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MICROPROBE ANALYSIS OF PHASES IN Nb-N ALLOYS

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June 1969

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I. INTRODUCTION

General interest in the refractory metals stems from their high melting points, strength at elevated temperatures, corrosion resistance, superconductivity and nuclear properties. The light elements hydrogen, carbon, oxygen and nitrogen which dissolve interstitially in these B.C.C. metals have the potential for improving the mechanical properties, but they can also adversely affect these properties. Several of these gas-metal systems have been studied by various methods including X-ray analysis, chemical analysis, metallography, anelastic methods, and gas pressure equilibrium studies. The present study is concerned with chemical analysis of the phases in dilute Nb (niobium)-N (nitrogen) alloys using the electron beam microprobe technique.

The Nb-N system contains several nitride phases, but it is the one which co-exists with the terminal solid solution which could possibly result in an improvement in mechanical properties and was therefore studied in this work. The phase equilibrium between the terminal solid solution and the nitride, Nb_2N , in Nb-rich alloys has been reported.¹⁻⁶ Nb_2N has a hexagonal close-packed structure, and is reported to have a temperature dependent composition. The limit of solubility of Nb_2N in the Nb solid solution has been determined in gas-metal equilibrium studies from 1550°C to 2100°C. Internal friction results on specimens quenched from temperatures up to 800°C indicated changes in heats of solution occurring in the solvus at around 800°C. However, the phase Nb_2N , existing at high temperature, is believed to be the same as that

in equilibrium at lower temperatures.³ It is one of the purposes of this study to measure the composition of both the Nb_2N precipitate and the Nb solid solution in equilibrium² with it in the temperature range from 800°C to 1200°C. This will be done by electron beam microprobe analysis of specimens equilibrated in this temperature range. The Nb rich portion of the Nb-N phase diagram is shown in Figure 1.³

Upon cooling of the solid solutions from high temperatures precipitation of Nb_2N may proceed in at least two modes, discontinuously and continuously, according to the particular composition, annealing temperature, and cooling rate.⁷ Furthermore, the effect of a third element, Zr (zirconium), is reported to have an influence on the precipitation of nitride, and therefore some effect on the properties of alloys.⁷ This behavior will also be examined herein by establishing the Zr distribution between precipitate and matrix in an Nb-N alloy containing Zr.

The application of the electron beam microprobe analyzer to these problems follows from its versatility in studying very small areas no larger than a few microns in diameter in a metallographic sample. The quantitative aspects of the analysis are the most important. The principle which allows the use of the characteristic X-ray lines of a given element to deduce composition is given by an excerpt from the pioneering work of Castaing.⁸ "In this new method the concentration of an element A in a given alloy is deduced from a comparison between the intensity I_A of an important characteristic line of element A emitted by the alloy under given conditions of electron bombardment

Figure 1. Solubility of Nb_2N in niobium according to Cost and Wert³.

and the intensity $I(A)$ of the same characteristic radiation when emitted by the pure element A under the same electron bombardment conditions."

The components of the electron microprobe analyzer include the main electron beam housing and generating equipment, specimen holding facilities with optical access and mechanical traversing provisions, one or more X-ray spectrometers and associated scalers and electronics, electron back-scatter detector and electronics, and meters for sample current and beam current. Much of the beam housing and spectrometer housing may consist of a large vacuum tank.

The principal of operation is briefly reviewed here. A well polished specimen is inserted into the sample holder within the vacuum chamber. A focused beam of electrons accelerated by voltages up to 50 kV is allowed to impinge on a selected area of the sample or it may be scanned across the sample. The X-rays from the sample are monitored by a spectrometer or spectrometers previously tuned to the characteristic X-ray wavelengths as determined from standard samples containing the elements to be analyzed for. The emission of the unknown is monitored under identical conditions of time interval, excitation potential, beam current and spectrometer setting as the standard. Further readings are taken on standard and unknown with the same parameters except that the spectrometers are detuned to wavelengths off the peak intensities to obtain background data. In order to quantitatively determine composition, appropriate steps must be taken to correct the raw intensity ratios for back ground, detector deadtime, drift,

contamination, fluorescence, absorption, and differences of average atomic number between the standard and unknown. The validity of the chemical analysis is critically dependent on the proper application of these corrections.

Before developing the theory of the method and the corrections which must be made to the raw data, some definitions must be made. These pertain to experimental quantities and to the physics of the excitation and absorption processes and will be presented in that order. The *peak* intensity for a particular element is the counting rate measured when the spectrometer is set to the Bragg angle of diffraction for a characteristic wavelength of the element. This peak position is obtained by scanning the counter and analyzing crystal through a range of Bragg angles and recording counting rate vs. angle. There is inevitably a *background* intensity level due to continuum radiation, overlapping characteristic radiation, cosmic radiation, and electronic noise. This background is measured with the counter at angular positions above and below the peak position at a distance equal to $5/2$ the peak width at one-half the maximum intensity of the peak (fwhm). The mean value of intensity at these two points is taken to be the background at the peak position. A *minimum detectable limit* is defined as a value of intensity above which the presence of the element is assured; in practice, the intensity at three-sigma from the peak of the distribution curve is used. The other instrumental corrections are for drift, deadtime in the detector, and surface contamination of the

