PHASE EQUILIBRIA STUDIES OF Cr_3O-TYPE STRUCTURES IN THE VANADIUM-RHODIUM-SILICON AND NIOBIUM-RHODIUM-SILICON TERNARY SYSTEMS

by

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I

INTRODUCTION

In the past few years there has been a great deal of interest and investigation concerning superconducting materials. The superconductor with the highest known transition temperature is Nb_3Sn, which has a Cr_3O-type crystal structure. The large number of systems, in excess of forty, which form the Cr_3O-type structure has prompted several investigations (1)(2)(3)(4) into the formation of this type structure. Most of these investigations have been concerned with determining the lattice parameters of the Cr_3O-type structures. However, some investigators have studied the factors effecting the formation of these compounds.

Pauling(5) and Geller(6) have proposed empirical relationships between the radii of the A- and B-atoms of these structures. Nevitt(7) has stated that the favorable CN(12) radius ratio R_a/R_b for the formation of the Cr_3O-type structure lies between 0.84 and 1.11, although this type of structure has not been found in several systems which fall within this favorable radius ratio.

The overall purpose of this investigation of Cr_3O-type structures by the Department of Metallurgical Engineering at the Virginia Polytechnic Institute was to try to resolve the differences between Pauling's and Geller's empirical relationships. It was also desired to obtain data which would aid in determining whether geometrical factors, or electronic bonding forces, or a combination of the two is the controlling factor in the formation of the Cr_3O-type compounds.

Therefore, phase equilibria studies were undertaken on two ternary systems, the vanadium-rhodium-silicon system and the niobium-rhodium-silicon system, to obtain information relating to atomic size and electronic structure effects on the formation of Cr_3O-type compounds. The vanadium-rhodium-silicon system was investigated to determine the extent of the solid solubility of silicon for rhodium in the vicinity of the stoichiometric Cr_3O composition line. The niobium-rhodium-silicon system had been previously investigated(4), however a more detailed investigation, in the vicinity of Nb_3Rh, was made to determine if any solid solubility of Si for Rh existed out to five atom per cent silicon.

Other investigators(1) have shown that Nb_3Rh, V_3Rh, and V_3Si do form the Cr_3O-type structure, whereas, no compound corresponding to Nb_3Si has yet been identified. In addition, this investigation was undertaken to determine when, and if, ternary solid solubility of these structures is possible.

II

LITERATURE REVIEW

Introduction

The Cr_3O-type structure is frequently referred to by several other designations, namely the β-W structure or the A_3B-type structure. The β-W structure was originally thought to be a high-temperature form of tungsten. However, later investigation(8) showed that β-W was actually an oxide of tungsten which did not exhibit any ordering.

The A_3B designation used to some extent in this thesis refers to the subgroups of the periodic table in which the constitutent elements lie. The A_3B designation is quite useful when ternary systems are involved but does not denote the ordering which is present in these systems. There are a number of compounds which form according to the A_3B stoichiometry but do not exhibit the ordering which is found in the Cr_3O-type structure.

Crystal Structure

The Cr_3O-type structure is an ordered, complex cubic structure consisting of eight atoms per unit cell. The atoms corresponding to the oxygen atoms occupy the body-centered-cubic positions, and the atoms corresponding to the chromium atoms form three mutually perpendicular interlocking chains with two atoms per cube face. Further discussion of the crystal structure will use the A_3B designation. Using this designation, the A-atoms correspond to the chromium atoms, and the B-atoms correspond to the oxygen atoms.

The location of the atoms in the unit cell 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.

Figure 1 shows a unit cell of the A_3B-type structure.

It would be convenient if there were some way of predicting the lattice parameter of A_3B-type compounds from the atomic radii of their component atoms. This brings up the question of what are the radii of the A- and B-atoms in this type of structure. Atomic radius or diameter does not refer to the size of an atom in a free space environment. It does, in fact, mean the radius of an atom as it appears in a specific crystal structure. It is a well-known fact that the size of an atom varies with changes in the number of nearest neighbor atoms (co-ordination number). An example of this is the allotropic transformation of iron from body-centered-cubic to face-centered-cubic with a resultant change in the radius of the iron atom. The exact mechanism which brings about the change in atomic radius is not so well understood. One theory is that the atomic radius of an atom is a function of the density of packing of hard, spherical atoms. Another theory states that the electronic bonding forces between atoms are the controlling factors regarding atomic radius. A third theory proposes that both factors, geometrical and electronic bonding forces, have an effect on the atomic radius.

Pauling(5) and Geller(6) have each proposed effective atomic radii for elements which form the Cr_3O-type structure. Each has also proposed an equation utilizing their atomic radii to predict lattice parameters of Cr_3O-type compounds. Pauling's equation is

$$a_o = 1.788\ (3/2\ R_a + 1/2\ R_b)$$

and Geller's equation is

$$a_o = 1.788\ (R_a + R_b)$$

where

a_o = lattice parameter

R_a = radius of the A-atom in the Cr_3O-type structure

R_b = radius of the B-atom in the Cr_3O-type structure

These two equations were derived from geometrical and nearest neighbor considerations using the hard-sphere atom concept.

Nevitt(7) has proposed that the favorable CN(12) radius ratio R_a/R_b for the formation of Cr_3O-type compounds fell between 0.84 and 1.11. Every known Cr_3O-type compound falls within these ratio limits. There are, however, numerous combinations of elements which fall within these limits but do not form the Cr_3O-type structure. This seems to indicate that electronic bonding as well as atomic size has a definite effect upon the formation of the Cr_3O-type structure.

Systems Previously Investigated

Prior to this investigation, three ternary systems had been examined under a long range program being sponsored by the Atomic

Energy Commission. Van Reuth(2) investigated the vanadium-silicon-tin system, finding ternary solid solubility between silicon and tin. Both binary compounds V_3Si and V_3Sn exist and have the Cr_3O-type structure. Barton(3) investigated the chromium-silicon-tin system and found no solid solubility of tin for silicon in the ternary system. Cr_3Si has been confirmed to have the Cr_3O-type structure; however, no compound corresponding to Cr_3Sn has been reported. Lassiter(4) examined the niobium-rhodium-silicon system with results similar to those of Barton. Nb_3Rh was known to exist, but there was no detectable ternary solid solubility of silicon for rhodium in the ternary system. Up to this point then, three ternary systems have been examined. The two systems which contained only one binary Cr_3O-type compound exhibited no ternary solid solubility between the B-elements, and the one system which contained two binary Cr_3O-type compounds exhibited complete ternary solid solubility between the B-elements.

Vegard's Law

Vegard's Law states that changes in unit cell dimensions should be linear with changes in composition, and several investigators(2)(4) have attempted to apply this law to the ternary solid solubility which occurs between the B-elements of certain A_3B-type compounds. According to Azaroff(9), Vegard's law should be obeyed most closely by those solid solutions which adhere rigorously to the Hume-Rothery rules. Even if the extension of the Hume-Rothery rules to a ternary solid solution between the B-atoms of binary compounds is valid, then only the rule concerning crystal structure can be applied with any degree of certainty. The condition for atomic size can certainly not be applied since an accurate determination of atomic size is one of the major unsolved problems in the A_3B-type structure. Likewise, electronegativity and relative valency are rather poorly defined quantities with respect to A_3B-type structures because the A-elements are transition elements with an unfilled d-band.

