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BRITTLE-DUCTILE TRANSITION IN VANADIUM

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BRITTLE-DUCTILE TRANSITION IN VANADIUM*

Benny A. Loomis and O. N. Carlson

ABSTRACT

Mechanical tests have been made on two grades of vanadium over a range of temperatures below 25°C to establish the existence of a brittle-ductile transition and the temperature range over which it occurs. Also, the effect of small amounts of metallic and non-metallic additions on the brittle-ductile transition in vanadium has been determined. Some of the physical properties of vanadium have been determined through the transition temperature. The results and conclusions of this investigation are summarized as follows:

1. There is a brittle-ductile transition in vanadium of 99.85 per cent purity at -65° ± 10°C. The transition occurs at the lower temperature of -110° ± 10°C in vanadium of 99.95 per cent purity. Both grades of vanadium regain some ductility at temperatures below -140°C.

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* This report is based on a Ph. D. thesis by Benny A. Loomis submitted March, 1958, to Iowa State College. This work was done under contract with the Atomic Energy Commission.

2. Small amounts of chromium, molybdenum, tantalum, zirconium, titanium, and thorium, when added to vanadium, have anomalous maxima and minima effects on the transition temperature of vanadium. The only metallic additions which lower the transition temperature of vanadium are titanium when present in amounts of 2.5 weight per cent or greater and possibly thorium when present in amounts less than one weight per cent.
3. The effect of adding small amounts of either hydrogen, oxygen, nitrogen, or carbon to vanadium is to raise the transition temperature. Hydrogen is the most effective in raising the transition temperature and carbon is the least effective. Oxygen and nitrogen have an effect intermediate to that of hydrogen and carbon.
4. The brittle-ductile transition in vanadium is apparently due to the interaction of dislocations with minute amounts of the interstitial solute atoms hydrogen, oxygen, nitrogen, or carbon. It is postulated that the transition in vanadium is accentuated by hydrogen atoms or ions assuming ordered positions in the vanadium lattice at temperatures below -65°C. This conclusion is based on the change of physical properties of vanadium near the transition temperature. There was no evidence for a low-temperature allotropic transformation in vanadium.

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I. INTRODUCTION

The presence of a brittle-ductile transition in many of the metallic elements and alloys has been observed in recent years. This type of transition is characterized by the existence of a narrow temperature range above which the metal has considerable ductility and below which there is a distinctive lack of ductility.

The early investigations into the nature of the brittle-ductile transition were concerned with the one occurring in steel because of its structural importance. These investigations, and subsequent ones, indicated that this type of transition was almost exclusively peculiar to metals with the body-centered cubic space lattice. The early investigators were not concerned so much about the mechanism of the transition as they were in preventing the brittle failure of many steel structures. For example, during World War II there was a number of failures of welded merchant ships and tankers. It was quickly recognized that the problem involved toughness and ductility of the steel in the presence of stress raisers such as notches. Since notches could not be avoided completely in a ship, it became obvious that it was necessary to build ships and other structures out of materials which were tough and ductile under conditions of service, even in the presence of notches. Hence, the problem was initiated of producing structural materials which had a brittle-ductile transition temperature below the required service temperature.

In recent years, the investigations have been expanded to include many non-ferrous metals which have a body-centered cubic lattice. However, of the body-centered cubic metals in the first, second, and third transition series of the periodic table, only vanadium remains to be examined for the existence of a brittle-ductile transition.

At the present time there are at least three possible applications for vanadium and its alloys (1):

1) Weldable, formable, high hot strength sheet alloy for airframe service at temperatures up to 650°C.
2) Fuel element cladding for fast reactors where interdiffusion, hot strength, and thermal conductivity are considerations.
3) As a diffusion barrier between titanium and steel in the manufacture of clads between these two elements.

Hence, it would seem that an investigation of the possible existence of a brittle-ductile transition in vanadium and some of its alloys would have considerable merit. Consequently, the purposes of this investigation are:

1) To ascertain whether or not there is a brittle-ductile transition in pure vanadium.

2) To determine the effect of various metallic and non-metallic additions on the transition temperature in vanadium, if such a transition exists.

3) To investigate some of the physical properties of vanadium, as a function of temperature through the transition range, for the purpose of ascertaining the possible mechanism of the transition.

II. LITERATURE SURVEY

As a result of the literature survey, it was decided that in order to determine the existence of a brittle-ductile transition in vanadium and its alloys, and to postulate an acceptable mechanism for the transition, the following investigations should be executed:

1) Mechanical tests on pure vanadium and vanadium alloys over a wide range of temperature.
2) Internal friction investigations on pure vanadium and vanadium containing small amounts of interstitial impurities.
3) X-ray investigations of massive polycrystalline samples and single crystals of vanadium over the temperature range in which the transition exists.

In the subsequent sections of this chapter, a summary of the results of investigations on other metals will be presented which are relevant to the three investigations just mentioned. In the final section, the current theories of the brittle-ductile transition in metals will be discussed.

A. Brittle-Ductile Transition in Metals

The existence of a brittle-ductile transition in a metal can be determined by many different mechanical tests. The temperature of the transition varies with the different tests and thus, it becomes necessary to select the test procedure which will help in an understanding of the problem.

When metals are tested in uniaxial tension at slow strain rates, the temperature of the brittle-ductile transition can be determined by plotting the total per cent reduction in area at fracture, i.e., the ductility, as a function of temperature. The transition temperature, as determined by this means, occurs in tungsten at about 250°C (2), near room temperature in molybdenum (3), at about -125°C in niobium (4), and near -150°C in iron (5). Chromium (6, p. 132) exhibits a brittle-ductile transition at 190°C when tested by bending. In the bend test the amount of deflection that can be given the metal as a function of temperature is determined. Tantalum (7), however, when tested in uniaxial tension does not exhibit a transition at temperatures down to -195°C, even though it has a body-centered cubic lattice similar to the metals just mentioned. A similar marked temperature dependence of ductility or reduction in area has not been observed in pure metals with close-packed structures (8). In fact, metals with close-packed structures may even exhibit an increase in ductility at low temperatures. Figure 1 illustrates the pronounced effect of temperature upon the ductility of tungsten, molybdenum, niobium, and iron which have a body-centered cubic lattice. Also plotted in Figure 1 is the ductility of zirconium and nickel which have close-packed structures and tantalum which has a body-centered cubic lattice. Although the ductility of zirconium is temperature dependent, it does not become brittle at low temperatures.

In most body-centered cubic metals other mechanical properties, in addition to the per cent reduction in area, are observed to be strongly temperature dependent. The total per cent elongation decreases sharply and the yield strength increases in a striking manner as the temperature is diminished through the transition. Also, a pronounced upper and lower yield point is usually observed in the load-elongation curves at temperatures near the transition. In addition to these properties, fractures at temperatures above the transition show a dull, fibrous rupture whereas bright, brittle, transgranular fractures are observed below the transition.

Information concerning the existence of a brittle-ductile transition in vanadium has not appeared in the literature. However, Pugh (9) has determined the tensile properties of 99.80 per cent pure vanadium at temperatures between -195°C and 1225°C. The results of this investigation

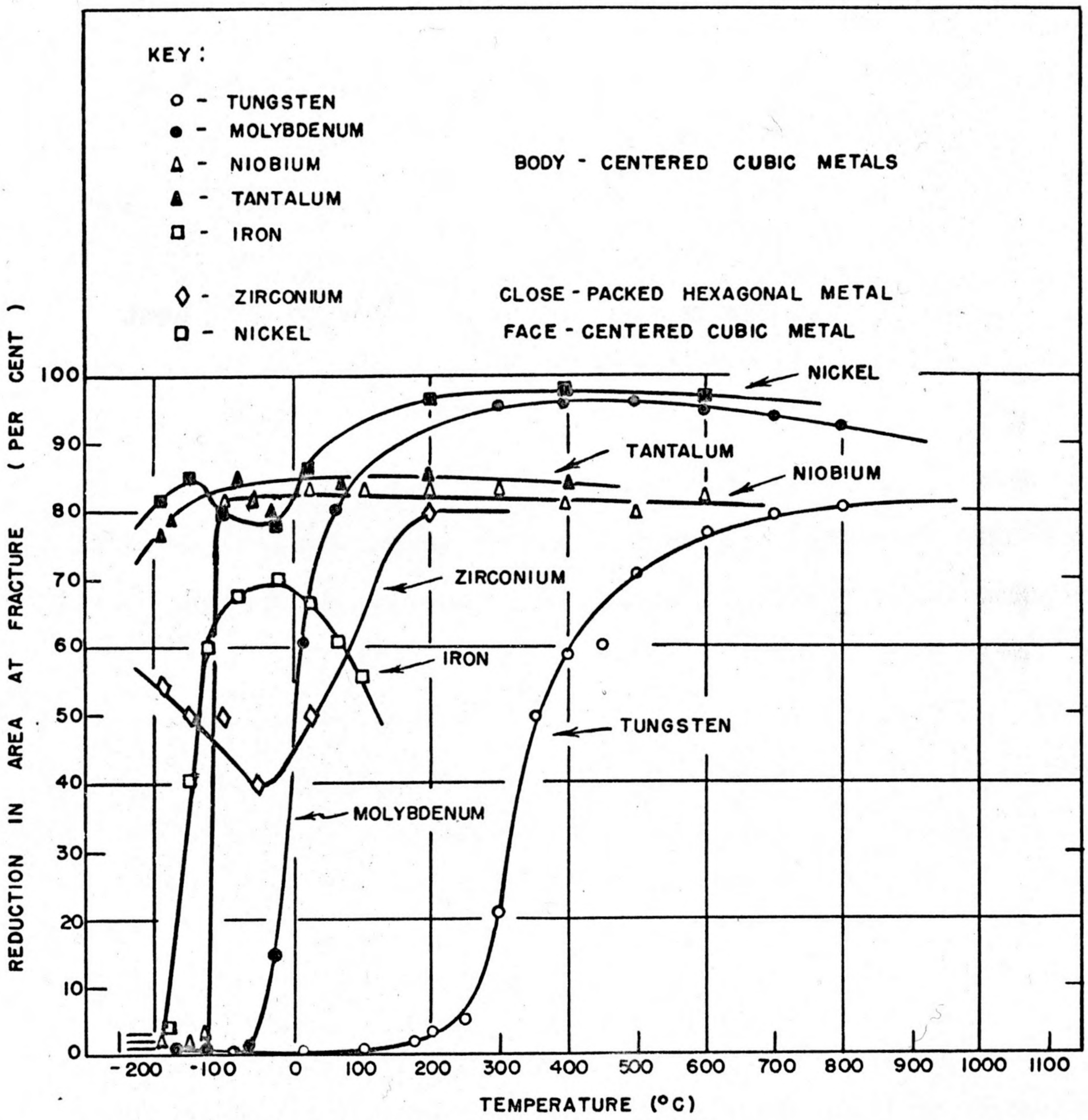

Figure 1. Ductility of metals at various temperatures

indicated that vanadium had no appreciable ductility at temperatures up to 775°C. Below room temperature, the strength was observed to increase very rapidly as the test temperature was diminished.

Roberts and Rogers (10a) have investigated the mechanical properties of hydrogenated vanadium wires in tension. They concluded, on the basis of tests at -196°C, 24°C, and 150°C, that there was a ductile-brittle-ductile fracture sequence in vanadium containing about .042 weight per cent hydrogen. However, this conclusion was based on a very limited number of tests.

In order to evaluate properly the effect of the metallic and non-metallic elements on the transition temperature in vanadium, it will be helpful to know the solid solubility of the various elements in vanadium. In Table 1 are listed what is considered to be the most reliable values of the solubility of the elements investigated.

B. Internal Friction Effects in Metals

One of the current theories of the brittle-ductile transition in metals concerns itself with the stress-induced ordering of the interstitial solutes carbon, nitrogen, oxygen, and hydrogen. Internal friction measurements over a wide range of temperature indicate the temperature at which this ordering effect takes place under an applied stress.

Table 1. Solid solubility of metallic and non-metallic elements in vanadium

Element	Solubility[a]
Tantalum[b]	25% at 900°C
Chromium[b]	Extensive at 700°C
Molybdenum[b]	10% at 900°C
Titanium[b]	Extensive at 900°C
Zirconium[b]	3% at 900°C
Thorium[c]	.1% at 25°C
Oxygen[d]	.25% at 25°C
Nitrogen[b]	1.0% at 900°C
Carbon[b]	1.0% at 900°C
Hydrogen[e]	.05% at 500°C

[a] All compositions listed in Table 1 and in subsequent discussions are on a weight per cent basis.

[b] The extent of solid solubility was obtained from an investigation by Rostoker and Yamamoto (10b).

[c] The extent of solid solubility was obtained from an investigation by Levingston and Rogers (11a, p. 122).

[d] The extent of solid solubility was obtained from an investigation by Allen, Kubaschewski, and von Goldbeck (11b).

[e] The extent of solid solubility was obtained from an investigation by Roberts and Rogers (10a).

