Directorate of Materials and Processes
Aeronautical Systems Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

Project No. 7350, Task No. 735001

(Prepared under Contract No. AF33(657)-7432 by ManLabs, Inc.,
Cambridge, Massachusetts; P. Stark, J. Ryan, S.V. Radcliffe, Authors)

MATERIALS RESEARCH AND DEVELOPMENT

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FOREWORD

This report was prepared by ManLabs, Inc. under Contract No. AF 33 (657)-7432. The program was initiated under Project No. 7350, "Refractory Inorganic Non-metallic Materials", Task No. 735001, "Refractory Inorganic Non-metallic Materials: Non-Graphitic". The work was administered under the direction of the Directorate of Materials and Processes, Aeronautical Systems Division with Lt. T. Lippart, and subsequently Lt. L. Jacobson acting as project monitors. The report covers work conducted from 15 October 1961 to 14 October 1962 under Phase I of the overall program.

The authors wish to acknowledge the assistance of Mr. R. Lundy in carrying out the experimental phases of the program.

Aeronautical Systems Division, Dir/ Materials and Processes, Metals and Ceramics Lab, Wright-Patterson AFB, Ohio. Rpt No. ASD-TDR-62-1087, Pt I. MECHANICAL BEHAVIOR OF INTERMETALLIC COMPOUNDS. Interim report, Jan 63, 101p. incl. illus., tables, 52 refs.

Unclassified Report

Suitable melting, casting and fabrication techniques have been developed for the preparation of the intermetallic compounds VNi_3 and VCo_3 in a form suitable for the study of mechanical behavior. The annealing behavior of arc-melted, rolled and extruded materials have been examined using

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ABSTRACT

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This technical documentary report has been reviewed and is approved.

W.G. Ramke
Chief, Ceramics and Graphite
Metals and Ceramics Laboratory
Directorate of Materials and Processes

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES
(continued)

LIST OF FIGURES
(continued)

LIST OF TABLES

I. INTRODUCTION

The mechanical properties of intermetallic compounds, which are defined here as intermediate phases in binary and higher order metal-metal systems in both the ordered and disordered state, are of interest for two principal reasons:

a. A number of these compounds possess desirable physical properties. To exploit these properties practically, the compounds must be fabricated into useful shapes and this requires a basic knowledge of their mechanical behavior.

b. The compounds themselves are being considered as materials for high temperature structural applications. Knowledge of their mechanical behavior is a prerequisite for the selection of the optimum material and treatment. Current knowledge of the mechanical behavior of intermetallic compounds is very limited and incoherent, compared with pure metals and primary metallic solid solutions. Except for some fundamental investigation of weakly ordered intermetallics, and the recent studies of Wood and Westbrook on AgMg[1] and Mote et al., on Ag-Al[2], work on this class of materials generally has been exploratory or ad hoc in nature. In the present investigation, an attempt is being made to provide a fundamental understanding of the mechanical behavior of intermetallic compounds through correlation with pertinent metallurgical phenomena and test parameters for a carefully selected series of binary compounds. The following six criteria were used in choosing the specific intermetallic compounds:

1. Types of crystal structures - The selected compounds should be model materials in the sense that they are representative of groups of compounds with the same crystal structure. This criterion is based on the general knowledge that the mechanical behavior of metals and alloys is largely dependent on their crystal structure. Thus, there may exist as many model intermetallic compounds as the number of different crystal structures that characterize such compounds. From a general point of view, it is desirable to select for investigation one or more intermetallic compounds representing each crystal structure. From such an investigation, it should be possible to establish that there exists a particular set of parameters for each crystal structure that essentially determine the mechanical behavior, or particular sets of parameters apply for certain groups of crystal structures, or a particular set of parameters applies for all crystal structures. However, in view of the relatively large number of crystal structures involved, additional criteria were employed in order to limit the selection to a reasonable number of compounds.

2. Potential importance of crystal structure - The different crystal structure groups represented by the selected compounds should contain

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[1] References are given at the end of the report.

Note: Manuscript released by authors November 1962 for publication as an ASD Technical Documentary Report.

members that possess potentially important mechanical properties at "low", "intermediate" and "high" temperatures. This criterion should increase the possibility that the information obtained from the investigation of model compounds would eventually help in attaining improved mechanical properties. For this purpose, it is not necessary that the selected compounds themselves possess outstanding properties.

A survey of intermetallic compounds which are composed of elements with high melting points, and therefore are potentially important for "high" temperature use, shows that the following crystal structures are common among them:

a. Ordered face-centered cubic and hexagonal close-packed compounds based on the composition AB_3, in which slight differences in stacking of the close-packed layers are described in terms of the compounds on which the crystals structure are based; i.e., the $TiAl_3$, $AuCu_3$, $MgCd_3$, VCo_3, and $TiCu_3$ type structures.

b. Disordered hexagonal-close-packed compounds; e.g., MoPt.

c. Face-centered cubic compounds based on the $MgCu_2$(C15) type crystal structure (Laves Phases); e.g., W_2Hf.

d. Hexagonal compounds based on the $MgZn_2$(C14) structure (Laves Phases); e.g., $TaCr_2$.

e. Body-centered cubic compounds based on the β - W(A15) structure; e.g., Cb_3Os.

f. Tetragonal compounds based on the β - Ur structure (σ Phases); e.g., W_3Os.

g. Cubic compounds based on the α-Mn(A12) structure; e.g., α Ta-Re.

With respect to properties at "low" and "intermediate" temperatures, the above crystal structures appear to offer a sufficiently wide range for study. Based on general knowledge of metals, both face-centered cubic and, to a lesser extent, body-centered cubic structures are considered potentially important. As a class of materials, intermetallic compounds are usually brittle at "low" and "intermediate" temperatures. However, there are undoubtedly factors involved which are not directly related to crystal structure.

3. Compounds existing in same binary system - The selected compounds should preferably include one or more series in which several different crystal structures are obtained by different stoichiometric ratios of the same two metallic elements. This criterion has the advantage that comparisons of mechanical behavior can be more easily made between different crystal structures if the same combination of atoms is used. Another advantage is that the same starting materials can be used in making the compounds. Thus, the contents of both substitutional and interstitial impurities

will tend to be the same, although this will also depend on their respective solubilities in the different compounds. This criterion greatly reduces the choice of compounds since there are only a limited number of binary systems in which there occur three or more compounds whose crystal structures are considered potentially important on the basis of the second criterion.

4. Three-d electronic structure - The selected compounds should preferably include one or more series in which the same crystal structure is represented by at least two combinations of elements. This criterion has the advantage that comparisons of mechanical behavior can be made between isomorphous compounds which are composed of element combinations such as A-B and A-C, where A is common and B differs from C in some electronic feature. An interesting variation to study is the extent to which the 3-d band is filled with electrons in compounds made up of transition elements.

5. Occurrence of ordering - The selected compounds should include some that are known to exhibit ordering. There is considerable evidence that the degree of both long- and short-range ordering affects mechanical behavior as determined by hardness, flow stress, rate of strain hardening, and creep rate measurements. It would be desirable to study effects of ordering in compounds that can also be compared in other ways, but evaluated by the same mechanical tests.

6. Upper melting points - The processing of the selected compounds into test specimens of sufficiently high purity should be feasible. This criterion requires considerable judgment and is difficult to satisfy without preliminary trials. As a precaution, it was decided to restrict attention to compounds possessing melting points below about 1500°C. It was believed that this limitation would increase the chances of successful melting and fabrication as compared with more refractory compounds.

Based on the above six selection criteria, a survey was made of possible model intermetallic compounds for study. It was decided that the three compounds occurring in the V-Co system and the four compounds occurring in the V-Ni system best satisfied the selection criteria. The phase diagrams for these systems[3] are shown in Figures 1 and 2 and the compounds selected for study are listed in Table 1 along with their significant physical properties.

The present report is concerned with the first year (Phase I) of this continuing program. During this period, emphasis has been placed on the melting, casting and fabrication of VNi_3 and VCo_3, and the study of the mechanical properties of these two compounds. In addition, the feasibility of the preparation and fabrication of the other selected compounds has been investigated, and an extensive review made of the literature dealing with the mechanical behavior of intermetallic compounds.* A block diagram illustrating the work sequence

*An invited paper based on this review was presented by Dr. Philip Stark at the Seminar on Intermetallic Compounds, AIME Fall Meeting, New York, October 1962.

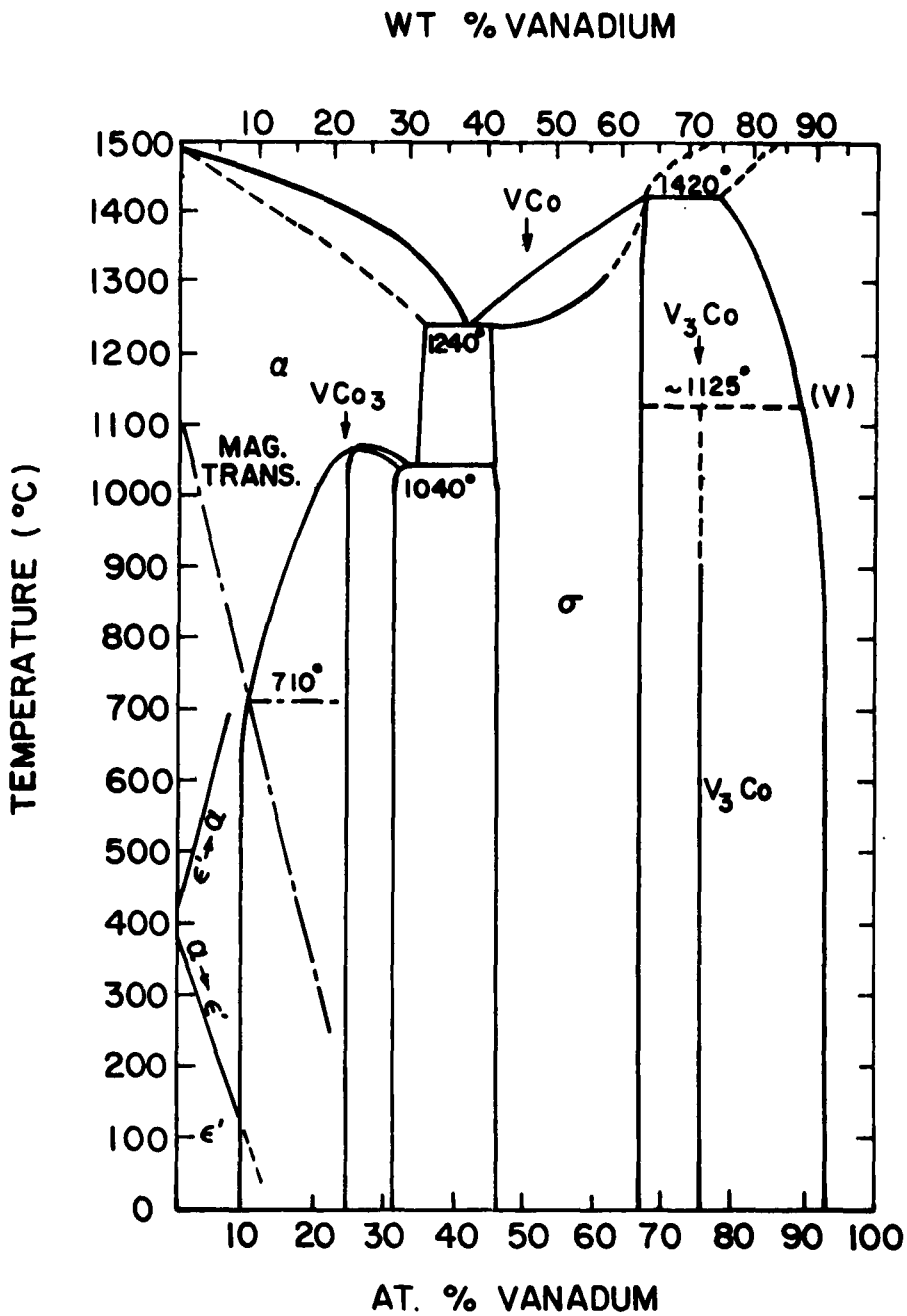


Fig. 1 - Binary phase diagram of Co-V

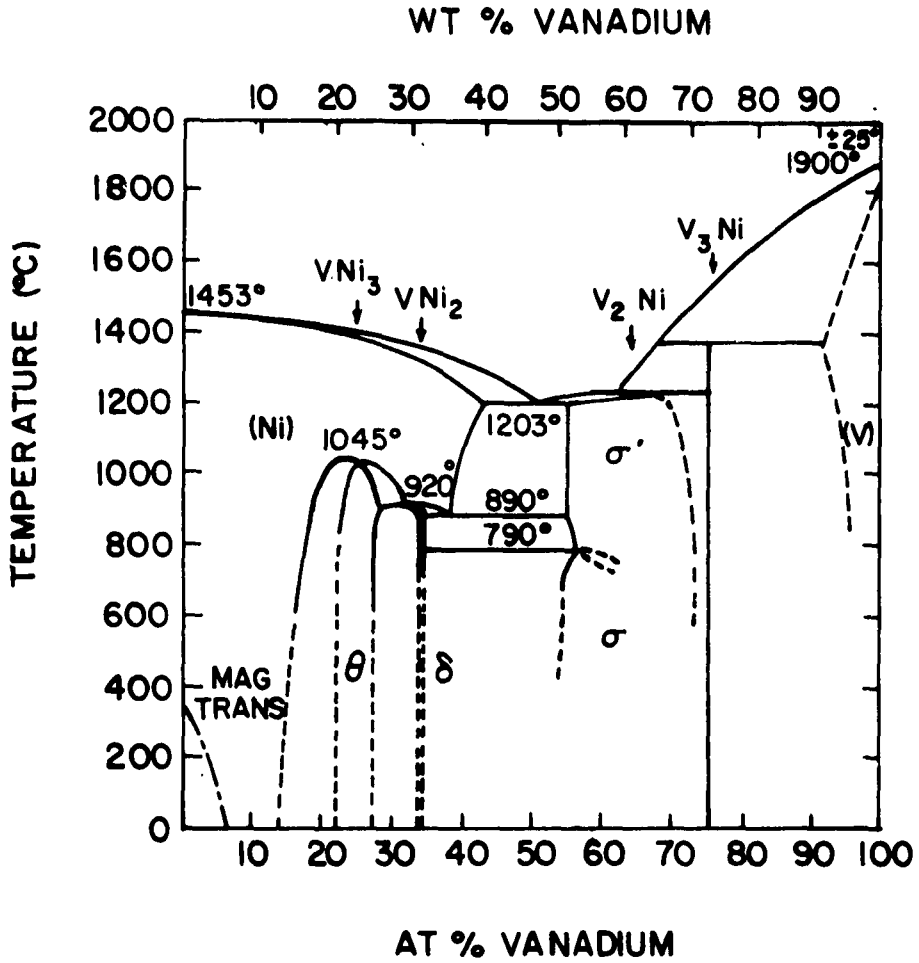


Fig. 2 - Binary phase diagram of Ni-V

Table I

Properties of Intermetallic Compounds Occurring in the V-Co and V-Ni Systems†

Compound	Crystal Structure	Lattice Constants	Homogeneity Range	Approx. Melting Point °C	Stable Temperature Range °C
VCo_3	ordered fcc ordered hcp(2)	---------- ----------	24-31 a/o V (23°C)	1400	below 1070
VCo_3	disordered fcc	----------		1400	1070 - 1400
VCo	tetragonal β-Ur	a = 6.246 A, c = 9.104 A, c/a = 1.458	46-66 a/o V (23°C)	1300-1400	below M.P.
V_3Co	bcc β-W (A 15)	a = 4.675 A,	75 a/o V (23°C)	1500	below 1125
VNi_3	ordered slight tetragonal distortion of cubic $TiAl_3$ type	a = 3.542 A, c = 7.213 A, c/a = 2.036	22-27 a/o V (23°C)	1400	below 1045
VNi_3	disordered fcc	----------		1400	1045 - 1400
VNi_2	orthorhombic (distorted fcc Ni solid solution)	----------	33.6-34.1 a/o V (23°C)	1350	below 920
VNi_2	fcc	----------	same	1350	920-1350
V_2Ni	tetragonal β-Ur*	a = 8.966 A, c = 4.641 A, c/a = 0.5176 (60 a/o V)	55?-73? a/o V (600°C)	1270	below M.P.
V_3Ni	bcc β-W (A 15)	a = 4.71 A	75(?) a/o V (23°C)	1500?	below ~ 1000

† The data is taken from reference (1), except where indicated otherwise.
* Possibly ordered below about 800°C.

involved is shown in Figure 3. Finally, the validity of a possible method of computing Young's modulus for intermetallic compounds has been examined. The ability to predict the elastic modulus would be helpful in selecting suitable compounds for study with reference to particular applications.

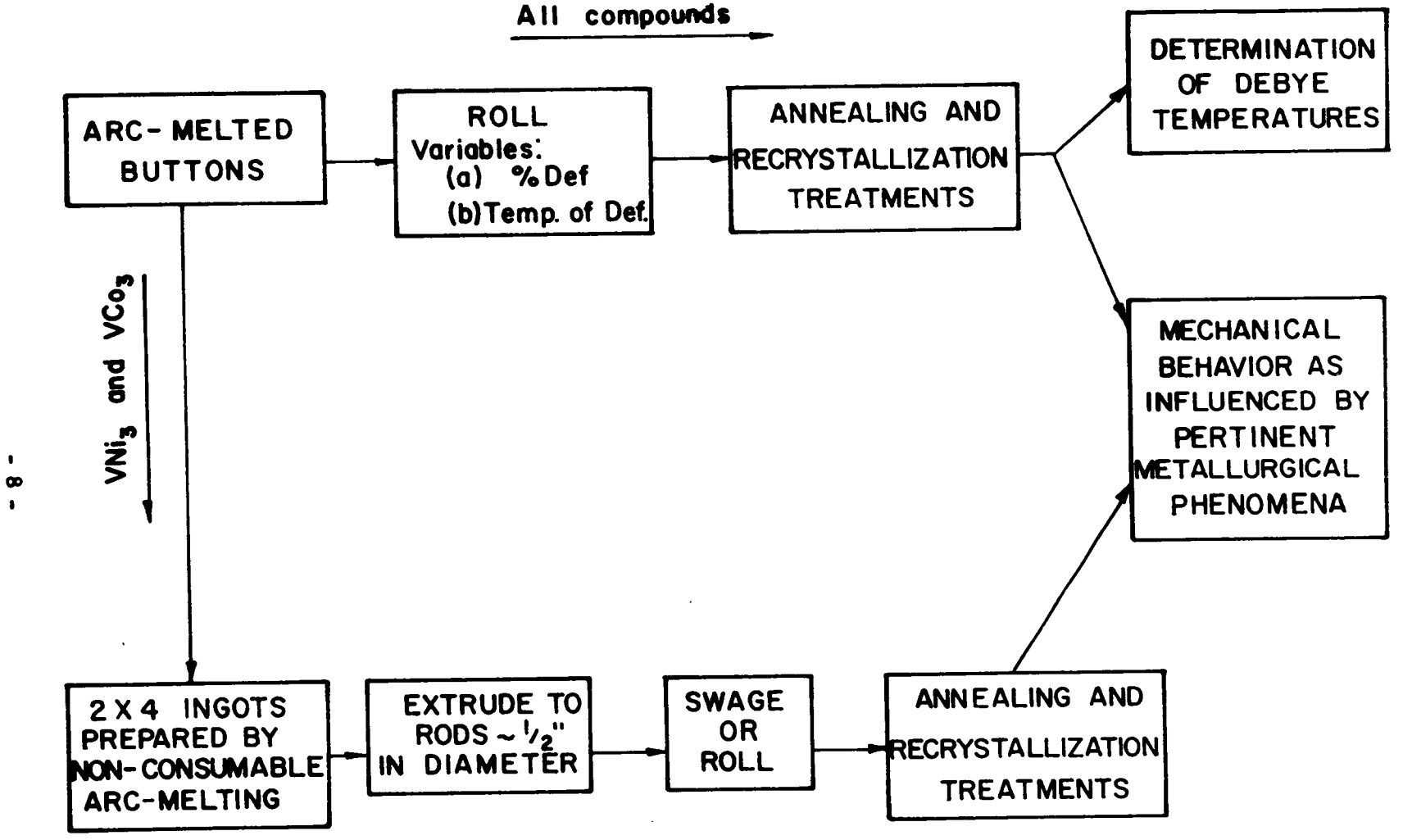


Fig. 3 - Block diagram illustrating work sequence in phase I.

