THE Cr₃O-TYPE COMPOUND IN THE NIOBIUM-RHODIUM-SILICON TERNARY SYSTEM

by

Perry Billups Lassiter

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INTRODUCTION

The Cr₃O-type structure appears in approximately forty known binary systems involving the transition element metals. At the present time, little is known concerning the factors affecting its formation. With the advent of the space age, the demands placed upon materials have increased considerably. The use of previously designated "exotic" materials has become an every-day occurrence. It is entirely possible that at some not too distant date, the Cr₃O-type compound will present a problem similar to the sigma phase problem now found in certain stainless steels. In addition, Cr₃O-type alloys exhibit some highly interesting electrical properties at very low temperatures.

Until recently, little work had been done to determine the conditions necessary to its formation. Seemingly the size factor or the electron configuration, or both, are of primary importance. The "size" of an atom is, of course, related to the energy relationships it enters into with its near neighbors. Although several theorists have proposed effective atomic radii for the Cr30-type compounds, little work has been done to confirm their theories experimentally. In addition,

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these sets of radii are not effective in predicting which atoms will form the Cr₃O-type structure. Until very recently, only binary alloys had been studied.

It was the purpose of this investigation to determine the effect of introducing a third element into the structure in order to obtain more information about the behavior of the A₃B phase in the ternary system, niobium-rhodium-silicon.

The ternary system investigated in this work, plus three other ternary systems, two of which have been completed, is part of a large scale investigation of factors affecting the formation of the Cr30-type structure. The overall investigation is being conducted by the Metallurgical Engineering Department of the Virginia Polytechnic Institute under sponsorship of the United States Atomic Energy Commission. Scope of Work In order that a complete analysis of the factors affecting the formation of the A_3B structure might be made at some future date, a tremendous amount of data must be established. Such facts as which combinations of A and B elements form the A3B structure and the extent of substitution of one B element for another in that structure will aid

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in future analysis of the effect of atomic "size" on the formation of the compound.

It is the purpose of this investigation to determine the extent, if any, to which the silicon atom will substitute for the rhodium atom in the Nb₃Rh compound. The ternary system niobium-rhodium-silicon was chosen because the niobium-rhodium binary system contains the A₃B phase while the niobium-silicon binary system does not. By introducing the silicon atom into the Nb₃Rh structure over a range of compositions having a constant amount of niobium, the extent of substitution of silicon for rhodium could be detected by measuring the change in lattice parameter.

An application of Vegard's Law to the data obtained on lattice parameters could be used to calculate the solubility limits. The knowledge of the solubility limits of a large number of combinations of A and B elements should at some future date yield information on the effects of atomic radii in the structure of the A₃B.

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LITERATURE REVIEW

Introduction The unique Cr30-type structure studied in this investigation was at first thought to have been analogous to a beta or high temperature form of Hagg and Schonberg⁽¹⁾ were able to show that tungsten. the so-called beta-tungsten does not exist as such, but is an oxide having the theoretical formula W_3O_* . The oxygen atoms in the compound are scattered randomly in the structure without evidence of ordering. A similar compound, Cr30 exists with the oxygen atoms in specific sites, thus comprising an ordered structure. The type of intermetallic compound studied in this work is referred to by various authors as either the beta-tungsten or the Cr3O-type compound. Actually, the term Cr₃O-type is more descriptive of the intermetallic compounds because they have the ordered structure which the term Cr30 denotes.

Other terms used to denote the structure are A_3B and A-15. In the first of these, A and B indicate the subgroup in the periodic table in which the constituent atoms lie. However, the term A_3B does not indicate whether or not ordering is present in the structure. The A-15 is merely one of a series of designations

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commonly used to describe the various crystal structures of metals.