Internal friction is defined as the conversion of the mechanical energy of an oscillating specimen into the energy associated with some internal mechanism operative in the specimen. This conversion of energy manifests itself in a decreasing amplitude of oscillation with time. Hence, the internal friction is commonly expressed in terms of the logarithmic decrement, δ, which is given by:

$$\delta = \log \left(A_n / A_{n+1} \right).$$

In this expression, A_n and A_{n+1} are the amplitude of successive oscillations. Internal friction is also sometimes expressed by:

$$Q^{-1} = \frac{\delta}{\pi} \quad ,$$

The number of mechanisms operative in metal specimens which can result in internal friction effects is large. Some of these mechanisms are stress-induced ordering of interstitial solutes, order-disorder transformations, and precipitation of second phases.

K̂e (11c) has proposed a mechanism whereby the stress-induced ordering of interstitial solutes in a body-centered cubic lattice may result in internal friction effects. If solute atoms occupy the octahedral interstitial positions in the lattice, then the lattice will be subjected to tetragonal deformation with the tetragonal axis aligned along one of the $\langle 100 \rangle$ directions, depending on which position the solute atom has occupied. If a tensile stress is applied along one of the $\langle 100 \rangle$ directions, then the solute atom will prefer to occupy a position such that the unique axis will be along the same direction. Thus, under fluctuating stress, solute atoms will diffuse in an attempt to maintain this state. Under suitable conditions of temperature and applied frequency, this diffusion process will absorb large amounts of the applied oscillation energy and result in an internal friction peak. A similar mechanism would be operative for interstitials preferring the tetrahedral position in the body-centered cubic lattice.

Chang and Gensamer (12) have made internal friction measurements on arc-cast molybdenum and a 0.20 per cent carbon steel at a frequency of 3.7 and 2.9 cycles per second, respectively. Their investigations on the 0.20 per cent carbon steel demonstrated that there was an internal friction peak at -173°C which was due to hydrogen. This internal friction peak was very close to the brittle-ductile transition in a 0.20 per cent carbon steel investigated by Eldin and Collins (13). In arc-cast molybdenum, an internal friction peak was located at about 27°C. This internal friction peak, likewise, occurred near the room temperature brittle-ductile transition in molybdenum.

Internal friction investigations on tantalum and niobium foils at ultrasonic frequencies have been performed by Marx, Baker and Sivertsen (14). Their results indicated that in niobium there were internal friction peaks at about 400°C and 600°C which were due to the stress-induced ordering of oxygen and nitrogen interstitials, respectively. Their results for tantalum indicated the existence of oxygen and nitrogen peaks at about 375°C and 650°C, respectively. Also, they observed, in the case of tantalum, anomalous peaks at -18°C and between -50°C and -80°C. These peaks were believed to be associated with the ordering of hydrogen ions into particular lattice positions.

The only internal friction investigations made on vanadium are those performed by Powers (15). His results indicated a stress-induced ordering of oxygen and nitrogen interstitials at 186°C and 272°C, respectively, when measurements were made at a frequency of 1 cycle per second.

C. X-ray Diffraction Investigations

The investigation of vanadium by x-ray diffraction techniques through the brittle-ductile transition temperature range was considered to be essential to this study. This was necessary for obtaining information as to the possible existence of an allotropic transformation or an ordering of impurities. Such an investigation has not been reported in the case of pure vanadium. However, Rostoker and Yamamoto (16) have postulated the existence of an allotropic transformation in metallic vanadium. They postulated, on the basis of a slight change in electrical resistance between -25°C and -33°C, that pure vanadium underwent a transformation from the room temperature body-centered cubic form to a body-centered tetragonal form in this temperature range.

X-ray investigations by Seybolt and Sumsion (17) of vanadium-oxygen alloys quenched from 600°C indicated that the terminal solid solubility of oxygen in vanadium was .95 per cent. Between .95 and 5.3 per cent oxygen in vanadium, they determined the existence of a two-phase region which consisted of the terminal solid solution and a compound. The compound had an ordered body-centered tetragonal structure and existed as a single phase between 5.3 and 8.3 per cent oxygen.

Rostoker and Yamamoto (10b) have made x-ray investigations and examined microstructures of vanadium containing up to 5 per cent nitrogen. Their investigations revealed that the terminal solid solubility of nitrogen in vanadium was about one per cent. Also, they determined by x-ray diffraction that a five per cent nitrogen alloy had a body-centered tetragonal lattice similar to that observed by Seybolt and Sumsion (17) for vanadium-oxygen alloys.

Rostoker and Yamamoto (10b) also made a similar study of the cast structure of vanadium-carbon alloys containing up to 10.5 per cent carbon. From 0.4 to 0.8 per cent carbon, the structure was observed to be one of coarse grains with a small amount of dispersed second phase. However, the microstructure of an alloy containing one per cent carbon showed interdendritic eutectic structure. With increasing carbon content, the amount of eutectic structure increased and the eutectic composition appeared to be between 3.5 and 5 per cent carbon. With greater than 5 per cent carbon additions, primary dendrites of an intermediate phase appeared in increasing amounts until at 10.5 per cent carbon, the microstructure was apparently one phase. An x-ray diffraction pattern of this phase identified the structure as close-packed hexagonal.

A detailed investigation of the vanadium-hydrogen system has not been made. However, neutron diffraction studies on $VD_{0.7}$[a] by Roberts (19) have demonstrated that an order-disorder transformation involving the deuterium atoms occurs at a temperature of -65 ± 10°C. Below this temperature, the deuterium atoms were ordered in a primitive cubic cell with a_o equal to 6.30 Å. This cell edge was twice that of the body-centered cubic vanadium lattice observed at liquid nitrogen temperatures with x-rays.

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[a] $VD_{0.7}$ contains 1.6 weight per cent deuterium.

D. Current Theories of the Brittle-Ductile Transition

The marked temperature dependence of the mechanical properties mentioned in a previous section are believed to arise from the interaction of dislocations with trace impurities. This has been postulated since the stress required to move a free dislocation is relatively insensitive to temperature and should be slight even at low temperatures. The trace impurities which could interact with the dislocations are principally the interstitial solutes carbon, nitrogen, oxygen and hydrogen.

Interstitial solute atoms can interact with dislocations in body-centered cubic metals by two important mechanisms. The first mechanism, which has been treated by Cottrell (20), arises from the relief of hydrostatic stress around the dislocation by the solute atoms segregating into the close vicinity of the dislocation. The second mechanism, discussed by Nabarro (21), involves the relief of both shear and hydrostatic stress around the dislocation by the solute atoms ordering into preferred interstitial sites.

Around a positive edge dislocation the atoms above the dislocation line are compressed, whereas the atoms below the dislocation are extended. The strain energy associated with this hydrostatic distortion could be reduced if the normal lattice parameter of the upper region were reduced locally and that of the lower region increased. In substitutional and interstitial solid solutions, the lattice will be subjected to a stress depending upon the amount of contraction or expansion resulting from the introduction of the solute atom in the lattice. Hence, the strain energy associated with this stress as well as that associated with the presence of the dislocation can be relieved by the solute atoms migrating to the expanded or contracted regions around the dislocation. In substitutional solid solutions, solute atoms which expand the lattice will migrate to the expanded region around the dislocation and solute atoms which contract the lattice will migrate to the compressed region. Likewise, if an atom in interstitial solution causes a local lattice expansion, it will migrate to the expanded region around the dislocation and vice versa.

It has been shown how the segregation of solute atoms around a dislocation will relieve the hydrostatic stress created by the edge dislocation. However, this process will not effect the stress field of a screw dislocation since it is ideally pure shear. It is doubtful, according to Bechtold (7), if the relief of hydrostatic stress around dislocations can by itself entirely account for the low-temperature yield behavior of the body-centered cubic metals, since screw dislocations will not be anchored. To interact with screw dislocations, solute atoms must be able to relieve shear stresses. There is a mechanism, as proposed by Nabarro (21), by which interstitial solute atoms in the body-centered cubic lattice can relieve shear stresses, and involves the production of non-symmetrical local distortion of the lattice. The interstitial solute atoms in the body-centered cubic lattice may be in either the face centres or the midpoints of the cube edges. If the atoms are at the centres of (001) faces or midpoints of edges perpendicular to (001), the lattice becomes tetragonal with (001) as the square base. The lattice is then distorted in the direction of the [001] axis. If the atoms jump to neighboring (010) interstitial sites, the lattice becomes tetragonal with (010) as the square base and the lattice is similarly distorted in the direction of the [010] axis. Interstitial atoms can, therefore, relieve shear stresses by arranging themselves in preferred interstitial sites, forming essentially an ordered array around the dislocation segments. This interaction should be about as strong with screw dislocations as with edge dislocations so that the entire dislocation line is anchored. Dislocations in face-centered cubic metals will not be anchored by this mechanism since neither interstitial nor substitutional atoms can relieve shear stresses by migrating into preferred interstitial lattice sites and producing a non-symmetrical local distortion. This is postulated to be the reason for the pronounced differences in the low-temperature mechanical properties of body-centered and face-centered cubic metals.

If an external force is applied to the dislocation with its surrounding atmosphere of solute atoms, it will start to move and thus leave its atmosphere of solute atoms behind; the energy of the locally distorted lattice is then raised, which means that the impurity atmosphere tends to restrain movement of the dislocation. If the applied force is insufficient to overcome the anchoring force, the dislocation cannot escape its atmosphere or else the atmosphere must move along with the dislocation. However, if the applied force is sufficient to overcome the anchoring force then the dislocation, once freed, will be under unnecessarily large external forces and should accelerate markedly when rapid flow under smaller forces becomes possible. This would result in a yield point which is observed in metals tested in tension. At high temperatures, thermal fluctuations can aid the escape of dislocations from their anchoring atmospheres and their propagation through the metal lattice. Hence, the metal will exhibit a temperature dependence of ductility since the propagation of dislocations through the metal is a necessary prerequisite for ductility. At low temperatures, the thermal fluctuations are not a sufficient aide to allow the dislocations to escape their solute atmosphere. Hence, local stresses may be built up either from an increasing external stress or from the piling up of dislocations at other dislocation groups, grain boundaries, impurity phases, etc. These local stresses can become of such magnitude that the cohesive strength across the crystal planes is exceeded and microcracks are formed and propagate through the metal which ultimately results in brittle failure. The amount of carbon necessary for an anchoring atmosphere in an annealed metal is extremely small, being approximately 10^{-6} per cent according to Bechtold (7). Therefore, the full effect of an impurity atmosphere can be expected even in the purest metals currently available.

A third mechanism is thought to be an operative in some metals in order to account for the presence or lack of a brittle-ductile transition. Bruckner (22) and others have postulated that brittle transgranular fracture may be related to mechanical twinning. The twins provide locally high stress regions which initiate brittle transgranular fracture at stresses well below the theoretical cleavage strength of the metal. In the investigation of tungsten (2) and molybdenum (3), mechanical twins were observed in specimens fractured in a brittle manner at low temperatures. No evidence of mechanical twinning was observed in tantalum (7) and hence, may be related to the absence of a brittle-ductile transition in tantalum.

III. MATERIALS

A. Preparation of Pure Vanadium and Alloys

The results of investigations on metals in which a brittle-ductile transition has been observed indicate that the transition temperature can be effected by such variables as grain size, amount of impurities in solution, amount and dispersion of second phases, and upon internal stresses. Hence, in this investigation it was necessary to establish some degree of uniformity with regard to these variables.

In this particular study two different grades of vanadium were investigated, i.e., different in the general impurity level in the base metal. The two grades were crystal-bar and bomb-reduced vanadium.

Bomb-reduced vanadium was prepared in this Laboratory by the reduction of C.P. grade vanadium pentoxide with calcium. Three separate reductions were made, each yielding approximately an 8 1/2 pound massive sample or regulus. The reguli were not suitable for processing directly into test specimens because of their porosity and the presence of entrapped calcium. Hence, the massive reguli were sectioned and arc-melted in 400-gram lots in a water-cooled copper mold under a helium atmosphere. The arc-melted material was subsequently given a 45 per cent reduction in thickness by rolling at 400°C if the material was to be used in the preparation of test specimens of pure vanadium. The work-hardened material was then recrystallized (Figure 2) by heating in a resistance furnace at 900°C for five hours under a vacuum of 10^{-4} millimeters of mercury. The recrystallized material had a hardness of Rockwell "A" 38 and an average grain diameter of .04 millimeter. This material was subsequently used in the preparation of test specimens.

