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DEGASSING OF NIOBIUM SINGLE CRYSTALS**

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ELECTRON BEAM FLOAT ZONE MELTING AND VACUUM
DEGASSING OF NIOBIUM SINGLE CRYSTALS*

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ABSTRACT

Niobium metal powder produced by electrodeposition from molten salts by CIBA Ltd. was electron beam float zone melted (EBFZM) for purification and growth of single crystals. It was necessary to EBFZM with a high oxygen partial pressure to reduce the carbon level. A high resistance ratio [$R_{300^\circ\text{K}}/R_{4.2^\circ\text{K}}$ (15 kgauss) = 6500] and low flow stress [$\tau_{ly} = 460 \text{ gm/mm}^2$] was obtained after a high temperature anneal (2350°C) in high vacuum (2×10^{-10} torr). Extensive material characterization results are reported for the niobium at various stages in the purification process. The impurity content determined by chemical analyses did not correlate with the resistance ratios; however, the flow stress exhibited an excellent correlation with resistance ratio. These results imply that interstitial impurity in solid solution is the impurity distribution most affecting dislocation motion.

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INTRODUCTION

Niobium, because of its high melting point, low vapor pressure, good corrosion resistance to molten alkali metals, good fabricability, low thermal neutron absorption cross section, and high superconducting transition temperature, has become a strong candidate for utilization in nuclear research and reactor technology. Many of these properties, particularly mechanical properties, are strongly influenced by impurities. This paper describes work performed within the Research Materials Program at the Oak Ridge National Laboratory on the purification and crystal growth of niobium single crystals. This material was used for basic studies concerning the effect of neutron irradiation upon the physical and mechanical properties of high purity niobium.

The purification mechanisms operating during electron beam float zone melting (EBFZM) of niobium have been described by several workers.^{1,2,3,4} Zone refining, as defined by Pfann,⁵ actually has been found to be a minor part of the total purification effect of EBFZM. Most zoning speeds reported for niobium have been too fast for effective zone refining. Speeds in the range of 1.3 to 37.6 cm/hr did not redistribute Ta and W in Nb,^{2,6} however, zoning speeds of 0.27 to 1.2 cm/hr resulted in a redistribution of Ta in Nb.⁷ In addition, layered or striated distributions of impurities have been reported in refractory metal single crystals^{6,8} which would indicate that EBFZM operations can cause a fluctuation in the growth rate. This would further reduce the effect of zone refining.⁹

The major purification mechanisms that occur during EBFZM of niobium are outgassing, volatilization and gas-metal reactions. In order to describe

these purification processes in greater detail, it is best to differentiate between the molten zone and the heated solid rod during EBFZM.

The molten zone is probably protected from any interaction with the residual gases in the vacuum environment by a protective sheath of evaporating metal atoms. Allen,¹⁰ using the pendant-drop method to measure surface tensions of the refractory metals, found that wide variations in vacuum from 10^{-4} to 10^{-7} torr had no measurable effect on the surface tension determinations. Because of the sensitivity of the surface tension to impurities, Allen concluded that the vaporizing metal atoms protected the surface from impinging residual gas molecules. From the geometry of the pendant drop and weight loss data, Allen also calculated that the refractory metals evaporated 230 to 2300 monolayers per sec while a vacuum of 5×10^{-6} torr would mean a gas impingement equivalent to two monolayers per sec. Thus, the molten surface apparently will be well screened from the vacuum environment.

The following purification processes can occur within the molten zone: preferential volatilization of metallic impurities that have higher vapor pressures than that of niobium at its melting point; removal of carbon and oxygen by the formation of CO with subsequent evolution of the gas from the molten zone; direct outgassing of oxygen, nitrogen and hydrogen until the solubility limit of these gases in the liquid has been attained; and the removal of oxygen by the formation and subsequent volatilization of NbO. It is important to note that the kinetics of these mechanisms are probably controlled by diffusion in the liquid which would be expected to be several orders of magnitude greater than diffusion in

the solid. In addition, it has been reported that there is good stirring in the liquid zone during EBFZM.^{6,8} Thus it is reasonable to expect that these mechanisms operate much more effectively in the liquid zone.