The ordered Cr30-type intermetallic <u>Crystal</u> Structure compounds have the cubic system space group notation Oh-Pm3n. More simply stated, the atoms analogous to oxygen in the Cr30 compound are found in body centered cubic lattice positions, and the atoms analogous to chromium are regularly interspersed, two to a cube face so that they form interlocking chains in all three mutually perpendicular axial directions of the cubic Figure 1 illustrates the Cr₃O-type structure. system. In describing the unit cell and in subsequent discussions of radii and coordination, the terms A and B will be used, keeping in mind that the structure is of the ordered type and that the A atoms fit in the chromium positions and the B atoms fit in the oxygen positions of the ordered Cr30-type structure.

The unit cell consists of eight atoms whose positions are as follows:

Six A atoms: 1/4, 0, 1/4; 1/2, 1/4, 0; 0, 1/2, 1/4; 3/4, 0, 1/2; 1/2, 3/4, 0; 0, 1/2, 3/4. Two B atoms: 0, 0, 0; 1/2, 1/2, 1/2.

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The coordination of the structure according to $Geller^{(2)}$ is as follows:

Each A atom is coordinated to:

Two A atoms at a distance $1/2 a_0$ Eight A atoms at a distance $1/4 a_0 \sqrt{6}$ Four B atoms at a distance $1/4 a_0 \sqrt{5}$

Each B atom is coordinated to twelve A atoms at a distance $1/4 = \sqrt{5}$.

Upon further analysis of the structure, however, it seems that in addition to the above, each B atom is coordinated to eight B atoms at a distance $1/2 a_0 \sqrt{3}$.

Laves⁽³⁾, using the popular concept of atoms being hard spheres, has shown from a geometrical standpoint the following relationship concerning atomic radius ratios.

> If A atoms touch A and B atoms $R_A/R_B = 0.81$ If B atoms touch B and A atoms $R_A/R_B = 0.29$

If R_A/R_B is greater than 0.81 A-A contacts are possible. If R_A/R_B is greater than 0.29 and less than 0.81 only A-B contacts are possible. If R_A/R_B is less than 0.29 only B-B contacts are possible. Some agreement is found between the description of Geller and the hard sphere concept of atoms where A-B contacts are present. The relationship between lattice parameter and atomic radius in both instances becomes:

$$a_0 = 4/75 (R_A + R_B)$$

 R_A and R_B = CN (12) β -W radii.

Geller used this equation to predict the lattice parameters of a number of A₃B compounds with reasonable but not perfect accuracy.

Pauling⁽⁴⁾, in his work with carbon atoms, derived the relation:

 $D_n = D_1 - (0.70 \log n)$

- D_n = inter-atomic distance between atoms with n bonds
- D_1 = inter-atomic distance between atoms with one bond

n = number of bonds between atoms.

From this and his theory of resonating covalent bonds for metals, Pauling modified the relationship to:

 $D_n = D_1 - (0.60 \log n)$

- D_n = inter-atomic distance between atoms with n bonds
- D₁ = inter-atomic distance between atoms with one bond
 - n = bonding electrons/CN,

indicating that it holds well in metallic structures. This, however, does not agree with Geller's derived radii for B-tungsten compounds. The controversy continues in several papers and as yet is unresolved. The final statement of Geller is that the relationship

$$a_0 = 4/\sqrt{5} (R_A + R_B)$$

is correct, while Pauling maintains that

$$a_0 = 4/\sqrt{5} (3/2 R_A + 1/2 R_B)$$

is correct.

Barton⁽⁸⁾, using Pauling's formula

$$R_n = R_1 - (0.3 \log n)$$

found a straight line relationship between lattice parameter and the number of bonding electrons per unit cell which holds true for any given A element when combined with several different B elements. Barton's work does not hold true, however, because the true value of R₁ is not known.

None of the above mentioned relationships will predict whether or not any combination of A and B elements will form the A₃B structure. It can be further noted that with any set of effective radii which conforms to the general theory of Geller or Pauling, a reasonable value of a_0 can be calculated.