An attempt was made to apply Vegard's law to a system which exhibited ternary solid solubility between the B-elements(2). The results from that system produced a rather large positive deviation from Vegard's law. It therefore appears that Vegard's law is of little value when attempting to predict the lattice parameters of ternary Cr_3O-type compounds.

III

EXPERIMENTAL PROCEDURE

Sample Preparation

The samples were prepared using powder metallurgical techniques. High purity elements were ground to less than -80 mesh powder and compacted in a one-half inch diameter steel die into pellets at pressures ranging from 100,000 psi to 130,000 psi without the use of a binding agent. Table I gives the chemical analysis of the two elements: vanadium and niobium. The silicon was Solar Cell grade and the rhodium was of 99.9+ per cent purity. The compacting pressure was varied to maintain a sample height of from three-eights inch to one-half inch. If the sample height exceeded one-half inch, the sample would not conduct the arc during the melting operation. After compaction, the samples were arc-melted in a controlled atmosphere furnace containing an atmosphere of welding grade Argon at just under one atmosphere pressure.

An attempt was made to melt each sample three times, inverting the sample between each melting, to obtain homogeniety. Those samples containing greater than 10 atom per cent silicon could be melted only once, because severe spalling resulted when a second melting was attempted. The high silicon content samples apparently absorbed large amounts of Argon during the melting causing porosity in the sample. When the sample was reheated, the entrapped gas expanded rapidly and caused the sample to spall.

After melting, each sample was encapsulated in Vycor tubing at a pressure of less than one micron of mercury. The encapsulated specimens were then placed in a furnace and given a homogenization anneal at 1000°C. for times varying from 100 hours to 1000 hours. The samples, which were arc-melted three times, were annealed for 100 hours. Samples, which were arc-melted only once, were annealed for 1000 hours.

Upon completion of the anneal, all but two specimens were water-quenched to room temperature to maintain the 1000°C. structure. Two samples were furnace cooled at the rate of 200°C. per day to try to determine the extent of ordering in the crystal structure.

Metallographic Examination

Metallographic examination was performed on selected samples in both the as-cast and annealed conditions. Polishing was done in accordance with standard metallographic practice. Etching was done in a vacuum-cathodic-etcher with etching times ranging from one-half to three minutes. Figure 2 shows a photomicrograph of sample NRS-11 at 500X.

X-Ray Examination

After metallographic examination, each sample was ground to -300 mesh powder for x-ray diffraction to determine the crystal structure and lattice parameter. Two x-ray diffraction techniques were used.

The first group of samples studied was examined using a 114.6 mm diameter Debye-Scherrer powder camera, chromium target x-ray tube, vanadium beta-filter, and Kodak No-screen x-ray film. Samples for the Debye-Scherrer camera were prepared by either rolling the powder into a 0.5 mm rod using Duco Cement for a binder or by coating the powder sample on a greased glass filament.

The second group of samples was analyzed on a Siemens Krystalloflex IV X-Ray Diffractometer using a chromium target x-ray tube and a vanadium beta-filter. The powder samples were contained in a lucite holder using parlodion for a binding agent.

The diffractometer was given a precision alignment using Conru's reversal method to insure accuracy in the lattice parameter measurements. The arrangement of the sample holder in the diffractometer was such that the sample surface was always tangent to the focusing circle to further insure lattice parameter accuracy.

The Debye-Scherrer films and the diffractometer traces were indexed according to standard procedures. Crystal structures were determined using Hull-Davey charts and published literature on the binary Cr_3O-type structure.

IV

RESULTS

The Vanadium-Rhodium Binary System

Four binary vanadium-rhodium samples, VRS-1, VRS-7, VRS-11, VRS-15, ranging from 72.04 atom per cent vanadium to 76.37 atom per cent vanadium, were prepared. Examination by x-ray diffraction showed that each of the four samples was a single-phase alloy of the Cr_3O-type structure. The lattice parameter of the samples varied with changes in per cent composition of vanadium. Sample VRS-1 had a composition of 74.47 atom per cent vanadium and 25.53 atom per cent rhodium. This corresponds closely to the stoichiometric composition V_3Rh. The measured lattice parameter of VRS-1 was 4.769Å which is in close agreement with Greenfield and Beck's(1) value of 4.767Å for V_3Rh. The lattice parameter for sample VRS-1 was the minimum lattice parameter measured on the vanadium-rhodium binary. The lattice parameters of the other samples increased with either an increase or a decrease in vanadium content. The lattice parameter of sample VRS-11 (76.37 atom per cent vanadium) showed an increase to 4.776Å and the lattice parameter of sample VRS-15 (72.04 atom per cent vanadium) had increased to 4.787Å.

The Vanadium-Silicon Binary System

Four binary vanadium-silicon samples, samples VRS-6, VRS-10, VRS-14, and VRS-18 ranging from 73.16 atom per cent vanadium to 81.30 atom per cent vanadium, were prepared. Examination by x-ray diffraction showed that each sample was a single phase alloy of the Cr_3O-type structure. The lattice parameters of the samples varied with changes in per cent composition of vanadium. Sample VRS-6 had a composition of 74.38 atom per cent vanadium and 25.48 atom per cent silicon which closely approximates the stoichiometric V_3Si composition. The measured lattice parameter of sample VRS-6 was 4.714Å which was in good agreement with Hansen's(10) value of 4.721 ± 0.003Å for V_3Si. The lattice parameter for VRS-6 was the minimum lattice parameter measured on the vanadium-silicon binary.

The lattice parameters behaved similar to those on the vanadium-rhodium binary. Deviation from the stoichiometric V_3Si composition caused an increase in lattice parameter. The lattice parameter increased to 4.720Å in sample VRS-10 (81.30 atom per cent vanadium) and to 4.724Å in sample VRS-18 (73.16 atom per cent vanadium).

The Vanadium-Rhodium-Silicon Ternary System

The ternary vanadium-rhodium-silicon samples were broken down into three general groups: samples containing approximately 75 atom per cent vanadium (samples VRS-2, VRS-3, VRS-4, VRS-5, VRS-12, and VRS-13), samples containing between 75 and 81 atom per cent vanadium (samples VRS-8 and VRS-9), and samples containing between 71 and 75 atom per cent vanadium (samples VRS-16 and VRS-17). The rhodium and silicon contents of the samples were varied so as to give a representative picture of the ternary system in the vicinity of the stoichiometric Cr_3O composition line. Table II gives the chemical analysis of each sample in the vanadium-rhodium-silicon system. Examination by x-ray diffraction showed that each ternary sample was a single-phase alloy of the Cr_3O-type structure. Lattice parameter measurements showed that an increase in the silicon content of the sample caused a corresponding decrease in the lattice parameter of the sample. This decrease occurred not only for samples along the stoichiometric Cr_3O-line, but also for the samples on either side of the stoichiometric 75 atom per cent vanadium line. Samples VRS-8 and VRS-9 (greater than 75 atom per cent vanadium) and samples VRS-16 and VRS-17 (less than 75 atom per cent vanadium) showed a decrease in lattice parameter across the ternary system with increasing silicon content. Lattice parameters for these alloys were larger than the lattice parameters for samples of corresponding silicon contents on the stoichiometric Cr_3O line. In other words, a minimum lattice parameter occurred along the Cr_3O composition line, and either an increase or decrease in vanadium composition (silicon composition remaining constant) caused an increase in lattice parameter.