specimen. *Deadtime* may be experimentally obtained and used to correct for the insensitivity of the detector to X-ray photons which arrive at the detector in the same small time interval. This correction raises the experimentally measured counting rates. The *drift* correction, though often ignored, is due to change in the electron beam current during the time when the necessary intensity readings are being made. This drift is compensated for by monitoring the electron beam current and normalizing all readings to the same beam current. *Contamination* due to cracking of oil and deposition of carbon on the sample gives an absorbing and emitting layer on the specimen which changes with time. The beam current, excitation potential, and time of analysis at a given spot influence the contamination rate. This fact is considered in the selection of these quantities. Maintenance of a good vacuum ($<10^{-5}$ Torr) and cold-trapping the diffusion pump decrease contamination.

The remaining corrections are termed *interaction corrections* because they pertain to the interaction of the incident electrons and generated X-rays with the atoms of the sample. The incident electrons collide with the electrons in the sample and are either slowed down or back-scattered from the surface. The *atomic number correction*, compensates for the efficiency with which the electron beam penetrates and fluoresces the sample. The X-rays generated within the sample are then partially absorbed before they leave the sample, and this is compensated for by an *absorption correction*. A third correction, called a *secondary fluorescence correction*, is used because the absorbed X-rays from some elements excite somewhat lower energy X-rays from other

elements. A complete expression for the weight fraction of element A is given in terms of a measured intensity ratio between the unknown and the standard, (K) corrected for instrumental errors and the correction factors named above:

$$C_A = K \frac{f_{a,s}(\chi)}{f_{a,u}(\chi)} \frac{1}{1 + k_{fA}} \frac{R_s}{R_n} \frac{(\bar{z}/A)_n (7.061 + \ln \bar{E} - \ln \bar{J}_n)}{(\bar{z}/A)_s (7.061 + \ln \bar{E} - \ln \bar{J}_s)}$$

Concentration of Component A = [Intensity Ratio] x [Absorbtion Correction Factor] x [Fluorescence Correction Factor] x [Atomic Number Correction Factor] (1)

Where subscripts A refer to element A, s to the standard, and u to the unknown. The Appendix discusses these factors more fully and gives references to the literature.

K = Ratio of Unknown and Standard X-ray Intensities, normalized to a beam current and corrected for counting losses.

$$\chi = \sum_i \left(\frac{\mu}{\rho} \right)_i^A C_i \operatorname{cosec} \theta$$

$\left(\frac{\mu}{\rho} \right)_i^A$ is the mass absorption coefficient of the *i*th element for A radiation,

C_i is the weight fraction of the *i*th element,

θ is the X-ray take-off angle.

k_{fA} = The secondary fluorescence contribution to the intensity of the A radiation from the other elements in the unknown and hence a function of voltage, composition, and all related factors.

(Cf. appendix)

R = backscatter loss factor: the term which corrects for the electrons lost from the specimen surfaces. It is a function of z , A , E , and E_c .

z = atomic number

$$\bar{E} = (E_o + E_c)/2.$$

E_o = electron beam voltage

E_c = X-ray line excitation voltage.

$\bar{J}$ = the mean ionization potential of the elements, which is not constant, but varies with J/z .¹⁰

A = atomic weight of element A .

The terms in brackets, the absorption factor, the fluorescence factor, and the atomic number factor, respectively, are functions of the amount of A in the unknown. (A recent review paper¹¹ contains more detailed discussions of these factors.) Hence this calculation gives C_A only to a first approximation, and this value of C_A , now different from K , is put back into the calculation and the process is iterated until the difference between $(C_A)_j$ and $(C_A)_{j+1}$ is less than some specified number, typically 0.05%. As can be seen, considerable supplementary information is needed for the quantitative analysis.

The application of the microprobe analyzer to light element analysis is not new and analyzing crystals having the necessary large lattice spacing have been produced. However, the quantitative analysis for very light elements such as carbon, nitrogen, and oxygen has not been successful, because most of the theories developed for the corrections did not apply at their long characteristic wavelengths (20-50Å)

and there was little understanding of the absorption process for these wavelengths. Initial attempts to correct microprobe data on light elements with the absorption values based on extrapolated quantities resulted in large errors of up to two times the true value in many cases. Lack of data and the use of improperly extrapolated values caused much of the error. The low level of fluorescent emission from the light elements compounds the problem, necessitating long counting times, which increases the chance for contamination. Nondispersive detectors alleviate part of the counting rate problem, but since they separate energies electronically instead of by crystal diffraction, their resolution is poorer and a serious background problem is made worse. In the present work the better resolution of crystal analysis is favored over the higher counting rates of the nondispersive detector.