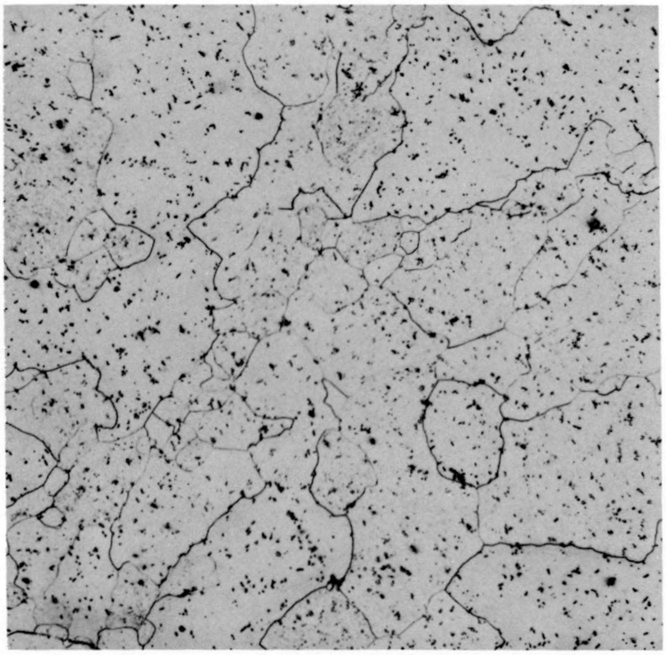

Figure 2. Recrystallized bomb-reduced vanadium (X250)

Approximately 500 grams of crystal-bar vanadium was prepared at this Laboratory by the decomposition of vanadium iodide on a vanadium filament heated by electrical resistance. The vanadium iodide was formed by the reaction of iodine with bomb-reduced vanadium. The as-deposited material was then arc-melted into rods 3/4 inch in diameter and subsequently swaged at room temperature into 7/16-inch diameter rods. The swaged material was then recrystallized (Figure 3) by heating in a resistance furnace at 1100°C for 48 hours under a vacuum of 10^{-4} millimeters of mercury. The recrystallized material had a hardness of Rockwell "A" 21 and an average grain diameter of .20 millimeter. This material was subsequently used in the preparation of tensile test specimens.

Figure 3. Recrystallized crystal-bar vanadium (X250)

Metallic additions to bomb-reduced vanadium were made by carefully weighing out sufficient amounts of the alloy constituents to make two 125-gram samples of identical composition. Each 125-gram sample was then arc-melted in a water-cooled copper mold under an inert helium atmosphere. After melting, each sample was again weighed to determine how much material had volatilized. If the weight change was not greater than .05 gram, the 125-gram samples were sectioned and mixed. The mixed pieces were then arc-melted into two 1/2-inch diameter rods that were six inches long. The alloy samples were not work-hardened and recrystallized, but they were given an annealing treatment by heating at 900°C for five hours under vacuum.

Non-metallic additions of oxygen, nitrogen, and carbon to bomb-reduced vanadium were made by first preparing master alloys of each of these elements. The oxygen and nitrogen master alloys were prepared by arc-melting bomb-reduced vanadium in an atmosphere of oxygen or nitrogen. The carbon master alloy was prepared by arc-melting bomb-reduced vanadium with high-purity graphite. An estimate of the composition of the master alloys was made by carefully weighing the vanadium before and after the introduction of the non-metallic elements. Oxygen, nitrogen, and carbon alloys were then prepared by arc-melting together portions of the master alloy and bomb-reduced vanadium in the manner described above for the preparation of samples containing metallic additions. These alloy samples were also annealed at 900°C for five hours under a vacuum of 10^{-4} millimeters of mercury.

The wires for the internal friction measurements were prepared by swaging a 3/8-inch diameter bar of crystal-bar vanadium to .030-inch diameter wire. The swaged wires were recrystallized by heating 24 hours at 900°C under vacuum. Hydrogen was added to the recrystallized wires by heating under an atmosphere of hydrogen at 500°C for 30 minutes and then allowing the hydrogenated wire to furnace cool under vacuum. Carbon was added to one wire for internal friction measurements by heating the wire in Shawinigan black at 900°C for 24 hours under vacuum.

B. Preparation of Test Specimens

The rectangular shaped bend test specimens were prepared by first milling the irregular shaped recrystallized specimens to the approximate final dimensions. These samples were then finished to the final dimensions by grinding on a Do-All surface grinder with a Norton 38A46-H8VBE grinding wheel. The bend test specimens had the dimensions of 2.25 x .375 x .25 inches.

The tensile specimens were prepared by first machining the heat treated material to within .010 inch of the final dimensions (Figure 4). The samples were then ground to

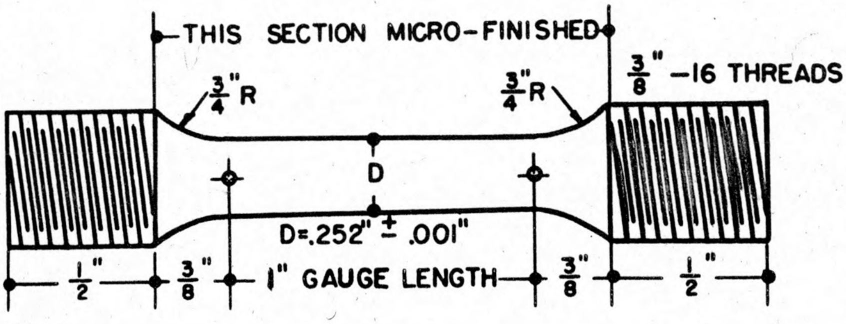

Figure 4. Dimensions of tensile test specimens

within .001 inch of the final dimensions on a cylindrical external grinder and polished to the final dimensions with 4/0 emery polishing paper.

C. Chemical Analysis of Vanadium

Crystal-bar and bomb-reduced vanadium and the vanadium to which carbon, nitrogen, oxygen and hydrogen was added were analyzed by a combination of chemical and spectographic methods. The analysis of both grades of vanadium is presented in Table 2. The alloys which were prepared to contain various amounts of metallic elements were not analyzed by quantitative procedures.

Table 2. Analysis of vanadium

Impurity	Composition (wt. %)	
	Crystal-bar	Bomb-reduced
C	.024	.08
N	.005	.02
O	less than .010	.015
H	.001	.006
Cr, Fe, Si	less than .02	less than .02

IV. APPARATUS AND EXPERIMENTAL METHODS

The transition from ductile to brittle behavior can be ascertained by many different tests, as mentioned in a previous section. In this investigation, two different mechanical tests were employed for the purpose of confirmation of the existence of a brittle-ductile transition in vanadium. The two mechanical tests employed were the slow tensile test and the bend test. Both tests were employed in the investigation of bomb-reduced vanadium whereas only the tensile test was utilized in the case of crystal-bar vanadium. For evaluating the effect of metallic additions on the transition in bomb-reduced vanadium, the slow tensile test was used exclusively. This was done since more data of a generally useful nature could be obtained. For the evaluation of the effect of non-metallic additions, i.e., carbon, nitrogen, and oxygen, the bend test was used because of the extreme brittleness of some of the alloys and subsequent difficulty experienced in machining them.

In the following sections of this chapter the equipment utilized and the procedure employed in performing the mechanical tests will be discussed in some detail. In the last two sections the x-ray cameras used and the internal friction apparatus will be described.

It would be appropriate at this point, for the purpose of clarification of the succeeding discussion, to mention that preliminary investigations indicated that a brittle-ductile transition occurred in vanadium at sub-zero temperatures when the tests were performed at slow strain rates. Hence, most of the equipment used in this investigation was adapted for investigations down to -185°C.

A. Tensile Testing Equipment and Procedure

All samples were tested on a Baldwin-Tate-Emery tensile machine at a strain rate of 1×10^{-4} inch per inch per second. The data were taken from autographic load-extension curves and measurements on the test samples. The extension data were obtained by attaching a microformer extensometer to a pair of knife edges which were in turn attached to the test specimen at the one inch gauge length. The arrangement was such that strains as small as $.5 \times 10^{-4}$ inch per inch could be determined from the load-extension curves. The microformer extensometer was removed from the sample when the elastic portion of the load-extension curve was well defined because of the possibility of ruining the microformer when brittle fracture occurred. The remainder of the stress-strain curve was determined by placing a dial gauge extensometer in contact with the moving crosshead.

The schematic diagram given in Figure 5 shows the essential components of the tensile testing apparatus. These components may be divided into three functional groupings:

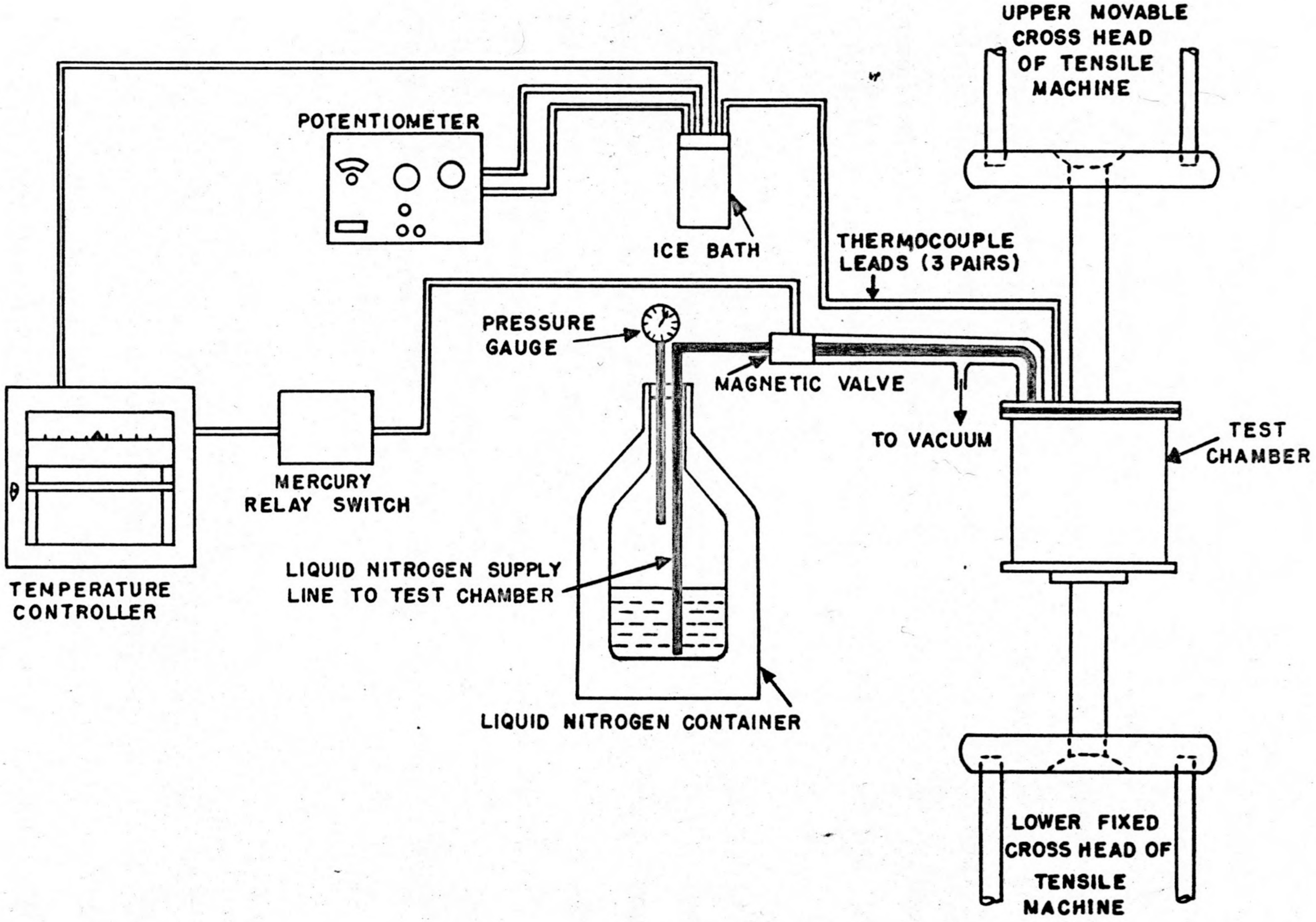

Figure 5. Block diagram of the low-temperature tensile testing apparatus

the refrigerant storage and supply system, the refrigerant flow regulating system, and the test chamber.

The refrigerant storage and supply system consisted essentially of a fifteen-liter Dewar flask equipped with a special head assembly. The essential components of the head assembly were a pressure gauge, a pressure relief valve, a packless needle valve, and an exhaust valve. The refrigerant, liquid nitrogen, was stored in the Dewar flask which trapped the vapor evolved and caused a build up of pressure on the surface of the liquid. This pressure was indicated by the pressure gauge and could be adjusted by means of the pressure relief valve. The pressure relief valve protected the Dewar flask from excessive pressure and maintained a constant supply pressure on the surface of the liquid nitrogen. This pressure forced the liquid up through the supply tube, which extended to the bottom of the Dewar vessel, and the amount of flow could be regulated by means of the needle valve installed in the supply line. The exhaust valve was used for reducing the Dewar pressure rapidly when desired and for building up an initial pressure.

