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A CHARACTERIZATION OF THE DEFORMATION BEHAVIOR OF THE Cr_2Nb ORDERED INTERMETALLIC SYSTEM

by

GREGORY EDMOND VIGNOUL, B.S., M.S.

DISSERTATION
Presented to the Faculty of the Graduate School of
The University of Texas at Austin
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This dissertation is dedicated to the late Professor John K. Tien, who with prescience, patience and a great deal of friendship pushed, prodded and sometimes even pulled me into the world of technical and scientific literacy.

Thanks Boss!

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Gregory Edmond Vignoul

Austin, Texas
April 1992

A CHARACTERIZATION OF THE DEFORMATION BEHAVIOR OF THE Cr_2Nb ORDERED INTERMETALLIC SYSTEM

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The mechanical deformation behavior of two Cr_2Nb ordered intermetallics was studied up to 1400 °C. Cr_2Nb and $Cr_2(Nb,V)$ have been shown to be potential candidates as high temperature structural materials. Microindentation has been utilized to investigate the static and time dependent deformation of these compounds. The microindentation hardness values over the temperature range of 25 to 1400 °C indicate that these compounds possess greater strength than nickel based superalloys and other ordered intermetallic compounds that have been more widely studied. Both compounds were shown to possess excellent intrinsic resistance to creep deformation. Furthermore, small additions of Vanadium to the Cr_2Nb compound has been shown to result in solid solution softening and an increase in the effective fracture toughness of the $Cr_2(Nb,V)$ compound. Additional investigation of these systems is warranted, and directions for continued study are discussed.

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I. INTRODUCTION

A. Ordered Intermetallic Compounds

It has become apparent over the past several years that the elevated temperature capabilities of the current generation of high temperature structural materials are approaching, or in fact have reached, their intrinsic limits. As a consequence, ordered intermetallic compounds have garnered increased attention as potential high temperature structural materials. Intermetallic compounds are regarded as promising candidate materials for high temperature application because they occupy an intermediate position with respect to strength and toughness between metallic alloys based on solid solutions or solid solutions with second phase strengtheners, on one extreme, and ceramics on the other.

Intermetallic compounds are superior to ceramics in terms of thermal conductivity, thermal shock resistance and the ability to employ traditional processing methods for the fabrication of intermetallic compounds that melt at temperatures less than about 2000 °C. Further, intermetallic compounds offer the possibility to tailor properties since they are amenable to conventional solid solution strengthening by means of ternary and higher order alloying additions whereas, in general, ceramic materials are not.

Intermetallic compounds have a number of properties that make them more appealing than disordered alloys for high temperature use. First, and perhaps foremost, intermetallic compounds tend to be intrinsically very strong as expressed by high yield and fracture stress and their strength tends to be maintained up to high temperatures. For example, the yield strength of TiAl is 450 MPa up to about 600 °C, and only then begins to drop with increasing temperature [1].

The inherent strength of intermetallic compounds is largely due to the long range-ordered structures possessed by these compounds. This ordered structure gives rise to the fact that the Burger's vector of a dislocation will, in general, be longer than the nearest neighbor distance characteristic of disordered materials. For example, in fcc materials the Burger's vector is a/2{110}, but in the fcc-based ordered structure $L1_2$ it is a{110}; that is, it is twice as long in $L1_2$ materials. The increased length of the Burger's vector in intermetallic compounds gives rise to two effects. First, complex dissociations of the total dislocation into several partial dislocations can occur, each separated from the other by a planar fault, such as an antiphase boundary (APB), supperlattice intrinsic stacking fault (SISF), or a complex stacking fault (CSF). These faults will have low energies only on certain atomic planes and thus the number of operative slip systems during deformation may be limited, especially at low temperatures. Secondly, anisotropy of fault energies can give rise to complex cross-slip or dislocation core transformation phenomena, as observed in Ni_3Al [2-4]. These complex dissociations may also mean that the dislocation core is non-planar (lies on no slip plane) and hence is only mobile when the temperature is sufficiently high to provide the necessary thermal energy to nucleate double kinks on the dislocation [5]. As a result, the strength of such compounds will be high at low temperatures.

Not only is the strength of intermetallic compounds maintained to high temperatures, the modulus also tends to be high and decreases more slowly with increasing temperature than does the modulus of disordered alloys. It has been demonstrated that the Young's modulus of an alloy based on Fe_3Al is significantly higher than that of an alloy based on a disordered Fe-base solid solution between ambient temperature and about 800 °C [6].

In addition to having relatively high strength and stiffness, intermetallic compounds also tend to have much lower self diffusion coefficients than do disordered alloys as a consequence of their long-range ordered structures. This has been shown in the case of CuZn, which has the bcc-based B2 structure and undergoes an order-disorder transformation. The activation energy for both Cu and Zn diffusion exhibits a discontinuous increase as the temperature is reduced below T_c, the order-disorder temperature [7]. As a result, the self-diffusion coefficients of an ordered compound can be several orders of magnitude smaller than those of a disordered alloy at a given temperature. Slow rates of diffusion bring with them the attendant advantages at elevated temperatures of improved microstructural stability and, since creep rate is often proportional to the diffusion coefficient of a given system, improved resistance to creep deformation [8].

To date, the overwhelming majority of research performed on intermetallic compounds has focused on relatively low melting compounds having fcc or bcc-derivative structures. Indeed, the most widely studied compounds are those having the fcc-derivative $L1_2$ structure such as Ni_3Al. While these studies have provided the scientific community with a detailed understanding of the deformation behavior of simple low-melting intermetallic compounds, virtually no such understanding exists for intermetallic compounds with melting temperatures in excess of 1600 °C. This is illustrated in Figure 1, which lists both the commonly studied intermetallic compounds and intermetallic compounds that are now gaining interest as a function of their melting temperatures. Virtually nothing is known about the deformation behavior of compounds that lie above the dashed line in this Figure.

In general, intermetallics of this genre do not have simple fcc- or bcc-derivative structures such as $L1_2$ or B2, they have many atoms per unit cell and are expected to be quite brittle at low temperatures. Consequently, there exists a basic need in the community for a detailed mechanistic understanding of the deformation behavior of complex intermetallic compounds such as the high melting Laves phases.

Thus, the goal of this dissertation has been to characterize the deformation behavior of complex, high melting Laves phase intermetallic compounds in order to ascertain their potential as high temperature materials. In particular, investigations of 1) strength as a function of temperature, 2) creep and resistance to creep, and 3) the

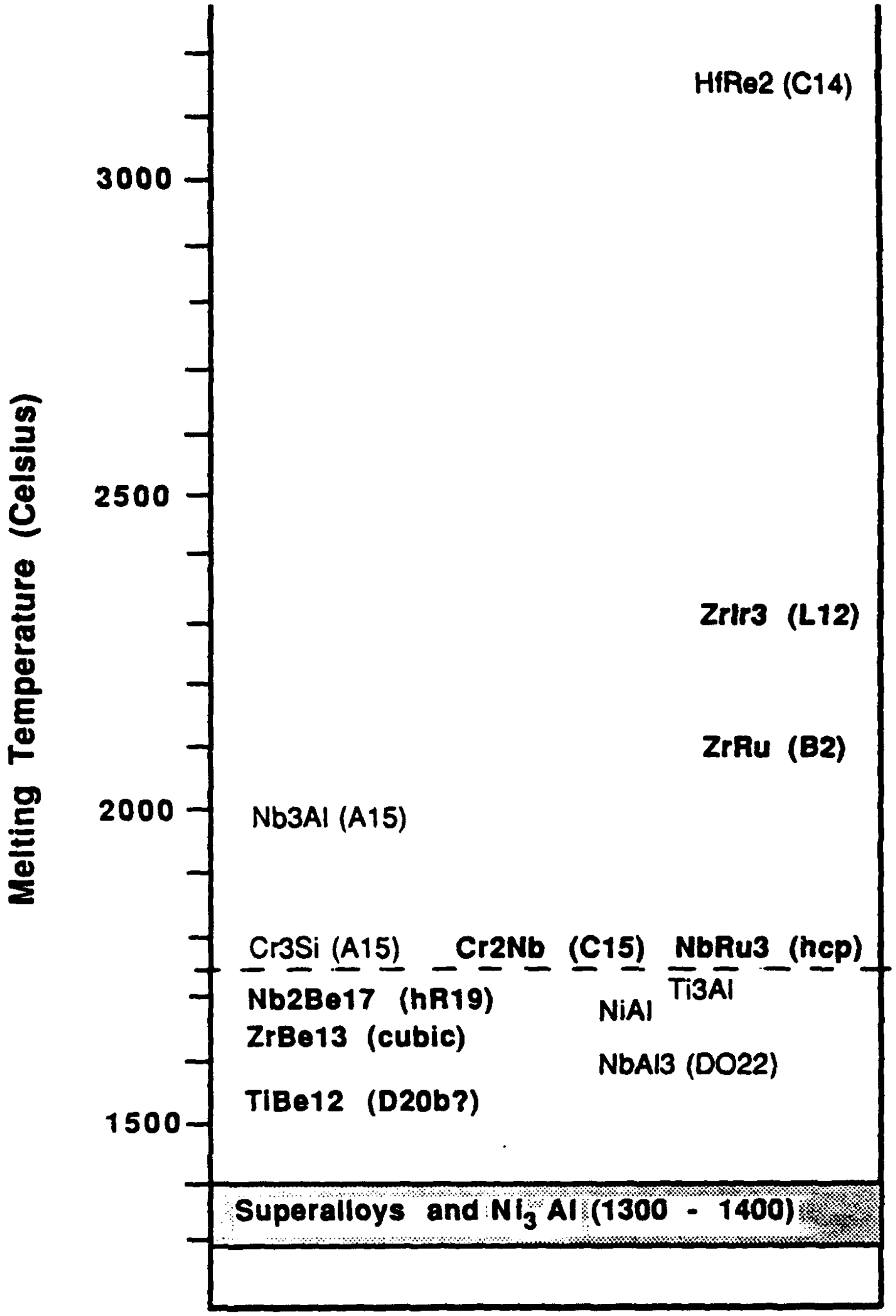

Figure 1. Ordered intermetallic compounds of current interest as a function of melting temperature

mechanical response of these compounds to ternary alloying additions were undertaken. These characterization steps are crucial in order to define basic behavior and identify potential and/or limitations prior to full scale development of a given high temperature material system. Current high temperature materials design philosophy dictates that potential materials systems for use at elevated temperatures must maintain good strength to high temperatures, good resistance to creep and a modicum of room temperature ductility or toughness. Consequently, the development of potential materials systems can only proceed when a basic first-level characterization, such as that utilized in this investigation, of the behavior of the systems has been performed.