Occurrence of A₃B Compounds The A₃B compound occurs in approximately forty known binary systems involving the transition element metals. The known A atoms are titanium, chromium, vanadium, zirconium, niobium, molybdenum, and tantalum. These combine with one or more of some twenty B atoms to form the A₃B compound.

Nevitt⁽⁹⁾ has shown that the A_3B compound forms only within certain favorable CN (12) radius ratio limits, and that all possible combinations within these

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limits do not form the compound. The favorable CN (12) radius ratio range is 0.84 to 1.11. The distribution of occurrence of the A₃B structure is roughly a statistical bell curve with a maximum at about 1.0.

The Niobium-Rhodium Binary System Greenfield and Beck⁽¹⁰⁾ report two intermediate phases in the Nb-Rh system, the ordered A_3B phase occurring at 75 atomic percent niobium and the sigma phase occurring at 60 atomic percent niobium. They also report a rhodium-rich phase which could be either another compound or a rhodium-rich solid solution occurring between rhodium and the sigma phase composition. The Nb₃Rh phase is reported by them to have a lattice parameter of 5.115A. The sigma phase has the complex tetragonal structure analogous to the iron-chromium sigma phase and has the following lattice constants:

> a = 9.774Ac = 5.054Ac/a = 0.517A

<u>The Niobium-Silicon Binary System</u> According to Knapton⁽¹²⁾, three intermediate phases, Nb₄Si, Nb₅Si₃, and Nb₃Si₂ are present in the niobium-silicon system. The Nb₄Si forms peritectially at about 1950°C and is

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isomorphous with Ta_4Si and Zr_4Si having the DO_{19} structure. Hansen⁽¹³⁾, in reporting the work of a number of other investigators, states that the Nb₄Si does not appear in high-purity, arc-melted compositions and indicates that carbon has the effect of causing the DO_{10} , Nb₄Si to form.

Hansen again reporting the findings of several investigators indicates that carbon influences the structure of the Nb₅Si₃ compound. The carbon-free Nb₅Si₃ has two crystal modifications. The low temperature modification is tetragonal with a = 6.57Aand c = 11.88A. The high temperature modification is also tetragonal having the lattice constants a = 10.01A and c = 5.07A. The carbon contaminated structure has the hexagonal D8g structure with a = 7.53A and c = 5.24A.

PROCEDURE

<u>Materials</u> All materials used in this investigation were powders of the highest commercially available purity. Table I gives the chemical analysis of these powders. Reasonable precautions were exercised in the handling of both materials and compacted specimens to prevent their contamination.

<u>Preparation of Specimens</u> The compositions listed in Table II were calculated in terms of weight percentages and weighed out on an analytical balance to plus or minus 0.001 grams. A specimen weight of approximately five grams was maintained throughout.

After careful mixing, the powdered specimens were pressed into cylindrical pellets one-half inch in diameter by approximately one-fourth inch long. Pressing was done in a Baldwin Testing Machine at a pressure of 100 K SI. Maximum pressure was held on the pellet for thirty seconds. No lubrication was used on the mold nor was a binding agent used in the powders. <u>Melting</u> Melting of all specimens was accomplished in the inert gas arc-melting furnace illustrated in Figure 2. An atmosphere of welding grade argon was maintained at a pressure just under one atmosphere

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during the melting and cooling of each alloy to prevent oxidation. Each alloy was melted three times and turned over between each melt. Melting losses did not exceed 0.01 grams (0.2 percent).

<u>Homogenization Anneal</u> After melting, each alloy was given a homogenization anneal for two weeks at 1100°C. Each specimen was encapsulated in fused quartz tubing at a pressure of less than one micron of mercury to prevent oxidation during the annealing process. All specimens were quenched from the annealing temperature in clear water to preserve the high temperature structure.

