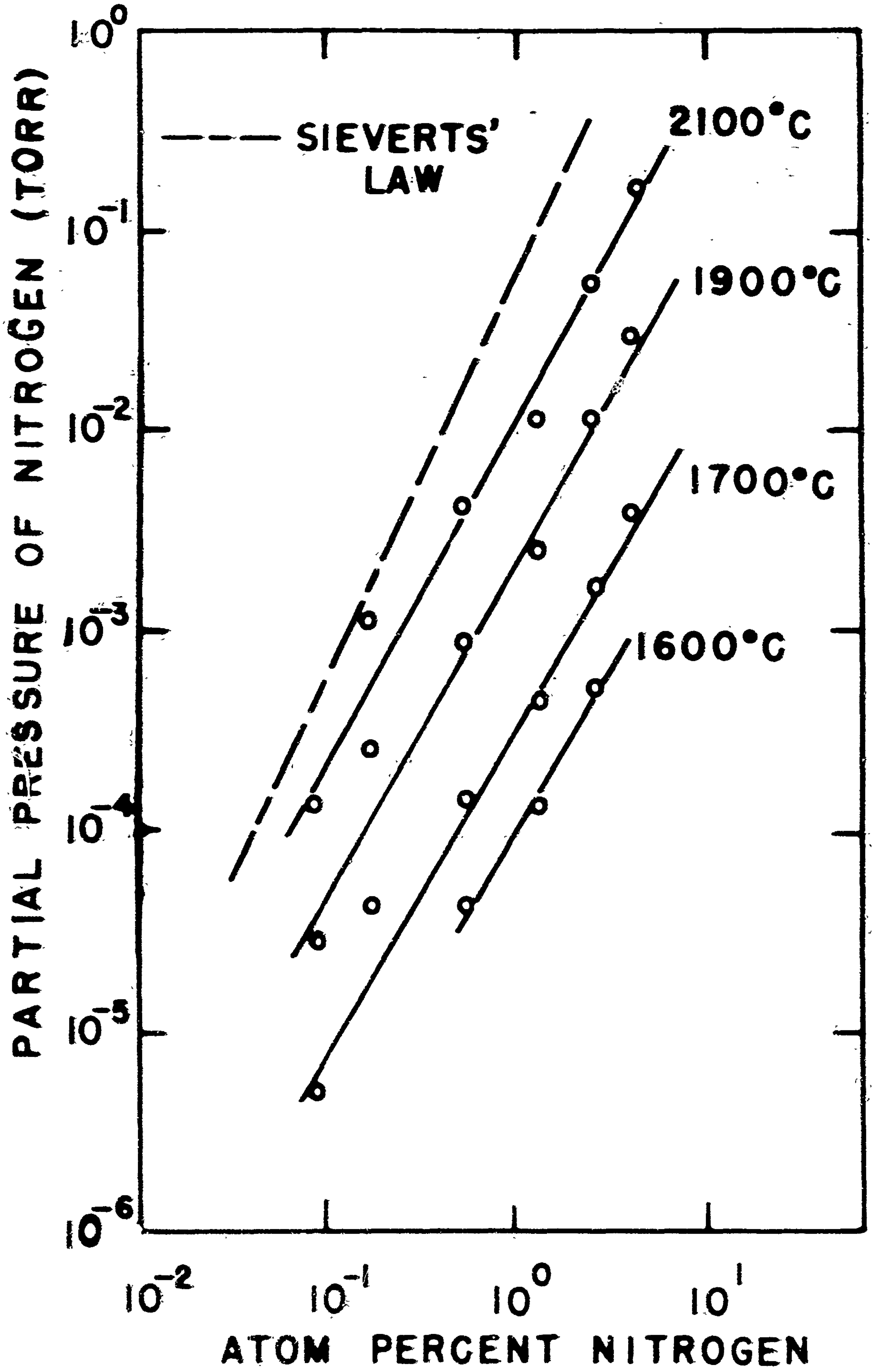

Fig. 3 Equilibrium nitrogen pressure vs. at % nitrogen in columbium at various temperatures