B. Laves Phases and Cr_2Nb

The Laves phases possess one of three related topologically close-packed structures of the general formula AB_2, for which $MgCu_2$ (C15), $MgZn_2$ (C14) and $MgNi_2$ (C36) are the prototype compounds. The C15 structure is cubic with 24 atoms per unit cell whereas the C14 and C36 structures are hexagonal with 12 and 24 atoms per unit cell respectively. These structures are shown in Figures 2-4 and are closely related in that they differ only in the stacking

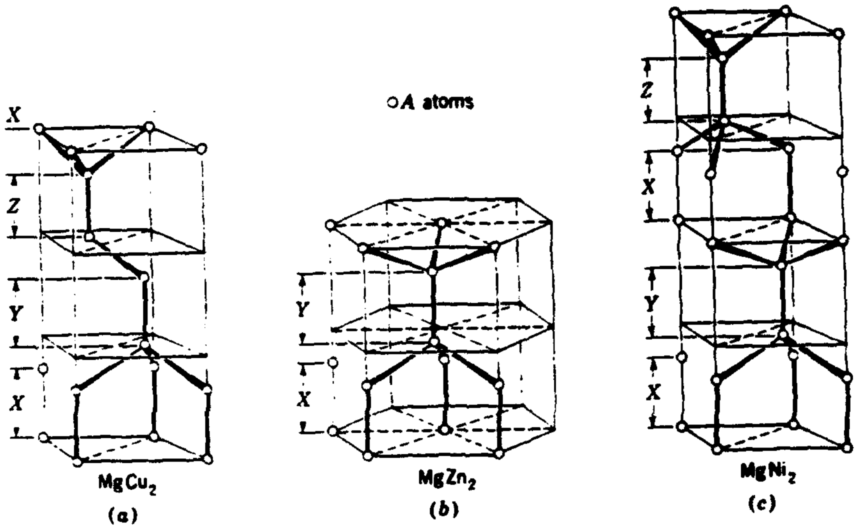

Figure 2. Distribution of A atoms and stacking of double layers in Laves phases [9].

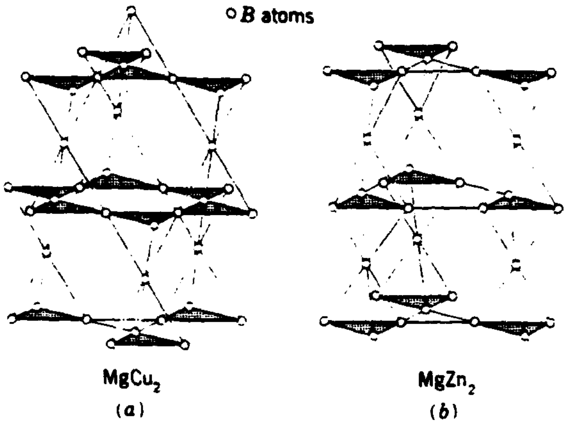

Figure 3. Distribution of B atoms and stacking of tetrahedra in Laves phases [9].

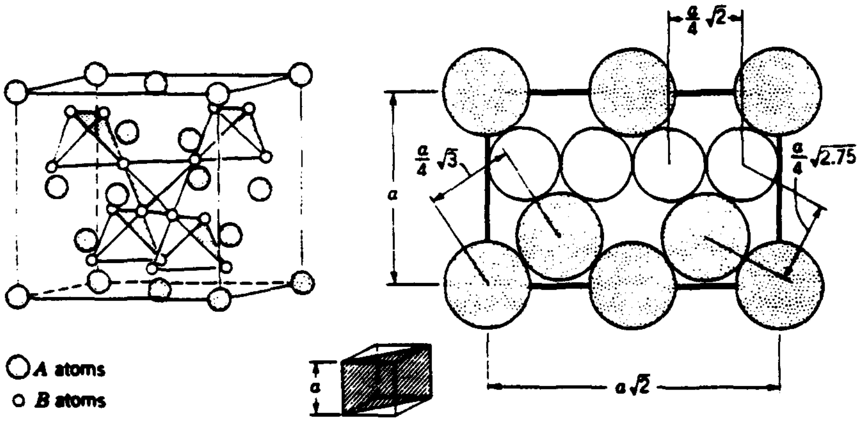

Figure 4. Distribution of A and B atoms in the cubic cell of MgCu2 (C15) structure. Left is a perspective view and right is a schematic arrangement in the (110) plane [9].

sequence of similarly built layers. Also, certain Laves phases undergo single or multiple phase transformations from one type to another as a function of temperature. It is generally believed that these transformations proceed by a shear, or martensitic, type mechanism which involves concerted motion of the different atomic layers.

The ordered intermetallic system chosen for study in this investigation was Cr_2Nb, a Laves-type intermetallic compound which melts at 1770 °C. The binary Cr-Nb phase diagram is shown in Figure 5. As may be seen, the Cr_2Nb intermetallic possesses two distinct Laves crystal structures; the C14 structure which is stable at temperatures above approximately 1625 °C and the C15 structure which is stable below this temperature. This transformation results in a 10% contraction of atomic volume and therefore it is expected that as-melted materials will exhibit poor structural and mechanical integrity as a result of transformation induced microcracking.

In addition to being selected because of its crystal structure type, this particular system was selected because it melts at a very high temperature as compared to intermetallic compounds currently being studied and the density of this system is comparable to the densities

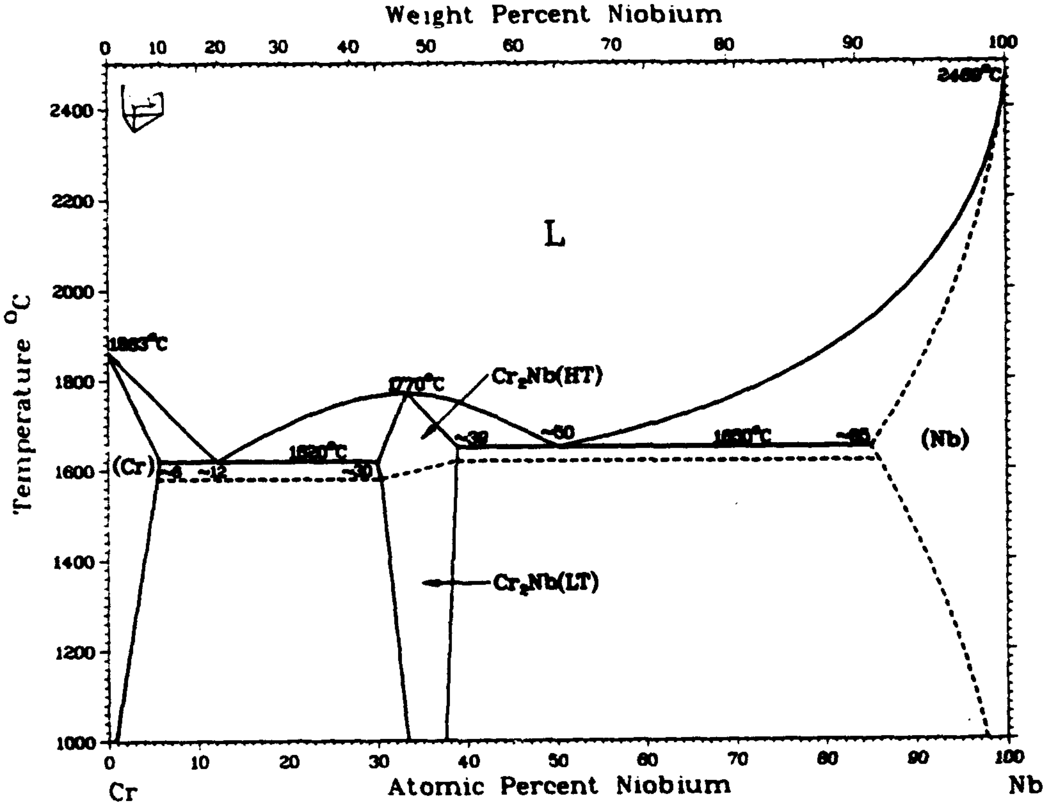

Figure 5. Binary phase diagram of Cr/Nb system [10].

possessed by the current generation of nickel-based superalloys. As alluded to above, this compound was expected to be quite brittle at low temperatures as a consequence of its complex crystal structure, limited symmetry and the high probability of severely limited operative slip systems available for deformation. Similarly, this system is expected on an a priori basis to be inherently quite strong and to maintain this strength to high temperatures as a consequence of the strong possibility that complex dislocation configurations, dissociations and interactions will occur during deformation [11].

The deformation behavior of a ternary Cr_2Nb compound containing 5.13 *atomic* percent Vanadium was also investigated. Vanadium was chosen as an alloying addition because of its role in intermetallic compounds with relatively wide phase fields as a solid-solution strengthener [12,13]. Further, it has been shown that Vanadium additions to intermetallic compounds in the titanium aluminide system can significantly enhance the ductility of these intermetallics [14,15].

The Cr_2Nb intermetallic system is considered an exotic in the sense that it is just beginning to be studied and as such is not produced outside of the laboratory. In fact, laboratory production prior to this work has meet with extremely limited success and has succeeded only in producing dual-phase material in very small quantities. Due to the extremely limited material availability and the difficulties inherent to the fabrication of large quantities of single phase compounds, the deformation behavior of these intermetallic compounds was characterized using the technique(s) of microindentation.