The heated solid rod can also be purified by preferential volatilization of metallic impurities, outgassing of oxygen, nitrogen, and hydrogen and formation and volatilization of NbO. However, the kinetics of these mechanisms will probably be much slower than in the liquid zone. In addition, the heated solid rod can interact with the residual gas environment. Thus the partial pressures of many of the gases in the EBFZM chamber become important in determining the degree of purification. Several researchers^{11,12,13,14} have determined the relationship between the equilibrium concentration of oxygen and nitrogen in niobium and their partial pressure in the gaseous environment. Also, whether the heated solid rod will be carburized or decarburized can be determined by the residual gas composition.¹⁵ Hence, the final purity of the EBFZM rod, and particularly the level of interstitial solid solution impurities, C, O₂, N₂, and H₂, will be affected by the degree of interaction between the heated solid rod and the residual gases in the vacuum environment.

EXPERIMENTAL PROCEDURE

A. Powder Consolidation

The starting material was a melting grade 60 mesh dendritic powder obtained from CIBA Ltd., Basle, Switzerland. This material had been prepared by electrodeposition from a molten salt. It was characterized by a low Ta and W content compared to niobium from other commercial sources

but contained appreciable amounts of Na. It was found that drop casting the powder into rod form by either arc melting² or electron beam melting¹⁶ introduced Ta and W impurities into the metal. Thus, a technique was developed to produce consolidated niobium rods directly from the powder by EBFZM.

The powder was first packed into 16 mm diameter copper tubing which had been carefully cleaned and etched. The tube was then evacuated with a liquid nitrogen trapped mechanical pump and sealed under vacuum. It was next cold swaged to 8 mm diameter. After etching off the copper tubing in nitric acid, a 6 mm diameter niobium powder rod compact was obtained that was strong enough to EBFZM. This rod was then zone melted for one pass in 5×10^{-6} torr vacuum at a zone speed of about 20 cm/hr for consolidation. It was found that prior outgassing passes in the solid state was ineffective in preventing "spitting" when the molten zone was formed. Thus, the powder compact was melted through completely on the first pass. A second zone pass was then made at 5×10^{-7} torr vacuum. The zoned rod was next cold swaged to 4.8 mm diameter rod. Table I lists the chemical analyses for both the starting powder compact and the as-swaged EBFZM rod at this stage.

B. EBFZM Procedure

Niobium single crystals with a resistance ratio [$R_{300^\circ\text{K}}/R_{4.2^\circ\text{K}} (15 \text{ kgauss})$] equal to 1400 had been produced by earlier work in this program, but this involved multipasses (10 to 17 passes) in ultrahigh vacuum (8×10^{-10} torr). It was also noted that the carbon impurity was difficult to remove unless

Table I

Chemical Analyses of Niobium Powder Compact
Before and After EBFZM

Element	Impurity Content (wt. ppm)	
	Powder Compact	After EBFZM
C	270	50
O	510	47
N	61	25
H	5	3
Ta	16	19
W	0.8	1.5
Na	10-1000	<1
K	8	<1
Cu	30	<1
Fe	20	2
Co	2	<1
Cr	2	<1
Ni	30	1
S	20	<1
Zn	4	<1
Si	10	1

the starting oxygen content was such that the $[O_2]/[C]$ ratio was greater than one. Hence, a standard EBFZM procedure was developed that produced niobium single crystals low in carbon content and yet used techniques not involving ultrahigh vacuum.

The following procedure was used: The specimen and a seed crystal were loaded into a Materials Research Corp. Model EBZ-94 electron beam float zone refiner. The system was evacuated overnight, attaining a base pressure of 5×10^{-8} torr. EBFZM passes were then made on the 4.8 mm diameter rod over an 18 cm length, using a zone speed of 10 cm/hr. During some of the initial passes, oxygen gas was introduced using a variable leak valve to maintain oxygen pressures in the range of 5×10^{-6} to 1×10^{-5} torr. The sequence that gave best results consisted of making three passes at 5×10^{-6} torr oxygen pressure, pumping overnight after closing the variable leak, and then zoning one pass at about 1×10^{-8} torr. This cycle could be completed in three days.