II. REVIEW OF LITERATURE

A. Considerations of Theoretical Strength

The highest strengths which have been achieved to date in ductile, polycrystalline bulk materials have been in the martensitic steels in which yield strengths of 300,000 to 350,000 psi can be developed by appropriate heat treatment[4]. A further increase to about 400,000 psi can be obtained through the application of thermal-mechanical treatments involving severe deformation of the alloy. Although these strength levels are much higher than those available several years ago, the design engineer is seeking still further improvements, not only at ambient temperatures, but also at elevated temperatures. Unfortunately, these martensitic alloys are not very heat resistant and their strength decreases rapidly with increasing temperature. It is clear that if present strength levels are to be substantially increased, then real metals must be able to develop higher fractions of their theoretical strength.

The theoretical or ultimate strength of a crystal is determined by the interatomic bonding forces existing within it. These forces are related directly to the elastic modulus, and as a first approximation, the theoretical strength of a perfect crystal can be computed as being about 5 to 10% of its elastic modulus. However, real crystals do not exhibit such high strengths, since they usually fail by plastic yielding or fracture long before the theoretical strength is reached. Such premature failure is a result of the presence of imperfections in the crystal lattice. It is known that wide variations in the actual strength of a solid can be achieved through changes in its fine structure. The martensitic reaction in steels is one example of the large influence structure may have on strength. Winchell and Cohen[5] have shown recently that the flow stress of iron-carbon-nickel martensites increases substantially with carbon content (40,000 to 240,000 psi) even though the interatomic bonding strength, as measured by Young's modulus, is decreasing in this range of compositions. However, the highest strengths achieved in these martensitic alloys is still far below the theoretical value.

Notwithstanding the important influence that structure has on the strength of real crystals, the ultimate or maximum strength is determined by the interatomic bonding forces existing within the lattice and, thus, a high elastic modulus is indicative of potentially high strength. As has been pointed out by Gilman[6], if the strengths which are currently available are to be increased by an order of magnitude, then it will be necessary to employ solids which possess very high elastic moduli and high resistance to dislocation motion within the lattice. Such solids are the hard metal compounds (i.e., carbides, nitrides, borides). However, these compounds inherently are also very brittle and, therefore, their use in structural applications is limited. Mechanical properties which are intermediate between those of primary metallic solid solutions and those of the hard metal compounds would be most desirable. Intermetallic compounds offer the possibility of achieving such an attractive compromise; that is, somewhat lower strengths but greater ductility and toughness than the hard metal compounds. These metal-metal compounds encompass a wide range of mechanical properties. Generally, those compounds which form

directly from solid solutions or from liquid-solid reactions behave more like primary metallic solid solutions while those which form directly from the melt (that is, melt congruently) approach the behavior of the hard metal compounds.

B. Mechanical Properties of Intermetallic Compounds

1. Elastic Behavior-The Elastic Modulus

Determinations of Young's modulus have been made for only a few of the known intermetallic compounds. Fortunately, in addition to some direct measurements of the elastic moduli of metal-metal compounds, there are a few experimental determinations of the Debye characteristic temperature, which is related directly to the elastic modulus. Thus, according to Debye theory[9], Young's modulus (E) is proportional to $m\theta^2$, where m is the mean atomic weight and θ is the characteristic temperature. This proportionality assumes that variations in Poisson's ratio and the mean atomic volume are negligible. There is evidence from experimental measurements[8,9] that gross trends in Young's modulus may be deduced from changes in θ.

Composition and degree of order have marked effects on the elastic modulus of intermetallic compounds. Nikolaeva and Umanski[10] determined the variation in characteristic temperature with composition for CoAl and NiAl, two brittle, high melting point compounds of the NiAl-type. Assuming $m\theta^2$ is proportional to E, their results show that (a) solutions of nickel and aluminum in NiAl and of cobalt in CoAl produce a decrease in Young's modulus, (b) the decrease in modulus is more pronounced in solid solutions containing vacancy-type defects than for solid solutions containing substitutional-type defects and (c) Young's modulus is a maximum at the stoichiometric composition (i.e., at the maximum degree of order). One would normally expect an increase in Young's modulus with increasing order and such behavior also is observed in Cu_3Au[11], Cu_3Pd[12] and CuZn[13]. However, there are a number of other compounds which exhibit a decrease in E or θ with increasing order. The reason for this difference in the behavior of Young's modulus with changes in the degree of order is not clear at this time.

Portevin and Guillet[14] examined the applicability of the rule of mixtures for predicting the elastic moduli of intermetallic compounds. Their limited data indicates that the elastic moduli of compounds whose bonding is essentially metallic are closely approximated by the rule of mixtures whereas the elastic moduli of those compounds whose bonding is predominantly covalent exhibit large positive deviations. However, their interpretation is open to criticism since they applied the rule of mixtures without correction to compounds whose component elements differ in crystal structure.

In selecting compounds for possible applications, it would be desirable if their elastic properties could be compared by computations from existing data. An estimate of the Debye temperature may be possible for congruent melting metal-metal compounds by using the semi-empirical Lindemann equation[15]. This type of calculation has been applied recently by Kaufman[16] to a number of NaCl-type compounds with reasonable success.

2. Plastic Behavior

2.1 Flow Stress

Effect of Ordering - The available experimental data[17,21] indicate that the flow stress of intermetallic compounds is a maximum at some intermediate degree of order and this behavior appears to be independent of the type of ordered lattice. However, the position of the maximum varies from one alloy system to another, and it may lie at or below the critical ordering temperature, T_c. This variation in the position of the peak strength results from the fact that the principal order-strengthening mechanism may vary from one system to another. It is probable that several different order-strengthening mechanisms are operative in the various experiments which have been reported, and the position of the strength maxima will be determined by the relative contributions of each mechanism. The strengthening theories which have been proposed[22,27] take into account the effects of short range order and partial long range order of the homogeneous and inhomogeneous types.

In addition to the strengthening derived from degree of order per se, two other strengthening effects should be noted. One involves the marked strengthening produced in systems where the ordering reaction involves a change in crystal structure[28,29]. These alloys are composed of partially ordered regions in a disordered matrix (inhomogeneous order) and the strengthening, which is a maximum at an intermediate degree of order, arises principally from the internal strains set up as a result of the misfit between the ordered and disordered regions. Such systems are analogous to precipitation hardening systems[29]. The second potent strengthening mechanism is the one proposed by Cottrell[30], and involves the interaction of dislocations with antiphase boundaries. The theory predicts a maximum in strength at a critical domain size of around 50 Å. Ardley[31] and Biggs and Broom[32] have observed a maximum in strength as a function of domain size in Cu_3Au, which they attribute to the Cottrell mechanism. In recent experiments on Fe_3Al[21], Lawley, Vidoz and Cahn observed a maximum in strength as a function of annealing time, which also appears to arise from Cottrell's domain size theory.

Yield points[17,31-33], yield-elongation regions over which stress remains relatively constant[31,32,34], and strain aging effects[31,35], have been observed in a number of intermetallic compounds. Such behavior can arise from both the Cottrell and Suzuki dislocation-locking mechanisms, which were originally proposed for metals and primary metallic solid solutions, and from dislocation locking mechanisms which are unique to ordering systems. These latter mechanisms involve dislocation interactions with order gradients.

Effect of Composition - Flow stress is greatly influenced by variations in composition within the single phase region of the compound. Changes in composition result in the introduction of point defects into the lattice which, in turn, alters the degree of order. Flow stress measurements on AgMg[1] have shown that sharp minima occur at the stoichiometric composition. Similar observations have been made by Kornilov[36] in Ni_3Fe. It appears that at low homologous temperatures, these minima are characteristic of the presence of a

compound. If one retains the high temperature Fe-Ni γ solid solution by quenching to room temperature, then the minimum disappears and the curve changes smoothly with composition. Generally hardness and tensile strength data obtained at low homologous test temperatures also exhibit minima at the stoichiometric composition. This off-stoichiometric or "solid-solution" hardening of the compound has been interpreted principally in terms of the introduction of lattice strains by either substitutional- or vacancy-type defects, although chemical and electronic effects also may play a role. The vacancy-type defect appears to be a more potent strengthener than substitutional atoms[38,39]. The substitutional defect can be a component element in excess of stoichiometry or a ternary solute addition. Quite clearly, the degree of hardening depends on the element selected as the ternary or excess addition, since the amount of lattice strain introduced varies with the substitutional defect. For example, excess silver[1]. However, the interpretation of the influence of substitutional defects per se on strength is complicated by the recent observations of grain boundary hardening effects resulting from oxygen and/or nitrogen absorption in binary compounds having either a stoichiometric excess of an active element (i.e., excess Mg in AgMg) or appropriate ternary additions[37]. These observations suggest that the true effect of either a ternary addition or an excess active element on strength cannot be evaluated until the anomalous grain boundary hardening is eliminated. This grain boundary hardening effect will be discussed further in Section 2.2.

Effect of Strain (Work-hardening) - It appears to be a general phenomenon[17,27,32,33,35] that a fully ordered alloy work-hardens much more rapidly than the disordered alloy and that, in general, compounds work-harden much more rapidly than metals. In fact, it has been suggested that the brittleness of intermetallic compounds results from their high rate of work-hardening. A number of hypotheses have been suggested to explain the enhanced work hardening rate of ordered lattices: (a) The difficulty of cross-slip in an ordered material resulting from the extended nature of the superdislocations[40] (b) the reduction in domain size of the ordered alloy with increasing deformation[27] and (c) the production of strips of antiphase domain by jogged superdislocations in the ordered material[33].

Effect of Grain Size - The only attempt to examine quantitatively the effect of grain size on the flow stress of a wrought compound has been by Wood and Westbrook in AgMg[1]. Their results indicate that grain size has only a small influence on the flow stress of AgMg at low homologous temperatures. Unfortunately, the treatments employed to vary grain size also may have varied the substructure, dislocation density and distribution of solute atoms, and it appears that this may be the reason for their data not obeying the usual linear relationship between flow stress and the inverse square root of the grain diameter.

Effect of Temperature and Strain Rate - There have been very few measurements of flow stress as a function of temperature for strongly ordered compounds and most of our knowledge of the high temperature strength of intermetallic compounds derives from hardness measurements. Because hardness tests cannot distinguish between variations in flow stress and variations in work-hardening characteristics (unless the elaborate Meyer analysis is applied), it generally is not possible to assess the actual change in flow stress

with temperature from such measurements. However, it can be said that the strengths of many intermetallic compounds, as measured by hardness, possess high heat resistance.

The first extensive study of the tensile behavior of an ordered intermetallic compound was carried out by Wood and Westbrook on AgMg[1]. Three regimes of deformation behavior are exhibited by this compound: (i) at low temperatures and moderate strain rates (~ 0.005 min.$^{-1}$) where the deformation is primarily by slip,(ii) at intermediate temperatures and low to moderate strain rates ($\leq$ 0.005 min.$^{-1}$) where interactions between solute atoms and dislocations play a prominent role in determining mechanical behavior, and (iii) at high temperatures and low strain rates where deformation is controlled by diffusion processes. The results at low temperatures already have been summarized. In the intermediate temperature range, the flow stress was found to be inversely proportional to the absolute temperature, and at a constant temperature, exponentially related to strain rate. At high homologous temperatures ($> 0.6T_M$) and for small deviations from stoichiometry, the flow stress is a minimum at the stoichiometric composition. However, hardness data obtained at equivalent homologous temperatures for AgMg[41] exhibit maxima at the 50-50 composition. The maximum in hardness at high temperatures was explained on the basis that deformation in this range is diffusion controlled and point defects enhance diffusion. From the flow stress measurements, it appears, at least for AgMg, that defects have a greater influence on slip than on diffusion when present in low concentrations.

Since intermetallic compounds are being considered for high temperature structural applications, their creep behavior is of prime importance. Studies on the creep behavior of metal-metal compounds have shown that the compounds generally possess greater creep resistance than either the pure components or the primary solid solutions of their components[36,42] and that both short and long range order enhance creep resistance[36,43].

2.2 Ductility

Effect of Temperature, Strain Rate and State of Stress - Although there are noted exceptions, a general shortcoming of intermetallic compounds is their poor ductility at low homologous test temperatures. Their brittleness is associated usually with grain boundary effects, since not only are most fractures intergranular but also single crystals exhibit more plasticity then do polycrystals. However, almost all intermetallic compounds exhibit some plasticity at elevated temperatures (0.7-0.9 of their melting point). Slow strain rates and a nearly hydrostatic stress state are also conductive to high plasticity. The application of these three factors has permitted the fabrication of a number of compounds by extrusion.

Effect of Prestraining - Savitskii[44] has reported that the extrusion of a cast material increases its plasticity in subsequent hot compression tests. Wood and Westbrook[1] also found that prestraining enhances the ductility of AgMg. As an example, an extruded silver-rich wire was ductile at room

temperature,whereas the same composition in the as-cast condition was completely brittle. For AgMg, explanations based on the existence of a coarse grain structure and compositional heterogeneities within the cast material cannot account for the observed difference in ductility. Extruded AgMg remained ductile even after an anneal which developed a grain size comparable to that found in the as-cast material. In addition, long-time homogenization treatments which appeared to eliminate gross compositional heterogeneities did not make the as-cast material ductile. Another example of the enhancement of plasticity by prior straining was observed in magnesium-rich AgMg. Prestraining in tension at slow strain rates and at high temperatures considerably increased the subsequent room temperature ductility. From the evidence available, it appears that prestraining per se may improve the ductility of intermetallic compounds.

Effect of Composition - It is known that the ductility of a compound can be affected significantly by compositional variations within the single phase field. For example, the tensile transition temperatures for AgMg compounds containing excess silver were found to be about 400°C lower than for those containing excess magnesium[1]. The intergranular brittleness of these magnesium-rich compositions has been shown[37] to arise from a hardening of the grain boundary regions relative to the bulk material. Although the specific hardening mechanism is not known, the phenomenon appears to be the result of preferential absorption of nitrogen and oxygen and their segregation to grain boundaries. This hardening is independent of the type of crystal structure, and is found in a large number of binary intermetallic compounds which have a stoichiometric excess of the "active" component element. It is not observed in those compounds in which the "active" element is less than the stoichiometric composition. An "active" element is one which has a high reactivity with, or solubility for, the gaseous impurities oxygen and nitrogen. Hardness measurements as a function of temperature show that the temperature at which the grain boundaries are no longer harder than the bulk material is approximately the temperature at which the onset of plastic deformation is achieved. Such a correlation strongly suggests that the presence of grain boundary hardening is at least partly responsible for the higher transition temperature of the magnesium-rich compounds compared to the silver-rich compounds. However, the brittle behavior of silver-rich compounds at temperatures close to liquid nitrogen apparently results from another cause since no grain boundary hardening is obtained for these compositions. It also should be noted that appropriate ternary solute additions can produce this grain boundary hardening effect in compositions which normally do not exhibit it (i.e., in the silver-rich compound). Furthermore, certain ternary additions and, to some extent, annealing treatments can modify or eliminate the effect.

C. Synopsis

In summary, intermetallic compounds encompass a wide range of crystal structures, bonding types and properties. These compounds are being considered for high temperature structural applications because their mechanical behavior generally is intermediate between that of the primary metallic solid solutions and the hard metal compounds. Although at low homologous temperatures many of them are brittle relative to metals, their room temperature impact strengths

are high compared with the more refractory compounds, and there are indications that their generally low ductility can be improved. It is clear that if an understanding of the mechanical behavior of intermetallic compounds is to approach that of the primary metallic solid solutions, and if some systematization and generalization of their behavior is possible, then more information is needed concerning the effects of pertinent metallurgical and test parameters. The objective of this present investigation is to provide some of this needed information.

III. EXPERIMENTAL PROCEDURE

A. Materials

The types and typical analyses of the starting materials used in preparing the selected V-Ni and V-Co compounds, are given in Table II. The acceptability of the various starting materials was confirmed by metallographic examination. The pellets were used for the bulk of the melting, which was by the non-consumable arc technique. The rods and wires were employed in an attempt to prepare the compound VNi_3 by electron beam melting. Since the procedure for alloying by the latter method, and indeed its feasibility, had not been established for these compounds, trial runs were made with materials that were readily available and not of the highest purity.

B. Melting Techniques

1. Arc-Melting

Non-consumable arc-melted buttons (1-5/8" dia. x 3/8" thick) of all the compounds were prepared in an MRC-type furnace under argon at a pressure of 260 mm of mercury and with a thoriated tungsten electrode. Before each melting, the chamber was evacuated, purged twice with argon and then back-filled to the final partial pressure.

Extrusion billets of VNi_3 and VCo_3, 2 inches in diameter by 3 to 4 inches in length, were prepared in the following manner. Arc-melted buttons of each compound (45 of them were required for a 3 inch billet and 60 for a 4 inch billet) were crushed into pellets, cleaned in aqua regia and then re-melted by non-consumable arc-melting to form the billet. Two billets were made of each compound. Each billet was cropped at the top to remove the shrinkage cavity and then machined to either 1-1/2 or 1-3/4 inches in diameter, depending upon the condition of its surface.

2. Electron Beam Melting

Attempts were made to prepare very pure specimens of VNi_3 in an electron beam zone-melting furnace,[45] both by forming the compound directly from its component elements and by zone-refining the arc-cast compound. In the attempts to prepare the compound VNi_3 from its pure elements, two types of anode were employed: (a) nickel wire tightly coiled about a bundle of straight vanadium and nickel wires and (b) vanadium wire closely coiled about a nickel rod. The vanadium: nickel ratio per unit length of the composite was chosen to yield an alloy lying in the VNi_3 single-phase field. In the case of the coiled wire anode, the nickel rod was melted first and the vanadium allowed to dissolve into the surrounding molten pool.

For the zone-refining of arc-cast VNi_3, a suitable anode was prepared by electron beam welding together several 1/8-inch diameter rods which were ground from a single button.

Table II

STARTING MATERIALS

Material	Source	Form	Diameter (Inches)	Typical Analyses (Wt. %)	
Vanadium	VCA	Pellets	0.250	99.6	V
	McKay	Wire	0.020	0.05	Fe
				0.05	C
				0.07	O
				0.03	N
				0.005	H
Mond Nickel	McKay	Pellets	0.370	99.9	Ni
				0.03	Fe
				0.003	Cu
				0.06	C
				0.001	S
				Trace	Si
	Whitehead	Rod	0.250	99.45	Ni(+Co)
				0.15	Fe
				0.06	Cu
				0.25	Mn
				0.05	C
				0.005	S
Grade A	McKay	Wire	0.020	99.4	Ni (max)
				0.05	Fe (max)
				0.25	Cu (max)
				0.35	Mn (max)
				0.05	Si (max)
				0.20	C (max)
				0.02	S (max)
Electrolytic Cobalt	McKay	Pellets	0.250 - 0.370	99.6	Co
				0.10	Ni
				0.08	Fe
				0.006	Cu
				0.006	Mn
				0.027	Si
				0.035	Al
				0.004	Zn+Cd
				0.001	Pb
				0.01	C
				0.035	O
				0.0007	H
				0.008	S
				0.003	P

C. Fabrication Methods

1. Rolling

A 2-inch high, 15 inch diameter mill was employed for the various rolling experiments. In order to prevent oxidation during heating and hot-rolling, the specimens were sealed in a stainless steel tube, after first purging with argon gas.

2. Swaging

The rods to be swaged were preheated in a Glo-Bar electric furnace in an atmosphere of argon. The swaging experiments were carried out using preheated "handspring" dies.

3. Extrusion

The extrusion of VNi_3 and VCo_3 was carried out in a 300 ton press fitted with a steel liner preheated to 480°C. A ram speed of 30 inches per minute was employed. Each billet was contained in a stainless steel jacket which was evacuated at room temperature to less than 0.03 microns and sealed.

D. Heat Treatment

Most of the heat treatments were carried out in a quartz vacuum tube furnace which was maintained at a pressure of less than 5×10^{-6} throughout the heat treatments. The specimens were held in recrystallized alumina crucibles to prevent contamination by the vacuum chamber walls. A record of each heat-treatment was made on a strip chart by a Honeywell Brown Electronik Potentiometer Recorder. Cooling was accomplished by "furnace-cooling", in which the furnace was shut off, and by "rapid quenching", in which the furnace was rolled back from the quartz vacuum tube. These two methods gave cooling rates of 2.5°C/min and 240°C/min respectively.