<u>X-Ray Techniques</u> A General Electric XRD-5 diffractometer was used for preliminary identification of the phases present and for indexing of the patterns. Specimens were prepared for the diffractometer by mounting in Bakelite and polished by standard metallographic techniques to obtain a flat surface. Filtered copper K radiation with a nickel filter was used in these preliminary investigations. Both annealed and as-melted specimens were x-rayed in this manner. <u>Precision Lattice Parameters</u> Since the wavelengths available for use with the x-ray camera equipment produced only one doublet in the back reflection region,

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a Debye-Scherrer camera was used in conjunction with Cohen's method to determine precision lattice parameters. Specimens were prepared for the camera by crushing in a diamond mortar and screening through a 325-mesh screen. A glass fiber coated with silicone grease was used as a specimen holder. Care was taken to see that the specimen was perfectly centered in the camera. Chromium K radiation was used in this phase of the investigation in order to shift the diffraction lines to as high an angle as possible in order to attain greater accuracy of lattice parameter measurement. Specimens were hand-polished according Metallography to standard procedures. Etching was done on a "Numec" cathodic vacuum etcher. An etch time of two minutes at 2.5 kilovolts with an argon etching medium at approximately 100 microns of mercury was used.

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RESULTS AND DISCUSSION

The Niobium-Rhodium Binary System The lattice parameter of the Nb₃Rh phase as determined with the XRD-5 diffractometer and with the Debye-Scherrer camera was 5.14 angstroms. This value does not agree with the value of 5.115 angstroms for Nb3Rh which was reported by Greenfield and Beck⁽¹⁰⁾. However, Greenfield and Beck's reported value was apparently calculated from theoretical considerations. The value of 5.115 angstroms is an average of individual lattice parameters calculated from each theoretically determined diffraction line. When Greenfield and Beck's observed data were processed in conjunction with Cohen's extrapolation method (11), a value of 5.138 angstroms was obtained for the Nb3Rh lattice parameter. It is to be noted that the diffraction data from this investigation and the observed data of Greenfield and Beck agree within the bounds of experimental error. Greenfield and Beck's theoretical data, however, differs significantly from both sets of observed data.

The precision lattice parameter determined in this investigation for Nb_3Rh was 5.141 angstroms, which is in close agreement with Greenfield and Beck. Because the structure of the Nb_3Rh compound is such that only one diffraction doublet appears in the back reflection region using chromium radiation, the Debye-Scherrer camera in conjunction with Cohen's method of extrapolation was used to determine all precision lattice parameters reported in this investigation. It is felt that this method produced more accurate values of a_0 because the extrapolation factor takes into account the standard errors of the Debye-Scherrer camera. If the back reflection focusing camera had been used, no accurate means for correcting standard error could have been utilized because the lattice parameter would have been based on only one diffraction line.

<u>The Niobium-Silicon Binary System</u> The 75 atomic percent niobium-25 atomic percent silicon alloy, which would correspond to the Nb₃Si compound if it existed, exhibited no evidence of the A₃B phase. X-ray analysis with the diffractometer indicated the presence of niobium and an unidentified phase having a lesser degree of symmetry than cubic. It is assumed that the second phase is the Nb₅Si₃ compound reported by Hansen⁽¹³⁾. The fact that niobium is present in the niobium-silicon binary alloy (NRS-6) rules out the possibility of the existence of Nb₄Si under equilibrium conditions because the composition of the Nb₄Si falls between niobium and

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the tentatively identified Nb₅Si on the niobium-silicon phase diagram. The absence of Nb₄Si is further substantiated by the fact that it has not been previously found in high purity, arc-melted alloys prepared by other investigators⁽¹³⁾.

<u>The Niobium-Rhodium Sigma Phase</u> The niobium-rhodium sigma phase reported by Greenfield and Beck was present in significant quantities in the Nb₃Rh composition in both the as-melted and the annealed condition. It was also present in some of the ternary alloys as subsequent discussion will reveal. The fact that a significant quantity of the sigma phase was present in the Nb₃Rh composition seems to indicate that the sigma phase forms preferentially to the A_3 B phase in both the as-melted specimens and in the specimens annealed at 1100°C for two weeks.