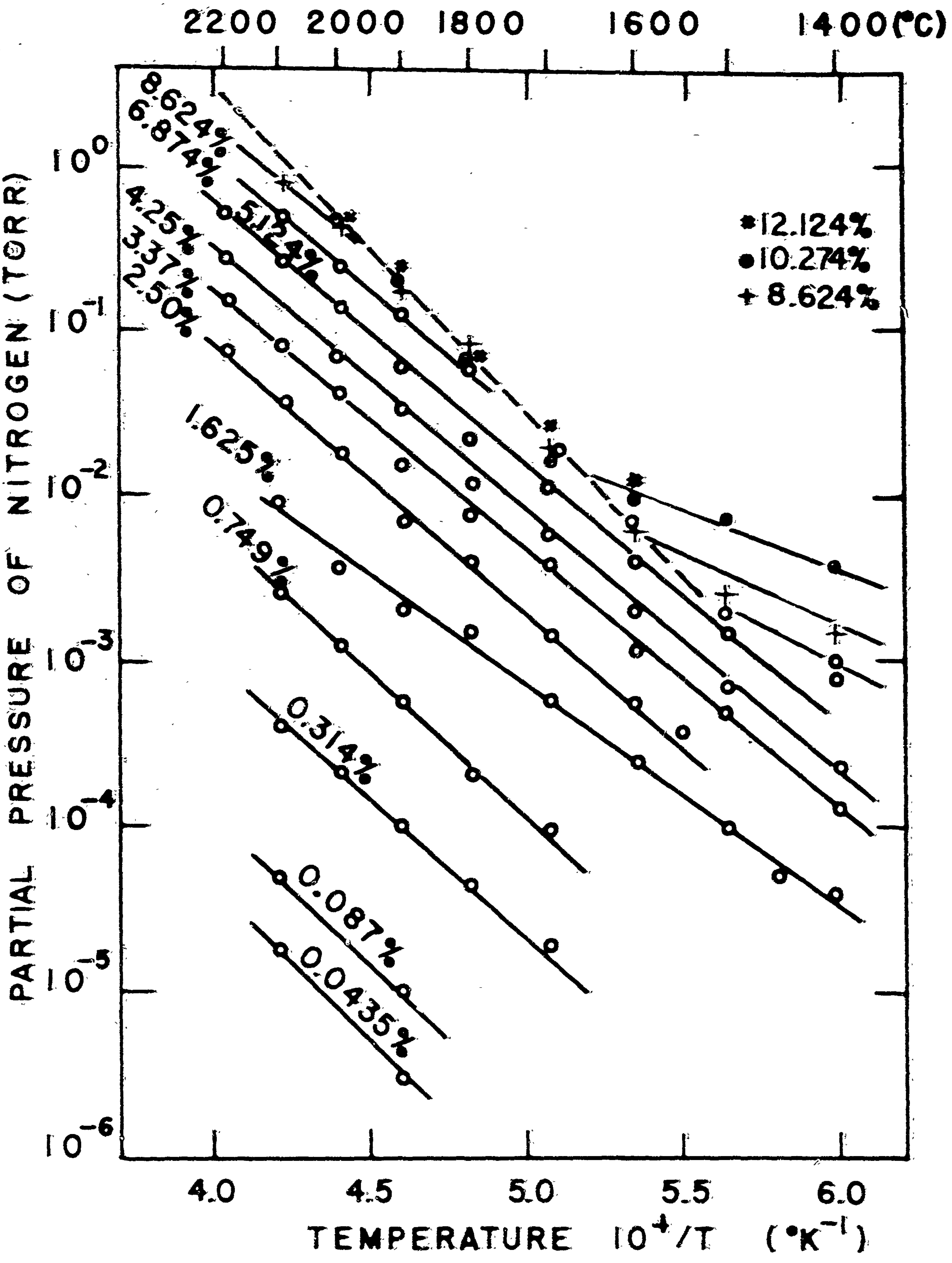

Fig. 4 Equilibrium nitrogen pressure vs. reciprocal temperature for Cb-.86% Zr alloy doped with various at % nitrogen