Recently Gray¹² has developed a set of absorption values for the light elements, as well as the microprobe and computer technique to handle them. In his work, the general pattern of attack consists of counting for long times and reducing the excitation voltage so that only the layers near the surface of the sample are probed. The background intensity for the standards is obtained by actual measurement, however the background for the unknown is synthesized from the backgrounds on the standards and the first approximation of composition of the unknown. This results in a greatly reduced time for an analysis and a proportionate reduction in error due to contamination. For example, to construct the background reading for the B analytical line of an unknown alloy containing A and B, intensity readings are made in the

following way: Measure intensity at the B analytical line on the A standard and the intensity at each side (peak angle $\pm 5/2$ FWHM) of the B analytical line on the B standard. These background readings for the standards are weighted according to the approximation of composition of the unknown, (the count ratio K) to give the synthesized background reading for the B line of the unknown. This constructed background may still be in error from two causes: for a compound B standard (CB) the C element may give an intensity contribution around the B line in the standard, and/or, an element D in the unknown may give an intensity around the B line in the unknown. Such interferences were sought, but not found, in the present work.

II. EXPERIMENTAL PROCEDURE

Specimen Preparation

Niobium rod produced by the Wah Chang Corp. was swaged to 0.035 in. wire, and the same size Nb wire with 0.86 wt.% Zr was purchased from the Kaweki Chemical Co.* The thermodynamic properties of the alloys with N have been determined using the same stock of material.^{3,13} The wires were nitrided at 1800°C after being outgassed at 2100°C for 2 hours in the 10^{-5} torr range, as described elsewhere.⁷ Two binary nitrogen alloys, nominally 2.0 wt.% N and 0.3 wt.% N were made, and about 3.6 wt.% of N was introduced into the Nb 0.86 wt.% Zr wire. The Zr containing wire was at 1800°C continuously for about 24 hours during the nitriding. The Nb-2.0 wt.% N alloy, radiation cooled from 1800°C was held at 1270°C for 180 sec and then quenched in dry helium. The other two alloys were directly quenched from the nitriding temperature. The Nb-0.86 wt.% Zr alloy was examined only in the helium quenched condition. The other alloys, however, were subsequently divided into small lengths, encapsulated in quartz, and annealed for extended periods of time at 800, 1000, and 1200°C to allow equilibration between the precipitated nitride phase and the solid solution. The annealing times

* The ingot analysis in weight percent are: Wah Chang - Nb, 99.762; O, 0.0093; N, 0.0048; H, 0.0003; C, 0.0043; W, 0.021; Ta, 0.058; Zr, 0.027; Ti, 0.004; Hf, 0.008; Fe, 0.005; others, < 0.096.
Kaweki - Nb, 98.915; O, 0.0313; N, 0.0033; C, 0.0041; W, < 0.05; Ta, 0.11; Zr, 0.86; Ti, 0.0242; Fe, 0.0022.

were chosen two or three orders of magnitude greater than the time needed for a nitrogen atom to diffuse to the precipitate particles. For example, using published values for $D(=0.0086 \exp(-34,920/RT)^{13})$, for $(\bar{X}^2)^{1/2} = 10$ microns and $T = 1050^\circ\text{K}$, the computed time is 18 min. Table I shows the specimen temperatures and annealing times used to produce equilibrium precipitate of nitride. Although oxygen diffusion is rapid enough to allow its diffusion throughout the specimens, probe analysis for oxygen demonstrated that the quartz capsule provided protection sufficient to prevent this contamination. The specimens were quenched in water after these anneals by simultaneously submerging and breaking the capsules.

TABLE I

Annealing Times and Temperatures for Nb-N Alloy

Specimen	Nominal N Content (wt.%)	Annealing Time (Hours)	Temperature ($^\circ\text{C}$)
1a	2.0	268	800
1b	2.0	116	1000
1c	2.0	60	1200
2a	0.3	120	800
2b	0.3	95	1000
2c	0.3	48	1200

The quenched specimens were mounted in a conductive resin to facilitate the probe analysis. They were polished through the 1/4 micron diamond wheel manually and then vibro-polished with 0.3 micron alumina. The polished specimens were etched to give the best definition of individual phase particles for optical examination. Since it is

desirable to have a flat surface for microprobe analysis, the specimens were repolished with 1 micron diamond, etched lightly in concentrated HF to delineate the areas of interest, rinsed in alcohol, and immediately put in the evacuated specimen holder in the microprobe. In order to get the most reproducible intensity readings, it was found necessary to completely eliminate the use of water and minimize the exposure to air after the final light etch.