Specimens requiring a brine quench were placed in a recrystallized alumina crucible and sealed in a quartz vacuum tube, which was first outgassed at a temperature of approximately 530°C and a pressure of less than 5×10^{-6} mm of mercury. The tubes were then heated in a Kanthal wound resistance furnace. At the end of the heating period, the specimen tubes were rapidly removed from the furnace and quenched in brine; simultaneously, the quartz tubes were broken to ensure effective quenching of the specimens.

E. Mechanical Testing

1. Hardness

Hardness measurements were made using a Leitz Durimet Microhardness Tester with a 500 gram load. Calibration was carried out at frequent intervals by the use of a standard test block.

2. Indentation Stress-Strain Measurements

For some specimen conditions where it was inconvenient or impossible to carry out compression or tensile tests, stress-strain characteristics were determined by the method of surface indentation measurements. In this method, the diameter of an impression made on the polished surface of a specimen by a spherical cemented carbide ball is measured as a function of indenting load. Two indentors, 1/32" and 1/64" in diameter, were used to achieve a wide range of strain using the same loads.

As previously determined[46] for copper and mild steel and several alloy steels, the stress-strain relationships can be expressed in terms of the mean pressure (P_m) applied by the spherical indentor and the diameter (d) of the resulting indentation as follows:

$$\text{stress: } \sigma = \frac{P_m}{c_1} = \frac{4W}{c_1 d^2}$$

$$\text{strain: } \epsilon = \frac{c_2 d}{D}$$

where W = applied load

D = the diameter of the indentor

C_1 and C_2 = constants

Values reported[46] for these constants are $C_1 = 2.8$, $C_2 = 20$. For the present application it was assumed that these constants remain the same for all heat treated conditions.

The loads used in indentation test varied from 1 kilogram to 10 kilograms. A Leitz microhardness tester was used in the range up to 2 kilograms, and a Kentron microhardness tester was used for higher loads.

3. Compression Testing

Compression samples were prepared from extruded rods by centerless grinding to 0.399" $\pm$ 0.001" in diameter and sectioning into approximately 1/2 inch long specimens. These specimens were held in a precision "V" block and flat parallel faces surface ground perpendicular to the axis. SR-4 (Type A-18) wire resistance strain gages were then mounted on the specimens for the determination of elastic modulus, elastic limit and stress-strain curve out to 0.01 strain. The modulus was measured on an Instron machine with a compression load cell by simultaneous recording of Instron load and strain gage output on a Baldwin strain indicator. Elastic limits were obtained by periodically unloading and measuring the residual plastic strain. Stress-strain curves were determined on a Baldwin 60,000 pound hydraulic testing machine. Strain-gages were used for strains up to about 0.01. The gages were then soaked

off in acetone and further plastic compression recorded by measuring the axial strain discontinuously, i.e. load-release method, with a micrometer. This technique has the advantage of inhibiting the onset of barrelling.

4. Tensile Testing

Tensile specimens, 2 in. long, were prepared from extruded rods by centerless grinding (0.050" diameter). After heat-treatment, the specimens were electropolished to reduce the gage section and ensure a smooth surface. This was accomplished by lacquering each end of the specimen so as to leave a center section one inch long exposed to the polishing solution. In the first tests carried out, some slipping in the grips was observed and the specimens fractured in the gripped portions, which was held in a modified pin chuck. Consequently, for later specimens, the entire length was electropolished before reducing the gage length further. This method of preparation reduced the number of fractures within the grips. However, some slipping still occurs and alternative methods of gripping the specimens are being investigated.

Tensile testing was carried out on a modified Polyani tensile machine of a design similar to that described by Adams[47]. In this machine, load is applied to the specimen by movement of the lower grips which are connected to a movable frame cross-head by means of a tie rod. The cross-head is driven by a constant speed synchronous motor through a translating screw and reduction gears. The upper grips are connected by means of a tie rod to a load measuring dynamometer, which is connected to the stationary part of the frame. Axiality of loading is facilitated by means of universal joints at the upper and lower ends of the tie rod and at the lower grips. Two interchangeable resistance strain-gage dynamometers (J. Langham Thompson, Ltd., England) of the proving ring type, with load ranges of 0 to 200 pounds and 0 to 500 pounds are used for load measurement. Constant voltage is supplied to the dynamometer by lead storage batteries (18 volts). Controlled variations in input voltage are provided by decade resistance in series between the batteries and the dynamometer. Dynamometer output voltage, corresponding to the applied load, is recorded on a Honeywell Brown Electronik Potentiometer Recorder together with the corresponding specimen extension. The latter is defined by the proportionality between the selected constant movable frame cross-head speed and the selected constant chart speed.

F. Metallography

1. Light Microscopy

Standard metallographic preparation technique using silicon carbide papers followed by diamond paste were generally used. For some specimen conditions, mechanical polishing produced artifacts and it was necessary to develop an electropolishing technique. Satisfactory electropolishing was achieved using an electrolyte of 4 parts conc. H_2SO_4 in 3 parts H_2O and a current density of 0.5 amp/cm^2. Microstructural examinations were always made on longitudinal sections parallel to the direction of working. In addition, a few observations were made on transverse sections. Grain size determinations were

made by the linear intercept method, taking the average of determinations on nine different areas.

2. Electron Microscopy

Negative parlodion replicas of suitably etched specimens were prepared by dry stripping with scotch tape using a 200 mesh nickel grid, and shadowing with chromium at 27.5°. Examination was carried out on the RCA-EMU2 and the Hitachi HU-11 electron microscopes.

In addition to the replica microscopy, some preliminary work was carried out on the development of a technique suitable for the preparation of thin-foil specimens for transmission microscopy. The technique attempted up to the present has involved the surface grinding of heat-treated sheet material to a thickness of 0.015 in., followed by hand polishing on water-lubricated silicon carbide paper down to a thickness of 0.004 in. Finally, the sheet has been electrothinned by a "window" technique, using the sulphuric acid-water electrolyte developed for electropolishing. The foils produced as yet have not been of good quality and will not be discussed in this report. With some modification, the technique appears likely to be quite suitable for these compounds.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. Melting and Alloying of Compounds

1. Button Ingots

Since very little was known about melting procedures for any of the selected compounds, it was decided that preliminary information should be obtained on small melts before proceeding on to large ingot sizes. Therefore, non-consumable arc-melted buttons of all the compounds were prepared from appropriate mixtures of vanadium, cobalt and nickel pellets. The chemical analyses of buttons prepared in this manner are given in Table III. Extensive analyses on a VNi_3 and a VCo_3 button, taking samples from along the diameter and through the thickness, revealed only minor variations in composition throughout the buttons.

Metallographic and microhardness examination of the as-cast buttons showed the VNi_3 and VNi_2 to be essentially single phase despite some coring (dendritic segregation) - see Figs. 4 and 5. In contrast, the V_2Ni consists primarily of two phases, with possibly a small amount of a third phase present (Fig. 6). The brittle, intergranular constitutent, exhibits a fine lamellar structure and apparently results from the eutectoid decomposition of σ the high temperature form of V_2Ni. The microstructure of the V_3Ni is composed of three phases (Fig. 7). The presence of the third phase arises from non-equilibrium cooling conditions; although the V-Ni phase diagram has not been clearly defined in this region, it appears that these phases may be V_3Ni, V_2Ni and σ'.

The microstructure of the VCo_3 shown in Fig. 8 is essentially single-phase, although dendritic segregation or coring is present. Some inclusions, pinholes and apparent grain boundary precipitate are visible in the structure. VCo cracked during cooling from the melting temperature and a satisfactory metallographic specimen could not be prepared. The as-cast structure of V_3Co (Fig. 9) consists of three phases, possibly V_3Co, VCo and a vanadium rich solid solution. Regions near the surface of the casting exhibit some intergranular cracks similar to those in VCo.

A measure of the relative brittleness of the as-cast buttons was obtained from observations made when attempting to cut them into sections for metallography and heat-treatment. VNi_3, VNi_2 and VCo_3 buttons could be cut with relative ease. The V_3Ni could be cut only with difficulty due to its high hardness. Some buttons of V_3Co could be cut without cracking, but others exhibited numerous macrocracks after cutting; this inconsistancy in behavior may be a result of variations in the volume percentage of σ phase and the number of microcracks formed during casting. In contrast with the preceding compounds, V_2Ni and VCo as-cast buttons could not be cut without shattering. The effects of homogenization on these compounds is discussed in a later section.

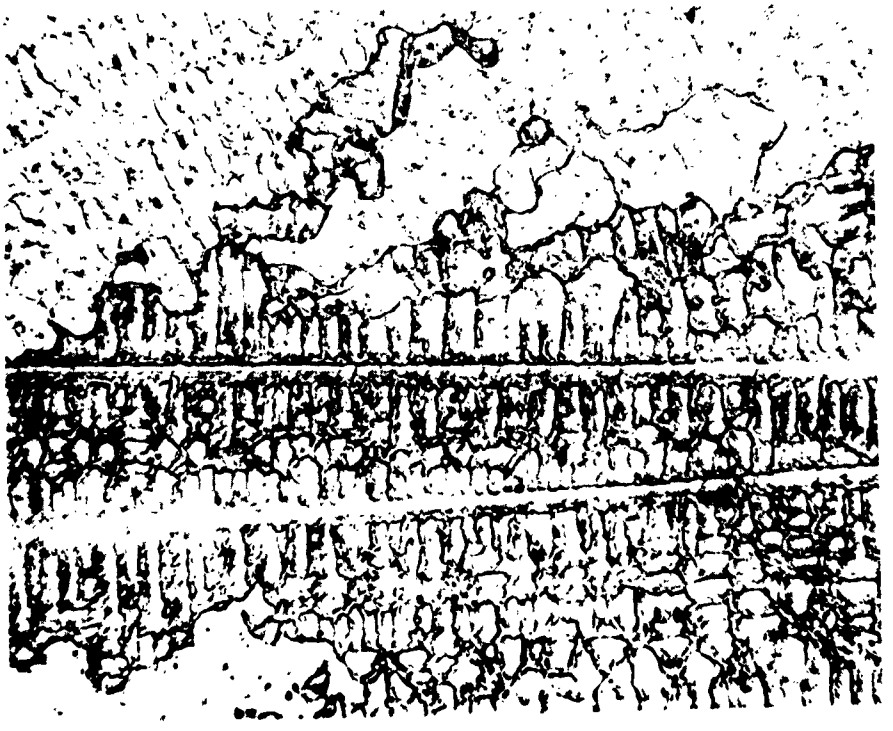
Table III

Chemical Analysis of Arc-Melted V-Ni and V-Co Buttons

Compound	Vanadium Homogeneity Range[2] (wt.%)	Stoichiometric Vanadium (wt.%)	ANALYSIS (WT.%)			
			Vanadium	Carbon	Oxygen	Nitrogen
VNi_3	19.7-24.4	22.5	22.1	0.022	0.026	0.007
VNi_2	30.5-31.1	30.3	30.1	0.016	0.041	0.008
V_2Ni	51.5(?)-70.2(?)	63.4	61.6	0.045	0.101	0.005
V_3Ni	None Indicated	72.3	71.4	0.043	0.099	0.034
VCo_3	21.5-28.0	22.4	23.3	0.016	0.033	0.012
VCo	42.5-62.7	46.4	44.2	0.046	0.091	0.015
V_3Co	None Indicated	72.2	71.6	0.034	0.109	0.010

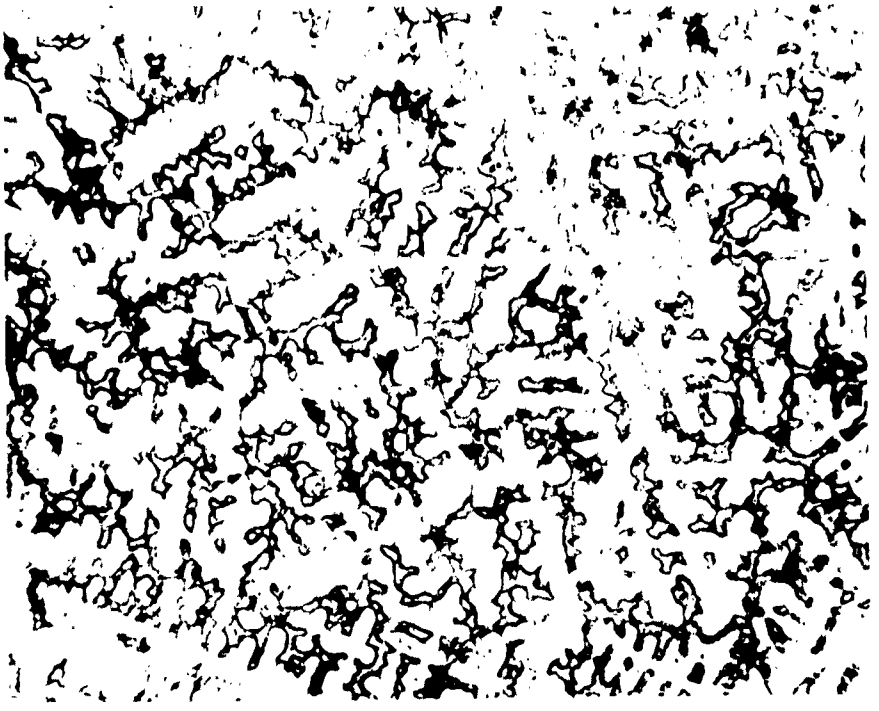
Aqua Regia 500X

Fig. 4 - Microstructure of as-cast VNi_3.

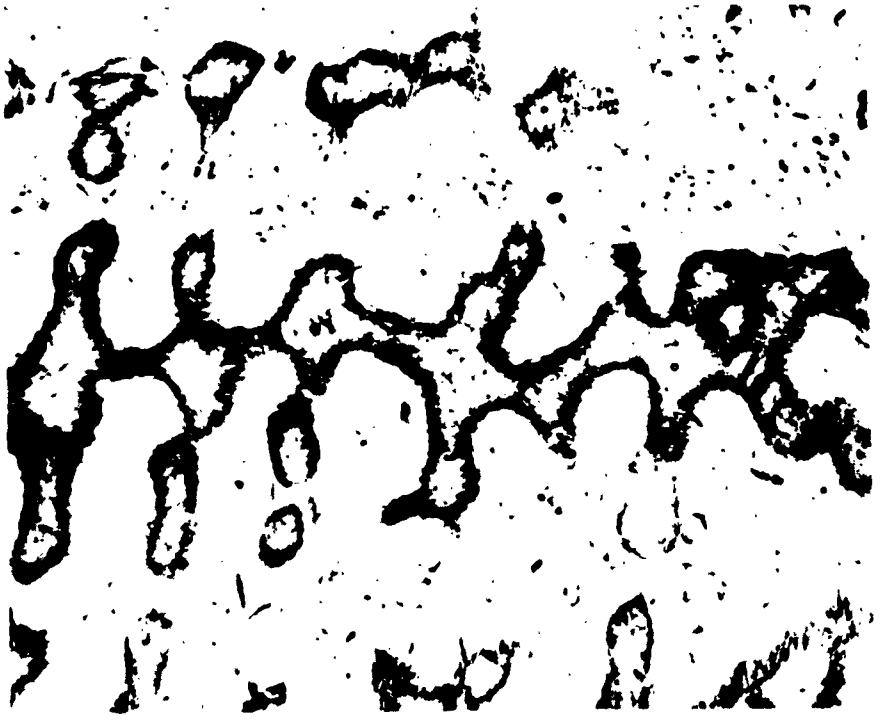


Aqua Regia 100X

Fig. 5 - Microstructure of as-cast VNi_2.

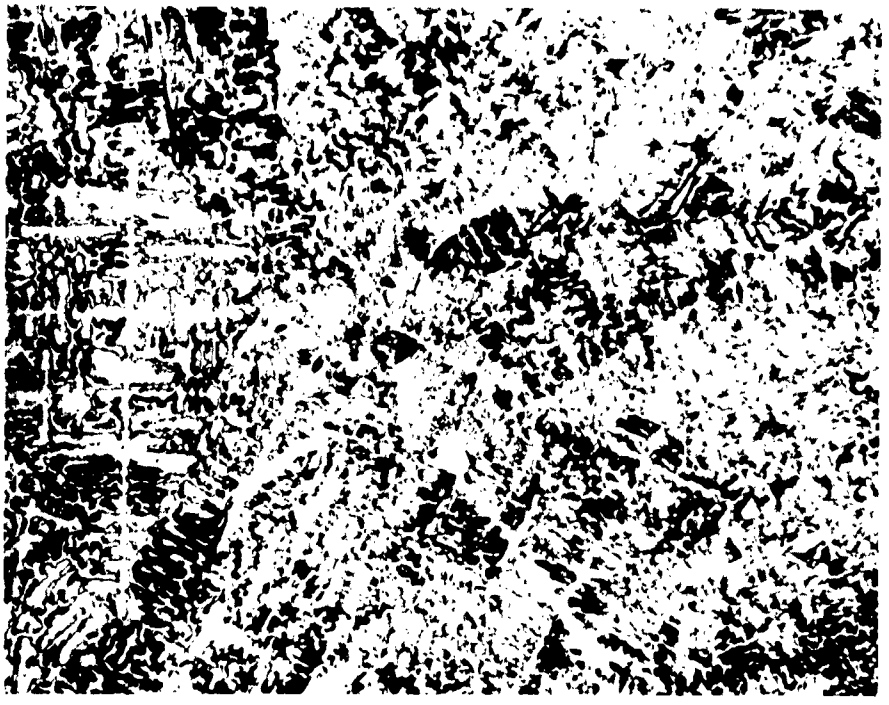


Aqua Regia 100X

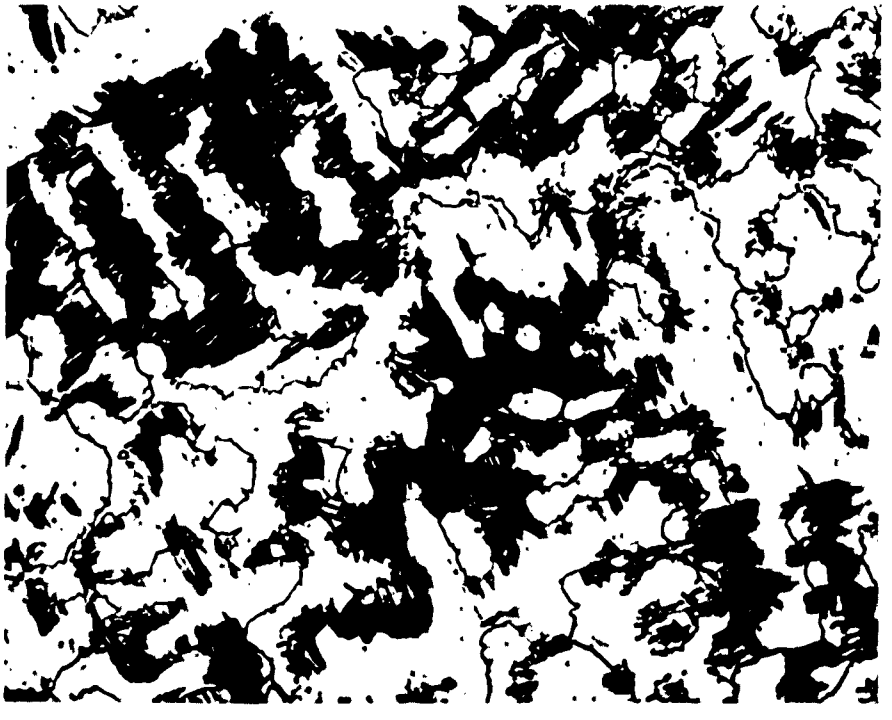


Aqua Regia 500X

Fig. 6 - Microstructure of as-cast V_2Ni.