C. Vacuum Outgassing Procedure

The as-zoned niobium single crystals were outgassed by heating to within 100 to 200°C of the melting point in ultrahigh vacuum. The system consisted of a bakeable stainless steel chamber capable of attaining a 1×10^{-10} torr pressure. A 20 kw r.f. power feedthrough was used to place an induction coil in the center of the chamber. The specimens were centered in the coil by hanging them on Nb hooks fastened to Ta wires. The specimens were heated to temperatures ranging from 2200 to 2350°C for times between 5 and 50 hours. The chamber pressure at temperature was 2×10^{-9} torr after 5 hours and 2×10^{-10} torr after 50 hours.

D. Material Characterization Procedures

The rods were examined for purity using several methods. Direct methods were: chemical analyses, such as neutron activation analyses for Ta and W, vacuum fusion analyses for O, N, and H, Leco combustion analyses for C, and spark source mass spectrographic analyses for other metallic impurities. Indirect methods were: resistance ratios measured between room temperature and liquid helium temperature in a 15 kilogauss magnetic field; and a flow stress measured at the lower yield point of the resolved stress-strain tensile curve. The tensile specimens were prepared by centerless grinding followed by chemical polishing. The tensile testing was done at room temperature on a table model Instron machine at a strain rate of $1.7 \times 10^{-4} \text{ sec}^{-1}$. The specimens were oriented with the tensile axis near $\langle 491 \rangle$ such that the Schmid factor for slip on the (101) $[\bar{1}11]$ system was 0.5.

EXPERIMENTAL RESULTS

Subsequent EBFZM and vacuum annealing of the consolidated niobium powder compact did not appreciably change the level of metallic impurities shown in Table I. The Ta content remained in a range between 15 and 23 wt. ppm. There was no systematic variation with position along the zone length, number of passes, or type of oxygen treatment. The range of Ta contents reported here was attributed to variations within the dendritic powder. The same was true for W which varied from 0.5 to 2.0 wt. ppm. All other metallic impurities were below the 1 wt. ppm level in both the EBFZM single crystals and the vacuum degassed specimens.

The major effect of EBFZM upon the consolidated niobium powder compact was a reduction of the interstitial impurities, C, O, N, and H. Table II lists the amount of these impurities remaining after various EBFZM treatments. The results show that zone melting without an oxygen treatment reduced the oxygen and nitrogen content but did not affect the carbon content. Introducing an oxygen partial pressure of 1×10^{-5} torr during the first pass of a three pass schedule resulted in a reduction of the carbon content. Using oxygen during additional passes of the EBFZM schedule further reduced the carbon content but the oxygen level of the zoned rod started to increase. A convenient schedule was found to be three passes at 5×10^{-6} torr oxygen pressure plus one pass at 2×10^{-8} torr vacuum. Rods with this treatment usually finished with 5-20 wt. ppm C, 50-150 wt. ppm O_2 , < 10 wt. ppm N_2 , and < 2 wt. ppm H_2 .

The vacuum degassing treatment was effective in further removing O_2 , N_2 and H_2 . The chemical analyses shown in Table II also include typical results obtained from outgassed samples. In addition, there usually was a loss of carbon, especially if the oxygen content prior to the anneal was 2 to 5 times the carbon level. However, carbon was not always reduced and during some anneals there was an increase in carbon content. This generally occurred when the oxygen to carbon ratio prior to the anneal was < 2.