Clearly, full scale characterization of the deformation mechanistics operative in these systems will require sufficient quantities of bulk material so that the gamut of testing, such as compressive and tensile yield and strain to failure, tensile creep, fatigue and creep/fatigue interactions, can be performed. However, until the problems associated with materials processing can be solved, the technique of microindentation is the one tool which allows a quantitative characterization to be performed on limited amounts of material. Indeed, the technique of high temperature microindentation has made this exploratory study possible.

II. EXPERIMENTAL BACKGROUND

A. Microindentation as a Function of Temperature

The use of indentation hardness as a means of studying the plastic yield properties of solids is well defined and has been accepted as a reflection of the constrained strength of a material [16-20]. It has been shown that when a material is deformed by a pyramidal indenter, such as that used during microVickers indentation, the shape of the indentation remains constant regardless of the size of the indentation and consequently that the stress and strain patterns in the deformed material remain geometrically similar. For this reason the yield pressure is essentially constant and is independent of the load L. Thus, if d is the diagonal length of the indentation then the yield pressure is proportional to L/d^2, and since this is constant $L = kd^2$, where the proportionality constant k depends only on the hardness of the material.

If pyramidal indentations are made in a material that exhibits ideal plasticity (a material which does not work-harden with indentation), it is found that there is a direct relation between yield stress σ_y of the material and the mean pressure P between the indenter and the material. As plastic deformation during indentation requires either shear-stress or shear-strain conditions, and because only about one-third of the applied pressure results in plastic flow, the mean pressure between the metal and the indenter is approximately three times the yield stress of the material. In fact, for a wide range of materials, it has been shown that $P = 3.2\sigma_y$ [21]. As H_v is calculated using the surface area of the pyramidal indentation rather than the projected area of the indentation, H_v is less than P by about 7% as determined from geometrical considerations. Thus, $H_v \approx 3\sigma_y$.

For materials that work-harden and therefore experience an increase in tensile yield stress with strain, the amount of work-hardening produced by the indentation process will vary with the geometry of the indenter used. It has been shown empirically that the indentation produced using a pyramidal Vickers indenter increases the effective yield stress of the material by an amount equivalent to a strain of about 8% and that this relationship holds irrespective of the initial degree of material work-hardening [21]. That is, if a material is deformed by an amount ε_0 , H_v at this stage of deformation will be approximately three times the yield stress of the material at a deformation of $\varepsilon = \varepsilon_0 + 8\%$.

B. Microindentation Fracture Toughness

The advent of indentation fracture mechanics has provided a fundamental basis for analyzing the complex deformation fracture response in brittle materials to controlled sharp-contact events [22]. Figure 6 shows a schematic of the indentation deformation fracture pattern for the Vickers geometry: P is the peak applied load and a and c are characteristic dimensions of the "plastic" impressions and the radial/median crack, respectively [23]. From dimensional analysis it has been demonstrated that these parameters relate directly to the hardness H and toughness K_c of the indented material,

$$H = P/\alpha_0 a^2 \tag{1a}$$

$$K_c = P/\beta_0 c^{3/2} \tag{1b}$$

where α_0 and β_0 are taken as numerical constants [23].

Explicit models of radial crack evolution within the elastic/plastic field of a sharp indenter for an isotropic, homogeneous material have shown that the net driving force on the crack system is a superposition of elastic (reversible) and residual (irreversible) components. At the indentation surface the elastic component is compressive, the residual

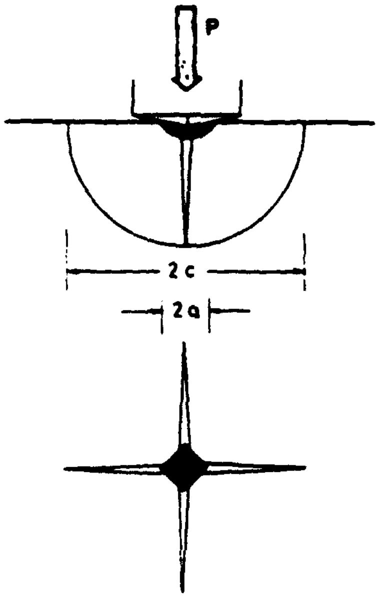

Figure 6. Schematic of Vickers produced indentation fracture system, peak load P, showing characteristic dimensions c and a of penny-like radial/median crack and hardness impression, respectively.

component is tensile and thus the radial cracks grow to their final lengths as the indenter is unloaded [24]. For sufficiently well developed cracks, c >> a, the pennylike cracks may be considered to be "center-loaded" at the deformation zone, in which case the driving force may be characterized by a residual stress intensity factor of the form:

$$K_r = \chi_r P/c^{3/2} \tag{2}$$

where χ_r is a constant that depends approximately on the square root of the ratio of Young's modulus to hardness, E/H, such that

$$\chi_r = \Phi^R (E/H)^{1/2} \tag{3}$$

where Φ^R is a material independent constant equal to 0.016 ± 0.004 for Vickers-produced radial cracks. If the crack system is subject to conditions of mechanical equilibrium both during and after the contact event, such that the radial cracks remain stable at $K_r = K_c$, then

$$K_c = \chi_r P/c^{3/2} = \Phi^R (E/H)^{1/2} (P/c^{3/2}) \tag{4}$$

Thus, material toughness can be evaluated in a straightforward fashion. It has been shown that this analytical method provides good agreement between toughness values obtained by microindentation and by conventional methods [25].

C. Microindentation Creep

In addition to allowing the characterization of static deformation characteristics of materials, it has been shown that the dynamic microindentation hardness behavior of a variety of materials at temperatures above $0.5T_m$ closely parallels the viscous creep characteristics of these same materials [26-28]. Viscous creep is generally described by a typical power-law creep relation of the form:

$$\dot{\varepsilon}_s = A\sigma^m \exp(-Q/RT) \tag{5}$$

where $\dot{\varepsilon}_s$ is the steady-state strain rate, σ the tensile stress, m is a constant on the order of 3 - 5 for materials exhibiting power-law creep and Q is the apparent activation energy for creep.

The microindentation hardness at these temperatures does not depend upon the shape of the indenter so that the strain rate must not be associated with indenter geometry, but rather with the rate at which the elastic/plastic boundary diffuses into the undeformed material ahead [28]. During microindentation creep the plastic zone is continuously increasing with time on load, and thus the use of a transient creep equation is physically more reasonable than a viscous creep relation.

Transient creep can be generally described by a relation of the form

$$\dot{\varepsilon}_{tr} = A_2\,\dot{\varepsilon}_s^{1/3} t^{-1/3} \tag{6}$$

where A_2 is independent of both stress and temperature and $\dot{\varepsilon}_s$ is the strain rate of steady state or viscous creep under the same constant stress σ. The validity of this relation has been experimentally demonstrated for a wide range of metals [29]. If Equation 6 and Equation 7 are combined, then it is seen that

$$\dot{\varepsilon}_{tr} = A_3 \sigma^{m/3} \exp(-Q/3RT) t^{-2/3} \tag{7}$$

This relation assumes that stress is substantially constant, is not too large and that every part of the sample is undergoing homogeneous deformation. Further, the following relationship exists between the microindentation stress (hardness) H and the time on load:

$$H^{-m} = A'\exp(-Q/RT)t \qquad (8)$$

This equation predicts linear logarithmic plots of microindentation hardness versus time on load whose slopes yield a measure of the stress exponent for creep, m, at each temperature.

The kinematics of the indentation process have been derived on the basis of assuming that this process corresponds to the plastic movement of a series of shells concentric with the indenter/material contact region, so that the growth of the indentation resembles the expansion of a hemispherical hole in a semi-infinite solid [28]. Further, it has been observed that for short loading times, the microindentation hardness rises rapidly to a relatively constant value which is independent of temperature. This deviation from the linearity of ln(H) versus ln(t) plots predicted by equation 9 is a direct result of the fact that at short loading times viscous creep, which characterizes the linear portions of these plots, can no longer take place effectively. Consequently, it has been postulated that the kinematics of the creep process during indentation can be analyzed using a transient creep "equation of state" of the form:

$$H^{-m/3} - H_0^{-m/3} = A_4 \exp(-Q/3RT)(t^{1/3} - t_0^{1/3}) \qquad (9)$$

where H is the microindentation hardness at time t, H_0 is the hardness immediately after attaining the full load at t_0, m is the stress exponent for creep and Q is the apparent activation energy for creep. Equation 10 predicts linear logarithmic plots of $(H^{-m/3} - H_0^{-m/3})$ versus $(t^{1/3} - t_0^{1/3})$ of slope unity, the interval on the abscissa between two lines for different temperatures T_1 and T_2 yielding an estimate of the activation energy of the microindentation creep process [28].

This analytical method has been validated for a number of different materials systems ranging from pure metals to ceramics. Further, the methodology has been applied to Ni_3Al and Ti_3Al and excellent agreement has been found between the values for m and Q determined by microindentation creep and by more conventional testing methods such as tensile or compressive creep [30].

III. EXPERIMENTAL PROCEDURES

The binary Cr_2Nb and ternary $Cr_2(Nb,V)$ intermetallic compounds were prepared via arc-melting/remelting in single heats of 125 grams each. As a consequence of the structural transformation and associated 10% volume contraction that occurs during cooling mentioned above, the as-received material exhibited significant macro- and microcracking. The crystal structure of each material was verified by x-ray powder diffraction using Cu kα radiation with a wavelength of 1.5414 Å.

The as-received materials were sectioned and metallographically prepared in order to determine the as-cast grain size, extent of residual casting porosity and material homogeneity. Each sample was surface etched using a solution of 33% HF, 33% HNO_3 and 33% H_2SO_4 for 30 seconds to 2 minutes prior to metallographic examination. Metallographic examination was performed via optical microscopy using Neumarski interference contrast.

Microindentation samples of each compound were sectioned to size (5 mm x 5 mm x 10 mm) and the surfaces metallographically polished prior to indentation. Each sample was annealed in vacuum at 1200 ± 2 °C for 96 hours to relieve residual stress incurred during fabrication.