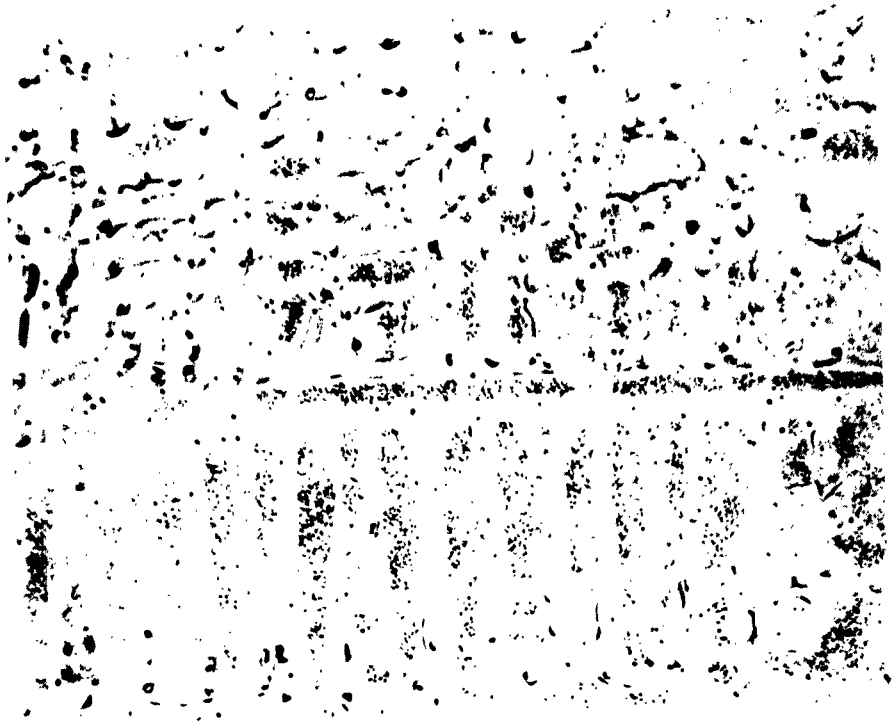


Aqua Regia 100X



Aqua Regia 500X

Fig. 7 - Microstructure of as-cast V_3Ni.



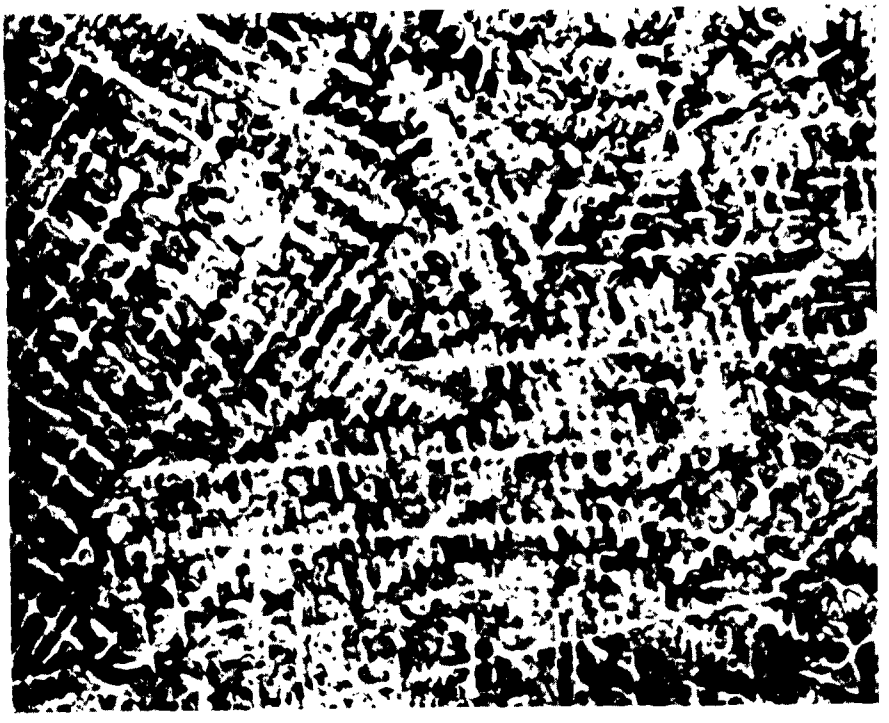
Acetic:Nitric:Water
1:1:1

100X

Acetic:Nitric:Water
1:1:1

500X

Fig. 8 - Microstructure of as-cast VCo_3.



Acetic Acid:Nitric Acid: Water
1:1:1

100X

Acetic Acid:Nitric Acid: Water
1:1:1

500X

Fig. 9 - Microstructure of as-cast V_3Co

2. Extrusion Billets

Arc-melted billets of VNi_3 and VCo_3 were prepared for extrusion to approximately 1/2 inch diameter rod. Each billet was cropped at the top to remove any shrinkage cavities and then machined to either 1-1/2 or 1-3/4 inches in diameter, depending on the condition of its surface. After machining, three of the billets still exhibited a few shallow blow-holes at the surface, and the fourth had a small number of circumferential surface cracks. However, it was decided that these were minor defects and that the billets should yield sound material after extrusion.

The vanadium, carbon and tungsten analyses of the four billets are given in Table IV. The two former were made on chips machined from the top, middle and bottom portion of each ingot. The tungsten content was determined on only one billet of each compound. It is seen that the compositions of the ingots lie within the homogeneity range of their respective compounds, and that the variation in vanadium content along the length of each billet is within the precision of the measurements. With the exception of the B1 billet, the impurity content is low. However the carbon contents were determined gravimetrically and should be considered as only approximate; carbon is now being re-determined conductometrically. Billet B4 contains essentially no tungsten and although billets B2 and B3 were not analyzed for tungsten, the quantity of insoluble residue on digestion of samples from these billets indicates that their average tungsten content is less than 0.05%. An overheating of the electrode during the melting of the first ingot is the cause of the higher tungsten content in B1 (0.23% W).

3. Electron Beam Melting

Attempts were made to prepare the compound VNi_3 from its pure elements by electron beam zone-melting. In the initial attempt, the anode was a random arrangement of straight vanadium and nickel wires enclosed in a closely wound nickel wire sheath. This arrangement of the component elements proved unsatisfactory since a uniform stable melting zone could not be maintained. Very little alloying occurred and the nickel-vanadium ratio varied considerably along the length of the composite due to dripping and running of the molten nickel.

The next three attempts to prepare the compound involved the use of an anode consisting of vanadium wire wrapped around a nickel rod. The melted rod was consistently found to be covered with a black layer which was apparently oxide. Two distinct metallic layers were observed beneath the outer oxide, indicating that complete alloying did not occur throughout the cross-section. The outer layer was vanadium rich V-Ni alloy and the inner core, which occupied about 90% of the cross-section, was essentially unalloyed nickel.

It was decided that no further effort should be spent in attempting to prepare the compounds by the electron beam zone melting technique.

Table IV

Chemical Analyses of VCo_3 and VNi_3 Billets

Compound	Billet No.	Section of Ingot Analyzed	Vanadium (wt.%)	Carbon (wt.%)	Tungsten (wt.%)
VCo_3*	B1	Average	22.2	0.014	0.23
	B2	Top	22.3	0.016	
		Middle	22.4	0.014	
		Bottom	22.1	0.022	
VNi_3+	B3	Top	22.3	0.014	
		Middle	22.3	0.003	None Found(< 0.02)
		Bottom	22.2	0.011	
	B4	Top	22.3	0.008	
		Middle	22.3	0.014	
		Bottom	22.3	0.008	

*Homogeneity Range: 21.5 - 28 wt.%
Stoichiometric Composition: 22.4 wt.%

+Homogeneity Range: 19.7 - 24.4 wt.%
Stoichiometric Composition: 22.4 wt.%

4. Electron Beam Zone-Refining

A preliminary investigation of the feasibility of zone-refining arc-cast VNi_3 was carried out. A suitable anode was prepared from several 1/8" diameter rods ground from a single button and welded together with the electron beam. Five traverses of the molten zone along the anode were made at the rate of approximately 0.2 in/min. The resulting microstructure consisted of large regular grains with boundaries which were slow etching and very difficult to distinguish. Each grain appeared identical, in contrast with the "light" and "dark" grains which were observed in the arc-melted structure (Fig. 10). Thus, it appears that the zone refining technique results in very small misorientations between grains, which suggests that the growth of single crystals of VNi_3 by this method may be feasible.

B. Primary Fabrication

1. Rolling of As-cast Compounds

The rolling experiments were multi-purpose in that they were intended: (a) to provide deformed specimens to study its effect on annealing time and temperatures, (b) to determine the feasibility of fabrication by rolling of as-cast compounds and (c) to furnish temperatures at which fabrication by extrusion is likely to be successful. A summary is given in Table V of the response of as-cast buttons of the selected compounds to rolling at temperatures in the range from 800 to 1200°C. The V_3Ni was not deformed above 800°C in order to avoid the formation of V_2Ni by peritectoid decomposition. The compounds V_2Ni and VCo were not rolled because of their brittleness in the as-cast condition. It is clear from the results obtained, that most of the as-cast compounds cannot be fabricated by rolling.

2. Extrusion of VNi_3 and VCo_3

The extrusion of the as-cast billets of VNi_3 and VCo_3 were carried out in a 300 ton hydraulic press fitted with a 2.04 inch inside diameter liner preheated to 480°C. A ram speed of 30 inches per minute was used. Each billet was contained in a stainless steel jacket which was evacuated at room temperature to less than 0.03 microns and sealed. The thickness of the jacket wall varied from 0.08 to 0.2 inches so that, in each case, the final diameter of the canned billet was 1.93 inches. The billets were preheated in an external furnace for 2 hours at temperatures of 1150 to 1250°C and were all successfully extruded to approximately 1/2 inch diameter rods. VNi_3 billet B3 stalled when attempts were made to extrude it at 1200°C and at an extrusion ratio of 16:1. However, the billet was re-canned and extruded successfully at 1250°C with an extrusion ratio of 10:1. The conditions and results of the extrusion experiments are summarized in Table VI.

The microstructure of the lead-ends of the as-extruded billets of both compounds were almost completely recrystallized, as illustrated in Fig. 11. However, as a result of a drop in the temperature of the billet during extrusion,

Aqua Regia 500X

Fig. 10 - Microstructure of zone-refined VNi_3.

Table V

Rolling of As-Cast Buttons

		Observations*					
		Temperature of Rolling °C					
Button	% DEF.	800	900	1000	1050	1100	1200
VNi_3	40		2			2	1
	60		2			2	1
	80		2			2	2
VNi_2	50						2
	80						1
V_3Ni	15	3					
	25	3					
VCo_3	50			2		1	
	60		2	2		1	
	80			2		2	
V_3Co	15				3		
	25				3		

* 1 = Edge cracks only
2 = Numerous cracks throughout specimen
3 = Fractured catastrophically

Table VI

Processing Data for Extrusion of VCo_3 and VNi_3 Billets
(To approximately half inch diameter rod)

Compound	Billet No.	Preheat Temperature (°C)	Die Size (inches)	Extrusion Ratio	Extrusion Ratio (Tons)	Comments
VCo_3	B1	1200	0.645	10:1	285	successful
	B2	1150	0.510	16:1	275	successful
VNi_3	B3	1200	0.510	16:1	330	Billet stalled
	B3R*	1250	0.645	10:1	275	successful
	B4	1250	0.645	10:1	270	successful

*Billet B3 Recanned.

Aqua Regia 500X

Aqua Regia 1500X

Fig. 11 - Microstructure of as-extruded VNi_3.

the tail-ends of the extruded rods contained a few unrecrystallized grains. Within the recrystallized grains of VNi_3 there are twins and fine structure. Neither of these structural features is seen in as-extruded VCo_3.

C. Secondary Fabrication of VNi_3 and VCo_3

Further fabrication of the 1/2 in. diam. extruded rods was necessary to provide material of a size suitable for the preparation of specimens for tensile testing. It was also desirable that this further fabrication be efficient enough to supply the needed material for all specimens from one casting of each compound so as not to introduce the variable of composition into the interpretation of test data. Three types of fabrication were examined: rolling, swaging, and further extrusion.

1. Rolling

The effects of both sequential hot and cold rolling of the as-extruded rod and of hot rolling annealed rod were investigated. In the case of the former, sections of VCo_3 and VNi_3 extruded rod were sealed in stainless steel tubing under argon and rolled at 1200°C to approximately 50% reduction. The rod sections were 1 in. long and were previously ground to 0.25 in. dia. Some edge and surface cracking occurred and the rolled pieces had to be surface ground to a thickness of 0.086 inches. The specimens of both compounds were then annealed at 1200°C for 1/2 hour, furnace cooled to 1000°C and held 3 days, and finally furnace cooled to room temperature. The specimens were next rolled at room temperature in 4 passes, with an anneal after the 3rd pass of 1000°C for one hour, followed by furnace cooling. The final thickness of the specimens were, VNi_3 = 0.037" thick and VCo_3 = 0.034".

For the hot-rolling experiments, specimens of as-extruded material were heat treated at 1200°C for 1/2 hour, furnace cooled to 1000°C and held for 3 days, and finally furnace cooled to room temperature. These specimens were sealed in stainless steel tubing under argon and rolled to approximately 50% reduction at the highest possible temperature within the ordered range (VNi_3 -975°C, VCo_3-1000°C). As in the cold-rolling experiments, some edge and surface cracking took place. Thus, although these compounds can be hot or cold rolled successfully, the process is wasteful of material because of the amount which must be ground away to remove rolling cracks.

2. Swaging

Sections of as-extruded rods of VNi_3 and VCo_3 were centerless ground to 0.400 inches in diameter, and swaged in air at 1200°C. Preheating was carried out in an inert atmosphere furnace. A reduction of 0.025 inches (i.e. approximately 12% reduction) was made on the first pass. The VNi_3 reduced with few observed defects, but the VCo_3 developed circumferential cracks. Both compounds began to break up on attempting a second pass after reheating to 1200°C.

The microstructure of the swaged compounds contained numerous cracks but did not show excessive grain growth. Possible causes of the cracking

are contamination picked up during the first pass, or chilling because of the small rod diameter. A solution to both problems would be to sheath the rods in stainless steel, which would prevent oxidation and help to retain the temperature for a longer period. However, in view of the success of the secondary extrusion technique discussed below, further work on hot-swaging was not attempted.

3. Extrusion

Sections of each compound as extruded from the original cast billet were centerless ground to 0.435" diameter. The sections (4 in. long) were built up to 1 in. diameter with a stainless steel jacket, evacuated and sealed. Extrusions to 0.09 in. diameter rods at temperatures above the ordering temperature were carried out under the conditions indicated in Table VII. The extrusions were successful and provided material of a suitable size and in sufficient quantity for tensile testing.

D. Homogenization and Annealing Behaviour

The effects of temperature and time on homogenization and annealing behaviour, as observed by metallography and microhardness measurement, were examined for all the compounds in the as-cast and the cast and rolled conditions. In the case of VCo_3 and VNi_3, the effects were also studied for the cast and extruded condition.

1. As-cast and As-rolled compounds other than VNi_3 and VCo_3

Temperatures in the range 1000°C to 1100°C were selected as the highest which could be used for the five compounds VNi_2, V_2Ni, V_3Ni, VCo and V_3Co without risk of decomposition. Two treatments were examined a) vacuum annealing at 1000°C for 5 days followed by furnace cooling to room temperature and b) same treatment as (a) followed by annealing at 1100°C for 1 hour, furnace cooling to 1050°C for 7 days and furnace cooling to room temperature (1050°C was the maximum safe temperature for prolonged operations of the furnace then available). Both as-cast and hot-rolled specimens were subjected to these treatments. The hardness results are summarized in Table VIII.

In the case of the VNi_2, both the as-cast and the rolled specimens exhibited similar hardness after annealing at 1000°C. The structures appear homogeneous and similar, except for the fine and more equiaxed grains developed in the initial as-rolled specimen. The microstructure is shown in Fig. 12, which is to be compared with the as-cast structure of Fig. 5. The annealed specimens exhibit a fine structure within the grains which is analogous to that observed in VNi_3 (see Fig. 11) and is probably associated with the order-disorder transition. Because of the homogenization resulting from the 1000°C anneal, the VNi_2 was not annealed further. In the case of the as-cast V_2Ni, the 1000°C anneal developed an essentially homogeneous structure which was substantially lower in hardness (Fig. 13A). The second anneal resulted in recrystallization and the development of a fine structure within the grains. (Fig. 13B). The slight increase in hardness arising from the second anneal may be due to this fine structure. In the case of the V_3Ni, neither annealing treatment greatly changed the distribution of the initial multi-phase

Table VII

Processing Data for Extrusion of VCo_3 and VNi_3 Billets to Small Diameter Rod for Tensile Specimens

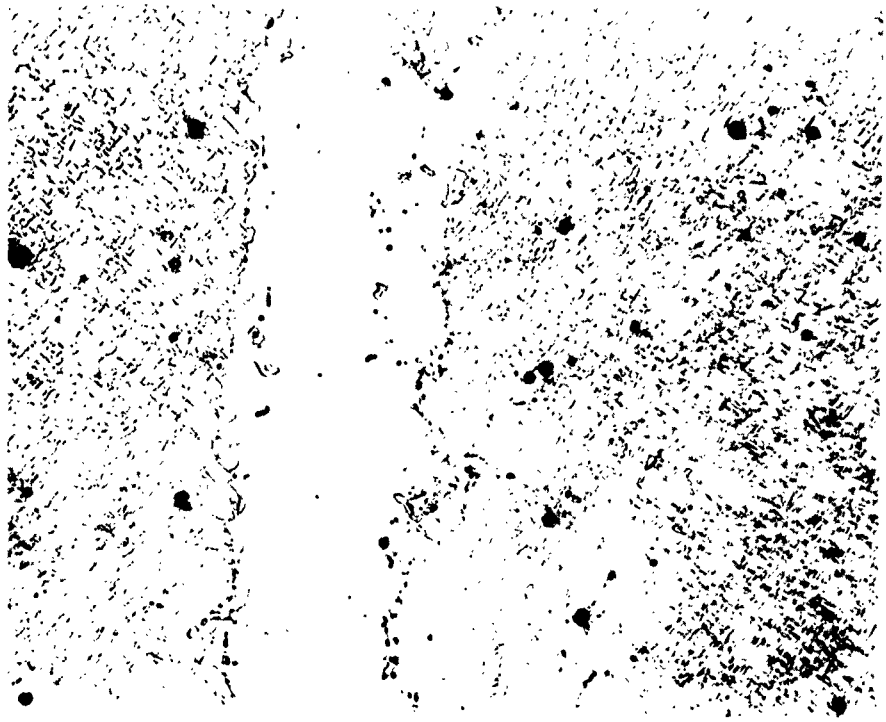
Compound	Billet No.	Preheat Temperature	Extrusion rate	Extrusion ratio (calc.)	Final Core Size
VCo_3	B-1	1200°C	30"/min.	16 to 1	0.090"
VNi_3	B-3	1250°C	30"/min.	16 to 1	0.090"

Table VIII

Effect of Homogenizing and Annealing Treatments on the Microhardness of Compounds other than VCo_3 and VNi_3

Condition	Microhardness (VPN 500 gm)									
	VNi_2		V_2Ni		V_3Ni		VCo		V_3Co	
	Cast	Rolled	Cast	Rolled	Cast	Rolled	Cast	Rolled	Cast	Rolled
Initial	*	544	1100	------	*	123-1010	1340	------	563-787	845
First Anneal: 1000°C for 5 days furnace cool	486	454	413	------	980	233-916	1040	------	1105	1113
Second Anneal: 1100°C for 1 hour furnace cool to 1050°C hold 7 days, furnace cool	----	---	490	------	960	1040	1070	------	880	880

*Cracked indents



Aqua Regia 500X

Fig. 12 - Microstructure of VNi_2 annealed at 1000°C for 5 days.

Aqua Regia (A) 500X

Aqua Regia (B) 500X

Fig. 13 - Microstructure of V_2Ni annealed at (A) 1000°C for 5 days (B) treatment A followed by 1100°C for 1 hr and 1050°C for 7 days.

structure. This was so for both the as-cast and the rolled material. The large hardness differences between the phases were also maintained - see Table VIII. Although the composition range of V_3Ni is unknown (see Fig. 2), it appears likely from these results that the vanadium content of the ingot (71.4 wt.% compared with the stoichiometric composition of 72.3 wt.%) falls outside it.