The metal standard specimens used were 99.98 per cent pure Nb metal and 99.98 per cent pure Zr metal. They were ground and polished through 1 micron diamond without the use of water in the cleaning and polishing operations. The N standard substance was single-crystal, oxygen-free aluminum nitride. This compound was chosen as a standard because it was the most suitable of the various compounds available. Count rates could not be reproduced at a given spot on a BN (boron nitride) specimen, and large apparent composition variations occurred from spot to spot. A single crystal of TiN (titanium nitride) behaved similarly. At 5 to 15 kV excitation, count rates from the aluminum nitride crystal varied less than from the other compounds. The greatest variation in apparent nitrogen concentration was found at 5 kV excitation and the electron beam penetrated through the thin crystal at 15 kV, yielding copper X-rays from the substrate. Hence the analyses were run at 10 kV, but appreciable variations in count rate from spot to spot still appeared. Only those particular analyses with large N count rates

were used. The aluminum nitride standard itself was analyzed qualitatively and was found to contain a small amount of silicon. Pure aluminum and silicon were used as standards to make a quantitative analysis for these elements in the nitride, and the nitrogen concentration was determined to be 60.4 wt.% (91.0 at.%). The choice of a standard substance for light element analysis is a difficult one. Even for carbon analysis where "pure" graphite or diamond is used, the counting rates for $CK\alpha$ have been found to vary widely. The aluminum nitride was not polished prior to use since its as-grown surface was flat.

In the Nb-N alloys, annealed at 800°C, 1000°C, and 1200°C (Figures 2,3), matrix areas and somewhat spheroidized precipitates were the two phases analyzed. In the Nb-0.86 wt.% Zr-3.6 wt.% N alloy, Figure 4, the outer cracked rim, A, the solid light layer, B, the needles which formed by growth and discontinuous precipitation in layer C and the grain boundary, E, were analyzed. The Widmanstätten precipitates and the matrix surrounding both them and the grain boundary nitride in layer D were analyzed.

Electron Probe Analysis

The analyses were carried out on an Applied Research Laboratory EMX electron microprobe analyzer at 10 kV electron beam accelerating potential. This low excitation potential was chosen because it was the optimum one for the aluminum nitride standard and also because it generated fluorescent radiation in the unknown only near the surface

Figure 2. Niobium-2.0 wt.% nitrogen alloy annealed and quenched from various temperatures: A, 800 C, B, 1000 C, C, 1200 C. Magnification 500X; etched in 95 HF, 5 HNO₃, parts by volume.

Figure 3. Niobium-0.3 wt.% nitrogen annealed and quenched from various temperatures: A, 800 C, B, 1000 C, C, 1200 C. Magnification 500X; etched in 65 HNO_3 and 35 HF for 1/4 sec.

Figure 4. Niobium-0.86 wt.% zirconium-3.6 wt.% nitrogen alloy with a non-equilibrium distribution of nitrogen. The areas marked A, B, C, D, and E, are described in the text. Unetched; magnification 240X.

of the sample and minimized both the absorption correction and excitation of the material below the precipitates. The disadvantage of the lower excitation voltage was that the analyses were more sensitive to surface contamination and charge build-up on the poorly conducting nitride particles. At low beam energies, the surface charge tended to push the beam off the edge of small particles. Large particles were selected to minimize this.

Counting times of 100 seconds were used for each position of the beam on the specimens to establish statistically significant information. The total number of nitrogen K α peak counts after 100 seconds on the aluminum nitride standard was typically 60,000, compared to a background of 15,000, giving a calculated peak to background ratio of 4 to 1. Drift of the beam current during the long counting times was corrected for by digitizing and recording the beam current during each analysis, and normalizing all intensity readings to the same beam current. The detector slit-width which determines the spectrometer resolution was 0.020 inches. The X-ray lines used in this analysis were the Nb L α (Nb L $\alpha_{1,2}$), N K α (N K $\alpha_{1,2}$), and Zr L α (Zr L $\alpha_{1,2}$), characteristic wavelengths. Three spectrometers having ADP (Ammonium-Dihydrogen-Phosphate), ADP, and PbSD (Lead-Stearate-Decoanate) crystals for wavelength discrimination permitted simultaneous measurement of all three elements. The detector was an argon and 10% methane gas filled proportional counter with a 2500 Å thick cellulose nitrate uncoated window. Pulse height discrimination was used in the nitrogen analysis

to exclude lines from Al, Zr, and Nb. Figure 5 gives typical spectrometer traces of the characteristic X-ray lines of the three elements being analyzed.

A summary of the procedure in analyzing for Nb and N in an Nb-N alloy is as follows:

1. The electron beam was focused and the beam current was selected to give the optimum count rate.
2. The first set of readings was the intensities of the peaks on the standards. The settings to obtain these are shown in Table II.

TABLE II

Spectrometer Settings for Standard Intensities

Specimen	Analyzing Crystal	Spectrometer Position	Wavelength (Å)	Bragg Angle
Niobium	ADP	Nb La	5.7240	32°33'
Aluminum Nitride	PbSD	N Ka	31.6037	18°23'

3. The second set of readings were to establish the background intensities for the standards and, by the procedure described above, for the unknowns. The settings to obtain these are shown in Table III.

TABLE III

Spectrometer Settings for Background Intensities

Specimen	Analyzing Crystal	Spectrometer Position	Wavelength (Å)	Bragg Angle
Niobium	ADP	Nb La $\pm 5/2$ FWHM	--	32°58', 31°54'
Niobium	PbSD	N Ka	31.6037	18°23'
Aluminum Nitride	ADP	Nb La	5.7240	32°33'
Aluminum Nitride	PbSD	N Ka $\pm 5/2$ FWHM	--	20°06', 16°45'

Figure 5. Spectrometer traces of N, Nb, and Zr X-ray lines, used for quantitative analysis. Arrows denote background positions.