Table II also lists some resistance ratios taken on niobium single crystals which had been given the various EBFZM and outgassing treatments and then subsequently used for chemical analyses. The highest resistance

Table II

Effect of EBFZM Schedules and Vacuum Degassing upon
the Interstitial Impurity Content and Resistance
Ratio of Niobium (Typical Values)

Treatment	Impurity Content in wt. ppm				Resistance Ratio $R_{300^\circ\text{K}}/R_{4.2^\circ\text{K}(15 \text{ kgauss})}$
	C	O	N	H	
1. After EBFZM of com- pacted powder	50	47	25	3	95
2. 3 EBFZM passes @ 1×10^{-7} torr	51	27	8	2	162
3. 1 pass @ 1×10^{-5} O ₂ 2 passes @ 5×10^{-8} torr	27	27	8	2	445
4. 3 passes @ 5×10^{-6} O ₂ 1 pass @ 2×10^{-8} torr	17	110	6	<1	331
5. Treatment 4 plus an- nealed 5 hr at 2350°C in 2×10^{-9} torr	26	20	1	<1	1480
6. Treatment 4 plus an- nealed 41 hr at 2350°C in 4×10^{-10} torr	9	18	1	<1	6370

ratios were obtained on the outgassed samples and ranged from 5000 to 7500. Attempts to quantitatively correlate the resistance ratios with impurity content were not successful, although there was a general trend that decreasing impurity content resulted in increasing resistance ratio. Figure 1 is a summary plot of total interstitial impurity content versus resistance ratio. Similar plots using atomic ppm instead of weight ppm and assigning various weighting factors to each impurity also failed to establish a good correlation between resistance ratio and impurity content.

The effect of centerless grinding tensile specimens from the niobium single crystals was evaluated using resistance ratio measurements. In all cases, the resistance ratio decreased upon grinding. However, vacuum annealing the tensile specimens generally resulted in resistance ratios near those measured on single crystals given the same EBFZM and annealing treatment. A typical sequence of treatments and resistance ratios would be: EBFZM 3 passes in 5×10^{-6} torr oxygen, 1 pass in 2×10^{-8} torr vacuum - 226; centerless grind tensile specimen and chemical polish - 187; anneal at 2350°C for 41 hours in 4×10^{-10} torr - 6440; and same overall treatment without centerless grinding - 6370.

All of the stress-strain curves obtained in the tensile tests exhibited a yield point. Figure 2 shows typical stress-strain curves for the as-zoned and annealed material. The vacuum outgassing anneal not only reduced the stress level at the lower yield point, but, in addition changed the general shape. However, the values for the resolved shear stress at the lower yield point for all of the niobium tensile specimens exhibited a strong correlation with the resistance ratios. Figure 3 shows this correlation.

DISCUSSION

The results of this study show that the oxygen treatment during EBFZM was effective in removing carbon from niobium. The probable sequence of events for the decarburization can be described as follows. Since the residual gases in the vacuum environment are not expected to interact appreciably with the molten zone due to a protective cloud of evaporating metal atoms, the oxygen enters the hot solid niobium rod near the molten zone. During each EBFZM pass at 10 cm/hr a point on the rod is molten for about three minutes. Using the diffusivity value of Powers and Doyle for oxygen in niobium,¹⁷ the estimated diffusion distances after three minutes ranged from about 1 mm at 1600°C to 3 mm at 2400°C. The equilibrium concentrations of oxygen in niobium expected at a partial pressure of 5×10^{-6} torr O_2 were calculated using the data of Fromm¹⁴ and varied from 12 wt. ppm at 2300°C to 421 wt. ppm at 1800°C. Thus, using temperatures where oxygen could diffuse distances on the order of the dimensions of the rod, it was possible to achieve oxygen contents of 10 to 200 wt. ppm in the heated rod adjacent to the molten zone. The molten zone then passed through the oxygen doped region. With the good stirring and fast diffusion rates in the liquid, the formation and evolution of CO could be expected with the resultant reduction of the carbon content.