Of the V-Co compounds, the VCo showed only a small drop in hardness after the 1000°C anneal and no further drop after the second anneal. No strong changes in microstructure from the original structure were apparent after either annealing treatment, as can be seen from Fig. 14. It will be recalled that, due to pronounced cracking, satisfactory micrographs could not be obtained from the as-cast VCo. The fact that this is possible after annealing indicates that some changes have occurred in the material, even though these are not apparent in the structure. In the case of the V_3Co, the hardness increases after the 1000°C anneal for both the as-cast and the as-rolled specimens. In addition, the microstructure (Fig. 15A) shows that homogenization has occurred but that there are still two phases present (compare with Fig. 9). The fact that the second annealing increases the amount of one of these phases (Fig. 15B), suggests that either the vanadium content of the ingot (71.6 wt.% compared with the stoichiometric composition of 72.2 wt.%) is outside the composition range of the compound, or that the reported[3] decomposition temperature of 1125°C is too high.

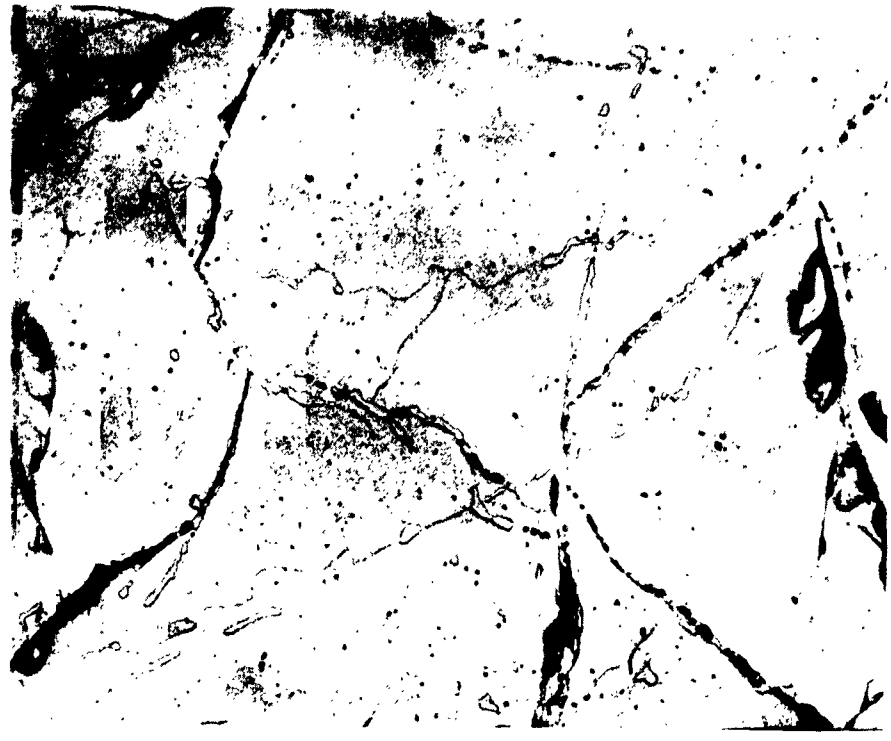
2. As-cast and As-rolled VNi_3 and VCo_3

For these compounds, only a limited study was made of the annealing of as-cast material. Instead, a more extensive study of the annealing of rolled material was made in order to guide the selection of extrusion conditions.

For the as-cast material, specimens of each compound were vacuum annealed at 1100°C for 6 hours. Cooling was accomplished by withdrawing the vacuum chamber from the furnace. For both compounds, small decreases in hardness took place and the dendritic as-cast structure was reduced considerably, although not eliminated. The annealed VNi_3 exhibited grain growth and fine structure within the grains. The VCo_3 showed a pattern of fine striations which are probably mechanical twins formed during the relatively rapid cooling from 1100°C, although there is some resemblance to the stacking fault structure reported for cobalt[48].

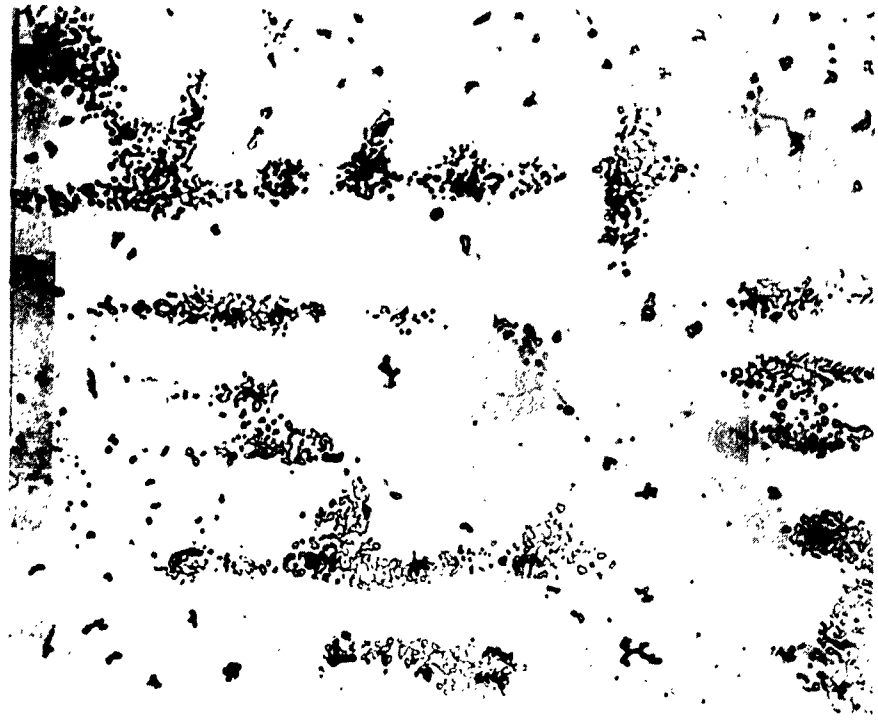
For the rolled condition, arc-melted buttons of VNi_3 and VCo_3 were reduced in thickness approximately 75% by rolling at 950 and 1000°C respectively. Specimens cut from this material were then vacuum annealed for 30 min. periods at a series of temperatures in the range from 800 to 1200°C. Again, cooling was accomplished by withdrawing the vacuum chamber from the furnace.

The effects of annealing temperature on the microstructure and hardness of as-rolled VNi_3 are shown in Figs. 16 and 17 respectively. It is seen that the compound is completely recrystallized after annealing at 1000°C and that a discontinuous increase in hardness occurs as a result of annealing above the order-disorder temperature (1045°C). The grain size of the specimens recrystallized at 1100 and 1200°C is very much larger than that recrystallized at 1000°C,

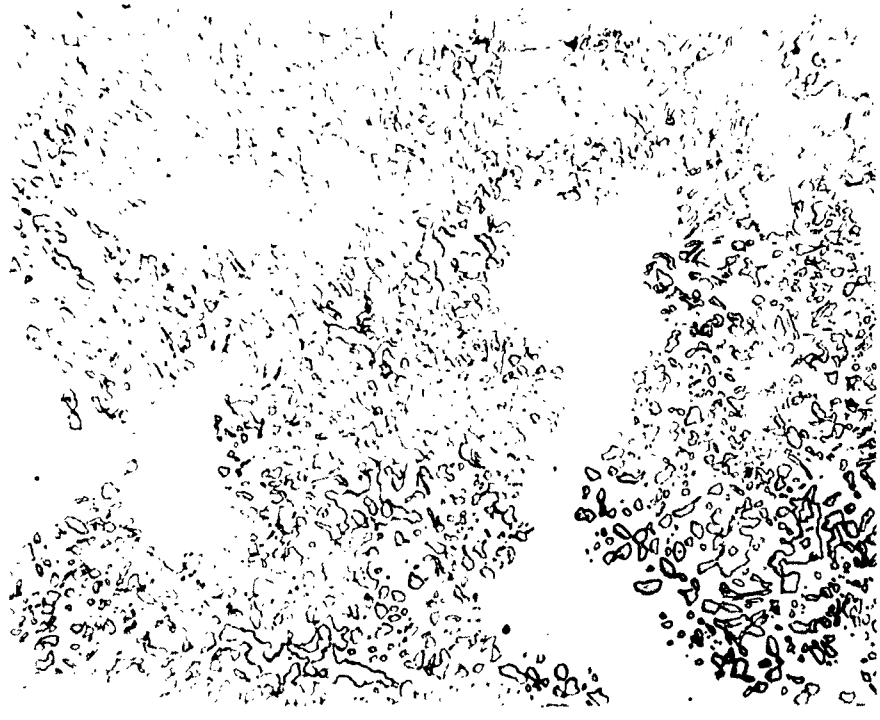


Aqua Regia 500X

Fig. 14 - Microstructure of VCo annealed at 1000°C for 5 days followed by 1100°C for 1 hr. and 1050°C for 7 days.

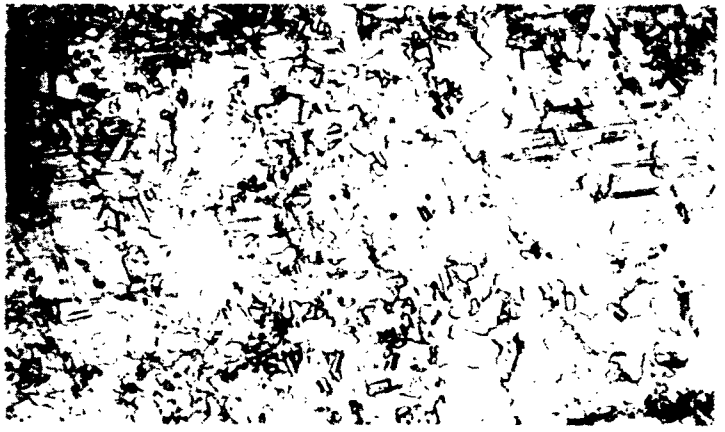


Aqua Regia (A) 500X

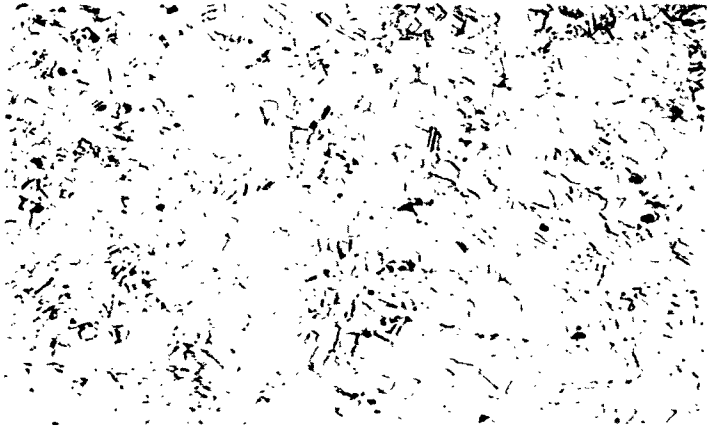


Aqua Regia (B) 500X

Fig. 15 - Microstructure of V_3Co annealed at (A) 1000°C for 5 days, (B) treatment A followed by 1100°C for 1 hr. and 1050°C for 7 days.



Aqua Regia 900°C 500X



Aqua Regia 1000°C 500X

Aqua Regia 1100°C 500X

Aqua Regia 1200°C 500X

Fig. 16 - VNi_3 deformed approximately 75% by rolling at 950°C and annealed for 30 minutes at the indicated temperatures.

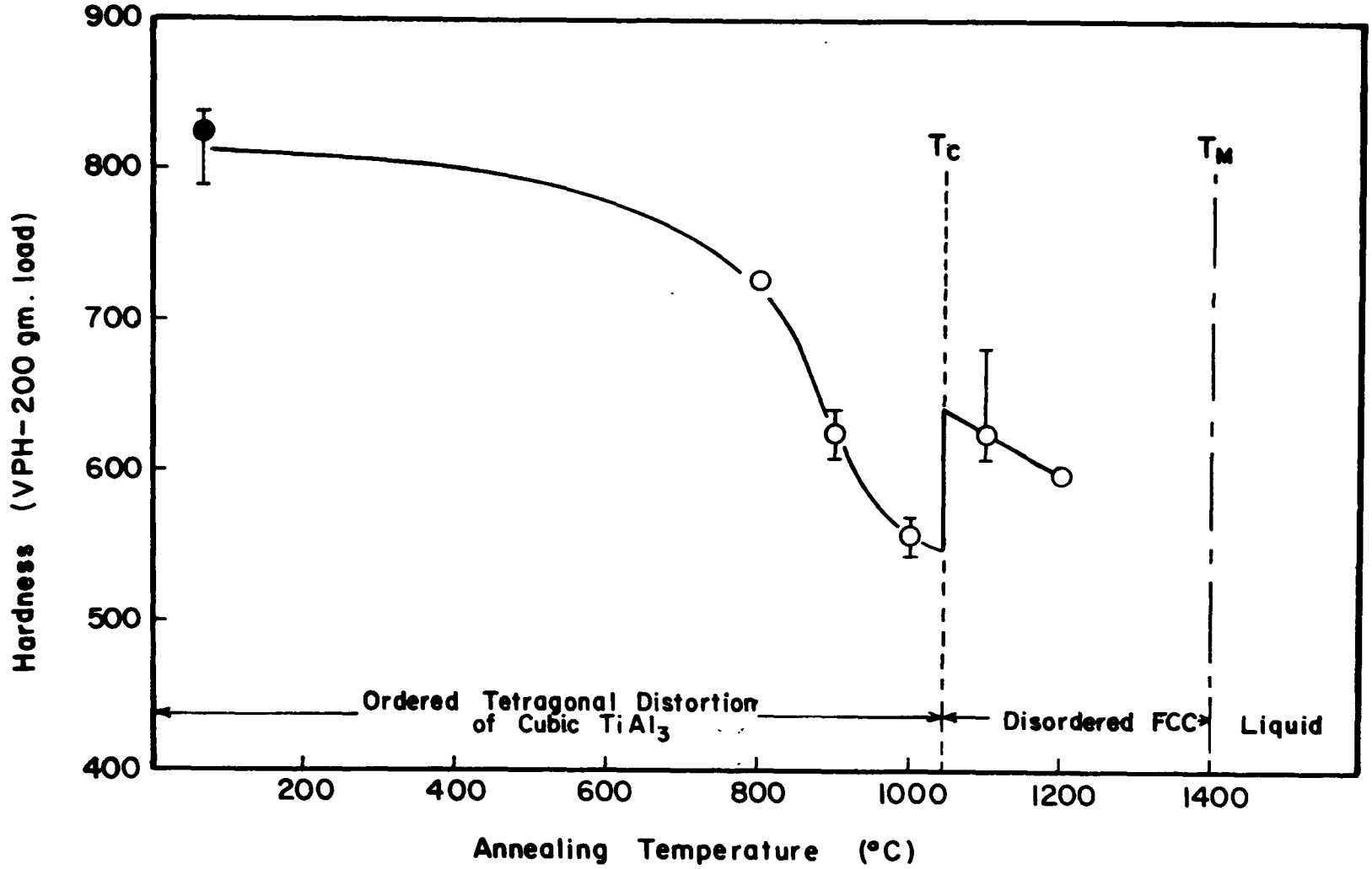


Fig. 17 - Hardness of VNi_3 as a function of annealing temperature. The as-cast compound was reduced in thickness approximately 75% by rolling at 950°C, annealed for 30 minutes at the temperatures indicated, and then vacuum-cooled to room temperature. The hardness of the as-rolled condition is shown by the solid point. Bars indicate the range of values.

which should result in their being softer not harder, and all three specimens exhibit recrystallization twins. The strong hardness increase observed is accompanied by marked differences in the internal structure of the grains. The grains in the 1000°C specimen are smooth (Fig. 18), whereas those in the 1100 and 1200°C specimens exhibit a fine substructure (Fig. 19). As will be discussed later, this structural feature is associated with the nature of the cooling cycle from the disordered state existing above the critical ordering temperature (1045°C). A similar substructure was observed in the as-extruded samples of VNi_3 which were cooled rapidly from 1200°C during processing.

The hardness changes accompanying the annealing of as-rolled VCo_3 are shown in Fig. 20. The hardness does not show a discontinuous increase upon annealing above the critical ordering temperature (1070°C) as was found for VNi_3. This observation is in agreement with the fact that there appears to be no difference in the interior structure of the recrystallized grains of VCo_3 formed on annealing above and below this temperature. The compound recrystallized almost completely at 1000°C and the structure formed at that temperature and higher consists of homogeneous equiaxed grains free from annealing twins or fine substructure. As for the VNi_3, substantial grain growth occurred on annealing above the critical ordering temperature.

3. Extruded VNi_3 and VCo_3

As pointed out earlier, the as-extruded billets of both compounds were found to be homogeneous and almost completely recrystallized. Accordingly, this material was used directly for a study of the effects on microstructure and mechanical properties of a variety of heat treatments designed to produce different degrees of order and grain size. The results of this work are discussed in the next section.

E. Mechanical Behaviour

1. Elastic Modulus of Compounds

The elastic modulus of a solid is related directly to interatomic bonding strength and, as discussed in Section II, the theoretical strength of a perfect crystal is approximately 5 to 10% of the elastic modulus. Although the relationships between actual and theoretical strengths are not clearly understood, a high elastic modulus is indicative of potentially high strengths. Accordingly, in selecting compounds for possible application, it would be helpful if their elastic properties could be compared by computations from existing data. As part of the present program, the feasibility of such a computation is being tested experimentally with reference to the compounds in the V-Ni and V-Co binary systems.

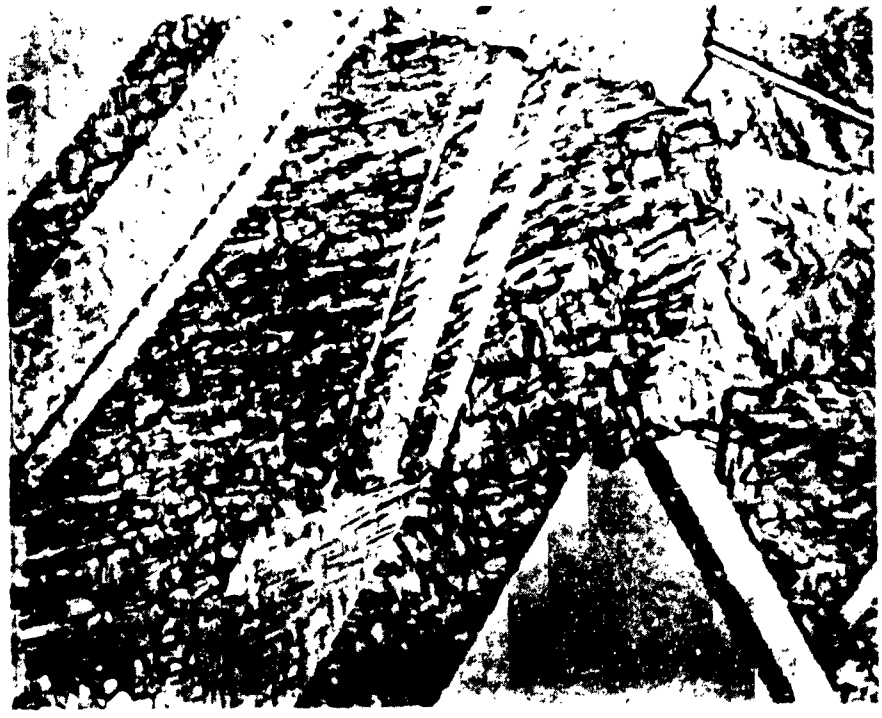
According to Debye theory[7], Young's modulus (E), for an isotropic material with a Poisson's ratio of 1/3 is given by:

$$E = 2.8 \times 10^5 \theta_D^2 M^{2/3} \rho^{1/3} \qquad (1)$$

Aqua Regia 1500X

Fig. 18 - VNi_3 deformed approximately 75% by rolling at 950°C and annealed for 30 minutes at 1000°C.

Aqua Regia (A) 1500X



Aqua Regia (B) 1500X

Fig. 19 - VNi_3 deformed approximately 75% by rolling at 950°C and annealed for 30 minutes at (A) 1100°C and (B) 1200°C.