All indentations were performed in a vacuum of 2-5 x 10^{-5} torr using a Nikon Model QM high temperature microhardness tester equipped with a diamond micro-Vickers indenter. The microhardness tester is designed so that both the specimen and indenter can be heated and controlled independently to an accuracy of ±5 °C at 1600 °C. Further, the applied load can be varied in step increments from 50 to 1000 grams. Given that the material used in this study was polycrystalline, multiple indents at each experimental condition were performed to insure sampling over several grains. The arithmetic average of the indentation diagonal lengths was taken to calculate the micro-Vickers hardness according to Equation 10 [31]:

$$H_v = 1854.4\,[L/d^2] \tag{10}$$

where H_v is the micro-Vickers hardness of the material, L is the applied load in grams and d is the mean indentation diagonal length in micrometers. The diagonal lengths of each indentation, as well as the lengths of any cracks associated with indentations, were measured using an optical microscope at a magnification of 400x to an accuracy of ±0.1 μm.

Indentation load hold time was chosen as 5 seconds to examine the deformation behavior of both systems as a function temperature, and was varied from 1 to 1000 seconds at constant temperature in order to study the creep behavior of these intermetallics. Loads were held constant at 300 grams for all aspects of this study. The indentation load application rate was maintained constant at 0.3 mm/sec throughout this study.

IV. RESULTS AND DISCUSSION

A. Microindentation as a Function of Temperature

Prior to examining the microindentation behavior as a function of temperature, microindentation hardness as a function of time at temperature was studied during annealing of the binary Cr_2Nb compound. As can be seen in Figure 7, the microhardness versus time at temperature curve exhibits classical stress relaxation behavior, indicating that the as-received compound accumulated significant residual stress during fabrication. This residual stress is a direct result of the isostructural shear transformation from the C14 structure to the C15 structure on cooling from the melt. The ternary $Cr_2(Nb,V)$ compound was subsequently subjected to the same annealing conditions so that valid intersystem comparisons could be made.

The observed microindentation hardness behavior as a function of temperature is shown in Figure 8 for the Cr_2Nb intermetallic and in Figure 9 for the ternary $Cr_2(Nb,V)$ system. Microhardness of the polycrystalline Cr_2Nb decreased with increasing temperature, from $H_V = 950$ MPa at 25 °C to $H_V = 322$ MPa at 1400 °C. While a slight peak in microhardness of this intermetallic was observed to occur at

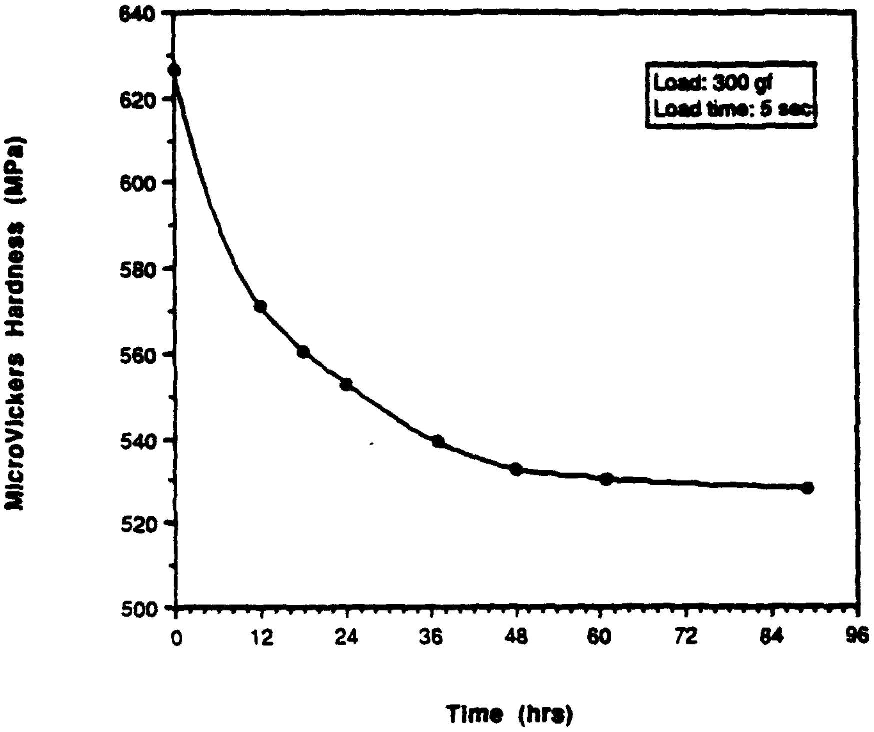

Figure 7. Microindentation hardness of Cr_2Nb as a function of time at temperature; T = 1200 °C

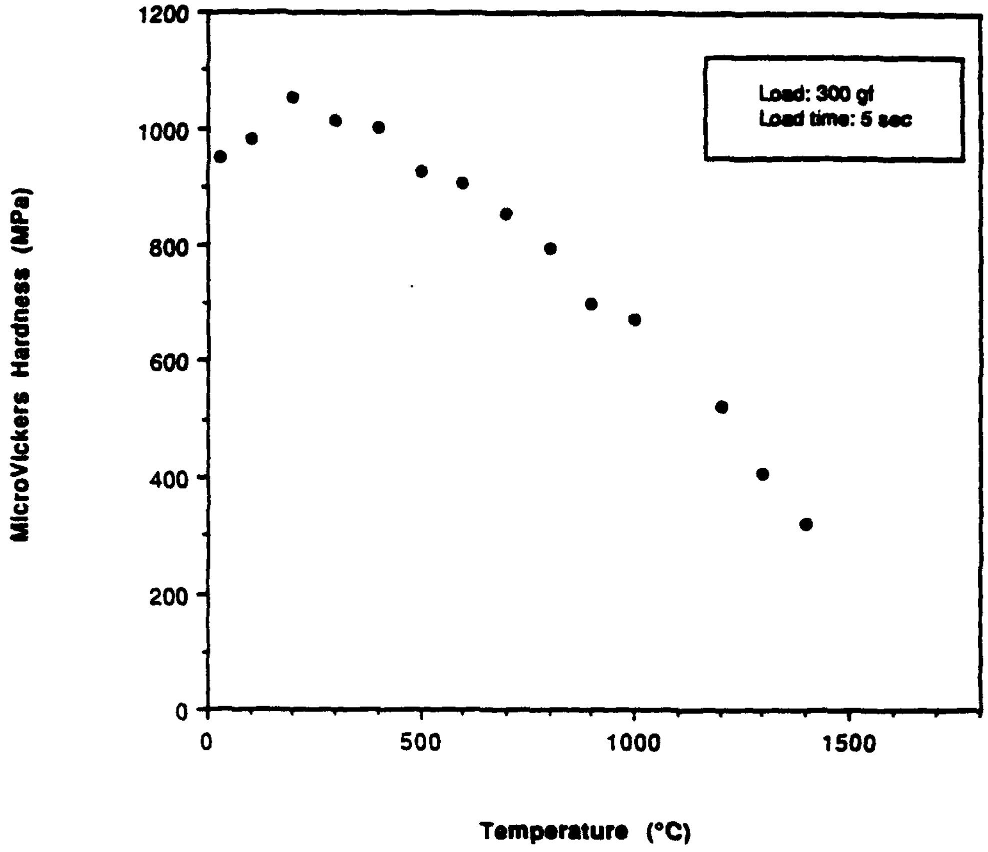

Figure 8. Microindentation hardness of Cr_2Nb as a function of temperature

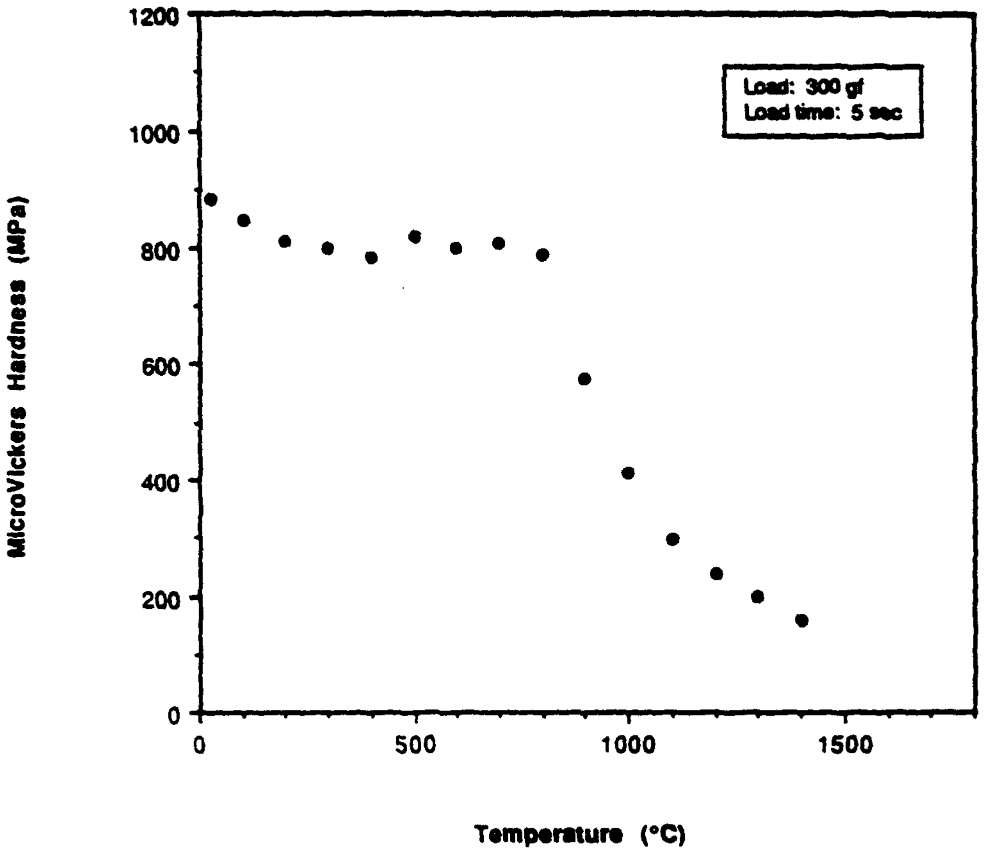

Figure 9. Microindentation hardness of $Cr_2(Nb,V)$ as a function of temperature

approximately 200 °C (H_V = 1040 MPa), this is not considered to be indicative of anomalous strength behavior since anomalous flow stress behavior is generally associated with cross-slip of dislocations to a sessile configuration and a subsequent thermally assisted change from sessile or "locked" to glissile dislocation configurations at elevated temperatures [2].