The vacuum outgassing anneal readily reduced the oxygen and nitrogen content of the niobium, and, in addition, generally removed carbon if an excess of oxygen was present in the niobium such that $[O]/[C] > 2$. Extrapolating the kinetic and equilibrium data of Fromm¹⁴ to lower pressures

and higher temperatures and taking residual gas partial pressures determined in the baked chamber at a total pressure of 1×10^{-9} torr, an estimate of the C, O₂, and N₂ concentrations was made. Using the times and temperatures of the anneals, it was found that the equilibrium concentrations should be attained. These estimated equilibrium concentrations after the outgassing anneal were: oxygen, 3×10^{-4} atomic ppm; nitrogen, 8×10^{-2} atomic ppm; and carbon, 1 atomic ppm. These values are all very much lower than the chemical analyses listed in Table II. In addition, a calculation of the resistance ratio (see below) expected for niobium with the above estimated impurity level, gives a value larger than the measured ratios obtained on the outgassed samples. In fact, the estimated resistance ratio (12,150) is about twice the highest measured ratio listed in Table II on outgassed niobium (6370). This is fair agreement considering the possible accuracy error ranges inherent in the calculations. However, the use of the data of Fromm¹⁴ outside the temperature and pressure range in which it was determined should be done with caution, since impurity concentration values estimated at temperatures above and partial pressures below this range apparently were too small.

The resistance ratios of niobium can be estimated from the chemical analyses using the data of Meyerhoff¹⁸ and Williams et al.¹⁹ Using their values for the change of resistivity with impurity content for Ta, W, O, N, and C in niobium and the temperature dependence of resistivity for low temperatures given by Meyerhoff,¹⁸ a resistance ratio was calculated for the several chemical analyses listed in Table II. The results are listed in Table III. The calculated resistance ratios based on the chemical

Table III

Calculated and Measured Resistance Ratios for
Niobium with Various Impurity Contents

Case	Resistance Ratios	
	$\rho_{295^\circ\text{K}}/\rho_{4.2^\circ\text{K}}$ (calculated)	$R_{300^\circ\text{K}}/R_{4.2^\circ\text{K}}(15 \text{ kgauus})$ (measured)
No Impurities	37,000	-
Ta, W Impurities only (20 wt. ppm Ta, 2 wt. ppm W)	19,400	-
Ta, W Impurities plus C, O, N estimated using Fromm ¹⁴ data for out- gassed Nb	12,150	-
1*	29	95
2	47	162
3	61	445
4	27	331
5	90	1480
6	138	6370

*Number refers to treatment listed in Table II and the calculated resistance ratio was based on the chemical analyses associated with each treatment listed in Table II.

analyses are all significantly lower than the actual measured ratios. A systematic error in the chemical analyses cannot account for the difference since no quantitative correlation could be found between the measured resistance ratio and impurity content as shown in Fig. 1. Thus the higher-than-predicted resistance ratio measurements indicate that only a portion of the total impurity content, as measured by chemical analyses, has a strong effect upon the resistivity. This infers that the interstitial impurities are not present in a single type of distribution in the niobium.

A case can be made to show that the impurity distribution in niobium most affecting resistivity is probably the unassociated interstitial atom in solution. For oxygen in niobium, Williams *et al.*²⁰ showed excellent agreement between impurity content determined by resistivity and that measured by internal friction. Other investigations^{21,22} have shown that these internal friction and elastic after-effect relaxations are due to unassociated oxygen atoms in solution at the octahedral site in the niobium lattice. In addition, clusters of interstitial atoms greater than 3 or 4 atoms did not contribute to the internal friction relaxations. Thus, it could be inferred that resistivity measurements probably are most sensitive to unassociated interstitial impurities in solution and clusters of more than 4 atoms would not contribute as much to the resistivity. A range of interstitial impurity distributions from single atoms to large clusters in the same niobium sample could then explain the discrepancy between resistance ratios and chemical analyses.

If the above model is assumed, then the strong correlation between the resistance ratio and the resolved flow stress as shown in Fig. 3,

indicates that the same impurity distribution, namely, the unassociated interstitial atom in solution, must also control dislocation motion in niobium. Thus thermal treatments, such as vacuum outgassing, can affect electrical and mechanical properties of niobium by changing either the amount or the distribution of interstitial impurities.