Figure 3 shows the location of samples in the vanadium-rhodium-silicon ternary system. Tables IV - XXI give x-ray diffraction data and Table XXII gives the lattice parameters for samples examined in the vanadium-rhodium-silicon system.

The Niobium-Rhodium Binary System

Three binary niobium-rhodium samples were prepared. Sample NRS-8 contained 72.67 atom per cent niobium, NRS-11 contained 74.36 atom per cent niobium, and NRS-13 contained 78.57 atom per cent niobium. X-ray diffraction showed that each binary sample was a two-phase alloy containing Nb_3Rh as one of the phases. The measured lattice parameter of Nb_3Rh in the two phase alloys was 5.135Å. The second phase present in samples NRS-8 and NRS-11 has been identified as "sigma-phase" as reported by Hansen(10). The niobium-rhodium sigma-phase has a tetragonal structure with $a = 9.774$Å, $c = 5.054$Å, and $c/a = 0.517$. Sample NRS-13 was composed largely of Nb_3Rh with a small amount of second phase present. However, not enough lines corresponding to the second phase were present to attempt an identification.

The Niobium-Rhodium-Silicon Ternary System

Four samples were prepared in the niobium-rhodium-silicon ternary system. The exact composition of each sample in the niobium-rhodium-silicon system is listed in Table III. X-ray diffraction showed that each ternary sample consisted of at least two phases; one of which was the sigma-phase. Several unidentified lines were present on each diffraction pattern indicating that at least one other phase was present in each ternary sample. In no instance was any trace of Nb_3Rh or any other ordered Cr_3O-type structure found in the ternary samples. Measured lattice parameters for the sigma-phase were $a = 9.885$Å and $c = 5.083$Å.

Figure 4 shows the location of the samples in the Nb-Rh-Si system. Tables XXIII - XXIX give x-ray diffraction data for samples examined in the niobium-rhodium-silicon system.

V

DISCUSSION OF THE RESULTS

The Vanadium-Rhodium Binary

Investigation along the vanadium-rhodium binary between 72.04 atom per cent and 76.37 atom per cent vanadium showed that all of the samples within this composition range had the characteristic Cr_3O-type structure. The lattice parameters within those composition limits ranged from 4.787Å to 4.776Å with a minimum lattice parameter of 4.769Å corresponding to the V_3Rh composition. This maintainance of the Cr_3O-type structure with changes in lattice parameter indicates that there is a range of vanadium solubilities along the binary for the formation of the Cr_3O-type structure. What was previously considered to be an intermetallic compound V_3Rh is actually an intermediate phase extending at least from 72.04 atom per cent vanadium to 76.37 atom per cent vanadium.

The Vanadium-Silicon Binary

The vanadium-silicon binary was investigated between 73.16 atom per cent and 81.30 atom per cent vanadium. Here too, the characteristic Cr_3O diffraction pattern appeared accompanied by changing lattice parameters with changes in vanadium composition. The lattice parameters ranged from 4.724Å to 4.720Å with a minimum lattice parameter of 4.714Å corresponding to V_3Si. The changes in lattice parameter with the changes in vanadium composition indicate a range of vanadium compositions for the formation of the binary Cr_3O-type structure. In this case what was previously thought to be an intermetallic compound V_3Si appears to be an intermediate phase with the Cr_3O-type structure and existing over a composition range from about 73 atom per cent vanadium to about 80 atom per cent vanadium.

There was a slight increase in lattice parameter from the stoichiometric composition to sample VRS-14 and a larger increase in lattice parameter from sample VRS-14 to sample VRS-10. This was a minor deviation from the behavior of the other three groups of binary samples, which showed a fairly large increase in lattice parameter at a small distance from the stoichiometric line. Since there was no indication of a second phase in either sample VRS-10 or sample VRS-14, the reasonable assumption was made that there was a solubility range for the formation of the Cr_3O-type structure between 75 and 80 atom per cent vanadium.

The fact that V_3Rh and V_3Si were reported as intermetallic compounds rather than intermediate phases may be explained by the assumption of several investigators(1)(6) that they had the stoichiometric ratio of elements necessary for the formation of the intermetallic compound. Examination of the vanadium-silicon binary diagram as given by Hansen(10) shows that samples were taken at five atomic per cent increments for the determination of the diagram. Considering that the original determination of the diagram did not recognize the existence of a solubility range for the formation of the Cr_3O-type structure, the value of 4.714Å for sample VRS-6 (74.38 atom per cent vanadium and 25.48 atom per cent silicon) may be a more accurate lattice parameter for the stoichiometric composition V_3Si than that given by Hansen.

Careful sample weighing did not preclude the loss of one or the other element during compaction or arc-melting. All of the samples prepared for the vanadium-rhodium binary and the vanadium-silicon binary were prepared using very careful procedures, however, none of the samples conformed exactly to the desired compositions. These results point up the absolute necessity of chemical analysis when working with systems of this type.

The Vanadium-Rhodium-Silicon Ternary System

A wide range of compositions, as shown in Figure 3 was investigated in the vanadium-rhodium-silicon ternary. Each of the samples examined by x-ray diffraction was a single phase alloy. This, in conjunction with lattice parameter changes with changes in rhodium and silicon compositions, indicated that there was complete solid solubility of silicon for rhodium along the stoichiometric composition line. There was a decrease in lattice parameter with a decrease in rhodium content; from 4.769Å at V_3Rh to 4.714Å at V_3Si.

As was discussed in the Literature Review, Geller proposed that the lattice parameter of a Cr_3O-type structure could be predicted by the equation

$$a_o = 1.788\ (R_a + R_b).$$

This equation was modified slightly to take into account the presence of two B-elements in the ternary system and resulted in the equation

$$a_o = R_a + \left[(\text{atom fraction } B_1 \times R_{b_1} + \text{atom fraction } B_2 \times R_{b_2})\right].$$

Calculations were then made of the lattice parameters of the four ternary alloys along the stoichiometric composition line using Geller's "β-W" radius values for vanadium, rhodium, and silicon(6). Agreement between the calculated and measured lattice parameters was very good, and for all samples measured and calculated values agreed within 0.003Å. In fact, agreement between measured and calculated values was better for ternary alloys than for binary V_3Rh and V_3Si.

Pauling's equation

$$a_o = 1.788\ (3/2\ R_a + 1/2\ R_b)$$

was also modified in the same manner as Geller's equation to give,

$$a_o = 1.788\ \left[3/2\ R_a + 1/2\ (\text{atom fraction } B_1 \times R_{b_1} + \text{atom fraction } B_2 \times R_{b_2})\right]$$

Calculations were then made for the same four ternary alloys using Pauling and Wells' values for the atomic radii of vanadium, rhodium, and silicon. These calculations gave a constant lattice parameter for all of the ternary alloys since Pauling and Wells reported the atomic radius of both rhodium and silicon to be 1.34Å.