The refrigerant flow regulating system consisted of the previously mentioned needle valve, a small packless magnetic valve, a Brown Electronik temperature controller, and a control thermocouple installed in the test chamber. Two additional thermocouples were placed in contact with the test specimen and connected to a portable potentiometer for purposes of checking the temperature gradient. When refrigerant was needed in the test chamber, as indicated by the control thermocouple, the controller energized and opened the magnetic valve. This allowed the liquid nitrogen to flow at a rate determined by the setting of the needle valve and the pressure in the Dewar flask. When additional refrigerant was not needed, the control thermocouple signaled the controller which de-energized and closed the magnetic valve and shut off the flow of liquid nitrogen. Copper-constantan thermocouples which had been calibrated down to the temperature of liquid nitrogen were used as the temperature sensing elements. The supply line, which was of flexible Tygon tubing, from the magnetic valve to the test chamber was insulated by a vacuum. This was accomplished by surrounding the Teflon tube supply line with Tygon tubing. To prevent the Tygon tubing from collapsing under the vacuum, a spiral of wire was placed between the Tygon and Teflon tubes. This arrangement provided an effective insulation and also rendered a degree of flexibility to the supply line. With this system of temperature control, a given test temperature could be maintained to ± 2°C.

The test chamber as shown in Figure 6 consists essentially of an inner can to confine the nitrogen vapor, an outer double-walled cylinder in which a vacuum is maintained, and this in turn is surrounded by Vermiculite insulation. The refrigerant, usually in the form of nitrogen vapor,

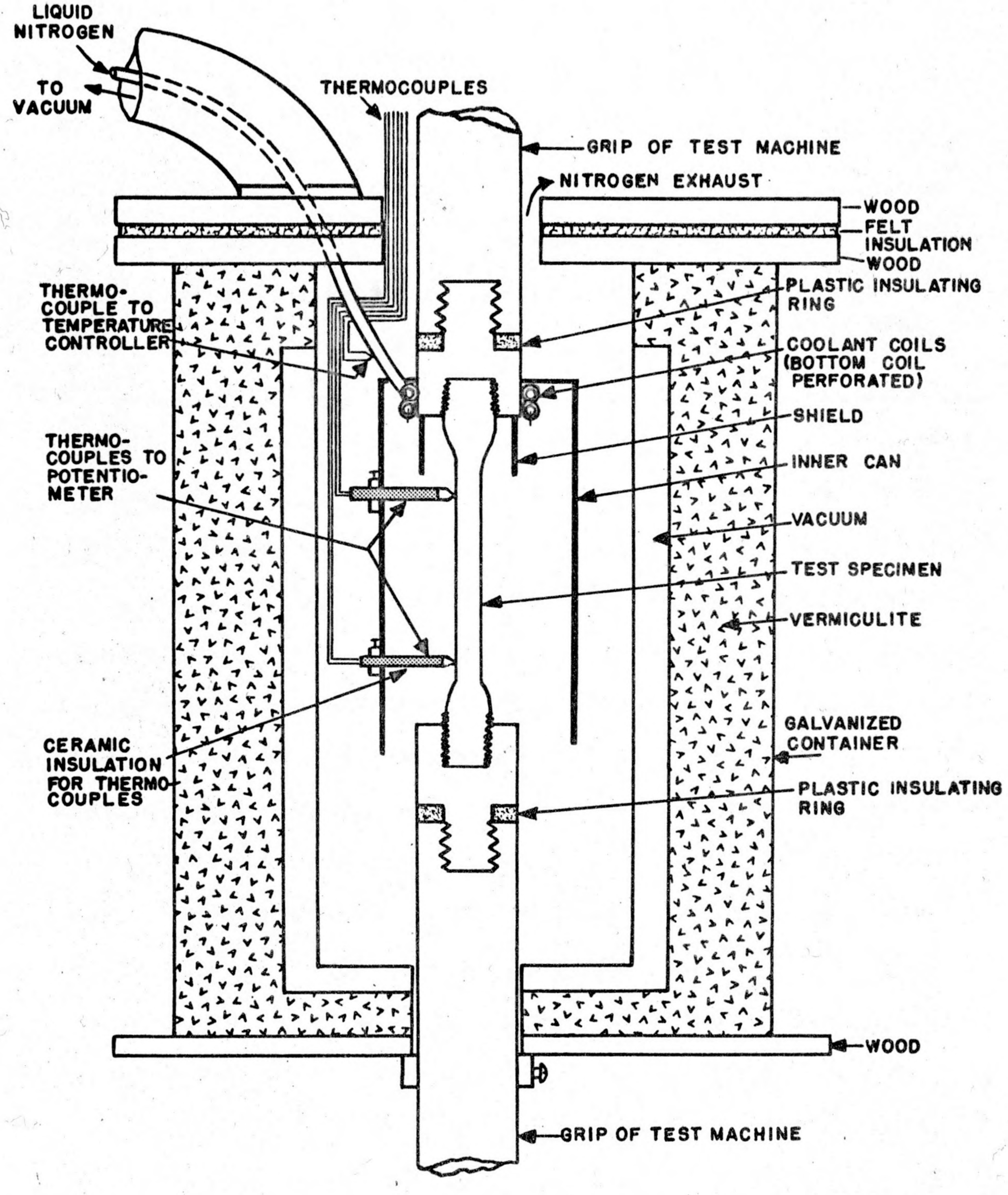

Figure 6. Low-temperature tensile test chamber

enters the test chamber through a copper coil wound on the upper grip of the test machine and escapes into the inner liner through the perforations in the bottom segment of the coil. The bottom segment of the coil is fitted with a shield to prevent the possibility of droplets of refrigerant contacting the specimen when the flow rates are such that liquid transfer to the test chamber occurs. The cold vapor, after it escapes through the perforations in the bottom coil, passes down around the test specimen and lower tensile grip where it remains until forced up and out of the test chamber by colder and denser vapor. As a result of this directed flow of refrigerant, the temperature gradient along the tensile specimen was about 2°C.

Tensile tests which were conducted above room temperature were performed by replacing the low-temperature test chamber with a resistance furnace and suitable insulation at both ends of the furnace. A given test temperature was controlled to ± 2°C by use of a Bristol temperature recorder and controller.

B. Bend Test Equipment

The bend test apparatus consisted of a double support giving a span of two inches, a load rod, and a dial indicator gauge to measure specimen deflection, all enclosed in either a low-temperature test chamber or a resistance furnace. The above apparatus was mounted on a small laboratory press. The low-temperature test chamber and control apparatus was the same as that used on the tensile testing apparatus. Likewise, the same resistance furnace and control apparatus were used for tests conducted above room temperature. The test temperature was measured at the specimen by means of a copper-constantan thermocouple. A plastic bag was placed around the entire apparatus and inflated with argon prior to testing in order to eliminate atmospheric condensation at low temperatures and sample oxidation at high temperatures. A strain rate of from .01 to .1 inch per minute was applied manually by means of the press level arm. The data pertinent to this particular investigation were obtained by applying an increasing load. The specimen was bent in .001-inch increments until it either broke or was bent .25 inches which was the extent that the apparatus would allow.

C. Low-Temperature X-ray Apparatus

The low-temperature x-ray investigations were carried out on both massive polycrystalline samples and single crystals of vanadium. The equipment and technique relevant to each of these investigations will be discussed.

The essential components of the low-temperature x-ray camera used in the investigation of massive samples of vanadium are shown in Figure 7. This camera was designed to replace the regular room-temperature specimen holder on the Norelco high-angle goniometer Geiger-counter x-ray diffractometer. The vanadium sample with dimensions of .75 x .50 x .25 inch was positioned in a groove of similar dimensions in the copper block. Wood's metal was used to assure an effective thermal contact between the copper block and vanadium specimen. Two calibrated copper-constantan thermocouples were used in this investigation. One thermocouple was placed in contact with the vanadium sample and the other was soldered to the incoming refrigerant line for control purposes. With the aluminum cover plate positioned to the back plate, this arrangement was then evacuated to less than 1×10^{-3} millimeters of mercury which eliminated all condensation of atmospheric water vapor on the sample and provided an effective insulation. Some atmospheric condensate was observed, however, on the aluminum foil window at temperatures below -100°C. The refrigerant supply and temperature control equipment was the same as that used on the tensile test apparatus. In this investigation, the Dewar flask was mounted on a rack and pinion type of jack so that the flask could be raised and lowered as the camera was rotated about its axis. The vertical movement of the Dewar flask and the associated flexibility of the refrigerant supply tube allowed the examination of the specimen without difficulty over a 2θ

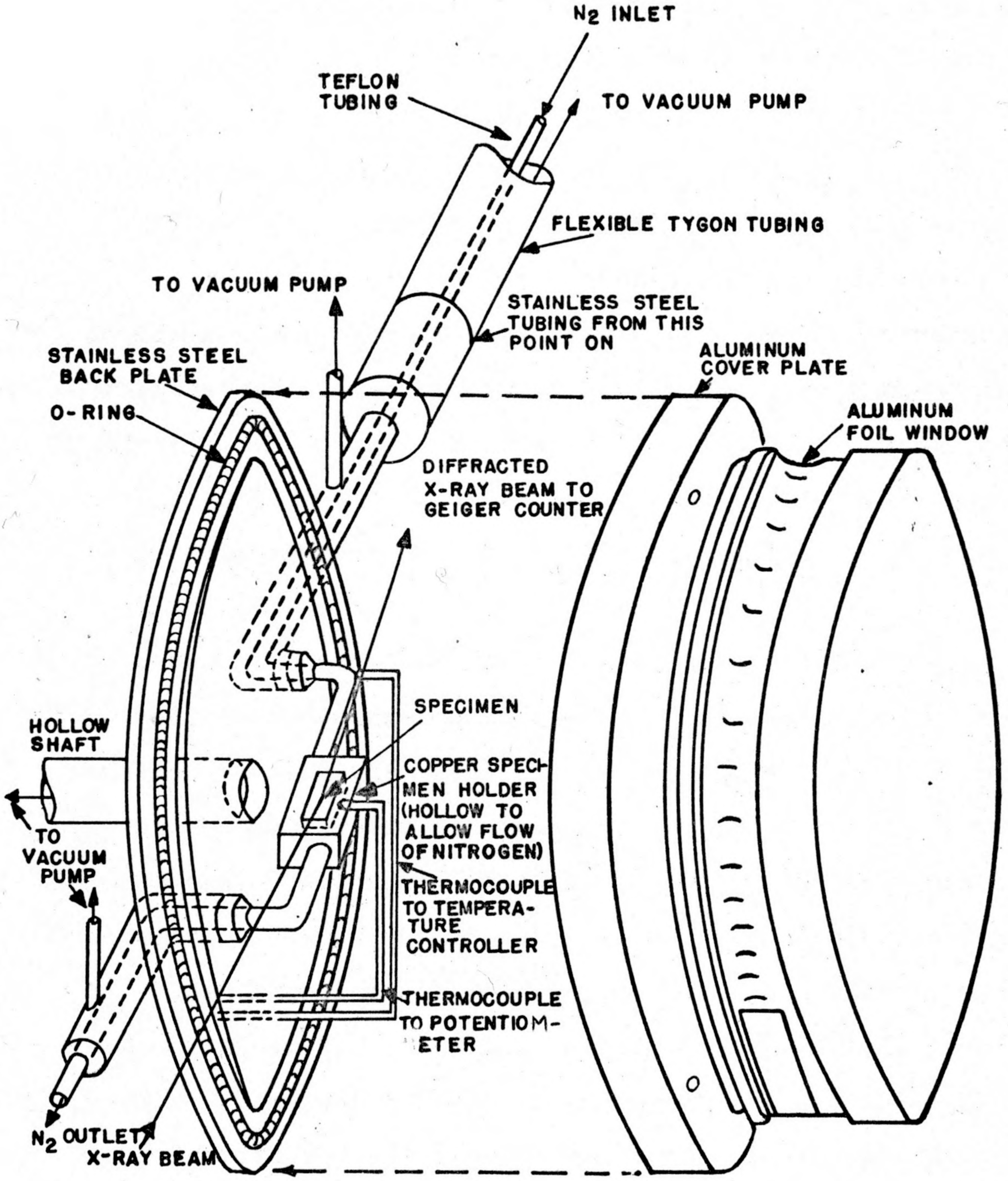

Figure 7. Low-temperature x-ray camera

range of 90°. Also, with this arrangement the temperature of the sample could be maintained at ± 1°C while the camera was rotated about the previously mentioned 2θ range. Copper Kα radiation was used throughout the investigation.

The examination of single crystals of vanadium was made by use of a Weissenberg camera. Single crystals were obtained from two sources. One source of single crystals was from the small droplets of vanadium spattered onto the copper mold during the course of arc-melting. The second source of single crystals was from the crystals deposited in the preparation of crystal-bar vanadium. The single crystal was cooled in the camera by directing a jet of cold nitrogen vapor onto the crystal. The temperature of the crystal was approximated by placing a copper-constantan thermocouple adjacent to it. The low temperature control system previously described was also used in this investigation. To eliminate atmospheric condensation on the crystal and camera, a plastic bag was placed around the camera and filled with helium.