CONCLUSIONS

1. An oxygen treatment during EBFZM was effective in reducing the carbon content of niobium.
2. Vacuum outgassing effectively reduced oxygen and nitrogen in niobium but did not affect the carbon content unless the starting $[O]/[C]$ ratio was greater than 2.
3. Specimens which were EBFZM three passes in 5×10^{-6} torr oxygen at 10 cm/hr and one pass in 2×10^{-8} torr vacuum and then outgassed for 41 hours at 2350°C in 4×10^{-10} torr vacuum had resistance ratios of about 6500 and resolved flow stresses near 460 gm/mm^2 .
4. The chemical analyses did not correlate quantitatively with the resistance ratios. Calculated resistance ratios based on the chemical analyses were much lower than the measured values. The resistance ratio probably measured mostly unassociated interstitial impurities in solution.
5. The resolved flow stresses correlated well with the resistance ratios. This implies that dislocation motion in niobium single crystals is affected strongly by unassociated interstitial impurities in solution.

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REFERENCES

1. E. Votava, *Phys. Stat. Sol.* 5, 421 (1964).
2. R. E. Reed, *Second International Conference on Electron and Ion Beam Science and Technology* (Gordon and Breach Science Publishers, New York, 1969), pp. 225-258.
3. L. C. Skinner and R. M. Rose, *Second International Conference on Electron and Ion Beam Science and Technology* (Gordon and Breach Science Publishers, New York, 1969), pp. 207-223.
4. H. C. Kim and P. L. Pratt, *Mat. Res. Bull.* 2, 323 (1967).
5. W. G. Pfann, *Zone Melting* (John Wiley & Sons, New York, 1966).
6. R. E. Reed, to be published. Abstract published in Program and Abstracts of ACCG Conference on Crystal Growth, National Bureau of Standards, August, 1969.
7. F. H. Cocks, R. M. Rose, and J. Wulff, *J. Less-Common Metals* 10, 157 (1966).
8. J. Barthel and R. Scharfenberg, *Crystal Growth*, H. S. Peiser, Ed., (Pergamon Press, New York, 1968), pp. 133-139.
9. J. Barthel and K. Eichler, *Kristall und Technik* 2, 205 (1967).
10. B. C. Allen, *Trans AIME* 227, 1175 (1963).
11. J. R. Cost and C. A. Wert, *Acta Met.* 11, 231 (1963).
12. E. Gebhardt, E. Fromm, and D. Jakob, *Z. Metallkde* 55, 423 (1964).
13. E. Fromm and H. Jehn, *Z. Metallkde* 58, 61 (1967).
14. E. Fromm, *J. of Vac. Sci. and Tech.* 7, S100 (1970).
15. H. R. Smith, C. de'a. Hunt, and C. W. Hanks, *Reactive Metals* (Wiley Interscience, New York, 1959), p. 131.

16. R. E. Reed, C. W. Dean, R. E. McDonald, and J. F. Emery, *Third International Conference on Electron and Ion Beam Science and Technology*, R. Bakish, Ed., (The Electrochemical Society, New York, N. Y., 1968), pp. 516-529.
17. R. W. Powers and M. V. Doyle, J. Appl. Phys. 30, 514 (1959).
18. R. W. Meyerhoff, J. Electrochem. Soc. 118, 997 (1971).
19. J. M. Williams, J. T. Stanley, and W. E. Brundage, Oak Ridge National Laboratory Rep. No. 4334 (1969), p. 9.
20. J. M. Williams, W. E. Brundage, and J. T. Stanley, Metal Science Journal 2, 100 (1968).
21. R. Gibala and C. A. Wert, Acta Met. 14, 1095 and 1105 (1966).
22. M. S. Ahmad and Z. C. Szkopiak, J. Phys. Chem. Solids 31, 1799 (1970).

FIGURE CAPTIONS

- Fig. 1 Resistance Ratio versus the Total Interstitial Impurity Content for Niobium Single Crystals.
- Fig. 2 Room Temperature Stress-Strain Curves for $\langle 491 \rangle$ Single Crystal Niobium Zoned Three Passes in 5×10^{-6} Torr Oxygen Plus One Pass in 2×10^{-8} Torr Vacuum.
- Fig. 3 Resistance Ratio versus Lower Yield Resolved Shear Stress for $\langle 491 \rangle$ Niobium Single Crystals Tested at Room Temperature.

Fig. 1

Fig. 2

Fig. 3