The deformation behavior as a function of temperature of the ternary $Cr_2(Nb,V)$ compound exhibited similar decreasing microhardness with increasing temperature to the binary compound, as is seen in Figure 9. Microhardness of the ternary decreased from H_V = 833 MPa at 25 °C to H_V = 158 MPa at 1400 °C. As indicated previously, Vanadium was originally chosen as a ternary alloying addition because of the potential for solid solution strengthening, either as a consequence of substitutional solution hardening or constitutional defect hardening. However, as may be seen in Figure 10, Vanadium addition to the Cr_2Nb intermetallic resulted in a decrease in strength of approximately 7% at 25 °C in the ternary compound as compared to the binary.

This decrease in strength over the entire temperature range investigated may be related to the phenomenon of solid solution softening which is observed in some bcc and hcp

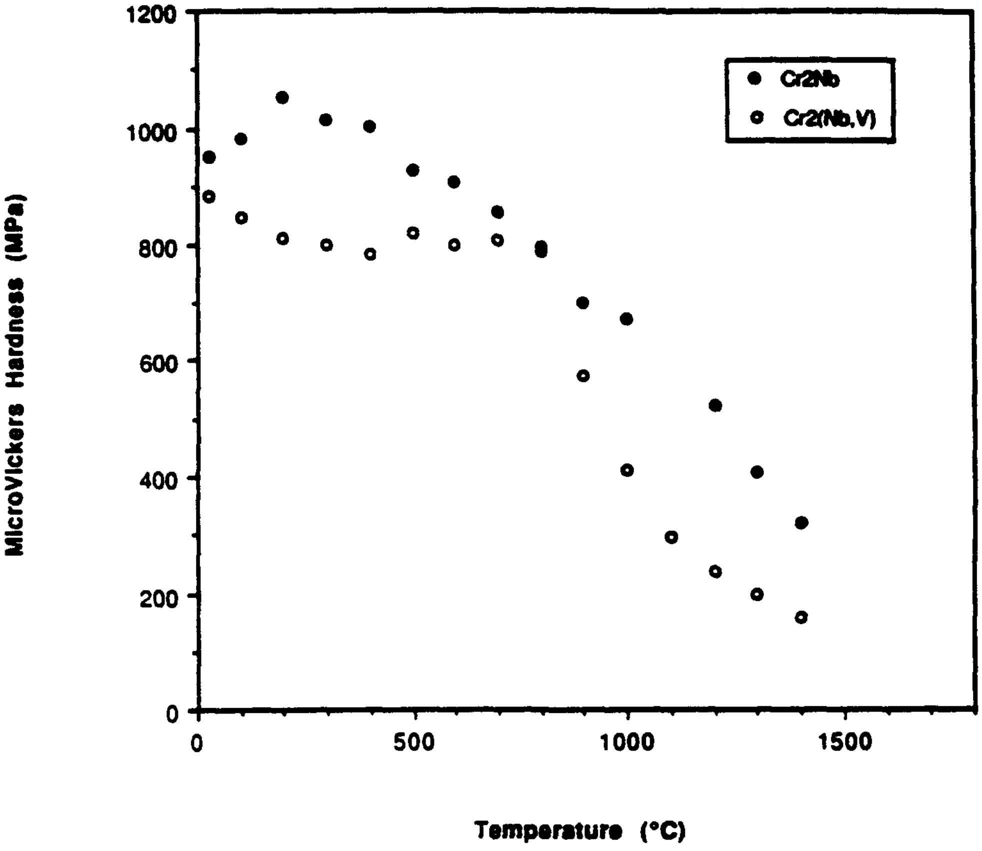

Figure 10. Effect of 5.13 a/o V addition on the strength of Cr_2Nb

metals which contain small amounts of impurities or alloying additions [32-35]. In these metals, solid solution softening occurs because screw dislocations have a relatively high Peierls stress and alloying either reduces the depth of the Peierls energy valley or aids double kink nucleation on the screw dislocations. Generally, the inherent lack of ductility in intermetallic compounds is the result of weak or brittle grain boundaries, an intrinsic lack of ductility within individual crystal grains, or a combination of these two factors. Given that indentations were performed within individual grains, it is clear that Vanadium serves to globally soften the individual grains in the material. The fact that solid solution softening is occuring as a result of Vanadium addition to the Cr_2Nb intermetallic is extremely interesting in that it provides the opportunity for effective ductilization and/or toughening of this system.

A logarithmic plot of microindentation hardness as a function of homologous temperature T/T_m, where T_m represents the melting temperature of the material, for the Cr_2Nb compound is presented in Figure 11. This Figure exhibits two linear regions of constant slope separated by a discontinuity which occurs at approximately 1090 °C. This discontinuity corresponds to the onset of enhanced plasticity,

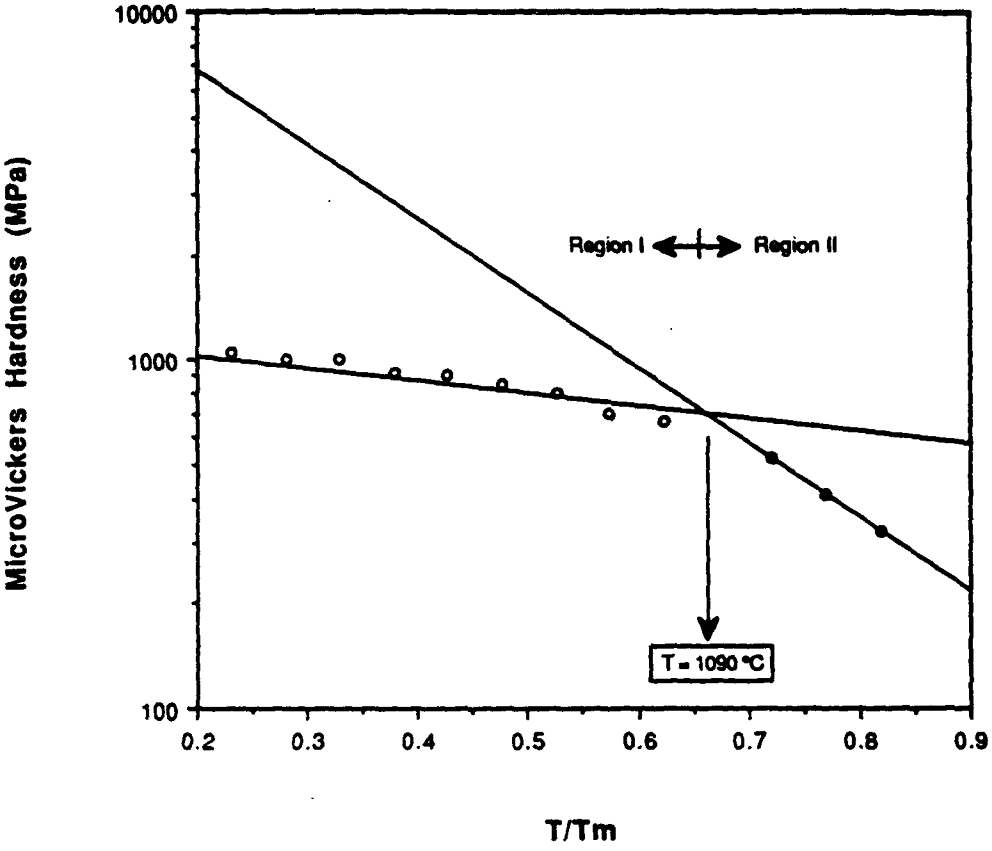

Figure 11. Microindentation hardness of Cr_2Nb as a function of homologous temperature

where region I exhibits elastic behavior associated with crack generation and/or propagation. Conversely, region II is indicative of increased plastic flow, both away from cracks and at crack tips. This observation is confirmed by the fact that the indentations below 1100 °C were accompanied by numerous cracks emanating from the corners and sides of the indentations, whereas indentations at or above 1100 °C exhibited significantly less cracking as measured both in terms of total number of cracks and crack lengths (see Figure 12).

Similarly, a logarithmic plot of the microindentation hardness as a function of homologous temperature for the $Cr_2(Nb,V)$ compound is presented in Figure 13 and shows a sharp transition in deformation processes at temperatures above about 800 °C. Again, this is indicative of the onset of enhanced plasticity at temperatures greater than approximately 800 °C. While it is tempting to call this discontinuity a ductile-brittle transition, examination of indentations performed at temperatures to 1200 °C indicates that cracking still occurs, although to a lesser degree than at temperatures below 800 °C.