D. Internal Friction Apparatus

The essential components of the low-temperature internal friction apparatus are shown in Figure 8. Prior to each low-temperature investigation the volume around the wire and inside the plastic shield was filled with argon to

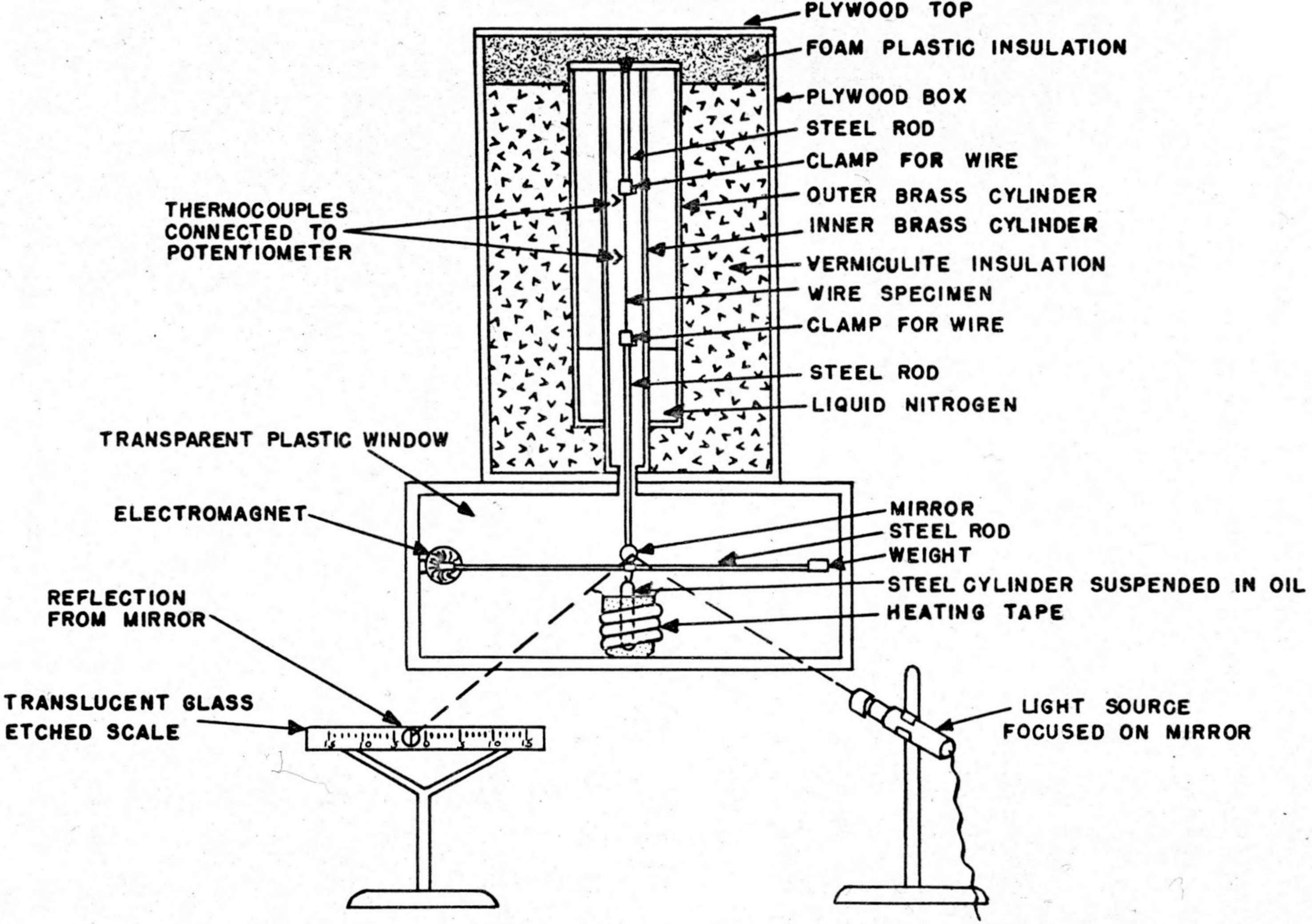

Figure 8. Low-temperature internal friction apparatus

reduce moisture condensation. However, the condensation could not be entirely eliminated below -75°C. The temperature of the wire specimen was estimated by two copper-constantan thermocouples in close proximity of the wire. Measurements indicated that the temperature gradient along the wire was less than 2°C. Liquid nitrogen was placed in the cylinder prior to each run and allowed to evaporate. The temperature of the wire specimen would then rise to room temperature at a rate of about one-half degree per minute. The temperature of the oil bath was maintained at 22°C throughout the course of the run. To measure the internal friction at a given temperature, the wire was put in torsional oscillation by means of an electromagnet and the amplitude of oscillation was observed on a translucent scale. The amplitude of each oscillation was then plotted on a logarithmic scale versus the oscillation number which generally extended to forty-two. The slope of this line divided by π was the internal friction. The temperature change of the wire specimen was, at most, one degree while data were being recorded for an internal friction determination at a given temperature. The internal friction of the wire specimen was determined at five-degree intervals up to room temperature.

To conclude the discussion of the apparatus and experimental methods it should be remarked that electrical resistance and dilatometric measurements were also made on vanadium. However, the equipment used was that ordinarily used in such experimental investigations. The electrical resistance was measured by use of a Kelvin double bridge and the thermal expansion of the vanadium samples was determined by use of a sensitive strain gauge.

V. EXPERIMENTAL RESULTS

The mechanical tests disclosed the existence of a brittle-ductile transition in metallic vanadium at sub-zero temperatures. In the following sections data are presented which substantiate the foregoing conclusions, together with data which indicate the pronounced effect that metallic and non-metallic additions have on the brittle-ductile transition in vanadium.

A. Transition in Unalloyed Vanadium

The mechanical properties of each of the unalloyed vanadium specimens tested in uniaxial tension are tabulated in Table 3. Also, several of the stress-strain curves obtained for crystal-bar vanadium are shown in Figure 9. At temperatures above -110°C, crystal-bar vanadium was observed to undergo considerable plastic deformation prior to failure (Figure 10); at -120°C and -140°C, this grade of vanadium fractured in a brittle transgranular manner (Figure 11) near the lower yield point and hence underwent little plastic deformation. However, tensile tests performed at -150°C and -179°C indicated that crystal-bar vanadium was able to again plastically deform at these temperatures. It should also be noted in Figure 9 that distinct yield points

Table 3. Mechanical properties of vanadium

			Ductility (%)				
Sample number	Vanadium grade	Test temperature (°C)	Total elongation	Reduction in area	Uniform[a] elongation	Proportional limit[b] (Psi)	Yield strength[c] (Psi)
BAL-148- 1	Crystal-bar	20	38.3	95.0	16.3	7,187	13,244
BAL-148- 2	"	0	37.1	95.0	15.1	7,085	15,789
BAL-148- 3	"	-20	38.7	95.0	16.7	11,134	21,053
BAL-148- 4	"	-40	35.2	95.0	14.5	11,134	16,296
BAL-148- 5	"	-60	32.9	95.0	15.9	10,267	21,253
BAL-148- 6	"	-80	38.6	95.0	17.6	12,170	19,777
BAL-148- 7	"	-100	39.2	95.0	20.2	11,831	25,000
BAL-148-11	"	-110	23.0	18.8	6.5	18,405	39,161
BAL-148- 8	"	-120	2.0	8.7	2.0	29,535	30,696
BAL-148- 9	"	-140	4.2	14.9	4.2	33,504	38,934
BAL-148-12	"	-150	13.4	18.8	4.0	54,048	55,668
BAL-148-10	"	-179	17.4	30.2	3.8	56,846	58,091

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[a] Uniform elongation is the elongation of the specimen before "necking" occurs.

[b] Proportional limit is the stress at the first observable deviation from the elastic portion of the stress-strain curve.

[c] Yield strength is the stress at .2 per cent offset from the elastic portion of the stress-strain curve.

Table 3. (Continued)

Sample number	Vanadium grade	Test temperature (°C)	Ductility (%)			Proportional limit[b] (Psi)	Yield strength[c] (Psi)
			Total elongation	Reduction in area	Uniform[a] elongation		
BAL-40-1	Bomb-reduced	22	36.04	45.82			
BAL-40-2	"	22	35.32	50.99		15,151	22,989
BAL-40-4	"	-32	33.67	36.65		20,707	26,970
BAL-40-3	"	-55	34.44	26.29		21,212	28,081
BAL-40-8	"	-71	2.92	1.20		18,182	23,000
BAL-40-9	"	-90	1.71	1.59		28,283	31,000
BAL-40-6	"	-105	2.41	3.19		50,000	54.545
BAL-40-7	"	-132	1.27	.80			

E3

Table 3. (Continued)

Sample number	Vanadium grade	Test temperature (°C)	Upper yield point[d] (Psi)	Ultimate tensile strength[e] (Psi)	Fracture strength[f] (Psi)	Type of fracture
BAL-148- 1	Crystal-bar	20	-[g]	28,747	2,053	Ductile
BAL-148- 2	"	0	"	29,554	2,024	"
BAL-148- 3	"	-20	"	31,984	2,024	"
BAL-148- 4	"	-40	"	29,453	2,024	"
BAL-148- 5	"	-60	"	35,934	2,053	"
BAL-148- 6	"	-80	"	36,410	2,028	"
BAL-148- 7	"	-100	"	40,741	2,058	"
BAL-148-11	"	-110	41,718	43,354[h]	2,965	Semi-ductile
BAL-148- 8	"	-120	58,650	-	51,688	Cleavage
BAL-148- 9	"	-140	59,426	"	52,254	"
BAL-148-12	"	-150	61,235	"	2,024	Semi-ductile
BAL-148-10	"	-179	63,070	62,656	1,660	"

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[d] Upper yield point is the stress at which there is a marked increase in deformation without an increase in load.

[e] Ultimate tensile strength is the maximum load prior to the onset of "necking" divided by the original cross-sectional area.

[f] Fracture strength is the load at fracture divided by the original cross-sectional area.

[g] No upper yield point was observed.

[h] No maximum load after the upper yield point was observed.

Table 3. (Continued)

Sample number	Vanadium grade	Test temperature (°C)	Upper yield point[d] (Psi)	Ultimate tensile strength[e] (Psi)	Fracture strength[f] (Psi)	Type of fracture
BAL-40-1	Bomb-reduced	22	-[g]	39,091	5,021	Ductile
BAL-40-2	"	22	"	37,576	4,545	"
BAL-40-4	"	-32	"	49,949	4,700	"
BAL-40-3	"	-55	"	49,697	5,252	"
BAL-40-8	"	-71	45,450	-[h]	44,444	Cleavage
BAL-40-9	"	-90	51,313	"	48,485	"
BAL-40-6	"	-105	61,111	"	61,111	"
BAL-40-7	"	-132	66,869	"	64,646	"