4. The Nb L α and the N K α peak intensities were measured on the unknown.

5. All measured counting rates were normalized to the same value of beam current.

6. The data were corrected for deadtime (~ 2 micro-seconds per count) to obtain the true number of counts.

7. The background intensity was subtracted from the peak intensity for each analytical line on the standards and the unknown to obtain the counts due to the characteristic X-rays only.

8. The ratio, K, of characteristic X-ray intensity in the unknown to that in the standards was taken for the elements present. For the N, characteristic X-ray intensity from the standard was corrected for its weight percent N.

9. The K ratios were corrected according to equation 1, using the computer program described by Gray.¹² The calculation was iterated as described in section I to give the weight fraction of each element in the unknown.

For the ternary unknowns the number of intensity readings had to be increased considerably. There were now three peak intensities to be measured on the standards and unknown and, in order to determine the backgrounds, readings had to be taken at 12 spectrometer positions instead of the 6 positions listed in Table III for the binary alloys.

A typical calculation of the results on one precipitate particle in the Nb-2.0 wt.% N alloy is given as an example: Drift- and dead-time corrected readings at the characteristic wavelengths on the two

standards and unknown, and the readings on the standards at the de-tuned position of the spectrometers are given in Table IV.

TABLE IV

Intensity Readings on Standards and Unknown

Specimen	Spectrometer Position	Corrected Counts (per 100 sec)
Niobium Standard	Nb L α +5/2	2410.3
" "	Nb L α -5/2	2370.0
" "	Nb L α	89765.9
" "	N K α	2443.7
Aluminum Nitride Standard	N K α +5/2	616
" " "	N K α -5/2	1232
" " "	N K α	7551.2
" " "	Nb L α	408.7
Unknown	N K α	3157
"	Nb L α	82890

Calculations are made which yield raw intensity ratios of 0.9053 for the Nb and 0.0353 for the N. Corrections are applied in a re-iterative manner to obtain the actual composition of the precipitate. The "effective" corrections are ones which convert the raw intensity ratios to the actual composition values in one step and are shown in Table V and presented in more detail in the Appendix.

TABLE V

Factors of Absorption, Fluorescence, and Atomic Number in Nb-N

Factors	Values	
	Niobium	Nitrogen
Absorption	0.9966	2.8858
Fluorescence	1.0000	0.9996
Atomic Number	1.0205	0.7239
Product of Factors	1.0170	2.0882

Using these "effective" corrections as factors to the raw intensity ratios, one obtains a composition of the precipitate of 92.2 wt.% Nb and 7.37 wt.% N (34.6 at.% N).

III. RESULTS AND DISCUSSION

The microprobe results of the Nb, Zr, and N concentrations are summarized in Tables VI and VII. The deviations listed are the scatter values for different points on the specimen. The tables list a value for the minimum detectable limits defined in Section I. Results of hardness measurements using a Knoop indenter with 1000 g load are shown in Table VIII. The hardness values are consistent with increased solubility at increased solubility at higher annealing temperatures.

Microprobe Analysis

The results of these measurements roughly agree with those of other techniques used in establishing the boundaries of the Nb-N solid solution and the Nb₂N¹⁻⁶ compound. The results of the Nb-2.0 wt.% N analysis are shown graphically in Figure 6. The values for solubility of N in Nb show the expected magnitude, however, they indicate a heat of solution value smaller by a factor of 2-3 than the value reported by Cost and Wert for this temperature range, but in good agreement with their value for low temperatures. The composition of the precipitate phase shows little change with temperature. Averaging the reported values in Table VI gives 6.8 wt.% (32.4 at.%) which is very near the composition Nb₂N.

The total amount of analyzed components in a microprobe analysis should approach 100%, but since the elements are analyzed for independently without normalization, the sum of the percentage reported will

TABLE VI

Concentration of Niobium and Nitrogen in Equilibrated Nb-N Alloys

<u>Region</u>	<u>Composition, wt.%</u>	
	<u>Nb-0.3 wt.% N</u>	
<u>800°C Annealed</u>		
Matrix	99.45 +0.13 -0.27	0.38 +0.70 -0.38
<u>1000°C Annealed</u>		
Matrix	99.22 +0.78 -0.34	0.01 +0.01
<u>1200°C Annealed</u>		
Matrix	99.75 +0.25 -0.64	0.18 +0.63 -0.18
Min. Detect. Limits	0.20	0.58
	<u>Nb-2.0 wt.% N</u>	
<u>800°C Annealed</u>		
Matrix	99.71	0.65 +0.72 -0.59
Precipitate	93.67 +1.92 -1.39	6.79 +0.83 -1.03
<u>1000°C Annealed</u>		
Matrix	99.67 +0.06 -0.06	0.80 +0.24 -0.17
Precipitate	93.13 +0.61 -0.72	6.82 +1.3 -1.0
<u>1200°C Annealed</u>		
Matrix	98.46 +0.80 -0.75	0.81 +0.55 -0.58
Precipitate	92.14 +0.83 -0.34	6.45 +0.56 -0.71
Min. Detec. Limits	0.184	0.823