As indicated in Figure 14, the microindentation hardness of both systems is significantly higher at any given

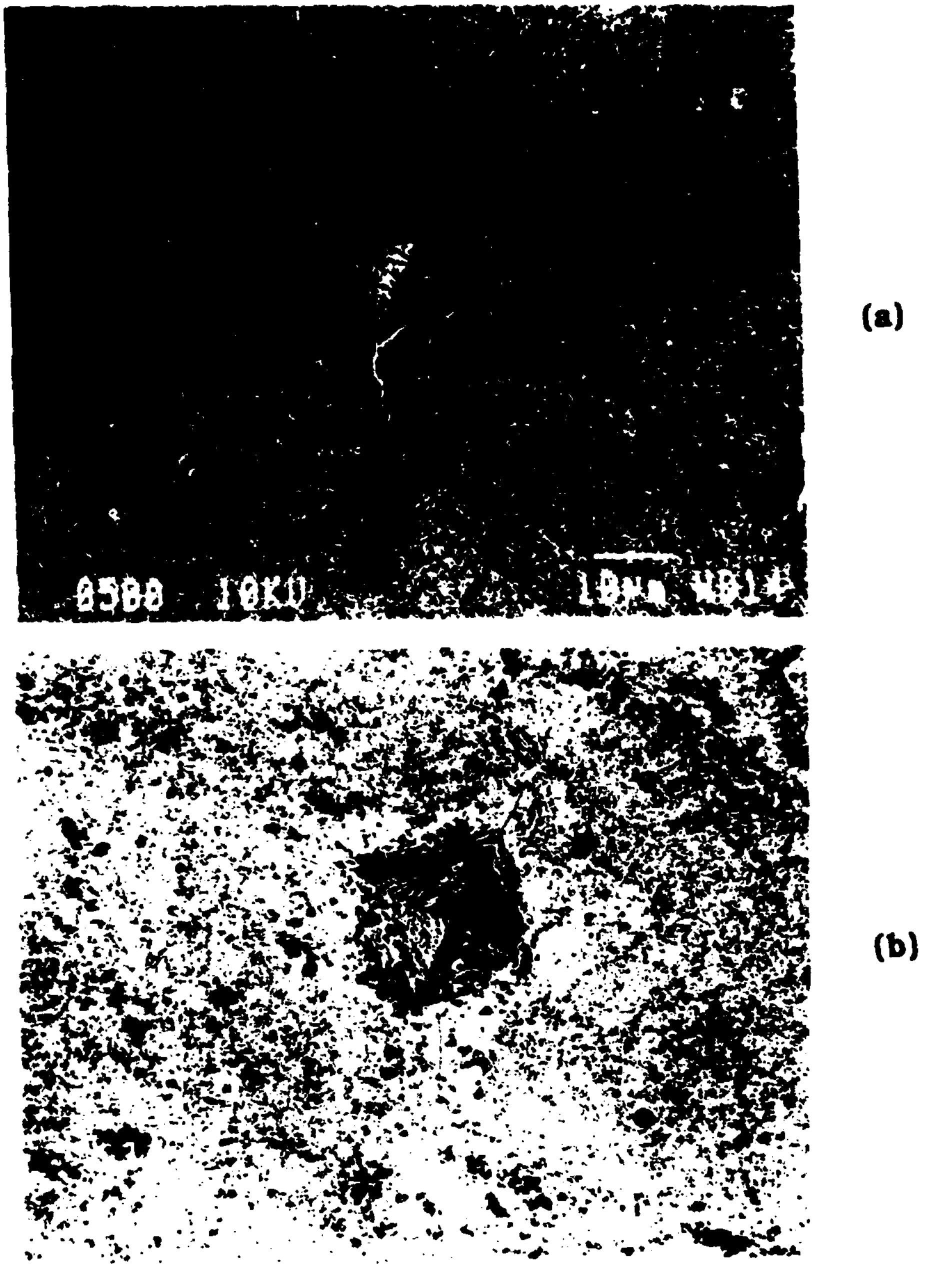

Figure 12. Micrographs of typical indentations in Cr_2Nb showing crack patterns and lengths at a) T = 500 °C and b) T = 1100 °C

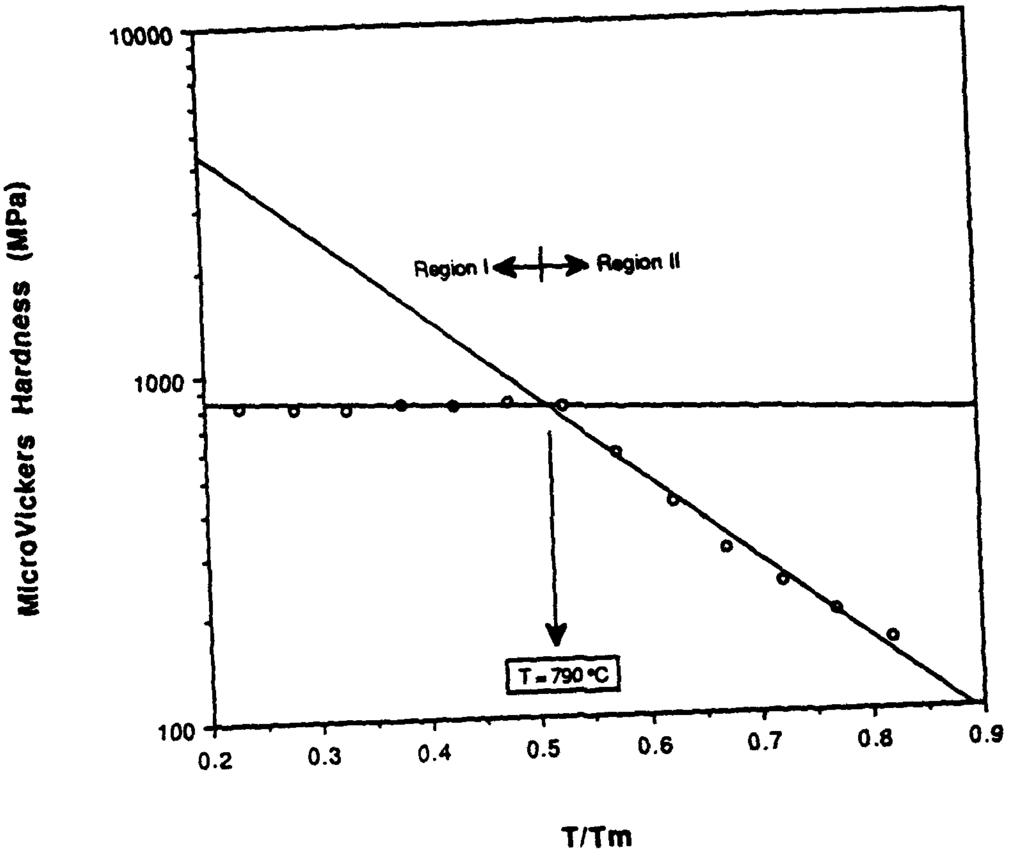

Figure 13. Microindentation hardness of $Cr_2(Nb,V)$ as a function of homologous temperature

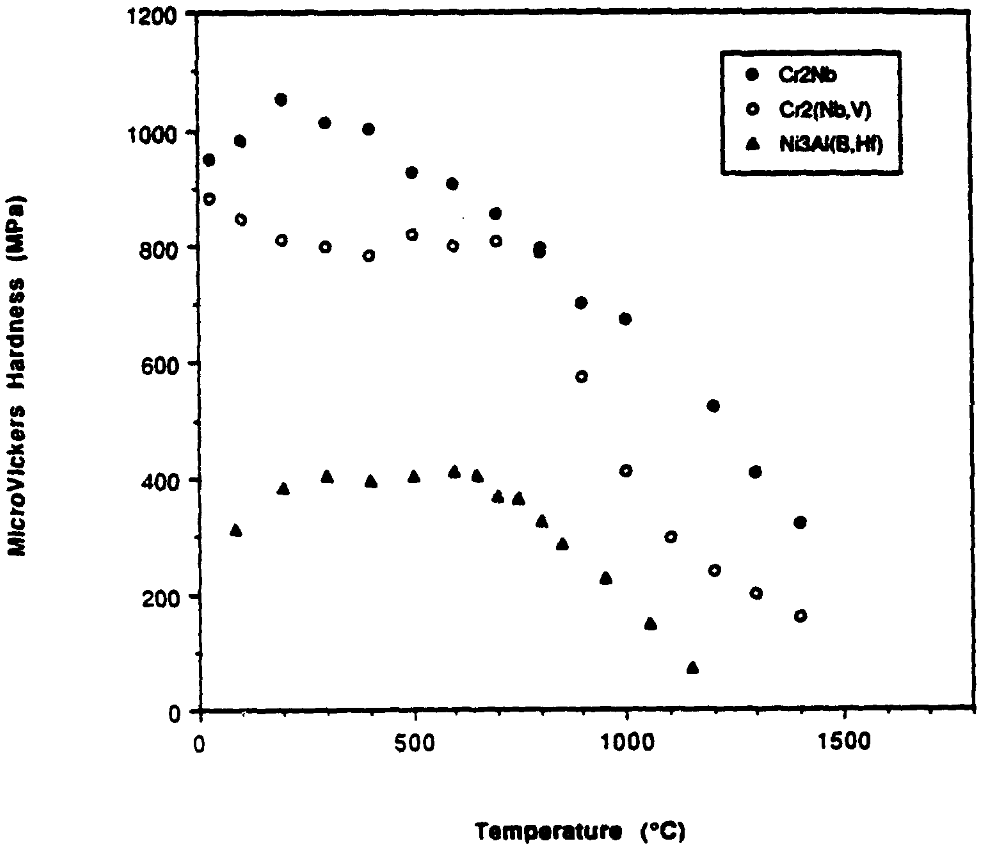

Figure 14. Comparison of microindentation hardness of Cr_2Nb, $Cr_2(Nb,V)$ and $Ni_3Al(B,Hf)$ as a function of temperature

temperature than that found for a $Ni_3Al(B,Hf)$ compound tested under identical experimental conditions. Indeed, at 600 °C, the temperature at which the peak in microindentation hardness occurs for the $Ni_3Al(B,Hf)$, the strength of the Cr_2Nb and $Cr_2(Nb,V)$ compounds is approximately 2.5 and 2 times greater respectively than that of the Ni_3Al intermetallic system. Further, the strength of the Cr_2Nb intermetallic at 1300 °C is comparable to or greater than the peak strength of the Ni_3Al intermetallic. This represents an effective increase in use temperature, as measured in terms of strength, of 700 °C over the Ni_3Al intermetallic alloy.