Results obtained from Geller's modified equation seem to lend credence to his argument for predicting the lattice parameter of stoichiometric Cr_3O-type compounds. An attempt was made to further extend Geller's equation to both binary and ternary Cr_3O-type alloys having compositions somewhat removed from the stoichiometric ratio; however, no suitable weighting could be determined for the atomic radii of the A- and B-elements.

The fact that the vanadium, rhodium, and silicon compositions can be varied within certain limits around the stoichiometric Cr_3O line with a resultant change in lattice parameter and no change in the characteristic x-ray diffraction indicates that there is an extensive single-phase region in the ternary system. This single phase region extends across the width of the ternary system from the vanadium-rhodium binary to the vanadium-silicon binary and ranges from a minimum of approximately 72 atom per cent vanadium to a maximum of approximately 80 atom per cent vanadium.

One of the more interesting aspects of the vanadium-rhodium-silicon system is the occurrence of a minimum lattice parameter at the stoichiometric Cr_3O compositions on both the vanadium-rhodium and vanadium-silicon binaries as well as in the ternary system itself. This minimum lattice parameter suggests that a maximum binding energy exists along the stoichiometric line and further points up the fact that electronic configuration in addition to atomic size is one of the controlling factors in the formation of Cr_3O-type structures. As the stoichiometric composition is approached, the attractive forces between the atoms are apparently increasing causing greater cohesion of the atoms. Atomic size in a structure is a function of the attractive and repulsive forces between atoms. In the Cr_3O-type structure the attractive forces seem to outweigh repulsive forces as the stoichiometric composition is approached. Therefore, Geller's equation is valid only in the region where the cohesive forces are a maximum. As composition deviates from stoichiometry, the cohesive forces are no longer a maximum and Geller's equation breaks down.

In view of the results obtained by varying the vanadium composition, the importance of the A-atom in the formation of the Cr_3O-type structure seems to have been seriously neglected. Changing the amount of the B-elements present, when solid solubility exists in the ternary system, does not seem to affect the formation of the Cr_3O-type structure; whereas, small changes in the amount of the A-element does seem to produce marked alterations in the formation of Cr_3O-type structure.

The Niobium-Rhodium Binary

There does not appear to be any solubility range for Nb_3Rh on the niobium-rhodium binary. The Nb_3Rh detected in samples NRS-8, NRS-11, and NRS-13 had, in each instance, a lattice parameter of 5.135Å. The lack of change in lattice parameter with changing composition indicates that there is no solubility range and that all Nb_3Rh formed will have the stoichiometric composition. The data obtained correspond closely to that given by Hansen(10) in that Nb_3Rh exists at 75 atom per cent niobium and is bounded by a two phase region, Nb_3Rh + sigma, on the low niobium side of the binary. The sigma-phase occurs at approximately 40 atom per cent niobium and extends over a solubility range of at least one atom per cent. The unit cell dimensions for the sigma-phase were apparently given for 40 atom per cent niobium, which is probably not the composition of the sigma-phase found in sample NRS-8. The composition range for the sigma-phase could explain the difference between the unit cell dimensions given by Hansen and those measured in sample NRS-8. The second phase found in sample NRS-13 (78.52 atom per cent niobium and 21.48 atom per cent rhodium) was not identified but may be a niobium rich solid-solution.

The Niobium-Rhodium-Silicon Ternary System

The compositions of the ternary niobium-rhodium-silicon alloys (NRS-7, NRS-9, NRS-10, and NRS-12) ranged from 72.26 to 78.50 atom per cent niobium and from 1.67 to 4.26 atom per cent silicon, with the remainder being rhodium. This range of compositions was used to investigate the possibility of solid solubility of silicon for rhodium in Nb_3Rh. All of the ternary samples contained at least two phases, one of which was the sigma-phase. The data from the ternary samples indicate that there is no solid solubility of silicon for rhodium in the Nb_3Rh structure in the ternary system. The ternary area encompassed by samples NRS-7, NRS-9, NRS-10, and NRS-12 seems to be largely composed of sigma-phase and an unidentified ternary phase or phases. The remaining phase or phases were probably ternary phases of niobium, rhodium, and silicon.

Lassiter(4) reported the presence of Nb_3Rh in the ternary system. However, his samples were annealed at 1100°C. The higher temperature anneal may have produced different phases other than those found in the samples annealed at 1000°C. Also, chemical analysis was not made of Lassiter's samples, so the compositions may have been outside the area examined in this work.

VI

CONCLUSIONS

The following conclusions resulted from the investigation of the vanadium-rhodium-silicon and niobium-rhodium-silicon systems at 1000°C.

The Vanadium-Rhodium-Silicon System

There is a range of solubilities for the formation of the ordered Cr_3O-type structure on the vanadium-rhodium binary. This range extends from approximately 72 atom per cent vanadium to approximately 76 atom per cent vanadium.

There is a range of solubilities for the formation of the ordered Cr_3O-type structure on the vanadium-silicon binary. This range extends from approximately 73 atom per cent vanadium to approximately 80 atom per cent vanadium.

There is a complete solid solubility of silicon for rhodium across the ternary system in the vicinity of the stoichiometric composition line.

There is a range of vanadium compositions for the formation of the Cr_3O-type structure in the ternary system. This range is between 72 and 80 atom per cent vanadium depending on the rhodium and silicon compositions.

A minimum lattice parameter occurs in the vicinity of the stoichiometric Cr_3O composition line. Either an increase or a decrease in vanadium content from stoichiometry will cause an increase in the lattice parameter of the Cr_3O-type structure formed.

A modified form of Geller's equation will accurately predict the lattice parameter of the stoichiometric Cr_3O-type compounds in the vanadium-rhodium-silicon ternary system because of the maximum cohesive forces which are present along the stoichiometric line.

The importance of the A-atom in the formation of the Cr_3O-type structure has been underestimated and should be investigated in greater detail.

The Niobium-Rhodium-Silicon System

The Cr_3O-type structure in the niobium-rhodium system forms only in the stoichiometric ratio Nb_3Rh.

There is a two-phase region bounding Nb_3Rh on the low niobium side of the binary. This two phase region consists of Nb_3Rh and sigma-phase which is tetragonal with a = 9.885Å and c = 5.083Å.

There is no ternary solid solubility of silicon for rhodium in Nb_3Rh.

Nb_3Rh was not found in the ternary portion of the niobium-rhodium-silicon system.

On the basis of the four ternary systems investigated to date, it appears that two binary Cr_3O-type structures must be present before a ternary Cr_3O-type structure can be formed.

VII

FUTURE WORK

In view of the wide range of solubilities found in both of the binary systems and in the ternary system, the vanadium-rhodium-silicon system should be investigated more extensively to determine the limits of the single-phase region exhibiting the Cr_3O-type structure. This investigation should include samples of no more than five atom per cent increments along the vanadium-rhodium and vanadium-silicon binaries. Also, representative samples should be made on both sides of the stoichiometric composition line in the ternary system.