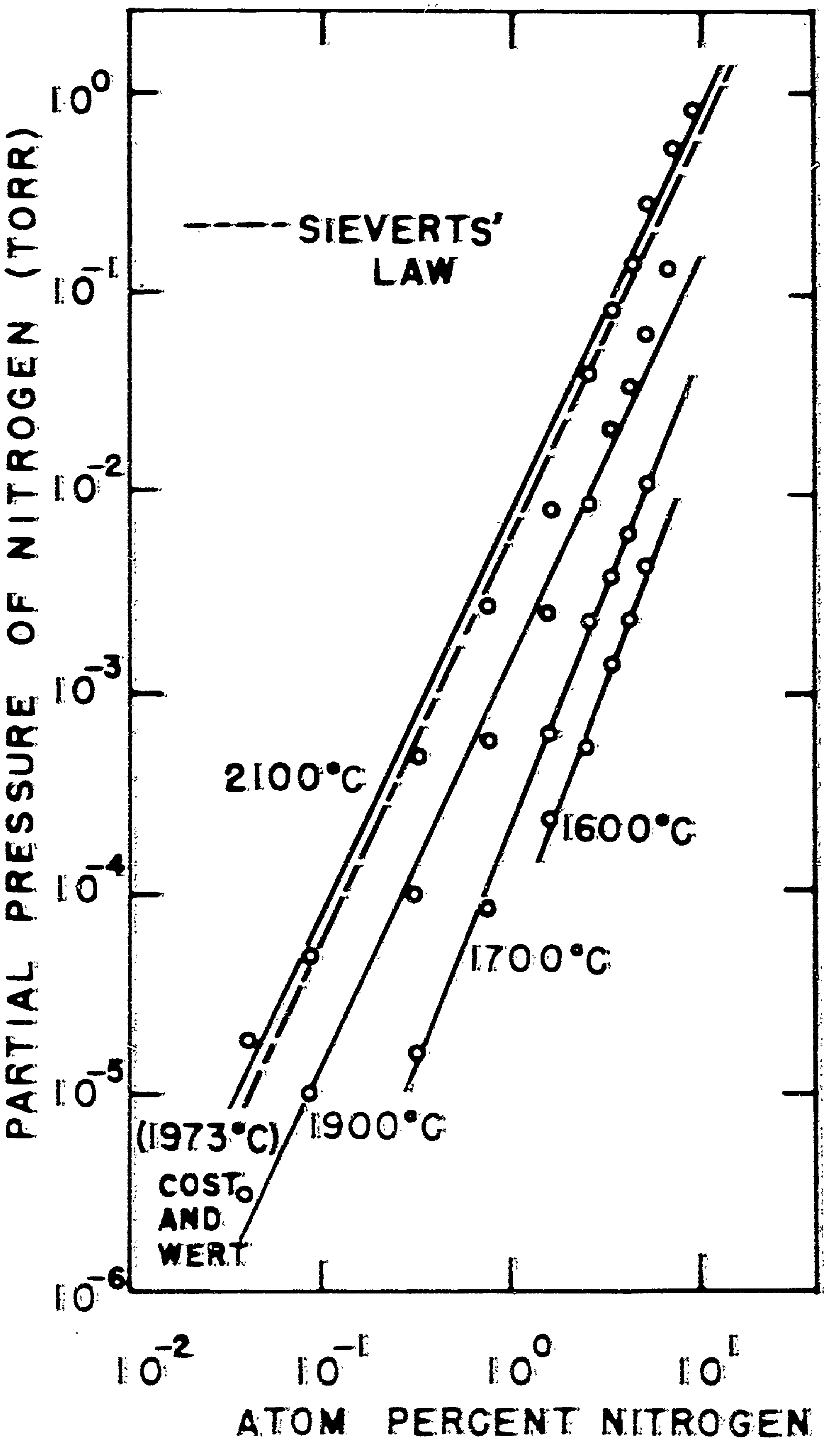

Fig. 5 Equilibrium nitrogen pressure vs. at % nitrogen in Cb-.86% Zr at various temperatures