TABLE VII

Concentrations of Niobium, Zirconium, and Nitrogen in
an Inhomogeneous Nb-Zr-N Alloy

<u>Region</u>	<u>Composition, wt.%</u>		
	<u>Nb</u>	<u>Zr</u>	<u>N</u>
(Cf. Figure 4)			
A. Thin outer layer	87.02	0.42	10.32
B. Thick inner layer	91.61	0.56	7.86
C. Large precipitate near discont. ppt.	91.34	1.64	7.16
Matrix adjacent to a large precipitate	98.17	0.62	0.25
D. Matrix in the grain center	96.25	0.88	2.03
Widmanstätten ppt.	95.02	0.78	2.62
E. Precipitate at grain boundary	91.56	1.04	6.74
<u>Minimum detectable limits</u>	0.20	0.14	0.58
Nominal wt.%	95.6	0.86	3.6

TABLE VIII

Knoop Hardness Measurements on the Alloys
(1000 Gm Load)

<u>Specimen</u>	<u>Annealing Temp.</u> (°C)	<u>Hardness</u> (KHN)
Nb-2.0 wt.% N	800	218
	1000	286
	1200	412
Nb-0.3 wt.% N	800	152
	1000	192
	1200	283
Nb-0.86 wt.% Zr- 3.6 wt.% N	(Quenched)	348
	(Nitride layer B, Fig. 4)	1423

Figure 6. Niobium-Nitrogen phase diagram at one atmosphere nitrogen according to Elliot and Komjathy with microprobe results of this study superimposed.

not total exactly 100%. Any substantial deviation from 100% reflects a possible omission of some component, the presence of large voids, changes in density of the sample, improperly prepared standards or experimental error.

Zirconium Distribution in Nb-0.86 wt.% Zr-3.6 wt.% N Alloy

The Nb-0.86 wt.% Zr-3.6 wt.% N alloy is of special interest because of the Zr present. This non-equilibrium specimen contains a large variation in microstructure since the nitrogen concentration has a gradient increasing from the specimen center outward, in addition to the presence of Zr and a gradient in cooling rate. There are more phases present than in the binary alloys and a different phase morphology, for example, the discontinuously precipitated Nb_2N . This precipitate has the form of long "fingers" or needles extending from the surface toward the specimen center. In the specimen center, nucleation rates exceeded the critical value and a Widmanstätten structure dominates.

The Zr is not evenly distributed in the various regions according to the probe analysis (cf. Table VII). Using estimated values of the diffusion coefficient of Zr, the Zr diffusion distance at 2100°C for two hours would be about 100 μm , and at 1800°C for 24 hours it is 70 μm . This is sufficient to allow a surface depletion by evaporation, and also to permit relocation during the nitriding process, but not during

Figure 7. Zirconium distribution across the Nb-0.86 wt.% Zr-3.6 wt.% N specimen diameter measured on a grain boundary nitride.

the quench. The results in Table VII show conclusively that nitride particles which coarsened and grew during the nitriding process are richer in Zr than the average and adjacent areas and the surface are depleted. The relatively fine internal precipitates formed continuously did not exhibit any contrast in Zr content. A survey across the specimen at 50 μ m intervals clearly shows the surface depletion of Zr (Fig. 7). The survey was made along the massive nitride layer at a grain boundary which is single phase.

The composition of the outer layer (layer A in Fig. 4) in this Nb-0.86 wt.% Zr-3.6 wt.% N alloy contains about 10 wt.% (43 at.%) nitrogen. R. Guard, et al.¹⁴ gives a constitution diagram for Nb-N which has a high temperature γ phase stable down to at least 1000°C. This face-centered-tetragonal phase contains an N to Nb ratio of from 0.75 to 0.80, corresponding to a formula of Nb_4N_3 , the same as the composition observed in the present study. The γ nitride was formed in this study despite the low maximum nitrogen pressure of about one torr during the nitriding process. This is thought to be a true nitride and not an oxygen stabilized compound because no oxygen was detected in a direct analysis for this element. Also Terao¹⁵ prepared this niobium nitride through decomposition of oxy-nitrides by heating in vacuo.

Hardness Measurements

The self consistency of the hardness values obtained on these specimens suggest that the heat treatments were correctly carried out.