TABLE I

Chemical Analysis of Niobium and Vanadium Used in the Ternary Systems

Niobium

Element	ppm	Element	ppm
Ta	2200	Co	20
C	130	Cr	20
O	120	Mn	20
Si	110	Ti	20
N	100	Sn	5
Ni	50	H	2
Zr	50	B	0.8
Fe	30		

Vanadium

V	99.69%	C	0.049%
O	0.105%	Fe	0.025%
N	0.080%	H	0.006%

TABLE II

Chemical Analysis of Samples in the Vanadium-Rhodium-Silicon Ternary System*

Sample No.	Atom Per Cent V	 Rh	 Si
VRS-1	74.74	25.53	0.00
VRS-2	73.86	20.85	5.29
VRS-3	74.64	15.41	9.93
VRS-4	74.94	10.47	14.57
VRS-5	74.45	5.61	19.93
VRS-6	74.38	0.00	25.48
VRS-7	75.46	24.53	0.00
VRS-8	78.39	16.18	5.41
VRS-9	80.61	7.81	11.57
VRS-10	81.30	0.00	18.69
VRS-11	76.37	23.65	0.00
VRS-12	73.36	19.04	7.59
VRS-13	75.46	10.20	14.33
VRS-14	79.30	0.00	20.69
VRS-15	72.04	28.03	0.00
VRS-16	71.91	18.38	9.71
VRS-17	71.87	10.71	17.42
VRS-18	73.16	0.00	26.83

*Chemical analysis performed by Ledoux and Company, Teaneck, New Jersey.

TABLE III

Chemical Analysis of Samples in the Niobium-Rhodium-Silicon Ternary System*

Sample No.	Atom Per Cent		
	Nb	Rh	Si
NRS-7	72.26	24.86	2.89
NRS-8	72.67	27.33	0.00
NRS-9	74.80	20.94	4.26
NRS-10	75.69	22.64	1.67
NRS-11	74.36	25.64	0.00
NRS-12	78.50	19.66	1.84
NRS-13	78.52	21.48	0.00

*Chemical analysis performed by Ledoux and Company, Teaneck, New Jersey.

TABLE IV

X-Ray Diffraction Data for Sample VRS-1

SIN Θ	d (Å)	h k l
0.3423	3.3463	110
0.4828	2.3725	200
0.5390	2.1251	210
0.5901	1.9411	211
0.6801	1.6842	220
0.7576	1.5119	310
0.8630	1.3265	320 α_1
0.8644	1.3266	320 α_2
0.8955	1.2784	321 α_1
0.8973	1.2780	321 α_2
0.9572	1.1960	400 α_1
0.9589	1.1959	400 α_2

TABLE V

X-Ray Diffraction Data for Sample VRS-2

SIN θ	d (Å)	h k l
0.3436	3.3336	110
0.4830	2.3715	200
0.5397	2.1223	210
0.5906	1.9394	211
0.6809	1.6822	220
0.7611	1.5049	310
0.8663	1.3214	320 α_1
0.8679	1.3213	320 α_2
0.8986	1.2739	321 α_1
0.9005	1.2735	321 α_2
0.9602	1.1922	400 α_1
0.9619	1.1922	400 α_2

TABLE VI

X-Ray Diffraction Data for Sample VRS-3

SIN θ	d (Å)	h k l
0.3436	3.3336	110
0.4845	2.3641	200
0.5412	2.1165	210
0.5917	1.9358	211
0.6826	1.6780	220
0.7630	1.5012	310
0.8682	1.3185	320 α_1
0.8702	1.3178	320 α_2
0.9004	1.2714	321 α_1
0.9022	1.2710	321 α_2
0.9619	1.1901	400 α_1
0.9640	1.1895	400 α_2

TABLE VII

X-Ray Diffraction Data for Sample VRS-4

SIN Θ	d (Å)	h k l
0.3493	3.2792	110
0.4853	2.3602	200
0.5422	2.1125	210
0.5934	1.9303	211
0.6837	1.6753	220
0.8699	1.3160	320 α_1
0.8726	1.3141	320 α_2
0.9022	1.2688	321 α_1
0.9042	1.2682	321 α_2
0.9647	1.1866	400 α_1
0.9671	1.1857	400 α_2

TABLE VIII

X-Ray Diffraction Data for Sample VRS-5

SIN θ	d (Å)	h k l
0.3477	3.2943	110
0.4868	2.3530	200
0.5441	2.1052	210
0.5952	1.9244	211
0.6860	1.6697	220
0.8732	1.3110	320 α_1
0.8749	1.3107	320 α_2
0.9052	1.2646	321 α_1
0.9076	1.2634	321 α_2
0.9677	1.1830	400 α_1
0.9695	1.1828	400 α_2

TABLE IX

X-Ray Diffraction Data for Sample VRS-6

SIN θ	d (Å)	h k l
0.3453	3.3172	110
0.4866	2.3539	200
0.5439	2.1059	210
0.5958	1.9225	211
0.6867	1.6680	220
0.8743	1.3094	320 α_1
0.8762	1.3088	320 α_2
0.9072	1.2619	321 α_1
0.9088	1.2618	321 α_2
0.9694	1.1809	400 α_1
0.9710	1.1809	400 α_2

TABLE X

X-Ray Diffraction Data for Sample VRS-7

SIN θ	d (Å)	h k l
0.3401	3.3680	110
0.4805	2.3838	200
0.5363	2.1358	210
0.5873	1.9504	211
0.6777	1.6902	220
0.7579	1.5113	310
0.8637	1.3262	320
0.8956	1.2782	321 α_1
0.8974	1.2779	321 α_2
0.9572	1.1959	400 α_1
0.9592	1.1955	400 α_2

TABLE XI

X-Ray Diffraction Data for Sample VRS-8

SIN Θ	d (Å)	h k l
0.3423	3.346	110
0.4833	2.370	200
0.5398	2.122	210
0.5911	1.938	211
0.7610	1.505	310
0.8666	1.321	320 α_1
0.8694	1.319	320 α_2
0.8997	1.272	321 α_1
0.9023	1.271	321 α_2
0.9619	1.190	400 α_1
0.9646	1.189	400 α_2

TABLE XII

X-Ray Diffraction Data for Sample VRS-9

SIN Θ	d (Å)	h k l
0.4850	2.3617	200
0.5419	2.1137	210
0.5929	1.9319	211
0.7645	1.4982	310
0.8706	1.3149	320 α_1
0.8732	1.3132	320 α_2
0.9027	1.2681	321 α_1
0.9059	1.2658	321 α_2
0.9655	1.1857	400 α_1
0.9677	1.1850	400 α_2
0.3433	3.3365	110

TABLE XIII

X-Ray Diffraction Data for Sample VRS-10

SIN θ	d (Å)	h k l
0.4861	2.3564	200
0.5432	2.1087	210
0.5946	1.9264	211
0.8739	1.3099	320 α_1
0.8756	1.3096	320 α_2
0.9068	1.2624	321 α_1
0.9085	1.2622	321 α_2
0.9691	1.1813	400 α_1
0.9710	1.1810	400 α_2