While a description of the specific deformation mechanistics involved in the Cr_2Nb systems is at present unknown, several studies on dislocations produced by deformation of other Laves phases possessing the C15 crystal structure provide some rationale for the high strength and lack of ductility exhibited by these systems. Specifically, it has been postulated that dislocation motion in these systems occurs as a result of a synchro-shear mechanism. This mechanism requires that dislocations are separated into quarter partials and that in order to move these partials require cooperative displacements of the two kinds of atoms in the crystal structure [36,37]. Accordingly, dislocation motion is expected to be difficult and further that self-pinning of the dislocations will occur if either type of atom is unable to move. Studies have shown that in $MgCu_2$ and $TiCo_2$ the dominant slip system is {111}<110> and that deformation proceeds by dislocation glide as a consequence of synchro-shear and is accompanied by the creation of numerous isolated extrinsic stacking faults on (111) planes [11,38]. These studies have also shown that dislocations of different Burgers vectors react to form networks which sometimes contain extended nodes and, at sufficiently high temperatures and low strain rates, well-defined subboundaries. Weak-beam imaging further showed separation of dislocations into two partial dislocations with a spacing of about 100 Å.

B. Microindentation Fracture Toughness

The microindentation fracture toughness of the binary Cr_2Nb compound was determined to be K_c = 1.33 MPa $m^{1/2}$ and was calculated on the basis of an average crack length of 40.05 μm and a Young's modulus of 219 GPa [39]. For comparative purposes, the fracture toughness for ceramic materials is generally reported to be in the range of 1 to 3 MPa $m^{1/2}$. Unfortunately, modulus data for the ternary

$Cr_2(Nb,V)$ intermetallic at ambient temperature does not exist. However, modulus does not vary significantly with small changes in material composition as a result of alloying and thus it is assumed that the Young's modulus of the $Cr_2(Nb,V)$ intermetallic is the same as that of the Cr_2Nb intermetallic. On the basis of this assumption and an average crack length of 36.25 µm, the microindentation fracture toughness of the $Cr_2(Nb,V)$ compound was determined to be $K_c = 1.63$ MPa $m^{1/2}$.

These results are quite interesting in that they show that small additions of Vanadium to the Cr_2Nb intermetallic system effectively increases the room temperature fracture toughness of this compound while maintaining good levels of strength. These results are supported by studies on titanium aluminide intermetallic compounds, which have shown that Vanadium additions are an effective method for increasing the ductility of these materials [14,15].

C. Microindentation Creep

The analytical method postulated by Atkins et. al. and discussed previously has been employed to characterize the microindentation creep behavior of the Cr_2Nb and $Cr_2(Nb,V)$ intermetallic compounds. A logarithmic plot of microindentation hardness as a function of time on load at 1000 °C for the Cr_2Nb intermetallic is shown in Figure 15. As can be seen, microhardness decreased with increasing time on load for load times greater than one second. At shorter load times, the microhardness values can be seen to increase rapidly in accordance with the discussion above. It was determined from this figure that the time required for the full load to be applied and power law creep to be dominant was 0.5 seconds, and this value has been used throughout the subsequent analyses to determine H_0 at each temperature for each compound.

Microindentation creep of the Cr_2Nb intermetallic was examined at T = 1000 and 1200 °C, and a logarithmic plot of microindentation hardness as a function of time at load is presented in Figure 16. From this figure it was determined that the average stress exponent for creep in this system was m = 24. In order to determine the activation energy for creep in this intermetallic, a logarithmic plot of $(H^{-m/3} - H_0^{-m/3})$ versus $(t^{1/3} - t_0^{1/3})$ was prepared and is shown as Figure 17. Note that the slopes of these lines are nearly unity, as predicted by equation 10. The plot indicates that the apparent activation energy for creep in this system is 478 kJ/mole.

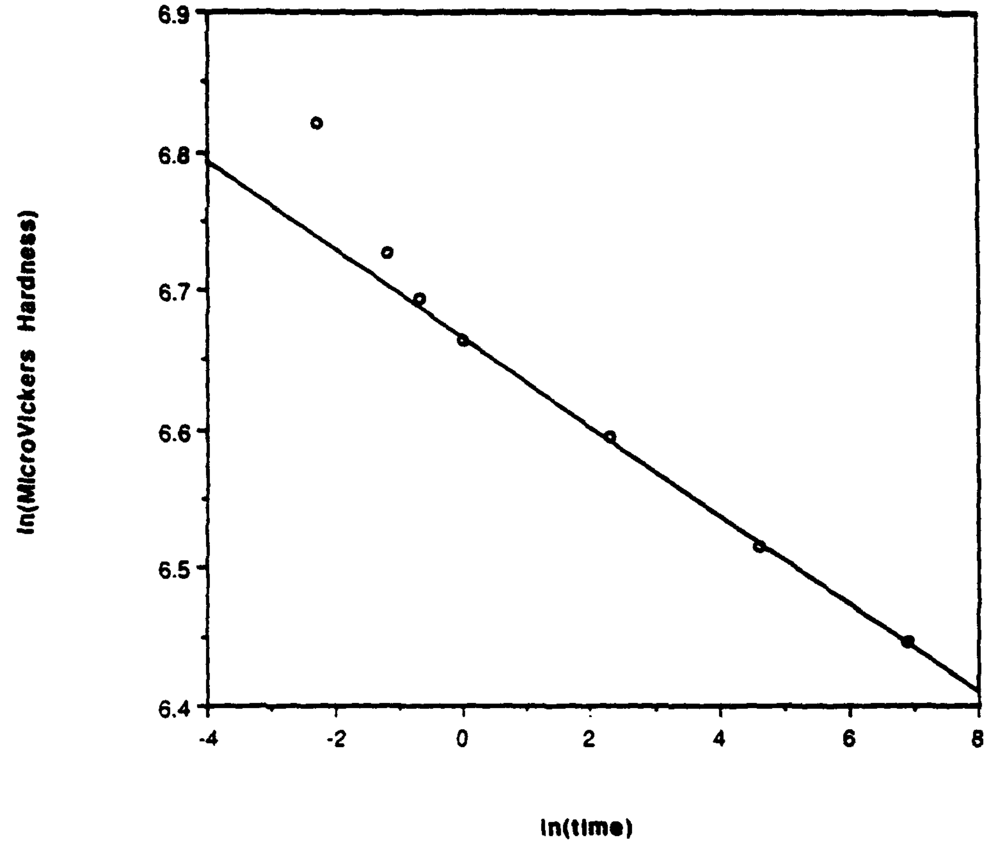

Figure 15. Microindentation hardness of Cr_2Nb as a function of time on load at T = 1000 °C