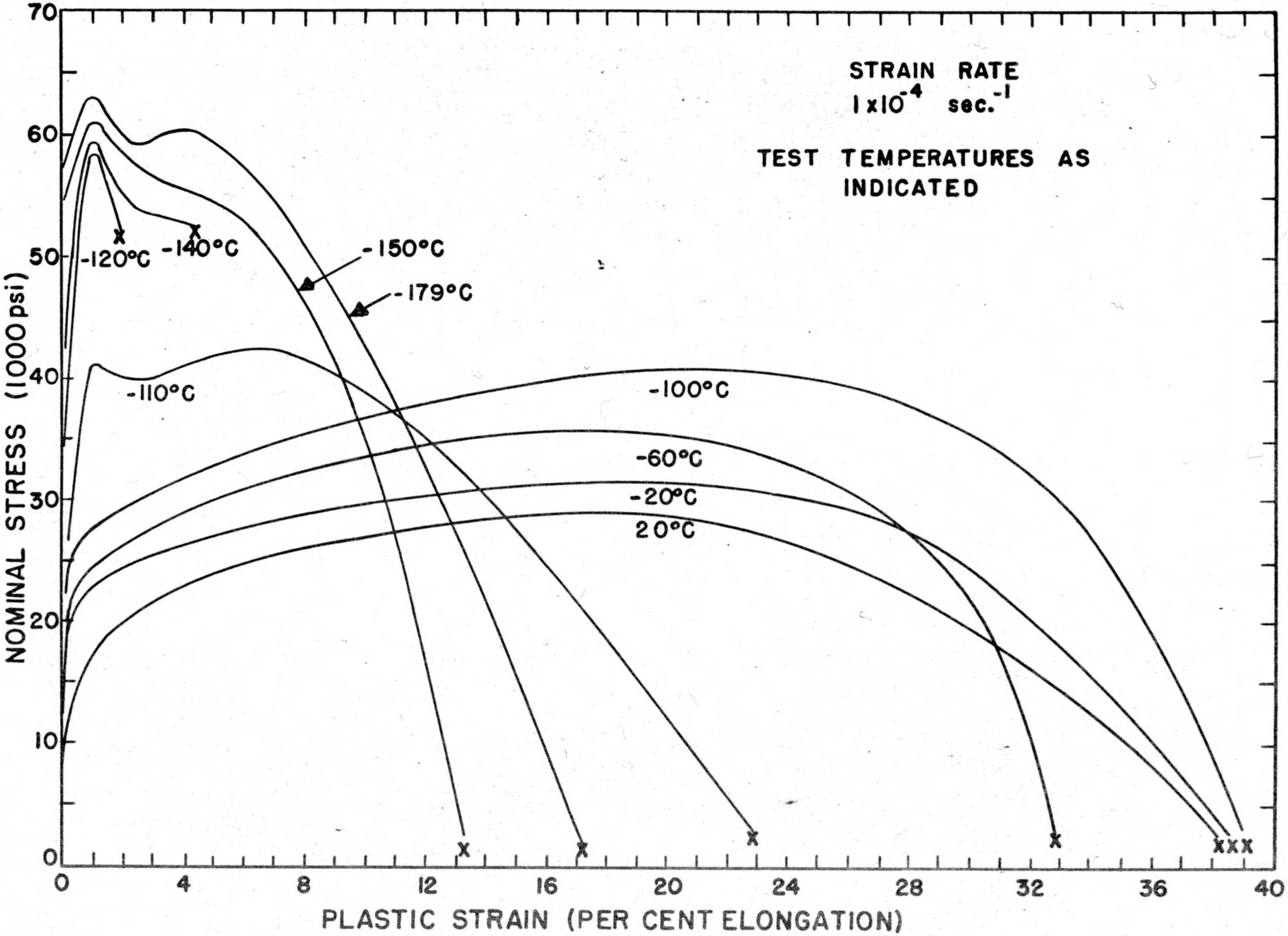

Figure 9. Stress-strain curves for crystal-bar vanadium

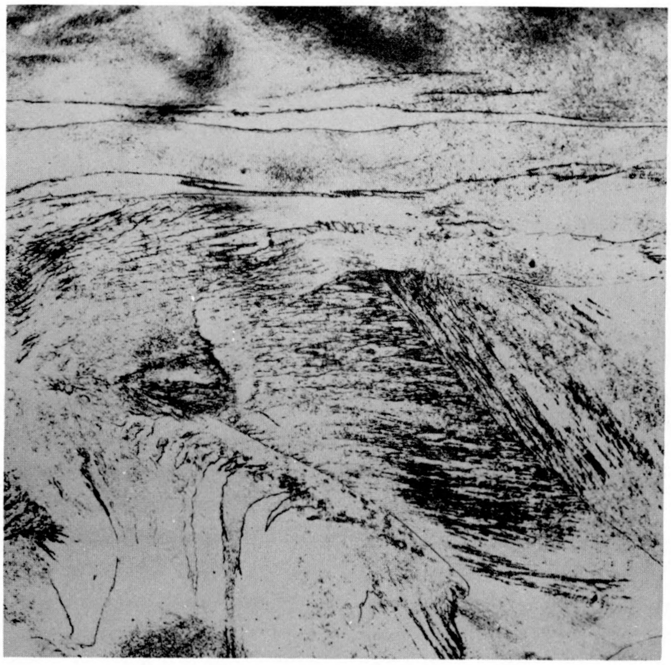

Figure 10. Deformation bands in crystal-bar vanadium after testing at -100°C

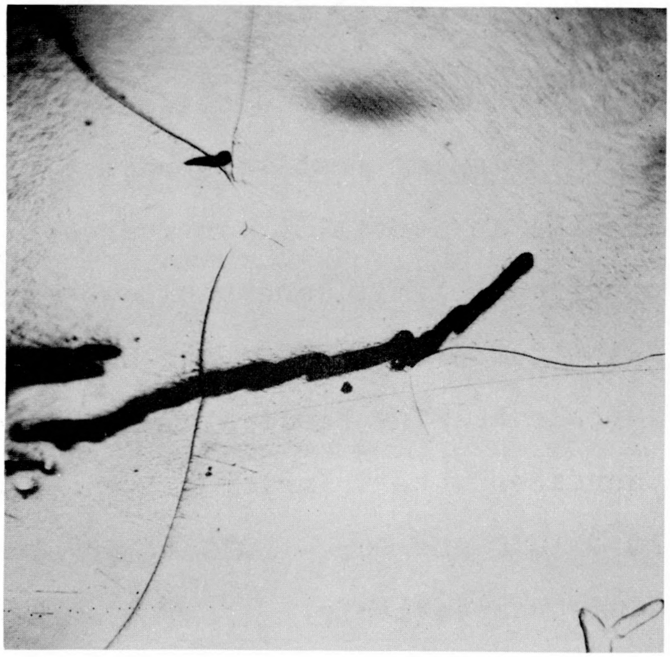

Figure 11. Transgranular crack in crystal-bar vanadium after testing at -120°C

in the stress-strain curves occurred only for test temperatures at and below -110°C.

Similar stress-strain curves were obtained for bomb-reduced vanadium. However, this grade of vanadium could not be plastically deformed to any great degree at temperatures below -55°C. Below this temperature, the metal fractured in a brittle transgranular manner near the lower yield point before undergoing much elongation or reduction in cross-sectional area.

The temperature dependence of the mechanical properties obtained from the stress-strain curves and from measurements on the test specimens is shown in Figure 12 and Figure 13. These curves show a temperature dependence of the mechanical properties similar to that exhibited by other body-centered cubic metals in which a brittle-ductile transition has been observed. With decreasing test temperature, there is a pronounced decrease in ductility, an increase in yield strength, proportional limit, and ultimate tensile strength at the transition temperature. On the basis of the plots of ductility versus testing temperature and the examination of fractured surfaces, the transition temperature was established at -110 ± 10°C and -65 ± 10°C in crystal-bar and bomb-reduced vanadium, respectively.

Young's Modulus of elasticity for both crystal-bar and bomb-reduced vanadium showed a peculiar type of temperature dependence (Figure 14). A minimum value of Young's Modulus

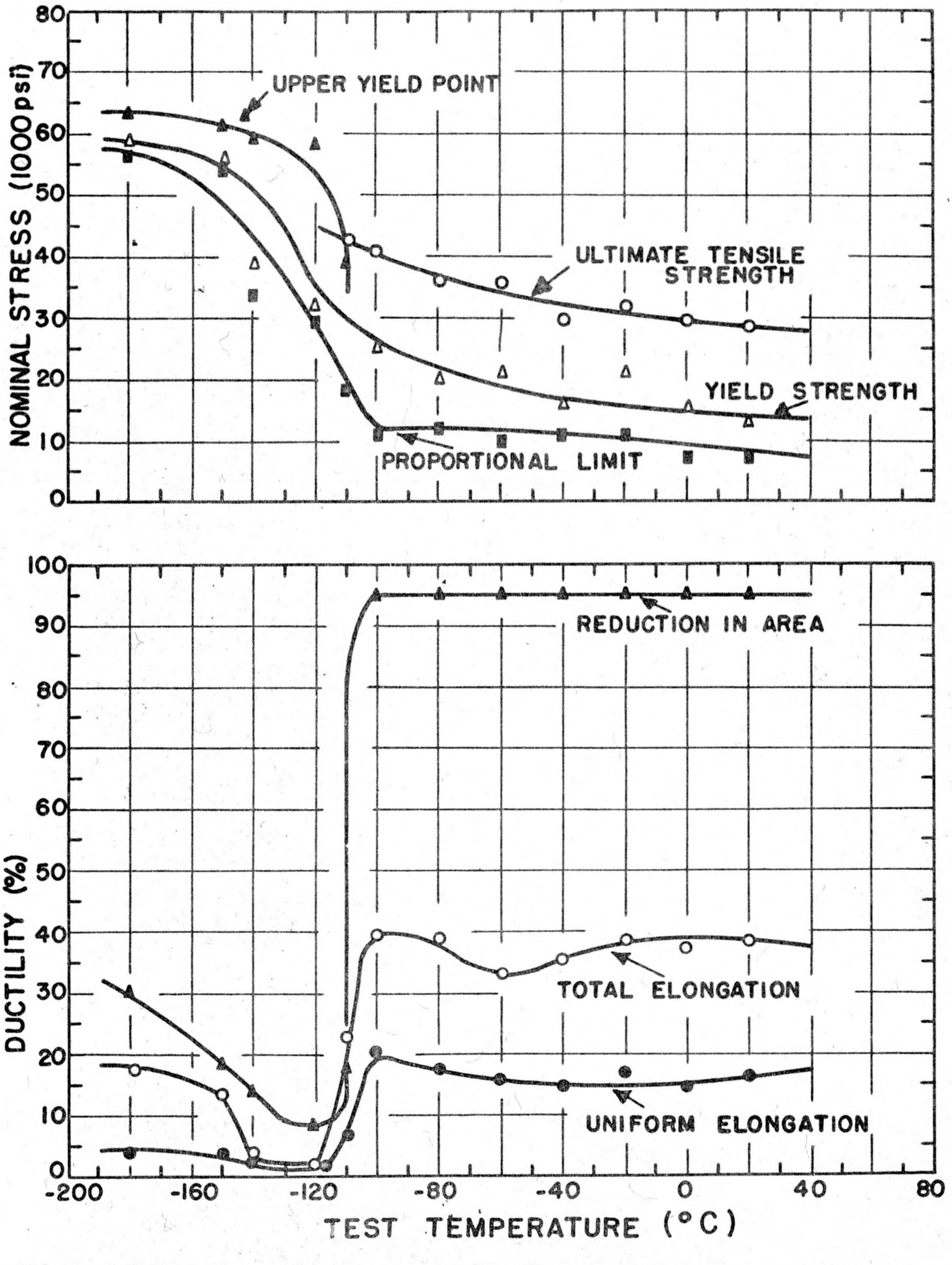

Figure 12. Tensile properties of crystal-bar vanadium at sub-atmospheric temperatures

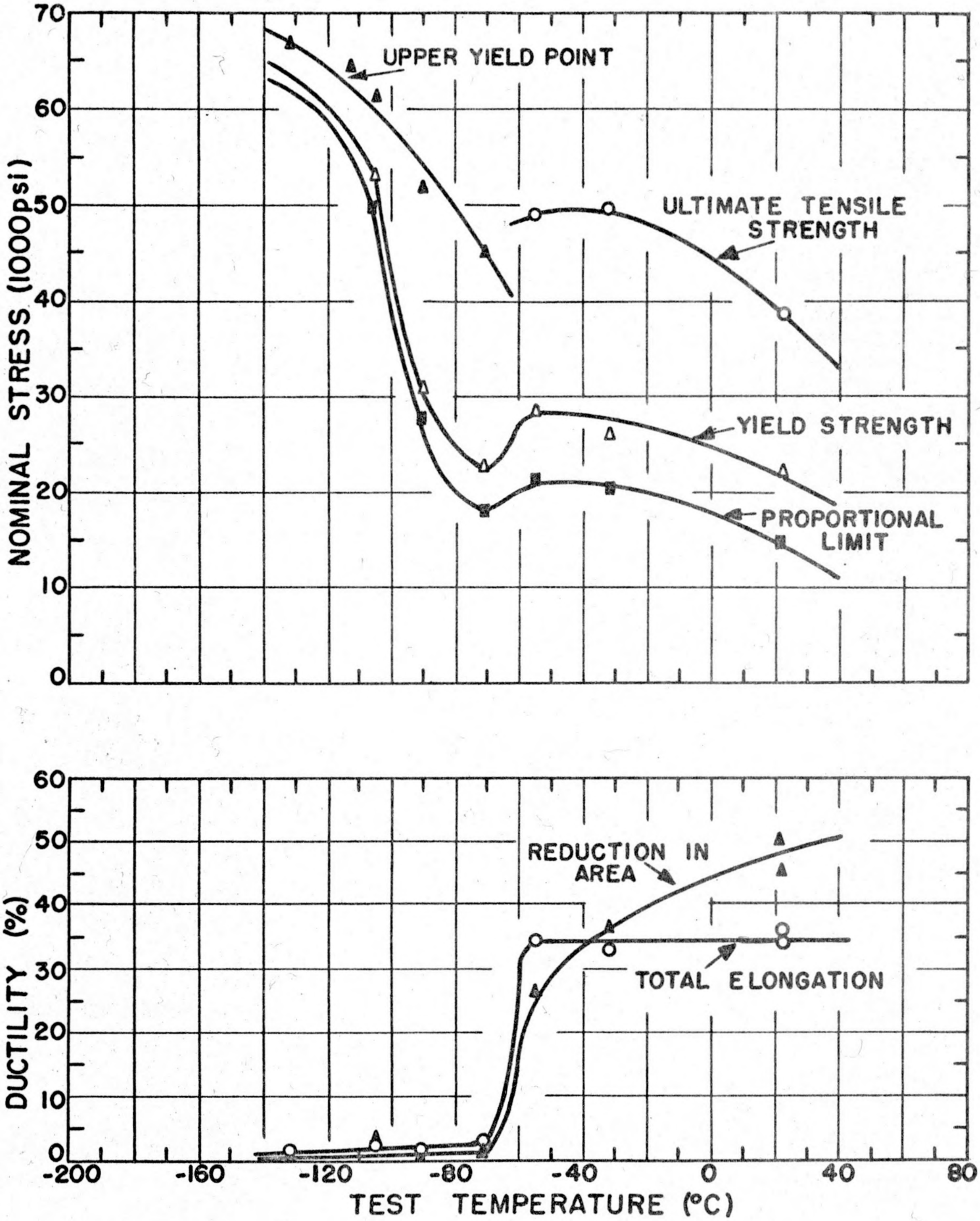

Figure 13. Tensile properties of bomb-reduced vanadium at sub-atmospheric temperatures