TABLE XIV

X-Ray Diffraction Data for Sample VRS-11

SIN θ	d (Å)	h k l
0.3404	3.3651	110
0.4802	2.3854	200
0.5368	2.1339	210
0.5892	1.9441	211
0.6786	1.6880	220
0.7576	1.5120	310
0.8633	1.3260	320 α_1
0.8650	1.3257	320 α_2
0.8955	1.2783	321 α_1
0.8974	1.2778	321 α_2
0.9572	1.1959	400 α_1
0.9589	1.1959	400 α_2

TABLE XV

X-Ray Diffraction Data for Sample VRS-12

SIN θ	d (Å)	h k l
0.3417	3.3522	110
0.4827	2.3730	200
0.5390	2.1251	210
0.5906	1.9394	211
0.6811	1.6817	220
0.7624	1.5024	310
0.8676	1.3195	320 α_1
0.8692	1.3193	320 α_2
0.8999	1.2721	321 α_1
0.9015	1.2720	321 α_2
0.9619	1.1901	400 α_1
0.9635	1.1901	400 α_2

TABLE XVI

X-Ray Diffraction Data for Sample VRS-13

SIN θ	d (Å)	h k l
0.3447	3.3230	110
0.4853	2.3602	200
0.5426	2.1110	210
0.5943	1.9273	211
0.8710	1.3143	320 α_1
0.8736	1.3126	320 α_2
0.9034	1.2672	321 α_1
0.9061	1.2655	321 α_2
0.9660	1.1850	400 α_1
0.9691	1.1833	400 α_2

TABLE XVII

X-Ray Diffraction Data for Sample VRS-14

SIN θ	d (Å)	h k l
0.3444	3.3259	110
0.4868	2.3530	200
0.5444	2.1040	210
0.5985	1.9138	211
0.8740	1.3098	320 α_1
0.8758	1.3093	320 α_2
0.9068	1.2624	321 α_1
0.9083	1.2625	321 α_2
0.9692	1.1811	400 α_1
0.9709	1.1811	400 α_2

TABLE XVIII

X-Ray Diffraction Data for Sample VRS-15

SIN θ	d (Å)	h k l
0.3379	3.3886	110
0.4782	2.3946	200
0.5346	2.1415	210
0.5857	1.9547	211
0.8952	1.2790	321 α_1
0.8964	1.2788	321 α_2
0.9572	1.1960	400 α_1
0.9583	1.1959	400 α_2

TABLE XIX

X-Ray Diffraction Data for Sample VRS-16

SIN θ	d (Å)	h k l
0.3401	3.3674	110
0.4815	2.3774	200
0.5388	2.1248	210
0.5897	1.9419	211
0.9003	1.2716	321

TABLE XX

X-Ray Diffraction Data for Sample VRS-17

SIN θ	d (Å)	h k l
0.4848	2.3614	200
0.5415	2.1139	210
0.5932	1.9303	211
0.8738	1.3102	320
0.9066	1.2629	321

TABLE XXI

X-Ray Diffraction Data for Sample VRS-18

SIN θ	d (Å)	h k l
0.4846	2.3628	200
0.5420	2.1128	210
0.5937	1.9287	211
0.8736	1.3104	320
0.8993	1.2625	321

TABLE XXII

Lattice Parameters for V-Rh-Si Samples

Sample No.	Lattice Parameter (Å)
VRS-1	4.769
VRS-2	4.755
VRS-3	4.745
VRS-4	4.728
VRS-5	4.718
VRS-6	4.714
VRS-7	4.777
VRS-8	4.752
VRS-9	4.734
VRS-10	4.720
VRS-11	4.776
VRS-12	4.754
VRS-13	4.728
VRS-14	4.715
VRS-15	4.787
VRS-16	4.756
VRS-17	4.725
VRS-18	4.724

TABLE XXIII

X-Ray Diffraction Data for Sample NRS-7

SIN θ	d (Å)	h k l	PHASE
0.4771	2.3996	321	Sigma
0.4914	2.3299	330	Sigma
0.5033	2.2745	- -	Unidentified
0.5160	2.2186	- -	Unidentified
0.5266	2.1737	411	Sigma
0.5395	2.1220	331	Sigma

TABLE XXIV

X-Ray Diffraction Data for Sample NRS-8

SIN θ	d (Å)	h k l	PHASE
0.4769	2.4019	321	Sigma
0.4910	2.3329	330	Sigma
0.4986	2.2962	210	Nb_3Rh
0.5030	2.2759	- -	Unidentified
0.5162	2.2180	- -	Unidentified
0.5262	2.1756	411	Sigma
0.5392	2.1222	331	Sigma
0.5461	2.0963	211	Nb_3Rh

TABLE XXV

X-Ray Diffraction Data for Sample NRS-9

SIN Θ	d (Å)	h k l	PHASE
0.4464	2.5645	- -	Unidentified
0.4773	2.3999	321	Sigma
0.4894	2.3393	- -	Unidentified
0.4915	2.3306	330	Sigma
0.5037	2.2728	- -	Unidentified
0.5164	2.2167	- -	Unidentified
0.5270	2.1725	411	Sigma
0.5398	2.1220	331	Sigma

TABLE XXVI

X-Ray Diffraction Data for Sample NRS-10

SIN θ	d (Å)	h k l	PHASE
0.4772	2.3987	321	Sigma
0.4913	2.3302	330	Sigma
0.5028	2.2767	- -	Unidentified
0.5160	2.2187	- -	Unidentified
0.5270	2.1725	411	Sigma
0.5395	2.1219	331	Sigma

TABLE XXVII

X-Ray Diffraction Data for Sample NRS-11

SIN θ	d (Å)	h k l	PHASE
0.4459	2.5675	200	Nb_3Rh
0.4775	2.3989	321	Sigma
0.4903	2.3363	330	Sigma
0.4982	2.2989	210	Nb_3Rh
0.5268	2.1744	411	Sigma
0.5459	2.0975	211	Nb_3Rh
0.8042	1.4236	320	Nb_3Rh
0.8347	1.3716	321	Nb_3Rh
0.8921	1.2834	400	Nb_3Rh

TABLE XXVIII

X-Ray Diffraction Data for Sample NRS-12

SIN Θ	d (Å)	h k l	PHASE
0.4775	2.3989	321	Sigma
0.4916	2.3285	330	Sigma
0.5030	2.2759	- -	Unidentified
0.5160	2.2187	- -	Unidentified
0.5272	2.2172	411	Sigma
0.5400	2.1212	331	Sigma

TABLE XXIX

X-Ray Diffraction Data for Sample NRS-13

SIN θ	d (Å)	h k l	PHASE
0.4464	2.5648	200	Nb_3Rh
0.4989	2.2960	- -	Unidentified
0.4984	2.2945	210	Nb_3Rh
0.5458	2.0975	211	Nb_3Rh
0.8315	1.3769	321	Nb_3Rh
0.8040	1.4240	320	Nb_3Rh
0.8919	1.2836	400	Nb_3Rh