An attempt was made to eliminate the sigma phase from the Nb3Rh composition by annealing at a temperature of between 1390 and 1505°C for two hours. The binary alloy which had been previously arc-melted, annealed at 1100°C for two weeks and quenched was re-compacted and sealed in quartz tubing at a pressure of less than one micron of mercury. The encapsulated specimen was then placed in a high temperature electric furnace and heated.

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The temperature was in excess of 1390°C for two hours. The alloy was quenched in clear water from 1505°C. The x-ray diffractometer pattern indicated the presence of even more sigma phase than in the original specimen which was quenched from 1100°C. The fact that more sigma phase was found in the higher temperature structure seems contradictory in light of the fact that sigma phase structures in other systems tend to diminish as the temperature is increased.

The A₃B Phase in Ternary Alloys The A₃B phase is definitely present in the ternary alloys. Both the diffractometer and the Debye-Scherrer camera, however, indicate that there is no measurable displacement of the diffraction lines which would indicate a substitution of silicon for rhodium in the Nb₃Rh structure. Table IV shows their precision lattice parameters.

The value of a₀ for specimen NRS-3 is slightly higher than that for the other two specimens. This small deviation is attributed to experimental error due to difficulty in reading the diffraction lines which had diminished to a very low intensity.

There is the possibility that a very small amount of silicon substitutes for rhodium in this structure, but in quantities of less than one percent. The

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intensity of the A₃B diffraction lines diminishes as the composition of the specimen moves away from the Nb₃Rh binary, giving further evidence that there is very little, if any, ternary single phase field associated with the A₃B. The presence of other phases in all ternary compositions also precludes the possibility of a single-phase, solid solution of silicon in rhodium in the Nb-Rh-Si system. <u>Non-A₃B Ternary Phases</u> There is definite evidence of a sigma phase in the ternary system out to at least 10 atomic percent silicon.

Because of the characteristic behavior of sigma phase structures in ternary systems, it is assumed that there is some substitution of silicon for the constituent elements in the Nb-Rh- sigma phase. The complexity of the sigma phase structure is such that an attempt to determine the extent of solubility of silicon in its lattice would be beyond the scope of this investigation.

It seems obvious that there are three phases present in all the ternary alloys. Positive identification of all the phases other than A_3B and the sigma phase was not attempted with the compositions prepared since the primary purpose of this investigation was to study the A_3B phase. <u>Metallography</u> The use of standard polishing techniques and the "Numec" cathodic vacuum etcher produced a microstructure which photographed with excellent quality.

Figures 3 and 4 illustrate the microstructure of the binary, Nb₃Rh composition in the as-melted condition. The melted compact was allowed to cool from the melted state on a water-cooled copper hearth. Note the presence of the acicular structure within the dendrites, indicating that some type of relatively low-temperature transformation took place. Neither of the phases has been identified.

Figure 5 illustrates the same alloy after being annealed at 1100° C for two weeks and quenched. Note that the same type of dendritic structure is evident, but that the second phase within the dendrites has spheroidized at the annealing temperature. X-ray analysis of the alloys indicates the presence of three phases, niobium solid solution, Nb₃Rh, and sigma phase in approximately the same relative amount in both the as-melted and the annealed alloy. The presence of all these phases in the annealed specimen indicates that complete equilibrium had not been attained after two weeks at 1100°C. Greenfield and Beck, however, report that their stoichiometric A₃B composition contained

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essentially 100 percent A₃B after being melted and annealed at 1000°C for three days. Melting and annealing Was done in a helium atmosphere. There is, of course, the possibility that the intended composition of the various alloys in this investigation as well as those in the work by Greenfield and Beck was not maintained throughout the melting of the compact. No reliable method for chemical analysis of niobium-rhodium alloys is known. It is assumed, however, that the actual compositions in this investigation are near to the intended composition.