Solution hardening of the matrix is apparent from the increasing hardness with increasing heat treatment temperature in both the Nb 0.3 wt.% N and in the Nb-2.0 wt.% N alloys. The massive nitride layer on the Nb 0.86 wt.% Zr 3.6 wt.% N has a hardness of 1423 KHN, in fair agreement with a value of 1500 for pure nitride.⁷

IV. SUMMARY AND CONCLUSIONS

The compositions of nitride and solid solution phases in equilibrated Nb-N alloys were measured by microprobe analysis. A non-equilibrium specimen of a Nb-0.86 wt.% Zr-3.6 wt.% N alloy was also studied. Hardness readings were made on all the specimens after the composition analyses using a diamond indenter with a 1000 g load. Specimens were prepared in a careful manner so as to minimize oxygen contamination and to provide representative materials for analysis. The phases studied in the equilibrated specimens were the metal-nitrogen solid solution and the dispersed and grain boundary precipitate, Nb_2N . A brief description of the microprobe analysis was given. The results of the study leads to the following conclusions:

1. Matrix compositions are obtained with the microprobe analyzer, but not to as great a precision as internal friction studies.

2. Nitride phases are satisfactorily analyzed provided they are massive enough and are equilibrated for sufficiently long times.

(Cf. Nb_2N and Nb_4N_3).

3. The distribution of a minor element (Zr) in an alloy can be traced effectively even when present in fractions of a wt.%.

4. Standard specimens of reactive elements must be carefully prepared and polished just prior to analysis and in the absence of water to prevent troublesome surface layers.

5. Compound standards for elements such as nitrogen must be characterized and analyzed initially to determine the actual amount of element present.

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APPENDIX

SAMPLE CALCULATION OF COMPOSITION OF Nb AND N

Since corrections to equation (1) are themselves a function of concentration, equation (1) is therefore more properly written as follows:

$$[\text{Intensity Ratio}] = [\text{Concentration of Unknown}]$$

$$[\text{Absorption Correction}] [\text{Fluorescence Correction}]$$

$$[\text{Atomic Number Correction}]$$

The bracketed correction terms themselves consist of many separate terms. A specific example of the use of these factors is given below for the determination of the Nb content of the Nb-N precipitates in the nominal 2.0 wt.% N-Nb alloy annealed at 800°C. A simplified form of these factors is considered here. Gray¹² gives a fuller discussion of their meaning.

The first factor given below corrects the drift- deadtime- and background- corrected intensity ratio, for the absorption of the characteristic radiation in the specimen. In the absorption correction the X-ray absorbing power of the specimen must be considered and also the depth below the surface at which the X-rays are produced. The latter factor involves the depth of penetration of the electron beam which in turn depends on the electron absorption process.

$$\frac{1 + \frac{\bar{h} R(0)}{R(\infty) + \bar{h} R(0)} \frac{\bar{\chi}}{\sigma}}{\left(1 + \frac{\bar{\chi}}{\sigma}\right) \left(1 + \frac{\bar{h}}{1+\bar{h}} \frac{\bar{\chi}}{\sigma}\right)} = \text{absorption factor}$$

$$\frac{1 + \frac{h R(0)}{R(\infty) + h R(0)} \frac{\chi}{\sigma}}{\left(1 + \frac{\chi}{\sigma}\right) \left(1 + \frac{h}{1+h} \frac{\chi}{\sigma}\right)}$$

Where the overscored symbols indicate values averaged over the composition of the specimen and subscripts refer to values for a given element.

$$\chi = \left(\frac{\mu}{\rho}\right) \operatorname{cosec} \theta$$

$\left(\frac{\mu}{\rho}\right)$ = mass absorption coefficient for

Nb L alpha line.

θ = X-ray take-off angle of the instrument (=52.5°)

σ = mass absorption coefficient for the electrons

$$= \frac{2.54(10^5)}{E_o^{1.5} - E_c^{1.5}}$$

E_o = electron beam acceleration potential (=10 kV)

E_c = critical excitation of the Nb L α line

h is a quantity which relates the absorption of electrons by X-ray excitation to that by other processes.

h is given approximately by $4.5 A/z^2$ where

A = atomic weight

z = atomic number

$R(\)$ is a geometric factor to account for the different directions of the electrons once scattering has occurred. $R(0)$ is taken as 1.1 and $R(\infty)$ is taken as 4.0 in all calculations.

The second factor corrects for the fluorescence of an element by X-rays of other elements in the specimen. In the present case this factor is essentially 1.00 since neither N nor Nb fluoresce each other to any significant extent.

$$k_{fA} = \left(0.5 P_{kL} C_N \frac{r_{Nb}^{-1}}{r_{Nb}} \omega_N \frac{A_{Nb}}{A_N} \left(\frac{\left| \frac{E_o}{E_c} \right|_N - 1}{\left| \frac{E_o}{E_c} \right|_{Nb} - 1} \right)^{1.67} \right)$$

$$\frac{\left(\frac{\mu}{\rho} \right)_{Nb}^N}{\left(\frac{\mu}{\rho} \right)^N} \left(\ln \frac{1 + \frac{(\mu/\rho)^{Nb}}{(\mu/\rho)^N} \operatorname{cosec} \theta}{\frac{(\mu/\rho)^{Nb}}{(\mu/\rho)^N} \operatorname{cosec} \theta} + \ln \frac{1 + \frac{\sigma}{(\mu/\rho)^N}}{\frac{\sigma}{(\mu/\rho)^N}} \right)$$

where

P_{kL} = a constant having the value of 2.4 for the fluorescence of an L line by a K line

C_N = weight fraction of N

r_{Nb} = ratio of the mass absorption coefficient on either side of the Nb L absorption edge termed the "absorption jump ratio."