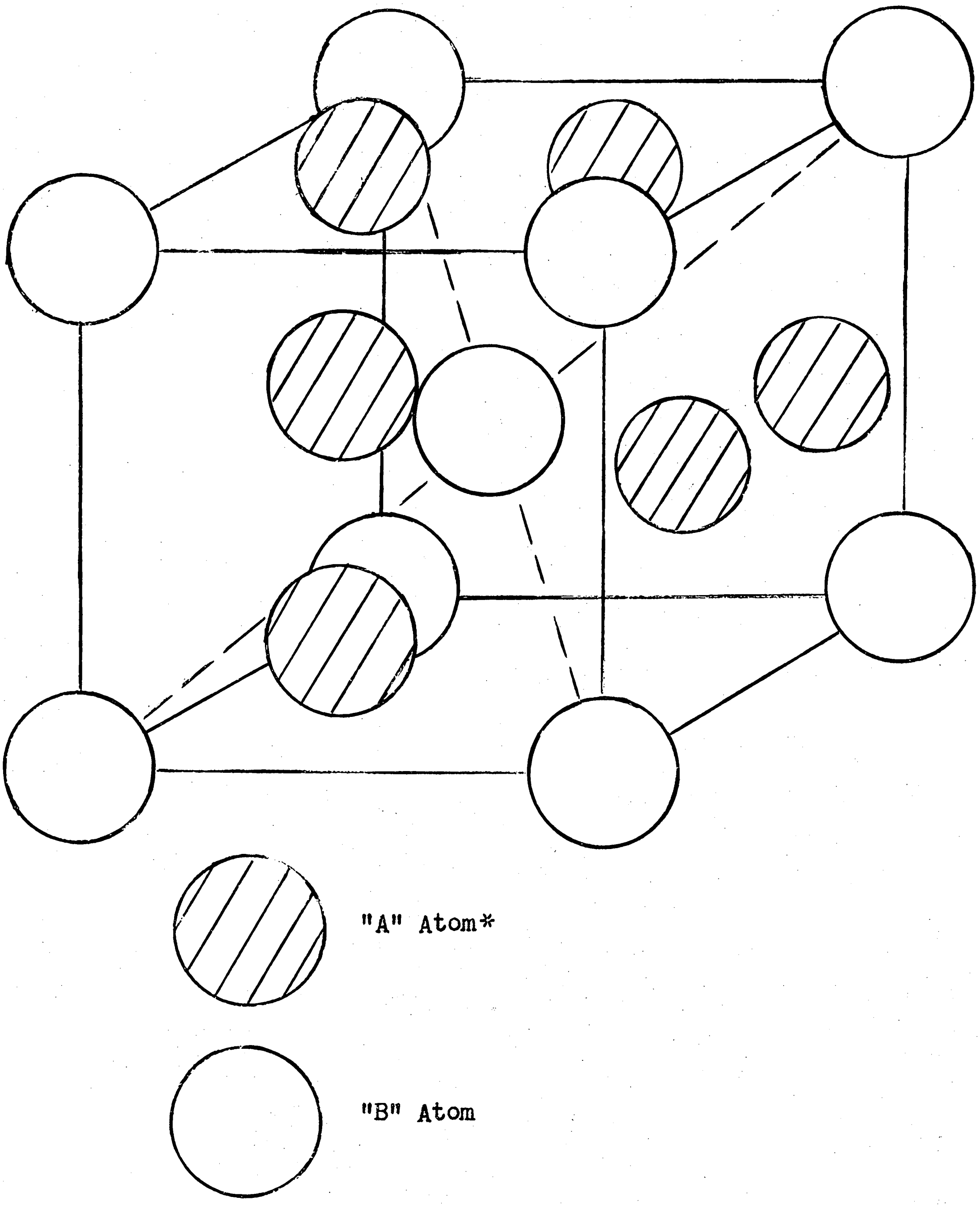

Figure 1 - Unit Cell of the Cr_3O-type Structure

*"A" atoms in rear faces omitted for clarity.