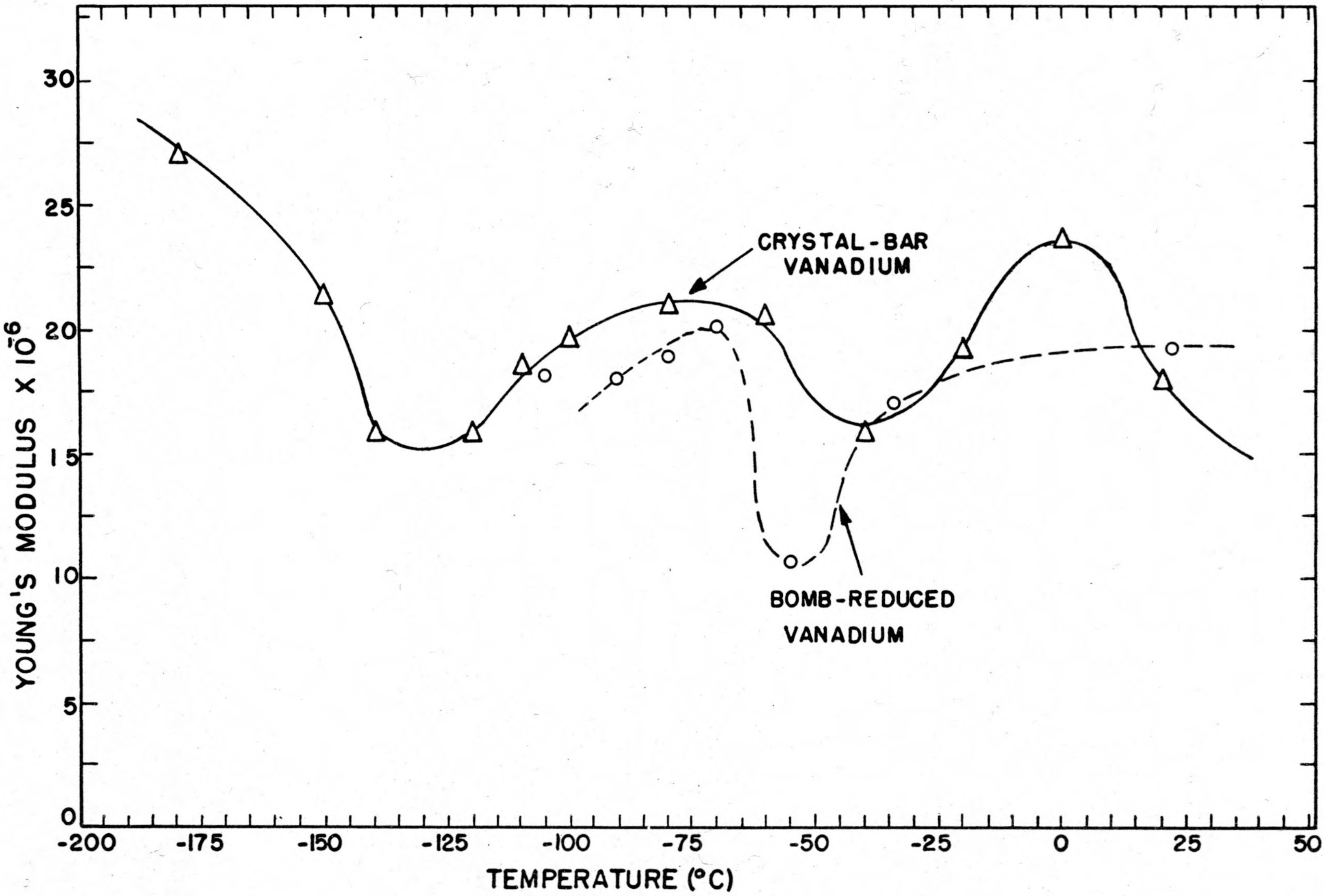

Figure 14. Young's Modulus of vanadium at sub-atmospheric temperatures

was observed for both types of vanadium at about -55°C. Also, a minimum value of Young's Modulus was observed for crystal-bar vanadium at about -130°C.

The bend tests on bomb-reduced vanadium, likewise, indicated the existence of a brittle-ductile transition. Typical bend test curves are shown in Figure 15 where the applied load is plotted against the specimen deflection for a given test temperature. At temperatures above -60°C it was not possible to break the bomb-reduced vanadium specimens whereas below -60°C the specimens broke before undergoing little if any plastic deformation. The results of these tests and others are shown in Figure 16 where the specimen deflection is plotted against the test temperature. The transition temperature according to this particular mechanical test was -70 ± 10°C. Below -145°C, it was possible to again plastically deform the vanadium specimens, as indicated in Figure 16, by the increasing amount the specimen could be bent before fracture occurred. However, the extent to which it could be deformed was limited.

B. Effect of Metallic Additions

The mechanical properties of each of the vanadium alloy specimens tested in uniaxial tension are tabulated in Table 4. The effect of metallic additions on the temperature of the brittle-ductile transition in vanadium was determined by plotting the ductility of the vanadium alloys as a

Table 4. Mechanical properties of vanadium alloys (Metallic additions)

			Ductility (%)					
Sample number	Nominal composition	Test temperature (°C)	Total elongation	Reduction in area	U.T.S. (Psi)	F.S. (Psi)	Type of fracture	Hardness Rockwell "A"
BAL-104-1-2	V+.25%Ta	108	19.01	41.8	36,853	1,077	Ductile	
BAL-104-1-3	"	60	9.50	36.40	43,319	3,483	"	
BAL-104-1-1	"	23	1.0	3.02	40,948	40,948	Cleavage	
BAL-104-1-4	"	-44	.44	.43	28,879	28,879	"	37
BAL-47-1	V+0.5%Ta	23	22.03	25.10	43.636	1,010	Ductile	31
BAL-47-2	"	-4	17.90	20.32	46,263	30,303	"	
BAL-47-3	"	-25	10.43	3.59	46,970	46,970	Cleavage	
BAL-47-4	"	-50	6.03	2.79	49,697	49,697	"	
BAL-128-2	V+1.0%Ta	55	12.52	17.0	42,675	1,061	Ductile	
BAL-128-3	"	40	22.67	32.1	46,284	26,008	"	
BAL-128-1	"	23	6.66	6.64	43.683	43,683	Cleavage	44
BAL-128-4	"	-24	2.02	.86	40,685	40,685	"	
BAL-129-1	V+.25%Cr	23	12.05	9.37	43,686	43,686	Cleavage	28
BAL-129-4	"	-22	2.89	2.53	35,158	35,158	"	
BAL-129-3	"	-32	4.43	4.08	40,326	40,326	"	
BAL-129-2	"	-50	1.61	2.04	38,798	38,798	"	
BAL-45-3	V+0.5%Cr	23	19.99	28.29	42,828	1,010	Ductile	30
BAL-45-1	"	-27	22.56	19.52	55,555	48,687	Cleavage	
BAL-45-4	"	-35	21.07	23.90	48,687	35,354	"	
BAL-45-2	"	-52	3.82	1.59	51,717	51,717	"	

Table 4. (Continued)

			Ductility (%)					
Sample number	Nominal composition	Test temperature (°C)	Total elongation	Reduction in area	U.T.S. (Psi)	F.S. (Psi)	Type of fracture	Hardness Rockwell "A"
BAL-103-1	V+1.0%Cr	23	21.10	42.90	45,090	38,477	Cleavage	42
BAL-103-4	"	0	22.93	38.20	54,545	43,030	"	
BAL-103-3	"	-23	4.04	2.85	48,065	48,065	"	
BAL-103-2	"	-43	6.63	6.06	61,818	61,818	"	
BAL-58-3	V+ .5%Ti	23	17.61	35.4	59,800	47,470	Cleavage	35
BAL-58-2	"	-41	18.57	22.2	59,800	53,540	"	
BAL-58-1	"	-50	8.40	12.6	60,100	60,100	"	
BAL-58-4	"	-81	7.39	10.4	62,730	62,730	"	
BAL-105-4	V+1.0%Ti	203	1.04	0.41	91,786	91,786	Cleavage	
BAL-105-3	"	149	5.54	1.01	40,000	40,000	"	
BAL-105-2	"	62	1.10	.21	88,518	88,518	"	
BAL-105-1	"	23	1.93	1.24	97,515	97,515	"	63
BAL-126-1	V+2.5%Ti	22	9.40	23.7	57,142	52,521	Ductile	37
BAL-126-2	"	-31	7.14	5.23	63,232	41,414	"	
BAL-126-4	"	-49	12.30	13.50	70,707	60,606	"	
BAL-126-3	"	-70	16.23	18.0	74.646	59,596	"	
BAL-125-1	V+.25%Mo	22	16.94	14.50	38,655	38,655	Cleavage	33
BAL-125-4	"	2	10.76	1.01	40,808	40,808	"	
BAL-125-3	"	-28	2.28	2.08	38,229	38,229	"	
BAL-125-2	"	-49	3.24	3.13	36,771	36,771	"	

Table 4. (Continued)

			Ductility (%)					
Sample number	Nominal composition	Test temperature (°C)	Total elongation	Reduction in area	U.T.S. (Psi)	F.S. (Psi)	Type of fracture	Hardness Rockwell "A"
BAL-46-3	V+ .5%Mo	-30	9.75	13.90	46,260	44,440	Cleavage	36
BAL-46-2	"	-40	8.62	7.94	46,360	46,360	"	
BAL-46-1	"	-50	7.99	5.16	48,990	46,770	"	
BAL-104-3-2	V+1.0%Mo	212	1.46	1.83	31,772	31,772	Cleavage	
BAL-104-3-3	"	149	1.23	.45	21,542	21,542	"	
BAL-104-3-4	"	54	2.64	3.88	35,560	35,560	"	
BAL-104-3-1	"	23	1.32	1.21	37,576	37,576	"	36
BAL-48-1	V+ .5%Zr	-25	22.26	34.66	51,414	13,535	Ductile	37
BAL-48-2	"	-50	19.05	34.26	56,970	34.343	"	
BAL-48-3	"	-62	3.00	2.79	46,263	46,263	Cleavage	
BAL-48-4	"	-75	2.08	1.20	36,200	36,200	"	
BAL-104-2-1	V+1.0%Zr	23	20.36	44.80	42,424	10,101	Ductile	32
BAL-104-2-2	"	-45	10.24	12.50	54.786	54,786	"	
BAL-104-2-4	"	-61	1.26	1.50	41,560	41,560	Cleavage	
BAL-104-2-3	"	-78	1.61	2.07	40,269	40,269	"	
BAL-124-4	V+4.0%Zr	-20	4.76	1.00	21.818	21,818	Cleavage	29
BAL-124-1	"	23	4.30	3.54	42,500	42,500	"	
BAL-124-2	"	110	.39	2.29	31,667	31,667	"	
BAL-124-3	"	300	5.37	2.61	26,956	26,956	"	

Table 4. (Continued)

Sample number	Nominal composition	Test temperature (°C)	Ductility (%)		U.T.S. (Psi)	F.S. (Psi)	Type of fracture	Hardness Rockwell "A"
			Total elongation	Reduction in area				
BAL-49-1	V+ .5%Th	-47	24.32	46.4	35,960	10,100	Ductile	23
BAL-49-3	"	-60	26.87	49.0	36,060	23,940	"	
BAL-49-2	"	-76	12.22	14.0	39,290	37,370	Cleavage	
BAL-127-1	V+1.0%Th	23	7.52	9.90	25,353	707	Ductile	19
BAL-127-2	"	-46	4.21	3.03	28,687	1,010	"	
BAL-127-4	"	-60	3.47	3.64	25,454	18,990	Cleavage	
BAL-127-3	"	-77	1.08	.40	20,202	20,202	"	