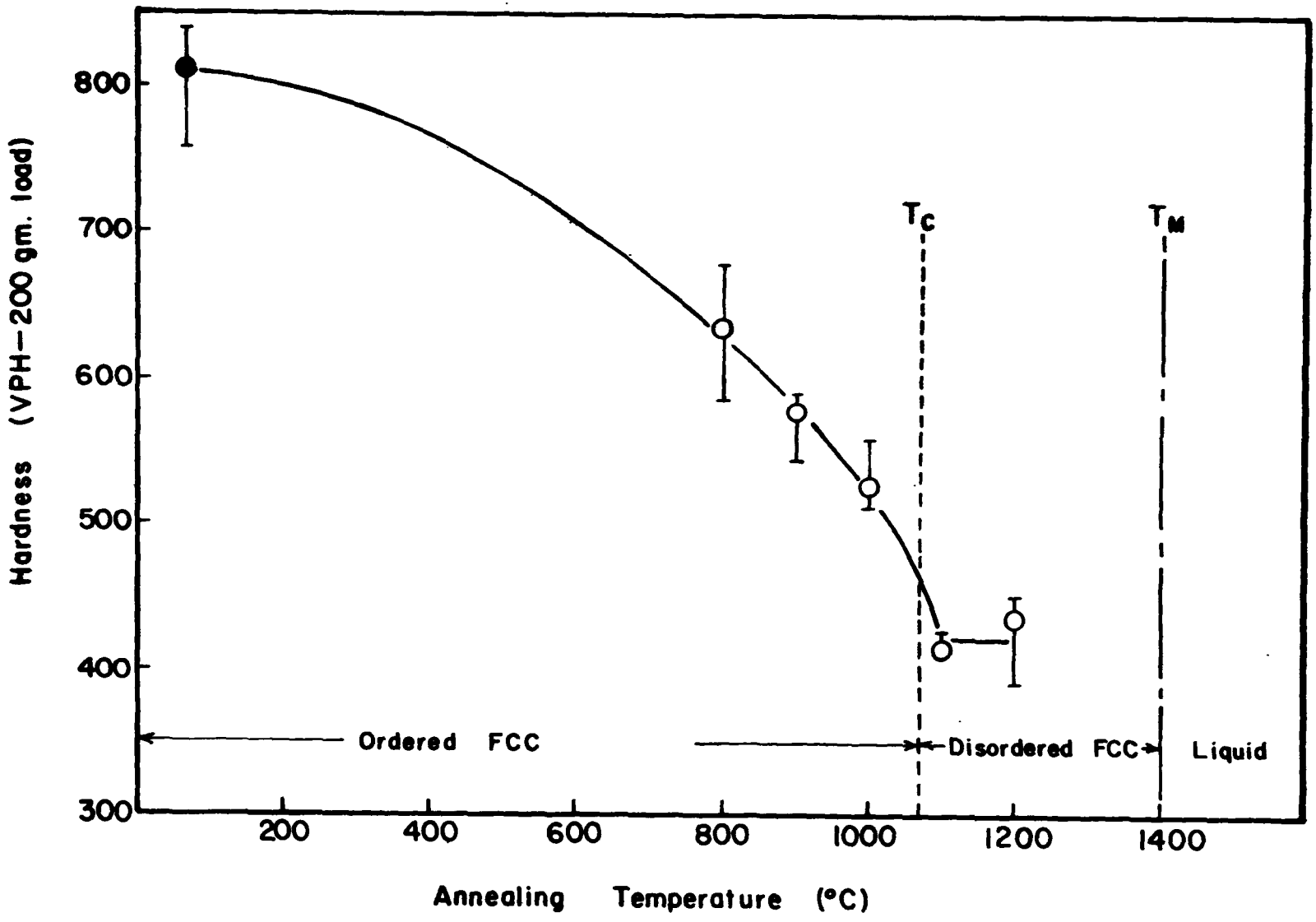


Fig. 20 - Hardness of VCo_3 as a function of annealing temperature. The as-cast compound was reduced in thickness approximately 75% by rolling at 1000°C, annealed in vacuum for 30 minutes at the temperatures indicated, and then vacuum-cooled to room temperature. The hardness of the as-rolled condition is shown by the solid point. Bars indicate range of values.

where θ_D = Debye temperature

M = mean atomic weight

ρ = density

Calculated values of Young's modulus for the pure elements are in reasonable agreement with measured values. As far as known, the only calculations made of Young's modulus for intermetallic compounds has been for Fe_3Al. It has been shown[49] that equation (1) can be used to estimate the elastic modulus of this compound.

Although measurements of θ_D are available for only a few materials, an estimate of this parameter may be obtained from the semi-empirical Lindemann equation (15):

$$\theta_D = C_L T_M^{1/2} v_a^{-1/3} M^{-1/2} \qquad (2)$$

where C_L = Lindemann constant

T_M = absolute melting point

v_a = atomic volume

M = mean atomic weight

C_L should be constant for chemically similar elements having the same structure. For elements with a face-centered cubic or hexagonal close packed structure, the Lindemann constant is found to be approximately 1.6×10^{-6} c.g.s. units[50]. Recently, Kaufman[16] has used the Lindemann equation to calculate the entropies of 35 different NaCl-type metalloid and halide compounds varying in bonding type from ionic (e.g., NaCl, KI) to semi-covalent (e.g., TiC, ZrN). The validity of this application is indicated by the fact that the calculated and observed entropies agree within a root mean square deviation of $\pm$ 13%.

In the present work, approximate calculations of θ_D and E have been carried out for the six compounds in the V-Ni and V-Co binary systems for which lattice parameter data are available. For the compounds, the Lindemann constant ($\overline{C}_L$) has been approximated as:

$$\overline{C}_L = y_A (C_L)_A + y_B (C_L)_B \qquad (3)$$

where y_A and y_B are the atom fractions of elements A and B, and $(C_L)_A$, $(C_L)_B$ are the Lindemann constants for the pure elements. The necessary values of C_L for the pure elements were calculated by substituting measured values[51] of Debye temperatures into equation (2). These calculated values are listed in Table IX. The melting point of each compound was taken as the liquidus temperature at stoichiometric composition, whether or not the compound decomposed before melting. The resulting values of Debye temperature and Young's modulus for the six compounds are given in Table X.

As part of the experimental check on the validity and usefulness of this approach, a preliminary determination has been made of the Debye temperature

Table IX

Calculated Values of Lindemann Constant (C_L) and Young's Modulus (E) for the Pure Elements from Measured Debye Temperatures

ELEMENT	STRUCTURE	$\theta(^{o}K)$	$C_L(10^{-6}$ c. g. s. units)	$E(10^{12}$ dynes/cm^2)	
				Exptl. (51)	Calc.
Co	hcp	390[11]	1.61	2.07	1.35
Ni	fcc	390[11]	1.59	2.07	1.35
V	bcc	340[12]	1.35	1.31	0.94

of VNi_3 from x-ray diffraction measurements on a specimen made from filings taken from the as-cast compound and annealed for 40 hours at 1100°C followed by rapid cooling. The experimental value of θ_D is 688°K compared with the calculated value of 375°K (Table X). The Young's modulus computed from Equation (1) by substituting the measured θ_D is 4.0×10^{12} dynes cm^{-2} (57.6×10^6 psi). The modulus corresponding to the calculated θ_D is 1.17×10^{12} dynes cm^{-2} (17.0×10^6 psi). A value of Young's modulus in compression of 2.28×10^{12} dynes cm^{-2} (33×10^6 psi) has been measured, as discussed in the next section, for a homogeneous, ordered VNi_3 specimen prepared from extruded rod. The corresponding θ_D computed by substituting Equation (1) is 523°K. From these results, it appears that (a) the experimental θ_D is too high and (b) the approximation used in Equation (3) leads to too small a value for the Lindemann constant and hence to too small a θ_D (these deductions still presume the validity of Equations (1) and (2)).

It is possible that the high experimental θ_D is due to incomplete homogenization and order in the specimen, and the parameter is being remeasured on filings taken from extruded rod and treated identically to the compression specimen. The solution of the second point, item (b) above, requires an alternative approximation for the Lindemann constant for compounds. It would appear most likely that all compounds having the same crystal structure might give the same value for C_L. Unfortunately, an examination of the thermodynamic data available for all compounds of the same structure-types as those in the V-Ni, V-Co series, has shown that there is insufficient data to compute the variations in C_L. Accordingly, in order to obtain an indication of the variations in C_L in intermetallic compounds in general, C_L was computed for all the compounds for which data could be found.

Of the 126 different structure types listed in Pearson[52], only 18 contain compounds with sufficient data. The compounds and their calculated C_L are listed in Table XI. Wherever more than one intermetallic compound existed in a given structure type, the average Lindemann constant, $\overline{C_L}$, was taken and used to calculated a Debye temperature for each compound. The deviation of this calculated θ_D from the measured θ_D is plotted in Fig. 21. It is seen that this deviation is less than 15% for some structure types (B8, B20, Be, C_1, and D53), so that it is possible to calculate unknown Debye temperatures within this accuracy for compounds of these types. However, it appears from these results that the method will not be reliable for general use.

2. Behaviour of VNi_3 and VCo_3

Experiments with these two compounds have been directed to determining the effects of temperature and time on the microstructure, hardness, and stress-strain characteristics. The starting material in all cases was as-extruded rod. Five heat treatments were examined. The first three were simple anneals of 30 minutes duration at 800, 1000 and 1200°C, respectively, followed by rapid cooling. These were designed to produce specimens having varying degrees of long-range order. Fully ordered specimens were produced by the fourth annealing treatment of 48 hours at 1000°C (just below the critical ordering temperatures T_c of both compounds) followed by furnace cooling to room temperature. The fifth

Table X

Calculated Debye Temperature (θ_D) and Young's Modulus (E)

Compound	Structure	C_L (c.g.s. units)	T_M (^oK)	θ_D (^oK)	E	
					(10^{12} dynes/cm^2)	10^6 psi
VNi_3	Tetragonal Distortion of Cubic $TiAl_3$	1.54	1673	374	1.17	17.0
VNi_2	Orthorhombic (Distorted FCC Nickel Solution)	1.52	1623	360	1.04	15.1
V_2Ni	Tetragonal β- Ur	1.44	1573	336	0.87	12.6
V_3Ni	BCC β- W	1.41	1773	348	0.90	13.1
VCo	Tetragonal β- Ur	1.48	1573	343	0.92	13.3
V_3Co	BCC β- W	1.42	1773	351	0.91	13.2

Table XI

Values of Lindemann Constant Calculated From Published Thermodynamic Data

Structure Type	Compound	Entropy (S_{298} cal/g. at)	θ_D (°K)	C_L (10^{-6} c. gs units)
B-3	AlSb	8.5	283	2.05
	CdTe	11.1	181.5	1.865
	MnS - β	9.35	244.5	1.050
B-4	BeO	1.68	116.5	1.545
	MnS - β^1	9.35	244.5	1.04
$B\text{-}8_1$	CoS	7.6	328	1.105
	NiS - β	7.25	351.5	1.305
B-13	NiS	7.25	351.5	1.67
B-20	CoSi	5.75	462	1.62
	FeSi	6.00	444	1.57
	MnSi	7.00	374	1.40
Be	CdSb	11.0	185	2.26
	SbZn	10.7	193.7	1.90
C_1	CeO_2	8.85	268	0.895
	HfO_2	8.00	310	1.05
C_3	Cu_2O	10.85	188	0.782
C_4	GeO_2	6.25	420	1.39
C_{12}	$CaSi_2$	11.0	185	4.70
Cm	VO_2	6.15	429	1.015
DO_{11}	Fe_3C	12.1	152	0.4725
	Mn_3C	11.8	161	0.567
DO_{24}	Ni_3Ti	14.25	107.2	0.283
$D5_1$	Al_2O_3 - α	6.25	423	0.800
	Cr_2O_3	9.70	229.5	0.475
	Fe_2O_3 - α	10.75	190.5	0.514
	Ga_2O_3	10.85	188.	0.340

Table XI (Cont'd)

Values of Lindemann Constant Calculated From Published Thermodynamic Data

Structure Type	Compound	Entropy (S_{298} cal/g. at)	θ_D (°K)	C_L (10^{-6} c. gs units)
$D5_3$	Ca_3N_2	12.7	137.0	0.425
	Mg_3N_2	10.5	199.5	0.538
$D5_8$	S_3Sb_2	19.8	41.7	0.784
HI_1	Fe_3O_4	17.5	62.6	0.183
	Fe_2O_3	10.75	190.5	0.900
LI_2	$AuCu_3$	18.55	53.6	0.424

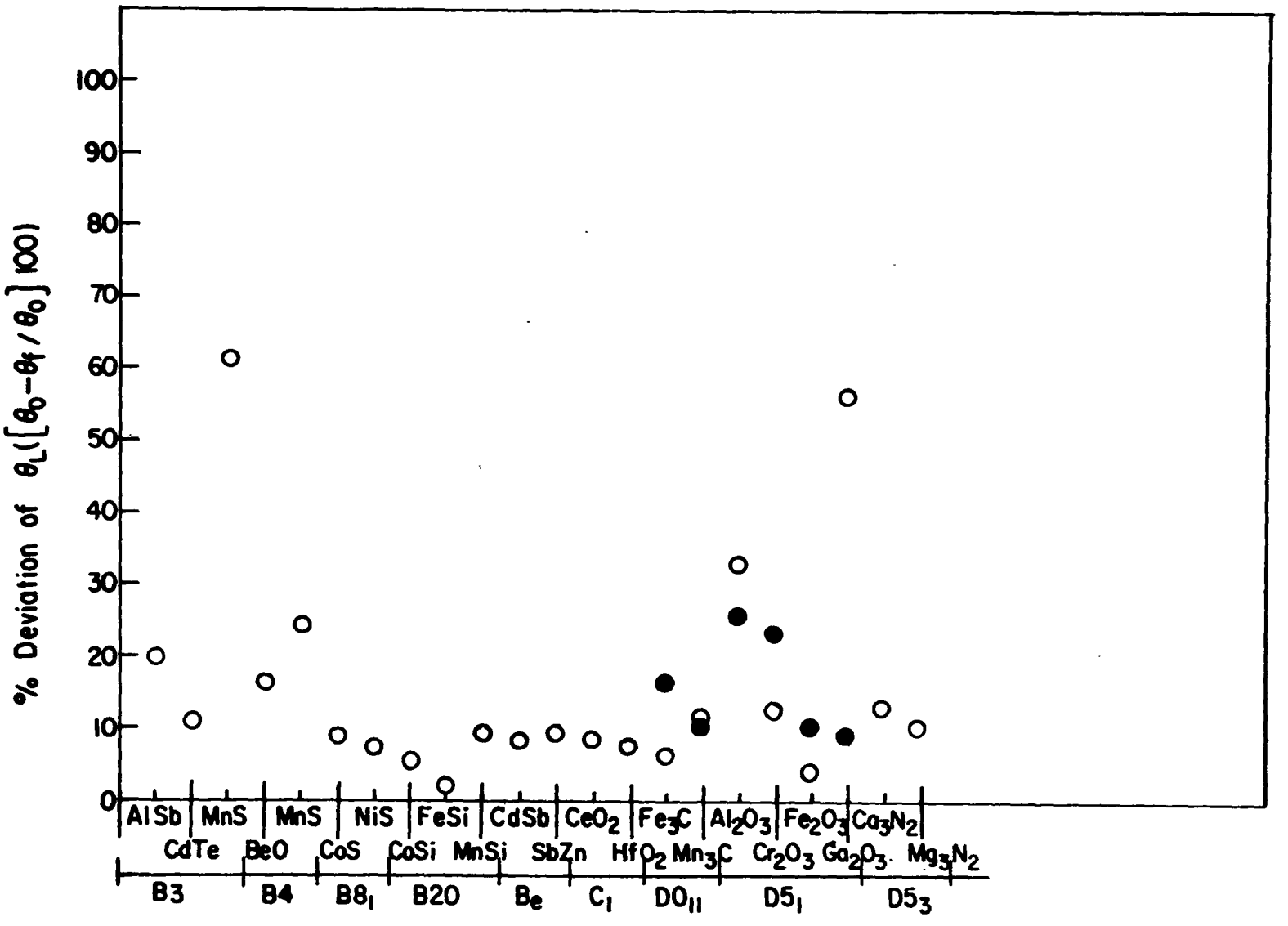


Fig.21 — The deviation of debye temperature $\left[(\theta_L \text{EXP.} - \theta_L \text{CALC.}/\theta_L \text{EXP.})\,100\right]$ in intermetallic phases.

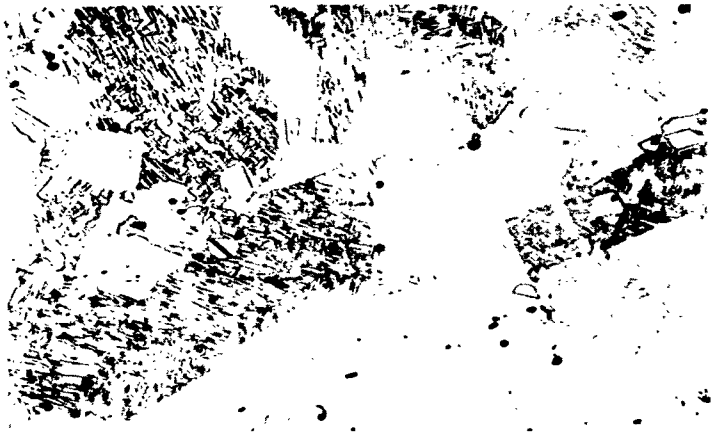
treatment was intended to provide fully ordered specimens of different grain size. The treatment consisted of annealing 30 minutes at 1200°C, furnace cooling to 1000°C for 48 hours, and finally, furnace cooling to room temperature.

In the case of VNi_3, little change in microstructure, except an increase in grain size, results from the simple annealing treatments at 800, 1000 and 1200°C (see Fig. 22). The fine substructure present in the as-extruded material (Fig. 11) is not removed by these treatments. However, the other two treatments, which both involved prolonged annealing just below T_c followed by very slow cooling, completely removed the fine substructure--see Figs. 23 and 24. The same result was obtained in a specimen of hot-rolled VNi_3 (75% reduction at 950°C) subjected to such treatment, as shown in Fig. 24. These light microscopy observations were confirmed by electron microscopy examination of surface replicas. Examples of the structural features visible at high magnification after the short and the prolonged annealing treatments are given for the extruded and the rolled materials in Figs. 25, 26 and 27. It should be noted that twins are present after all these treatments.

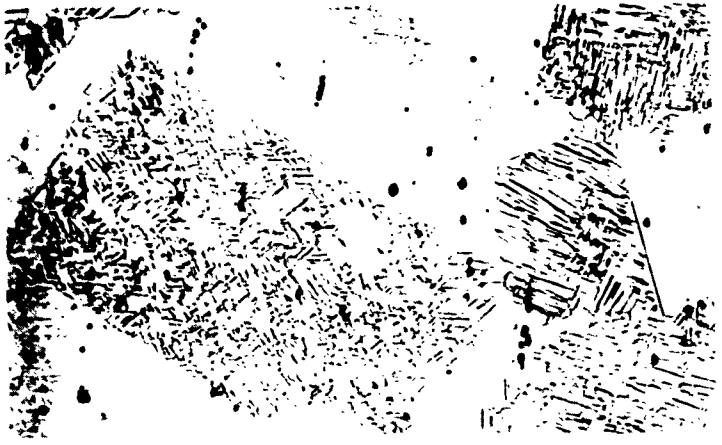
The changes in the grain size and hardness of VNi_3 which resulted from the different annealing treatments are shown in Fig. 29. The grain size increases only slowly with increasing annealing temperature up to T_c, but increases considerably above T_c. However, the large grain size established by annealing above T_c transforms to a finer grain size when the specimen is subsequently ordered by holding at 1000°C, instead of cooling rapidly to room temperature. The resulting grain size is smaller than that obtained by a direct 30 minute anneal at 1000°C, but is similar to that from a direct 48 hour anneal at 1000°C. Direct annealing at that same temperature for a longer time (168 hours), further reduces the grain size. In keeping with the earlier interpretation that as-extruded VNi_3 is almost completely recrystallized, the hardness is constant with increasing annealing temperature for direct 30 minute anneals, with the exception of a small decrease at 1000°C. However, both types of prolonged annealing at 1000°C cause substantial softening. These results, together with the accompanying microstructural changes, indicate that the substructure observed in as-extruded VNi_3 is responsible for its high hardness. It seems likely that the distinctive microstructure is a reflection of the formation of a partial long-range order structure or the retention of a high degree of short range order, rather than the retention of the disordered high-temperature phase. The structure appears in the as-extruded material because of the high rate of cooling from the extrusion temperature, which is well above T_c (see the retention of hardness on cooling rapidly from 1200°C, Fig. 29).