ω_N = fluorescent yield for nitrogen, the probability of the ionized

atom emitting an X-ray photon of that energy.

$\left(\frac{\mu}{\rho}\right)_m^n$ = mass absorption coefficient of element m for the n characteristic wavelength.

The last factor corrects for the efficiency with which the characteristic radiation of the elements is excited by the electron beam.

$$\left(\frac{\bar{R}}{R_{Nb}} \frac{\left(\frac{Z}{A}\right)_{Nb} [\ln 1.166 E - \ln J_{Nb}]}{\left(\frac{Z}{A}\right) (\ln 1.166 E - \ln J)} \right)$$

= Atomic number factor

where

R = fraction of the ionization remaining when the losses due to back-scattered electrons are removed.¹⁶

$E = \frac{E_o + E_c}{2}$ = mean excitation potential.

J = the "ionization potential" defined as follows:¹¹

$$\frac{J}{z} = 14.0(1.0 - e^{-0.1\bar{z}}) + \frac{75.5}{\bar{z} \bar{z}/7.5} - \frac{\bar{z}}{100 + \bar{z}}$$

The following table gives values for the quantities defined above, the atomic properties, and the experimentally determined quantities for the example calculation of the amount of Nb and N in the precipitate phase.

TABLE AI

Variables and Constants to Calculate Correction Factors

Common Designation	Program Designation	Nb	N
Atomic Properties of Unalloyed Elements			
Atomic number	AT.NO	41	7
Atomic weight	AT.WT.	92.906	14.007
Analytical line wavelength	WAVE	5.724	31.600
Analytical line excitation	EC	2.371	0.400
Absorption edge of analytical line	EDGE	5.230	30.990
Fluorescent yield	W	0.035	0.002
Calculated Factors for Unalloyed Elements			
J Factor	PF	552.565	134.835
Overvoltage ratio	U	4.22	20.00
Backscatter factor	R	0.772	0.959
Z/A	WS	0.4413	0.4998
$E_0 + E_c/2$	E	6.1855	5.2000
$\ln 1.166 \bar{E}$	VAL	8.8832	8.7097
σ	SIGMA	9080.55	8096.97
h	HS	0.2487	1.2864
$1 + \chi/\sigma$	US	1.0887	1.2627
$f(\chi)$	FS	0.9077	0.7373
$f(\chi) R/S$	FACT	0.61862	0.37184
Absorption jump ratio	--	5.36	29.16
Mass Absorption Coefficients of Unalloyed Elements			
Nb L alpha line absorption coeff.		639	357
N K alpha line absorption coeff.		14607	1688
Calculated Factors for Alloyed Elements			
Mean backscatter factor	RAL	(0.7778)	
Mean atomic number $\bar{Z}$	ZAL	(38.0489)	
Mean $(\bar{Z}/A)$	WSAL	(0.4408)	
Mean h value $\bar{h}$	HAL	(0.2683)	
Mean J factor $\bar{J}$	PAL	(510.34)	
CHI of alloy, χ	YP	(17011.68)	
Calculated Factors for Elements in the Alloy			
Mean overvoltage ratio	VAL	1.0848	3.1010
$f(\chi)$ alloy	FAL	0.9108	0.2555
Absorption coefficient of unknown for Nb $L\alpha$		(611.2)	
Absorption coefficient of unknown for N $K\alpha$		(13496.3)	

A summary of calculated factors for the elements in the alloy show the different relative magnitudes of the factors for the two components in Table AII.

TABLE AII

Summary of Correction Factors in an Nb₂N Type Phase

Correction Factor	Program Designation	Values	
		Nb	N
Absorption	$(f_u(\chi)/f_s(\chi))$	1.00343	0.34652
Fluorescence	FIDI $(=k_{fA}^s)$	1.00000	1.00005
Atomic number (total correction/ absorption x fluorescence)		0.97780	1.38140
Product of factors		0.98116	0.47857
Reciprocal product of factors		1.0135	2.0895

The Nb composition is given by the same relation stated earlier:

$$\frac{I_u}{I_{std}} = C_A \frac{f_u(\chi_u)}{f_s(\chi_s)} [1 + k_{fA}] [AT.No.Corr.]$$

$$.905315 = C_{Nb} (1.00343) (1.00000) (0.97780)$$

$$\therefore C_{Nb} = 0.92273 \text{ wt. fraction}$$

By the same procedure,

$$C_N \approx 0.07210 \text{ wt. fraction.}$$

Therefore we see that in the case of Nb there isn't any fluorescence contribution to the X-ray intensity by the N, and the absorption effect is low (0.997), but the atomic number factor contributes about 2% (1.0205). The N on the other hand, has a large contribution from the

absorption (2.886) and the atomic number factor (0.724), but no real contribution from fluorescence.