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CONCLUSIONS

The following conclusions were derived as a result if this investigation:

- No measurable amount of silicon was found to substitute for rhodium in the Nb₃Rh compound. There is, however, the possibility that a very small amount, less than one atomic percent, substitution occurs.
- The precision lattice parameter of Nb₃Rh is
 5.141 angstroms.
- 3. The niobium-rhodium sigma phase (Nb₃Si₂) extends into the niobium-rhodium-silicon ternary system to at least ten atomic percent silicon.
- 4. The presence of an acicular type microstructure in the Nb3Rh composition (as-melted) indicates that a martensitic type transformation occurs on cooling.

FUTURE WORK

Of primary importance in considerations for future work would be the establishment of equilibria relationships in the niobium-rhodium system. A binary equilibrium diagram of the system would prove very valuable in the overall investigation of the Nb3Rh compound. At this time, very little is known about the niobium-rhodium system except that at least two intermediate phases are present. Also of interest would be the determination of equilibria relationships of the sigma phase in the niobium-rhodium-silicon systems.

TABLE I

Composition of Constituent Materials

Niobium^a

	ppm		ppm
C	130	Ta	2200
0	120	Si	110
N	100	В	0.8
Н	2	Zr	50
Fe	30	Co	20
Cr	20	Sn	5
Ni	50	Mn	20
Ti	20		

Rhodiumb

99.995% +

Silicon^C

Solar cell grade

Source:

- a E. I. duPont de Nemours and Co., Inc., Wilmington, Del.
- b Jarrel-Ash Co., Newtonville 60, Mass.
- c E. I. duPont de Nemours and Co., Inc., Wilmington, Del.

TABLE II

<u>Composition of Alloys Prepared</u> <u>in the Nb-Rh-Si System</u>

Specimen No.	At. 🔏 No	At. % Rh	<u>At. % Si</u>
NRS-1	75	25	0
NRS-2	75	20	5
NRS-3	75	15	10
NRS-4	75	10	15
NRS-5	75	5	20
NRS-6	75	0	25

TABLE III

X-Ray Diffraction Data for Nb3Rh

hk1	d Spacing (angstroms)	Obser v ed Intensity ^a
200	2.552	70
210	2.285	100
211	2.088	60
220 ^b	1.81	5
310 ^b	1.63	5
320	1.422	20
321	1.371	30
400	1.284	35
420 ^b	1.15	5

a Determined from height of diffraction peaks from diffractometer pattern.

b Observed on diffractometer pattern only.

TABLE IV

Precision Lattice Parameters of Nb3Rh in Nb-Rh-Si System

Specimen No.	Lattice Parameter (angstroms)
NRS-1	5.141
NRS-2	5.143
NRS-3	5.147
Greenfield and Beck ⁽¹⁰⁾	
Theoretical	5.115
Observed	5.138







Figure 2. Inert Atmosphere Arc-Melting Furnace



Figure 3. The Nb3Rh Microstructure As Melted 250X



Figure 4. The Nb₃Rh Microstructure As Melted 1500X



Figure 5. The Nb₃Rh Microstructure Annealed Two Weeks at 1100°C and Water Quenched, 250X

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ABSTRACT

A series of compositions across the niobiumrhodium-silicon ternary diagram from Nb₃Rh to 75 atomic percent niobium-25 percent silicon, were prepared by arc-melting compacts of high-purity powders. Both x-ray diffractometer and camera techniques were used to analyze the resulting structures.

No measurable amount of silicon was found to substitute for rhodium in the Nb₃Rh structure. The 75 percent niobium-25 atomic percent silicon composition contains niobium plus an unidentified phase assumed to be Nb₅Si₃. The Nb-Rh sigma phase extends into the ternary system to at least 10 atomic percent silicon. All ternary alloys investigated contained three phases. These phases were one or more unidentified phases combined with either A₃B or sigma or both.