In the case of VCo_3, for which no substructure was apparent in the extruded material, the annealing treatments do not lead to the striking changes in structure and hardness found for VNi_3. As can be seen from the micrographs in Fig. 28 and the grain-size measurements in Fig. 30, the principal structural change apparent with increasing annealing temperature is an increase in grain size for temperatures of 1000°C and higher. The increase, which is not discontinuous across T_c, is accompanied by the development of twins. The hardness changes on annealing are correspondingly small. There is essentially no change up to 1000°C,

Aqua Regia 800°C 500X



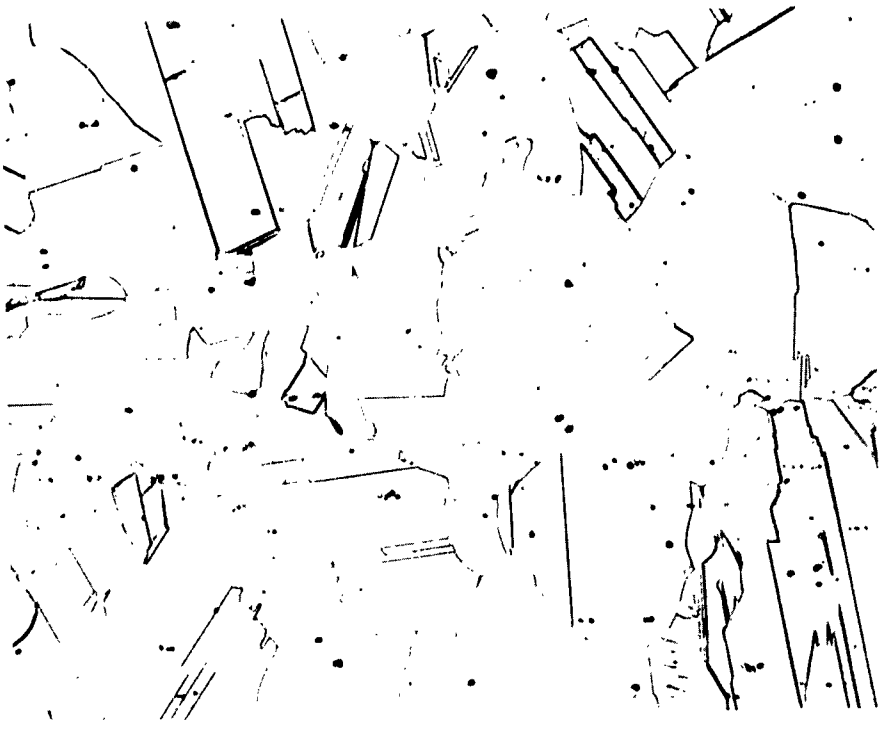
Aqua Regia 1000°C 500X



Aqua Regia 1200°C 500X

Aqua Regia 1200°C 2500X

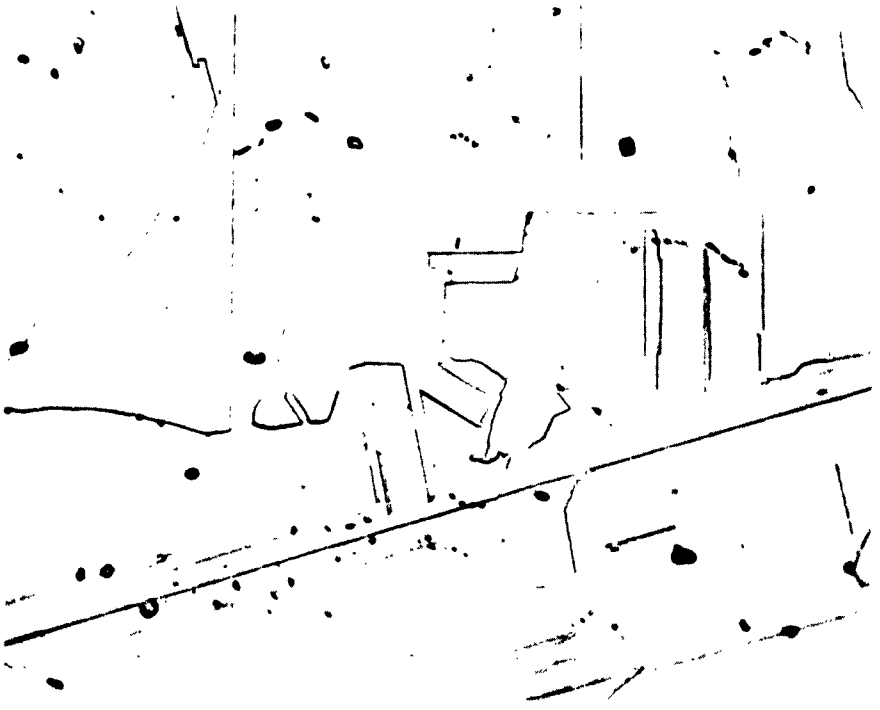
Fig. 22 - Microstructures of extruded VNi_3 annealed at the indicated temperature for 30 minutes and rapid cooled.



Aqua Regia (A) 500X

Aqua Regia (B) 500X

Fig. 23 - Microstructure of extruded VNi3 following (A) annealing at 1200°C for 30 min, furnace cooling to 1000°C for 48 hours followed by furnace cooling to room temperature (B) annealing at 1000°C for 48 hours followed by furnace cooling to room temperature.

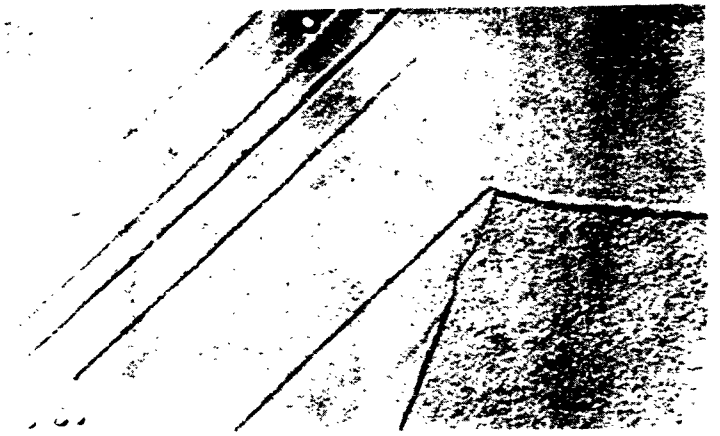


Aqua Regia (A) 1500X

Aqua Regia (B) 1500X

Fig. 24 - Microstructure of VNi_3 following annealing at 1200°C for 30 min., furnace cooling to 1000°C for 48 hours followed by furnace cooling to room temperature for (A) rolled specimen (B) extruded specimen.

Aqua Regia (A) 5000X

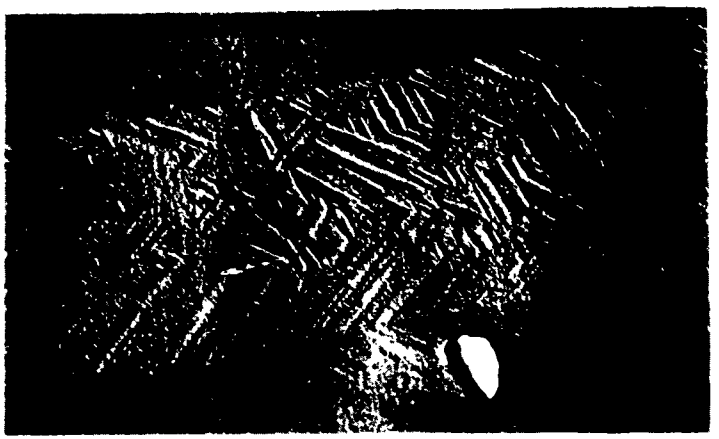


Aqua Regia (B) 5000X

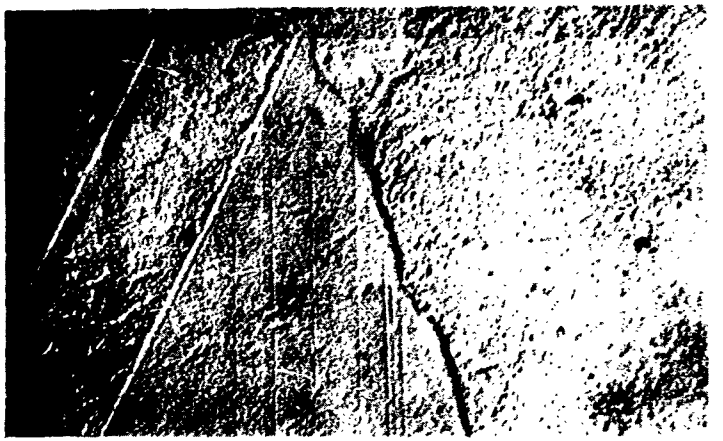
Aqua Regia (A) 20,000X

Aqua Regia (B) 20,000X

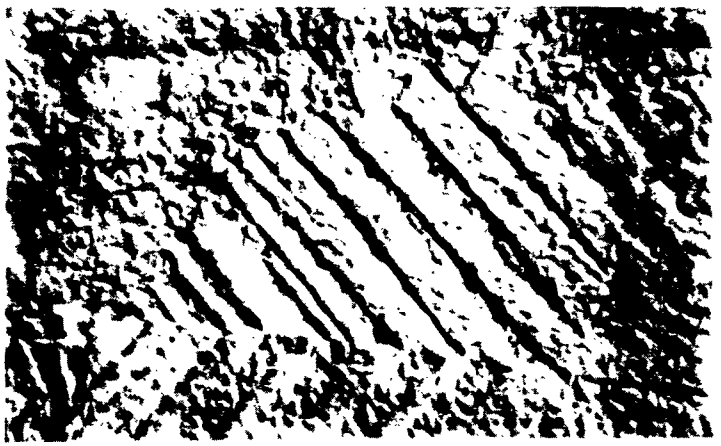
Fig. 25 - Electron micrographs of extruded VNi_3 following annealing at 1000°C (A) for 30 min. followed by rapid cooling and (B) for 48 hours followed by furnace cooling.



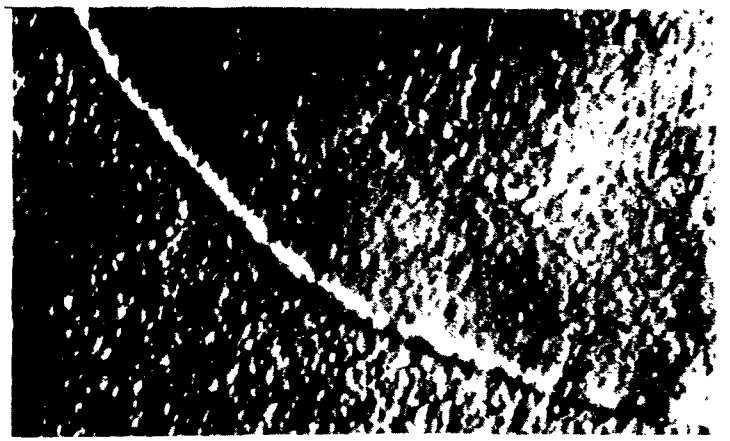
Aqua Regia (A) 5000X



Aqua Regia (B) 5000X



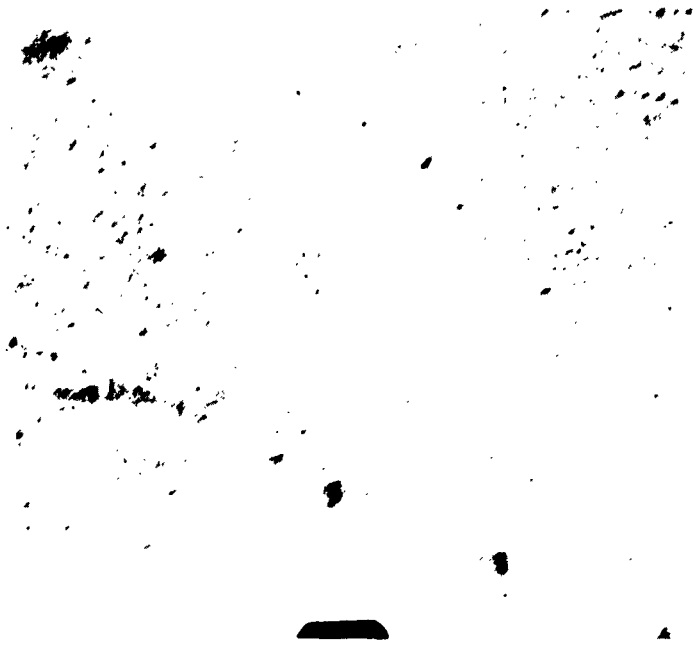
Aqua Regia (A) 20,000X



Aqua Regia (B) 20,000X

Fig. 26 - Electron micrographs of extruded VNi_3, following annealing at 1200°C (A) for 30 min. followed by rapid cooling and (B) for 48 hours followed by furnace cooling.

Aqua Regia (A) 5000X

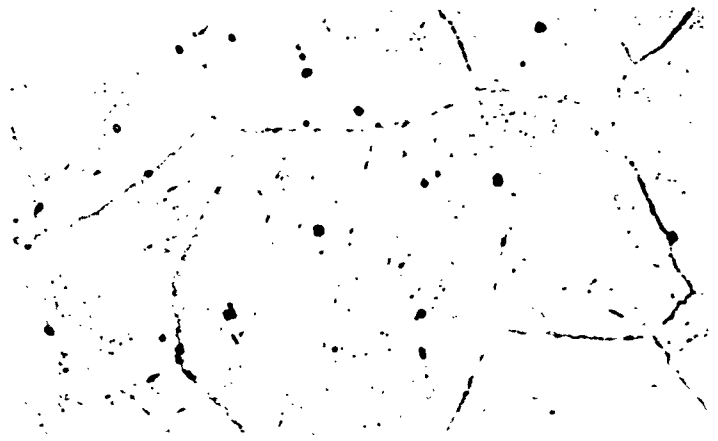


Aqua Regia (B) 20000X

Fig. 27 - Electron micrographs of hot-rolled VNi_3 annealed at 1200°C for 30 min., furnace cooled to 1000°C for 18 hours and furnace cooled to room temperature.

Aqua Regia (A) 800°C 500X

Aqua Regia (B) 1000°C 500X



Aqua Regia (C) 1200°C 500X

Aqua Regia (D) 1000°C 500X

Fig. 28 - Microstructures of extruded VCo_3 annealed at (A) 800°C for 30 min. rapid cooled, (B) 1000°C for 30 min. rapid cooled, (C) 1200°C for 30 min., rapid cooled and (D) 1200°C for 30 min., furnace cool to 1000°C for 48 hours, furnace cool to room temperature.

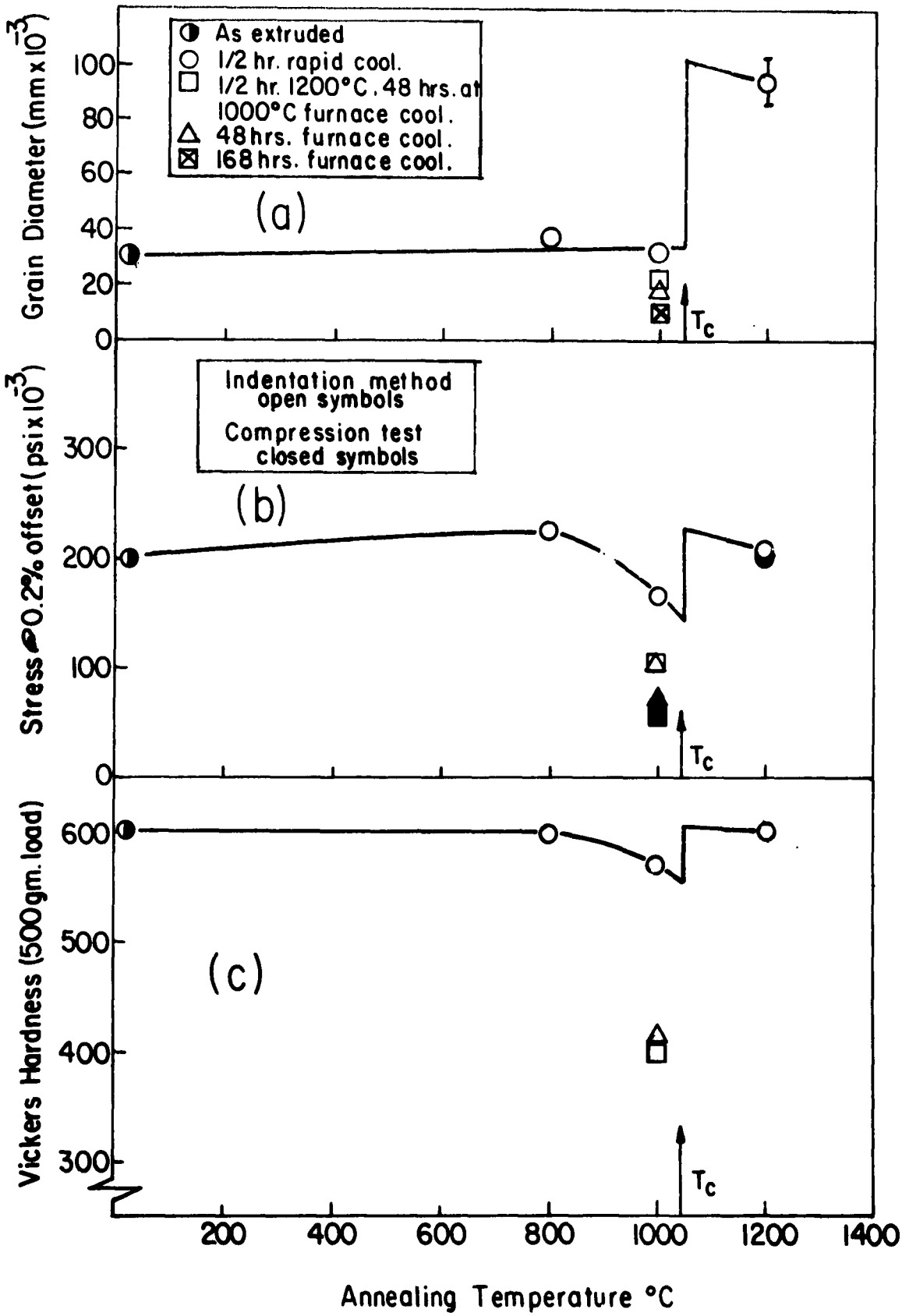


Fig. 29- Effect of indicated annealing treatments on (a) grain size (b) yield stress (c) hardness of as extruded VNi_3.