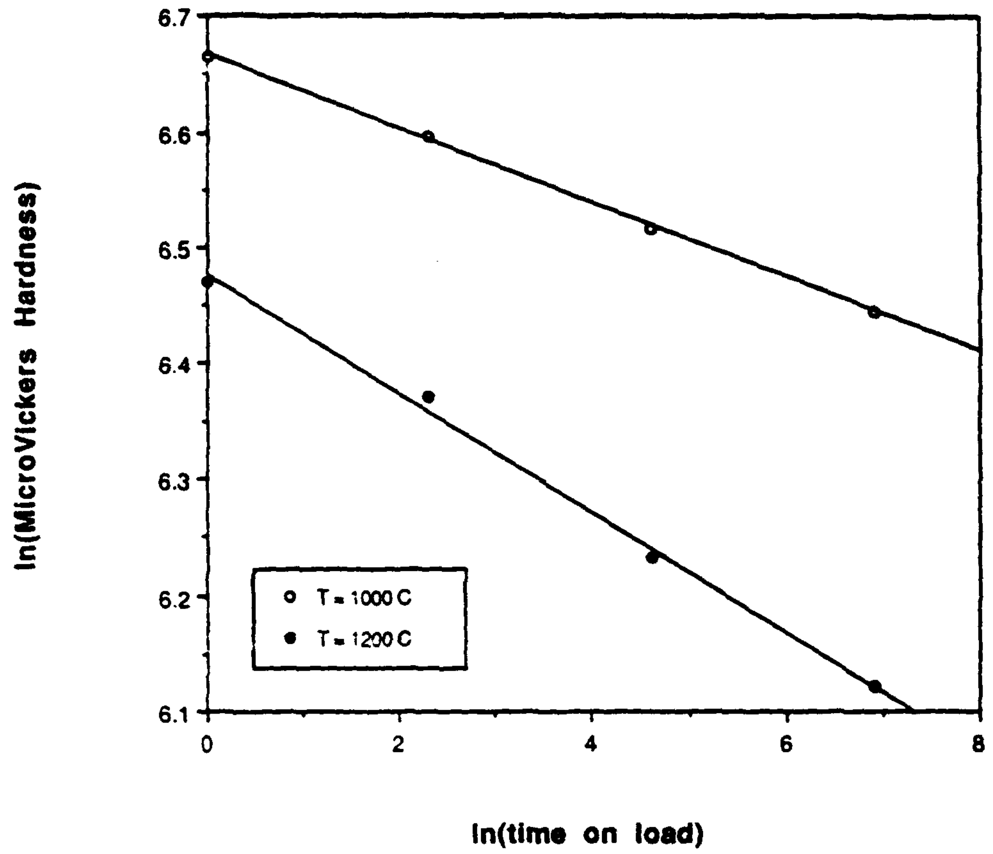

Figure 16. Microindentation hardness of Cr_2Nb as a function of time on load

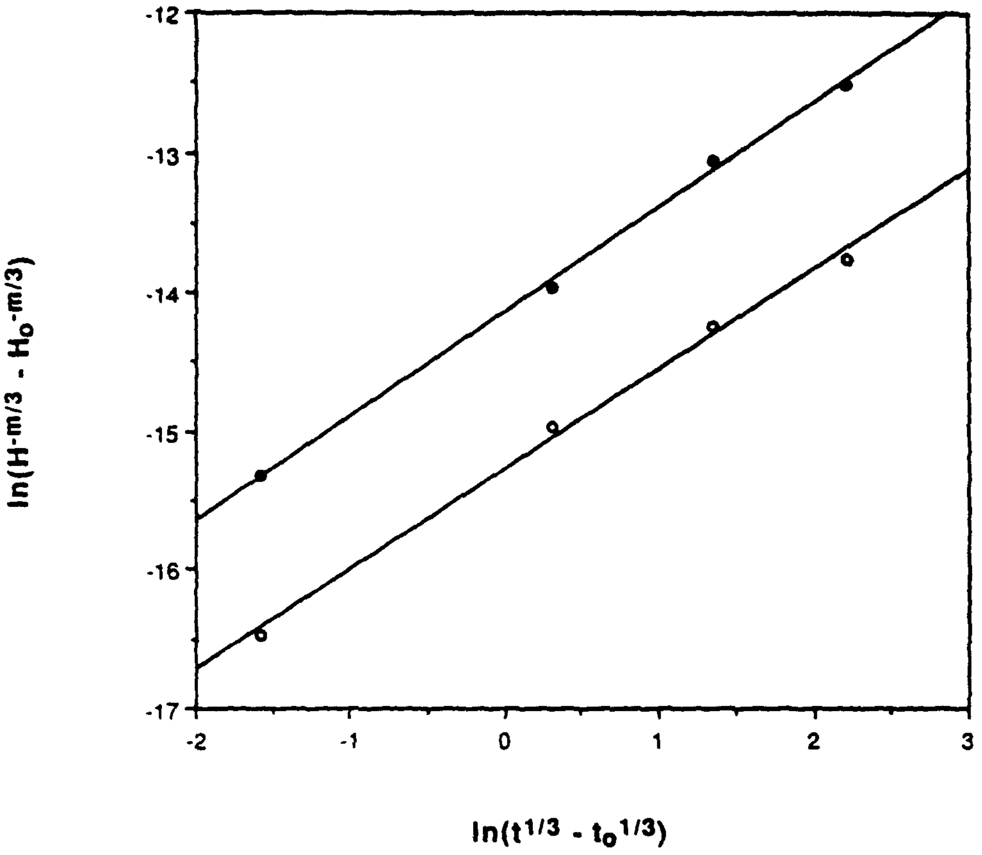

Figure 17. Corrected microindentation hardness of Cr_2Nb as a function of time on load

The creep behavior of the $Cr_2(Nb,V)$ intermetallic was similarly studied, with the data presented in Figure 18. The value of the average stress exponent was determined to be m = 16 and that of the apparent activation energy for creep in this system to be 385 kJ/mole.

While no activation energy data for self-diffusion in either the binary or ternary Cr_2Nb intermetallic systems is currently available, this activation energy can be approximated as $Q_{sd} = 142T_m = 291$ kJ/mole, where T_m is the melting point of the material in degrees Kelvin. It should be noted that while this approximation is generally good to within ± 5% of the experimentally determined activation energy for self-diffusion in pure metals, it is at best a cursory indicator for self-diffusion in ordered compounds.

The values of m and Q obtained for these two intermetallic compounds are unusually high relative to materials exhibiting typical power-law creep behavior, where m is generally between 3 and 8 and $Q_{creep} = Q_{sd}$. These values are surprising in that such high stress exponents and activation energies for creep are normally associated with complex multiphase systems, such as high-volume fraction γ' superalloys and oxide dispersion strengthened (ODS) alloys and not with single phase systems. In fact, the observation of

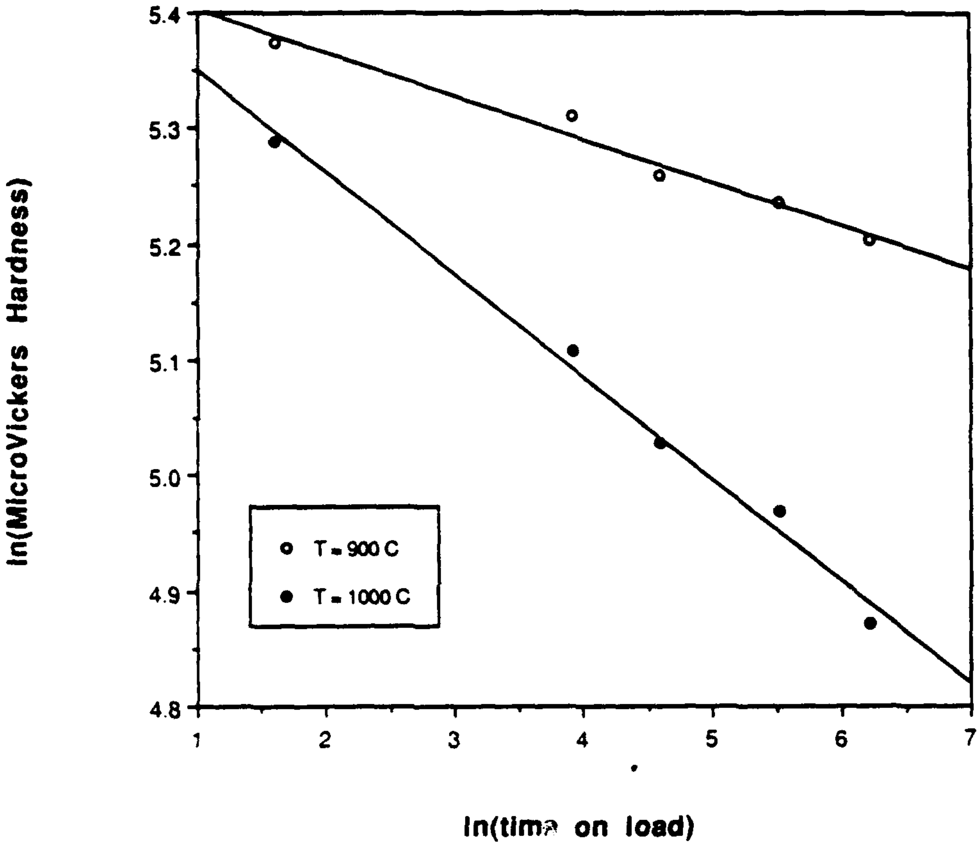

Figure 18. Microindentation hardness of $Cr_2(Nb,V)$ as a function of time on load

such "abnormally" high values has been shown to be indicative of the existence of an effective resisting stress against creep deformation in a variety of such complex material systems [40-42].

As the high values of m and Q obtained for the Cr_2Nb and $Cr_2(Nb,V)$ intermetallics imply, these systems appear to be highly resistant to creep. In fact, this resistance is much greater than these intermetallic's high melting temperature would suggest. While the actual mechanistics for this apparent creep resistance have yet to be fully explored, it is believed that the resistance to creep is, at least in part, due both to the fact that deformation occurs via a complex synchro-shear *mechanism* in these systems and that this deformation is accompanied by extensive faulting and dislocation-dislocation interactions.

V. CONCLUSIONS

The basic characterization of deformation behavior in materials systems intended for use at high temperatures is clearly of fundamental importance in the quest to identify and develop the next generations of high temperature structural materials systems. Such systems must possess high strength at temperatures in excess of 1200 °C, good resistance to creep and sufficient ductility at low temperatures to fulfill minimum design requirements. As it is apparent that materials systems capable of meeting the demands imposed by such advanced applications as hypersonic flight will be non-traditional and exotic, it is critical not only that potential materials systems be identified, but also that successful characterization methodologies be developed and implemented in an effort to allow study of systems with complex crystal structures and available only in limited quantities.

The Cr_2Nb ordered intermetallic system is a potentially attractive alternative to current high temperature materials systems, both technologically and from a fundamental scientific standpoint since virtually nothing is known about the mechanistics of deformation of complex intermetallic compounds. Consequently, the deformation characteristics of the Cr_2Nb and $Cr_2(Nb,V)$ intermetallic systems have been investigated and as is evident from the results of this study, these intermetallic systems are intrinsically quite strong and this strength is maintained to very high temperatures. Indeed, if it is assumed that the relationship $H \approx 3\sigma_y$ is valid for these systems then it is obvious that the strength of these intermetallics is comparable to or greater than that found for the most advanced high temperature structural materials systems in use today and is maintained to significantly higher temperatures than is acheivable with these systems.

While these intermetallics remain brittle even at high homologous temperatures, there is evidence that enhanced plasticity, or dislocation mobility, occurs at temperatures greater than 800 °C for the ternary compound and at temperatures greater than 1100 °C for the binary compound. While Vanadium addition to the Cr_2Nb intermetallic did not result in solid solution strengthening as originally postulated, it is clear that alloying additions of Vanadium to this system can be utilized to increase the fracture toughness of this intermetallic system while preserving the excellent strength to high temperatures exhibited by this system. Obviously, the possibility of ductilization through alloying of these compounds is extremely attractive.

Further, it is not inconceivable that alloying additions may stabilize the low temperature C15 crystal structure of this intermetallic system. In fact, alloying additions have long been used to enhance stability of one phase in a material system over another [49]. This is of significance because if the C15 structure can be stabilized preferentially to the high temperature C14 structure then the structural transformation on cooling exhibited by this compound can be ammeleorated and processing via traditional melt techniques may be employed without a concommitant loss of structural integrity.

Finally, it has been determined that the creep resistance of these intermetallics is intrinsically quite high and can best be rationalized by the incorporation of a resisting stress against creep into the descriptive microindentation creep concept. Although specific deformation mechanistics for creep in these intermetallics have not been determined explicitly, it can be inferred from dislocation studies in other C15 Laves phase materials that there exist strong pinning or resisting forces to dislocation motion in these materials. Such pinning points are the direct result of the complex crystal structure and the synchro-shear glide mechanisms of deformation.

Clearly, these intermetallic compounds exhibit great potential as high temperature structural systems. Indeed, at a recent research update meeting with the Office of Naval Research it was recognized by ONR that the Cr_2Nb intermetallics are the most attractive of all ordered intermetallic systems being investigated by ONR in terms of strength and creep resistance. However, in order to fully characterize the deformation behavior of these intermetallics, significantly more work must be done. Specifically, it is imperative that viable processing techniques be found to fabricate bulk samples of these materials that possess complete structural and mechanical integrity. Until this is achieved, it will be very difficult, if not impossible, to fully understand the operative mechanistics of deformation since dislocation studies of bulk deformed samples cannot occur until bulk samples can be fabricated.

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