Figure 2 - Photomicrograph of Sample NRS-11, 500X

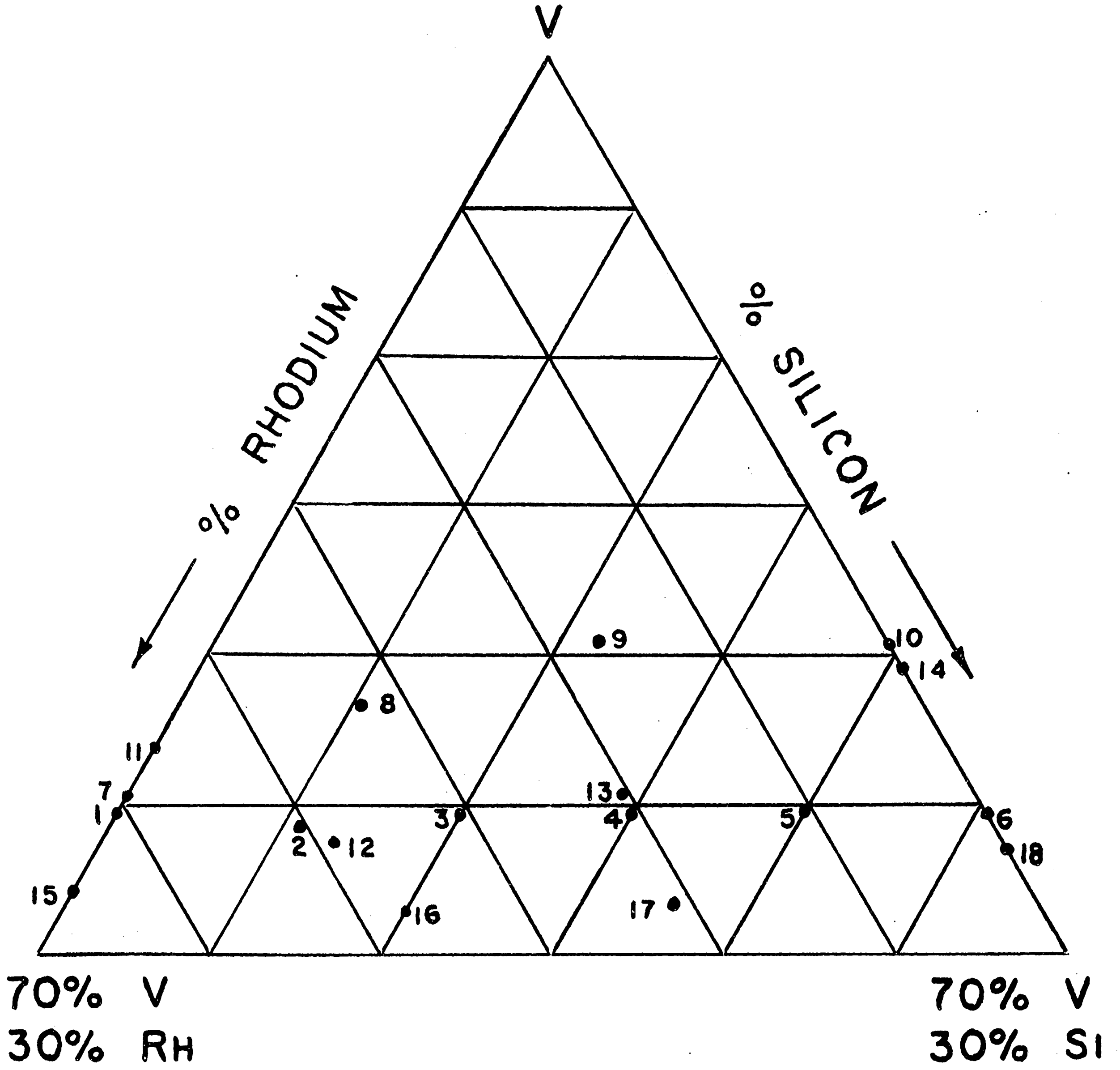

Figure 3 - Location of Samples in the Vanadium-Rhodium-Silicon System

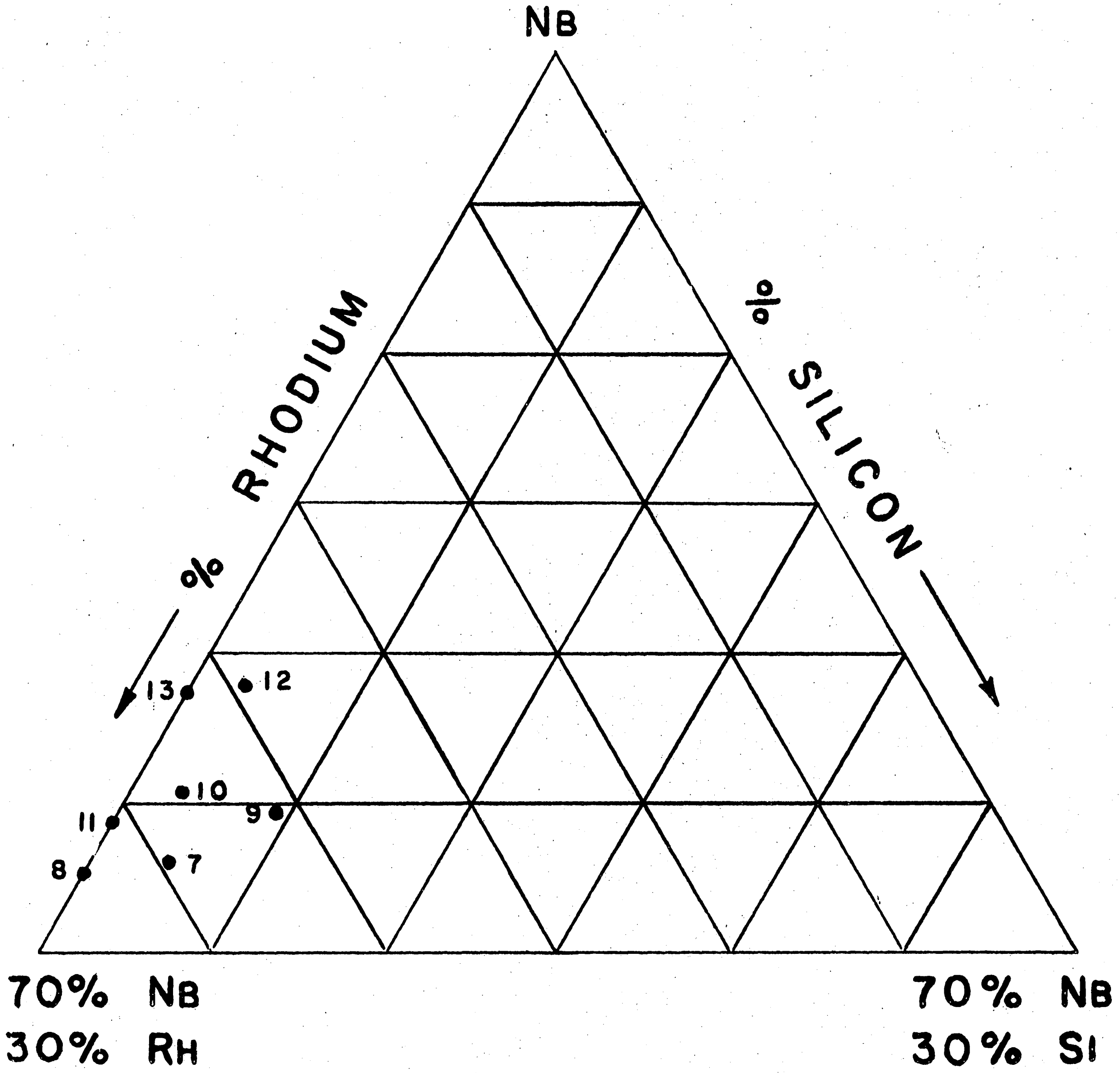

Figure 4 - Location of Samples in the
Niobium-Rhodium-Silicon System

VIII

BIBLIOGRAPHY

1. Greenfield, P. and Beck, P. A.: Intermediate Phases in Binary Systems of Certain Transition Elements, Transactions AIME, Volume 206, p. 265 (1956).

2. Van Reuth, E.: Unpublished Thesis, V. P. I., June, 1960.

3. Barton, E. E.: Unpublished Thesis, V. P. I., July, 1961.

4. Lassiter, P. B.: Unpublished Thesis, V. P. I., August, 1962.

5. Pauling, L.: A Set of Effective Metallic Radii for Use in Compounds with the β-Wolfram Structure, Acta Crystallographica, Volume 10, p. 374 (1957).

6. Geller, S.: A Set of Effective Coordination Number (12) Radii for the β-wolfram Structure Elements, Acta Crystallographica, Volume 9, p. 885 (1956).

7. Nevitt, M. V.: Atomic Size Effects in the Cr_3O-Type Structure, Transactions AIME, Volume 206, p. 265 (1956).

8. Hagg, G. and Schonberg, N.: β-Tungsten as a Tungsten Oxide, Acta Crystallographica, Volume 7, p. 351 (1954)

9. Azaroff, L. V.: <u>Introduction to Solids</u>. McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

10. Hansen, M.: <u>Constitution of Binary Alloys</u>. McGraw-Hill Book Co., Inc., New York, N. Y., 1958.

IX

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ABSTRACT

Phase equilibria studies of two ternary systems, the vanadium-rhodium-silicon system and the niobium-rhodium-silicon system, were made to obtain information about the formation of the Cr_3O-type structure in these systems. All samples had compositions in the vicinity of the stoichiometric Cr_3O composition line and were prepared by powder metallurgy techniques. The compacts were then arc-melted, given a homogenization anneal, and examined by x-ray diffraction.

Complete solid solubility of silicon for rhodium was found across the V-Rh-Si system in the Cr_3O-type structure. A large range of vanadium compositions for the formation of the Cr_3O-type structure in the V-Rh-Si system was also found. A minimum lattice parameter was found for samples closely approximating the stoichiometric Cr_3O composition in the V-Rh-Si system. Either an increase or a decrease in vanadium composition from stoichiometry caused an increase in the lattice parameter of the Cr_3O-type structure formed.

No solid solubility of silicon for rhodium was found in the niobium-rhodium-silicon system. Apparently the only Cr_3O-type structure which forms in the Nb-Rh-Si system is of the stoichiometric composition Nb_3Rh.