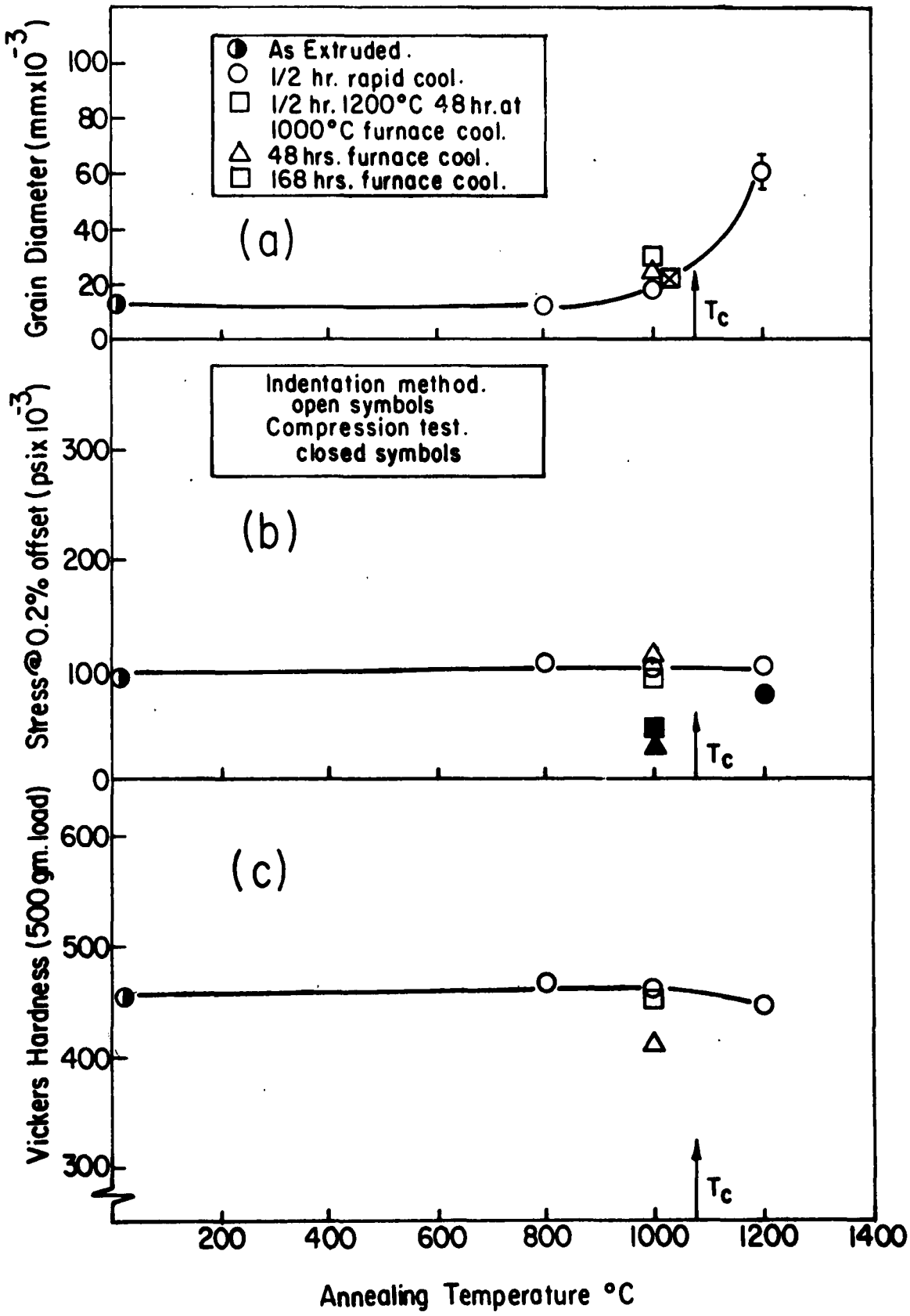


Fig.30-Effect of indicated annealing treatments on (a) grain size (b) yield stress (c) hardness of as extruded VCo_3.

but the larger grain size developed at 1000°C is accompanied by slight softening. Even prolonged annealing at 1000°C produces little further softening. It is interesting to note that the considerable softening which occurs on fully ordering VNi_3 reduces its hardness to a value close to that for fully ordered VCo_3. These various results suggest that in VCo_3, ordering takes place more rapidly than in VNi_3, and is not suppressed at the cooling rates used after extrusion or in the annealing experiments.

The stress-strain behavior of VNi_3 and VCo_3 for several of the annealed conditions was examined by indentation (i.e. compression) stress-strain measurements on metallographic specimens, compression testing on 0.4 in. diameter cylinders and tensile testing on 0.05 in. diameter wires. The yield stress values obtained for the different conditions of VNi_3 and VCo_3 by the two compression methods are compared in Figs. 29 and 30, respectively. It is seen that there is good qualitative agreement for both compounds between the values from the two methods. However, the quantitative agreement is not good and it appears that different values of the constants in the indentation stress-strain equation would be appropriate. Despite these differences, the trend of the yield stress values with annealing temperature closely resembles that of the hardness. The substantial loss of strength accompanying the removal of the substructure in VNi_3 should be noted -- the yield strength falls from about 200,000 psi to only some 50,000 psi. Such a large change is unusual for order strengthening, but the observation appears to provide some substantiation for the current view that a type of order-hardening could be responsible for the yield-strength increases of similar magnitude or greater in the Fe-Ni base "maraging" alloys. For VCo_3, where no substructure was observed, the analogous change in yield stress was much smaller -- falling from only 72,000 psi to about 38,000 psi.

The stress-strain characteristics obtained from the compression tests are summarized in Table XII - which gives the Young's modulus, elastic limit, yield stress and strain-hardening exponent. It is seen that all these parameters except the latter, are smallest for the specimens which are disordered at 1200°C before ordering at 1000°C. This is in keeping with present ideas on the factors governing the initial flow stress and work-hardening rate of ordered structures. The various characteristics are illustrated for VNi_3 in Fig. 31, by stress-strain curves for three degrees of order.

In addition to the above observations, there is some evidence from compression stress-strain data that strain-aging may take place in these compounds. However, several series of specimens are currently in testing and a discussion of this point together with a fuller comparison of the stress-strain behavior for various degrees of order and grain size will be made in a subsequent report.

Because of mechanical problems in gripping and aligning the small diameter wires which it has been necessary to use for tensile tests, the data from such tests is at present more limited than for the compression tests. Also, because of these difficulties - which lead to errors in strain measurement and to premature failure -- the accuracy of the data obtained up to the present time is less.

Table XII

Compression Data for VNi_3 and VCo_3

Compound	Treatment*	Young's Modulus		Elastic Limit (10^3 psi)	Yield Stress (0.1%, 10^3 psi)	Strain Hardening Exponent ($\sigma = \sigma_0 \epsilon^{\eta}$)
		10^6 psi	10^{12} dyne cm^{-2}			
VNi_3	#1-1200°C-1/2 hr. R.Q.	38	2.62	~70	193	.12
	#4-1200°C-1/2 hr. F.C. #4-1000°C-2 days F.C.	33	2.28	10	50	.35
	#5-1000°C-2 days F.C.	38	2.62	36	65	.33
VCo_3	#1-1200°C-1/2 hr. R.Q.	44	3.03	16	72.5	.37
	#4-1200°C-1/2 hr. F.C. #4-1000°C 2 days F.C.	43	2.97	8	37.5	.48
	#5-1000°C 2 days F.C.	44	3.03	13	44	.48

*F.C. = Furnace Cool
R.Q. = Rapid Quench

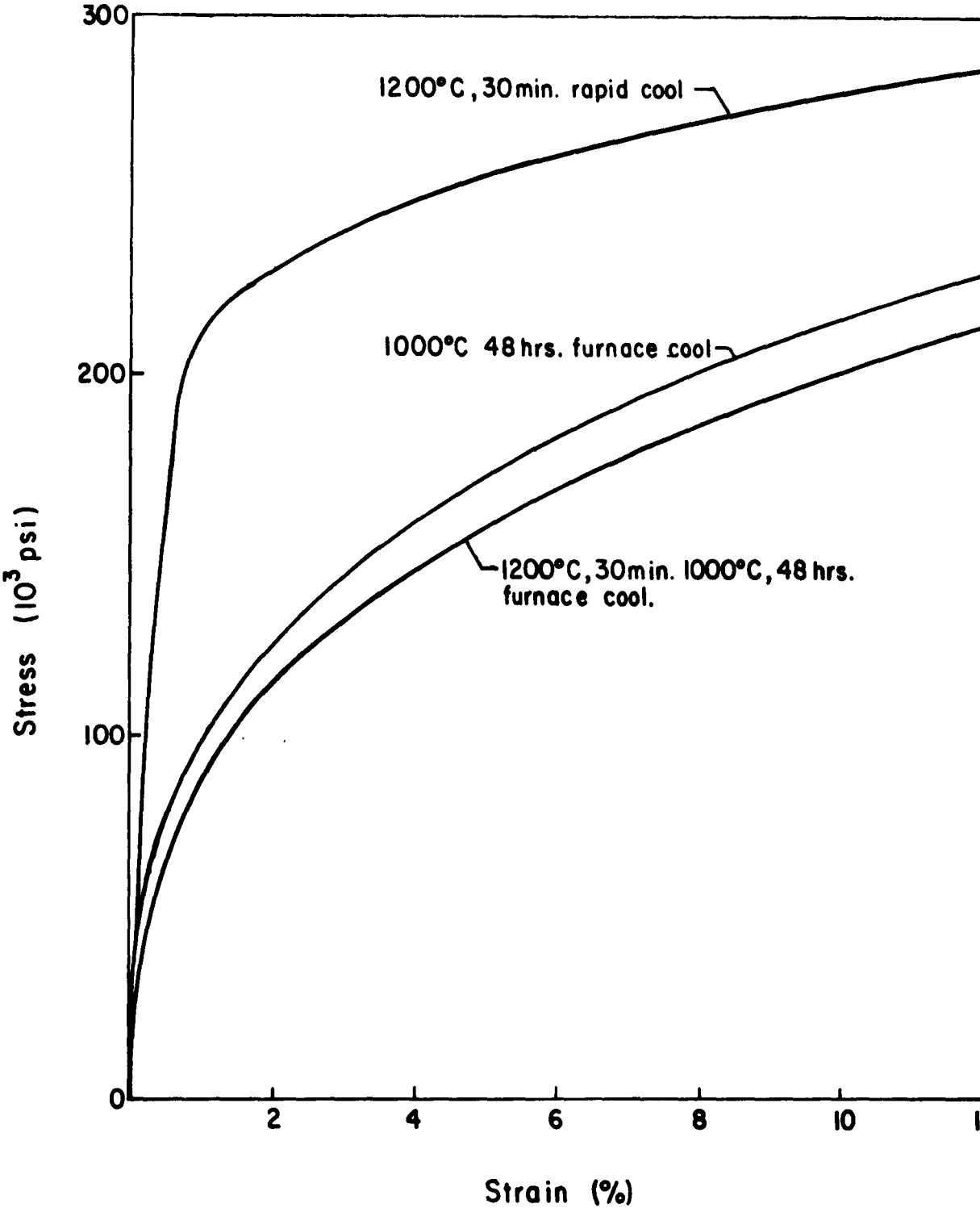


Fig.31-Compression stress-strain curves for VNi_3 subjected to indicated annealing treatments.

As shown by the results presented inTable XIII, fracture takes place within 1 to 3% plastic elongation (as much as 1.8% strain was achieved in compression without failure) and the apparent yield stresses are always lower than those observed in the compression tests. It is considered that these low values are incorrect and that they will be found to approach the compression values as the method of testing is improved.

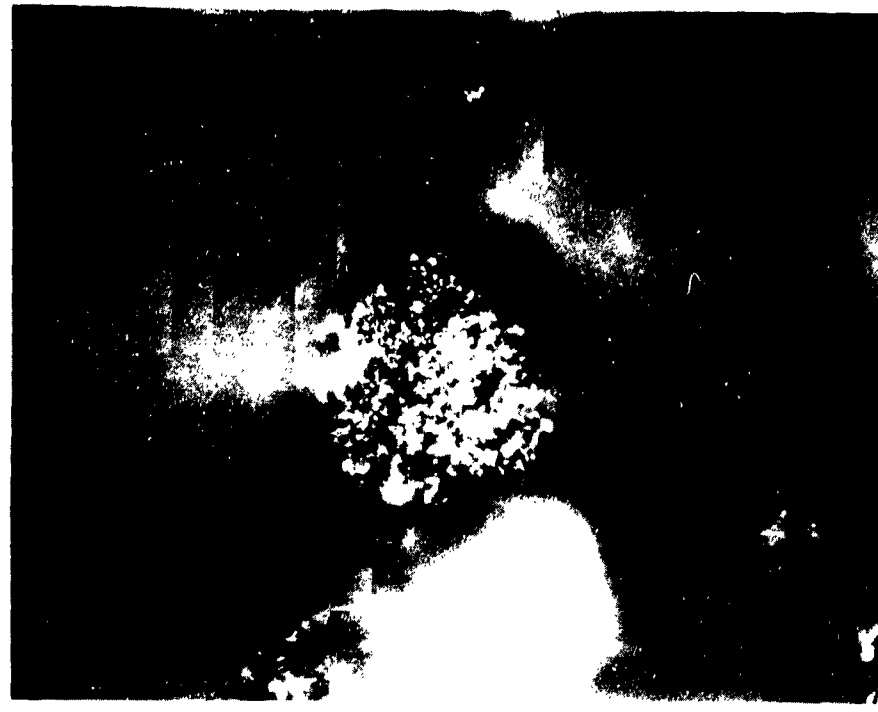
A characteristic feature of the mechanical behavior of intermetallic compounds is the relatively brittle nature of their tensile fracture. VNi_3 and VCo_3 appear to be no exception to this. Accordingly, as part of the study of their mechanical behavior, the fracture surfaces of tensile specimens are being examined by several fractographic techniques in an attempt to elucidate their mode of failure. Two annealed conditions of both compounds have been examined by light microscopy - (a) "disordered" - 1200°C for 30 min., rapidly cooled to room temperature and (b) "ordered" - 1200°C for 30 min., furnace cooled to 1000°C for 120 hours and furnace cooled to room temperature. In the "disordered" condition, the VNi_3 fracture surface appears granular or "sandy" (Figure 32A), whereas the VCo_3 fracture is much coarser and large facets with twins and ripple markings are clearly visible (Fig. 33A). In the "ordered" condition, the VNi_3 fracture surface is brightly faceted but rough, making photography difficult. Twins and straight slip markings are visible on the facets (Fig. 32B). Grain boundaries have also been observed. In contrast, the "ordered" VCo_3 fracture is less rough and exhibits a heavily distorted surface with few facets. However, even with the distortion, some twins can be distinguished (Fig. 33B). Although the coarser features discussed above are readily apparent, higher magnification is necessary to resolve the details of the fracture facets. A suitable technique is being applied to prepare carbon replicas of the surfaces for study by electron microscopy.

Table XIII

Tensile Test Results for VNi_3 and VCo_3

Compound	Treatment*	Yield Stress 0.5% offset (psi x 10^3)	Total Elongation (%)
VNi_3	1200°C-1/2 hour R.Q.	35.5	1.0
	1200°C-1/2 hour F.C. 1000°C-2 days F.C.	35.4	1.5
	1200°C-1/2 hour F.C. 1000°C-5 days F.C.	31.5	1.7
VCo_3	1200°C-1/2 hour R.Q.	34.9	3.1
	1200°C-1/2 hour F.C. 1000°C-2 days F.C.	30.8	3.2
	1200°C-1/2 hour F.C. 1000°C-5 days F.C.	33.4	2.5

*R.Q. = Rapid Quench
F.C. = Furnace Cool



As Fractured (A) 800X

As Fractured (B) 800X

Fig. 32 - Tensile fracture surfaces of VNi_3 specimens prepared by annealing at (A) 1200°C for 30 minutes and rapidly cooled (B) 1200°C for 30 minutes, furnace cooled to 1000°C for 120 hours and furnace cooled to room temperature.

As Fractured (A) 800X

As Fractured (B) 800X

Fig. 33 - Tensile fracture surfaces of VCo_3 specimens prepared by annealing at (A) 1200°C for 30 minutes and rapidly cooled (B) 1200°C for 30 minutes, furnace cooled to 1000°C for 120 hours and furnace cooled to room temperature.

V. SUMMARY AND CONCLUSIONS

During the first year (Phase I) of this continuing program, the principal objectives have been to (a) review the literature on the mechanical behavior of intermetallic compounds (b) develop suitable melting, casting and fabrication techniques for VNi_3 and VCo_3 and the study of the mechanical properties of these two compounds, (c) study the feasibility of the preparation and fabrication of VNi_2, V_2Ni, V_3Ni, VCo and V_3Co and (d) examine the validity of a possible method of predicting Young's modulus for intermetallic compounds. The work undertaken and the conclusions reached may be summarized as follows:

(1) An extensive review of the relevant literature was completed. Based largely on this, an invited lecture was presented by one of the authors of this report at the AIME Seminar on the Properties of Intermetallic Compounds held at the 1962 Fall Meeting in New York.

(2) Small ingots (1 5/8 in. diameter by 3/8 in. thick) of all the selected compounds were prepared by non-consumable arc-melting under a partial pressure of argon. The ingots all exhibited cored microstructures despite the chill casting technique used. In addition to arc-melting, attempts were made to prepare VNi_3 by electron beam zone melting. The technique proved unsatisfactory.

(3) Some preliminary experiments were made of electron-beam zone refining of arc-melted VNi_3. The results indicated that this technique may prove satisfactory for the preparation of single crystals of the compound.

(4) The response of the as-cast ingots to hot-rolling (15 to 80% reduction in thickness) were examined, (a) as a method of fabrication, (b) to provide specimens suitable for the study of annealing and recrystallization characteristics and (c) to indicate the range of possible extrusion temperatures. The ingots were protected from oxidation during rolling by sheathing with stainless steel. The V_2Ni and VCo ingots were not included in these rolling experiments since they proved to be so brittle as to shatter during cutting for metallographic examination. The results showed that rolling at temperatures in the region of 1200°C was successful, except for edge cracking, for VNi_3, VNi_2 and VCo_3. Rolling of V_3Ni and V_3Co was restricted to temperatures of 800 and 1050°C respectively, because of their likely decomposition at higher temperatures. Both fractured badly, but as it is possible that the V_3Ni compound may remain stable to as high as 1200°C, it may deform more readily at higher temperatures. In the case of V_3Co, it is doubtful whether a higher temperature can be used. These results indicated that extrusion at high temperatures should definitely be feasible for VCo_3, VNi_3 and VNi_2 and possibly for V_3Ni and V_3Co. The likely response of V_2Ni and VCo is uncertain.

(5) Extrusion billets of VNi_3 and VCo_3 (2 in. diameter by 3 to 4 in. long) were prepared by remelting batches of the smaller ingots in a non-consumable arc-furnace. As predicted from the results of the rolling experiments, the billets of VNi_3 and VCo_3 were extruded successfully to approximately 1/2 in. diameter rod at temperatures in the region of 1200°C. Extrusion ratios of both 10:1 and 16:1 were used for VCo_3, whereas only 10:1 was possible for VNi_3.

As for the rolling, the compounds were protected from oxidation during extrusion by sealing in stainless steel jackets. The microstructures of the as-extruded compounds consist almost entirely of recrystallized, regular grains. VNi_3 exhibits twins and a fine structure within the recrystallized grains; VCo_3 shows neither of these structural features.

(6) Secondary fabrication of extruded VNi_3 and VCo_3 to provide material for tensile testing was attempted by hot-rolling, hot-swaging and further extrusion. Rolling was successful, but wasteful of material due to edge-cracking. Swaging was unsuccessful under the conditions tried. Extrusion was completely satisfactory and provided wire lengths 0.090 in. diameter suitable for the preparation of tensile specimens.

(7) Homogenization and annealing studies of the as-cast and rolled compounds showed that simple annealing treatments are sufficient to homogenize VNi_3, VNi_2, V_2Ni and VCo_3. V_3Ni, VCo and V_3Co did not homogenize under the same conditions and will require much more prolonged annealing.

(8) The method of computing Young's modulus, E, which involved an estimate of the Debye temperature θ_D, has been applied to the six V-Ni and V-Co compounds for which the necessary data is available. For VNi_3, E and θ_D were measured experimentally and found to differ considerably from the calculated values. It is possible that the experimental θ_D is too high because of incomplete order in the x-ray powder specimen used. The low calculated θ_D arises from the value of the constant, C_L, assumed for the calculation by the Lindemann approximation. Computation of C_L for intermetallic compounds in all systems for which suitable data is available shows that for certain structures C_L can be estimated to within 15%. However, there are many structure types for which the accuracy is much lower.

(9) The effect of annealing temperature and time on the microstructure, hardness and stress-strain characteristics of extruded VNi_3 and VCo_3 were examined. The annealing conditions were designed to introduce different degrees of long range order and grain size. In VNi_3 a fine substructure exists in the as-extruded condition and this persists after all treatments except those leading to complete order. The removal of the substructure is accompanied by marked loss of hardness and the yield strength falls from about 200,000 psi to only 50,000 psi. Only minor changes in grain size result from annealing, except for specimens heated to temperatures above T_c and rapidly cooled. In VCo_3, no initial substructure is visible and the yield strength decrease accompanying complete ordering is smaller - falling from about 72,000 psi to 38,000 psi. Again, changes in grain size are small, except for annealing above T_c.

(10) Yield strength changes resulting from the above treatments on VNi_3 and VCo_3 were measured by indentation (compression) stress-strain testing, compression testing and tensile testing. The results from the two types of compression testing are in fair agreement, but it appears that the values of the constants in the indentation stress-strain equation must be changed for these compounds. The compression tests have provided reliable, reproducible measurements of Young's

modulus, elastic limit, yield stress and strain-hardening exponent. All the parameters except the latter are smallest in fully ordered specimens, which is in keeping with current ideas on the mechanical behavior of ordered structures. Difficulties in tensile testing from specimen slipping and premature fracture have been experienced, and only limited tensile data has been obtained up to the present.

(11) Fractographic examination of the surfaces of VNi_3 and VCo_3 specimens broken in tension have shown differences in fracture mode for the two compounds in various conditions of order.

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