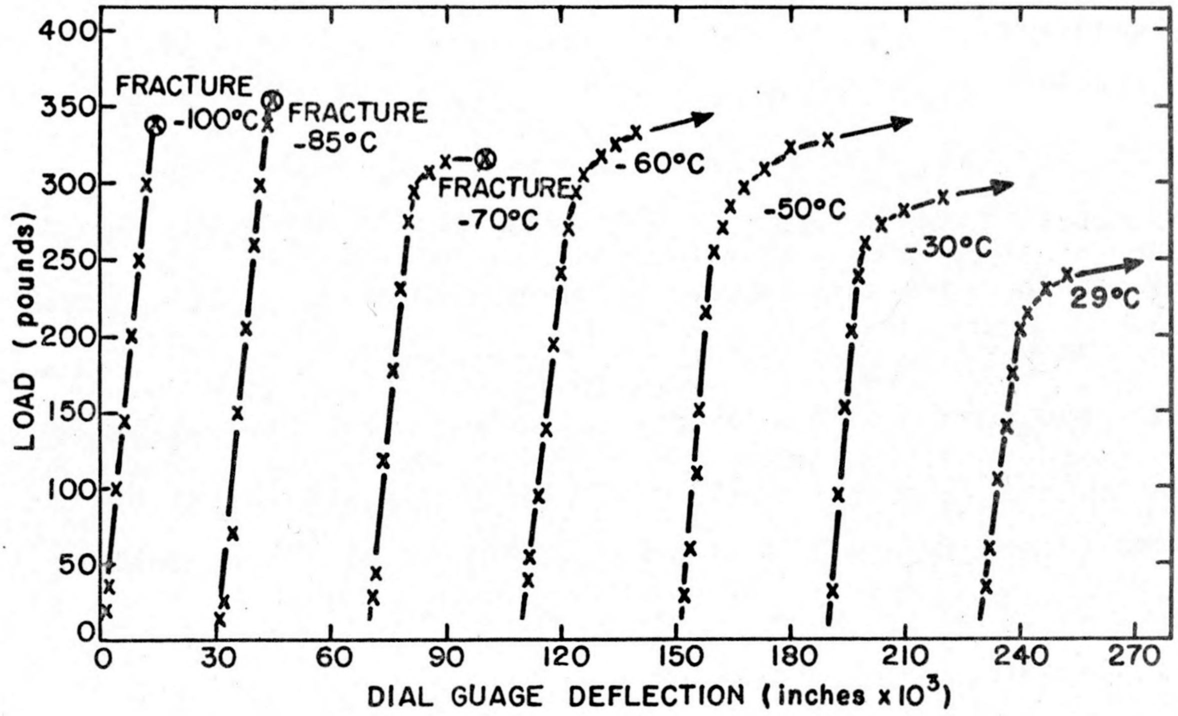

Figure 15. Bend test curves for bomb-reduced vanadium

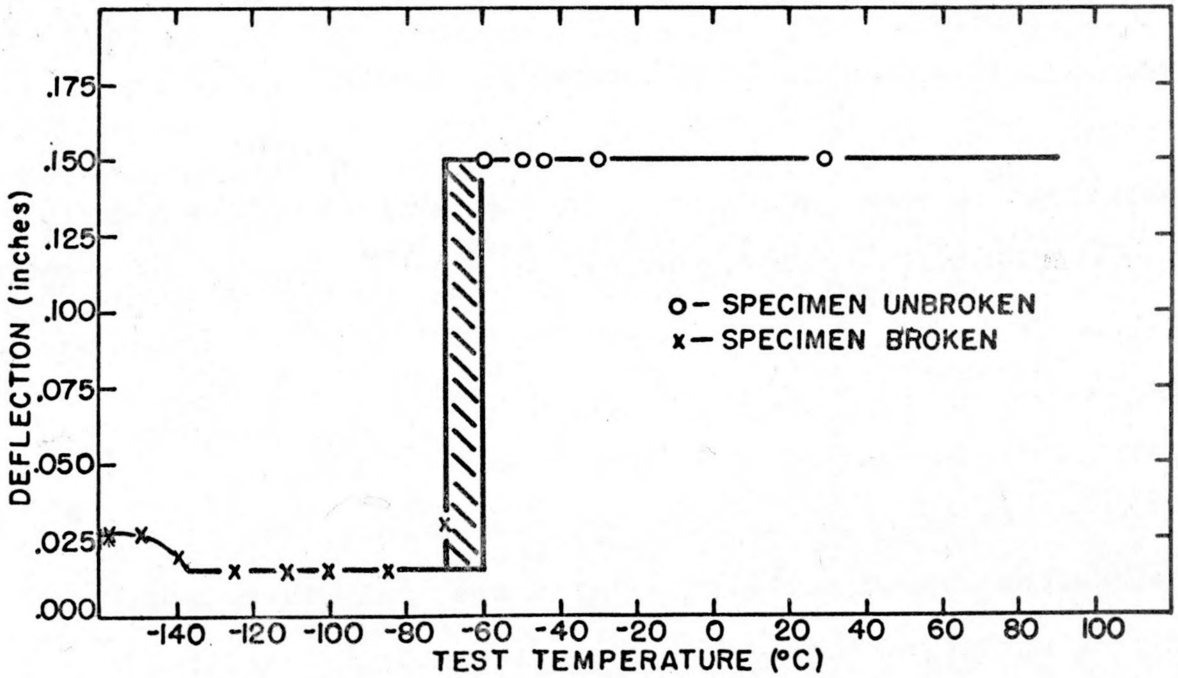

Figure 16. Deflection of bomb-reduced vanadium at subatmospheric temperatures

function of test temperature in Figures 17, 18 and 19. The transition temperature of these alloys was determined to be that temperature at which there was a pronounced decrease in reduction in cross-sectional area or total elongation with decreasing test temperature. Since this decrease in ductility occurred over a range of temperature, the transition temperature was chosen as the middle of this range. The nature of the fracture was also given some consideration in the selection of the transition temperature. However, in several of the alloys the fracture appeared to be of a cleavage type at temperatures at which the alloy possessed considerable ductility.

The transition temperature of the vanadium alloys appears as plotted points in Figure 20 where the transition temperature is plotted against the weight per cent of metallic addition. Since only four specimens of each composition were tested, it was not possible to locate accurately the transition temperature. Therefore, the transition temperatures of the alloys shown in Figure 20 must be considered only as approximate. In most cases, however, the accuracy of the transition temperature is believed to be ± 10°C.

For the majority of the metallic additions studied, their effect was generally to raise the transition temperature of unalloyed vanadium. The only metallic additions investigated which lowered the transition temperature of vanadium were titanium when present in amounts greater than

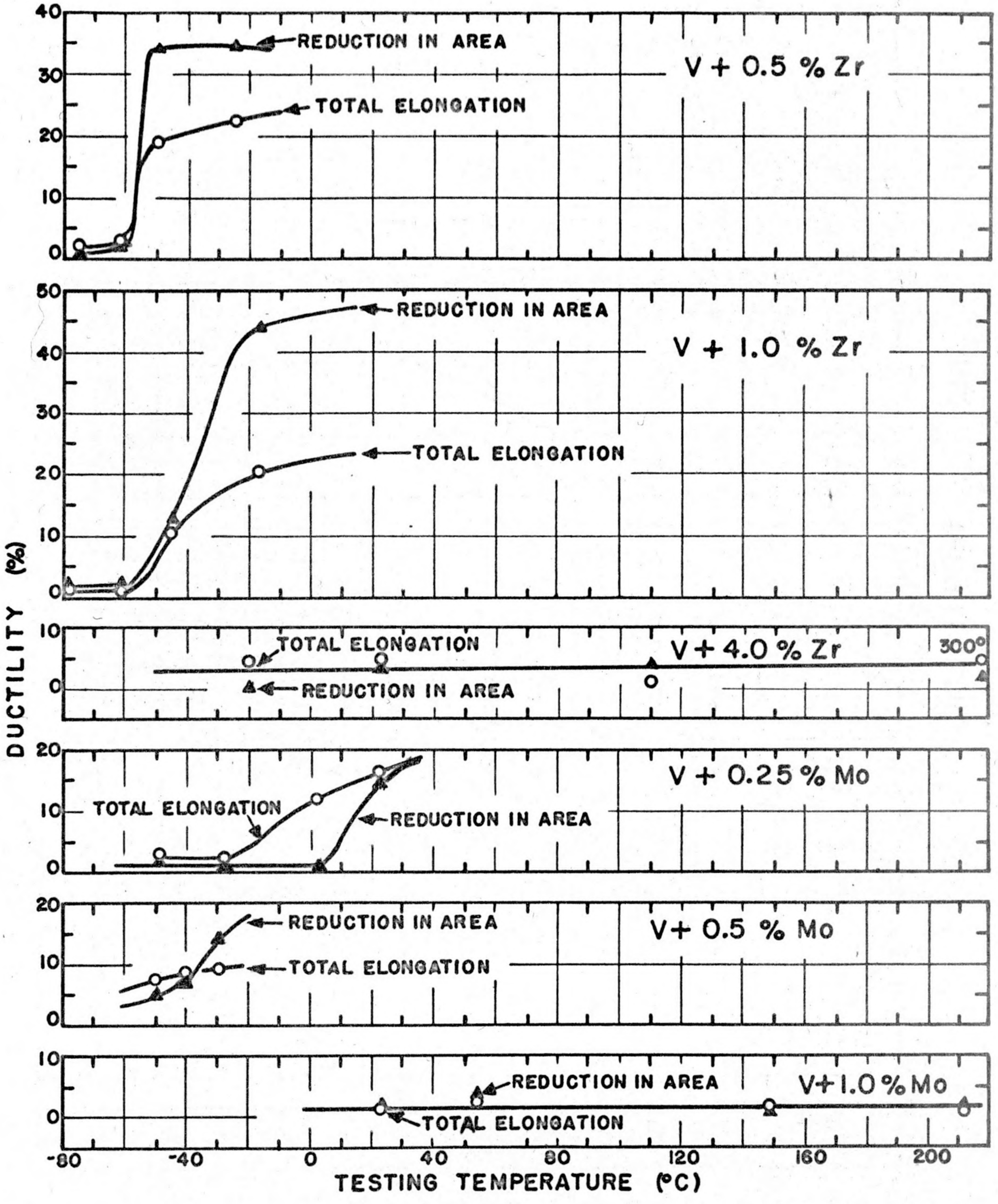

Figure 17. Ductility of vanadium containing small amounts of zirconium and molybdenum

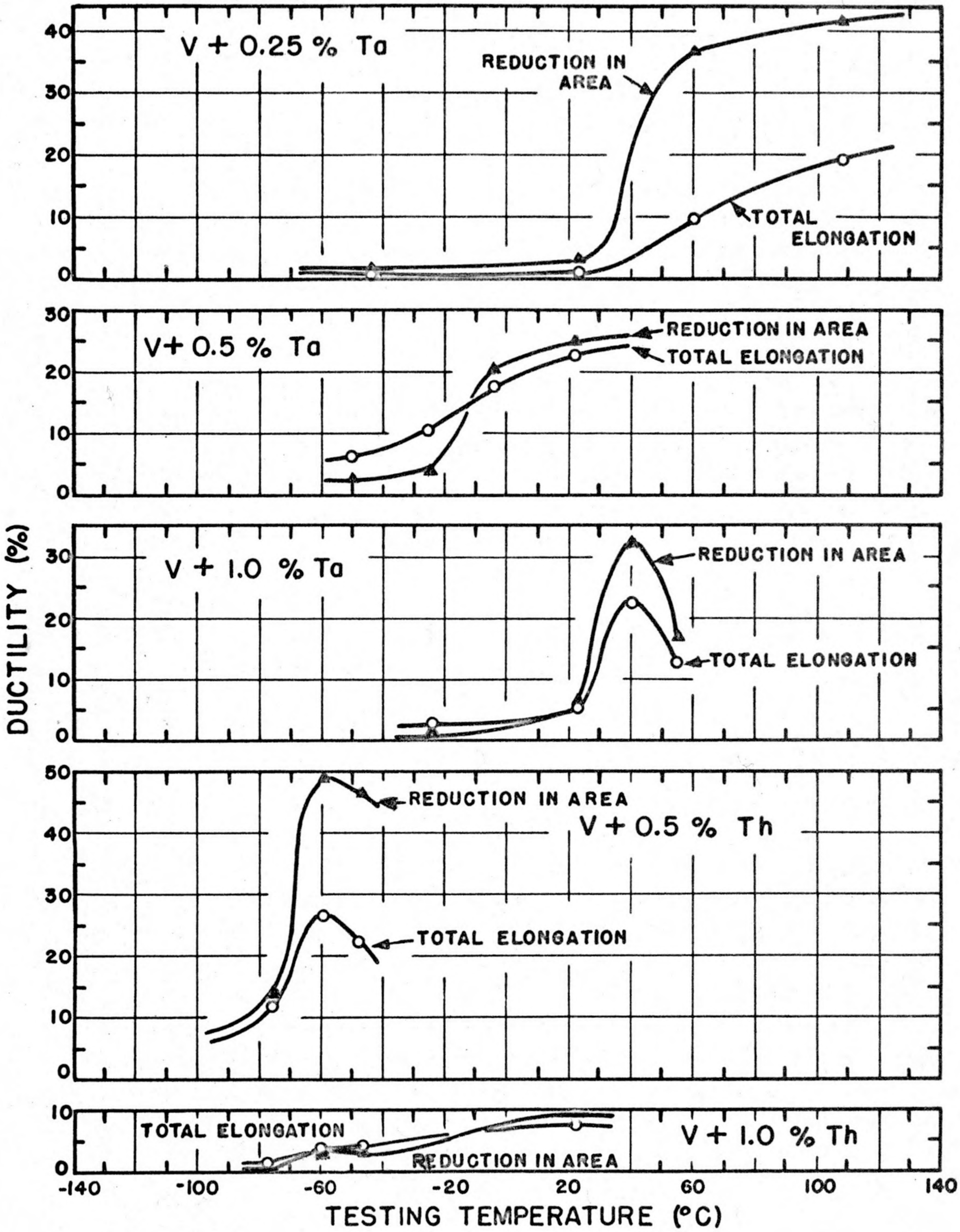

Figure 18. Ductility of vanadium containing small amounts of tantalum and thorium

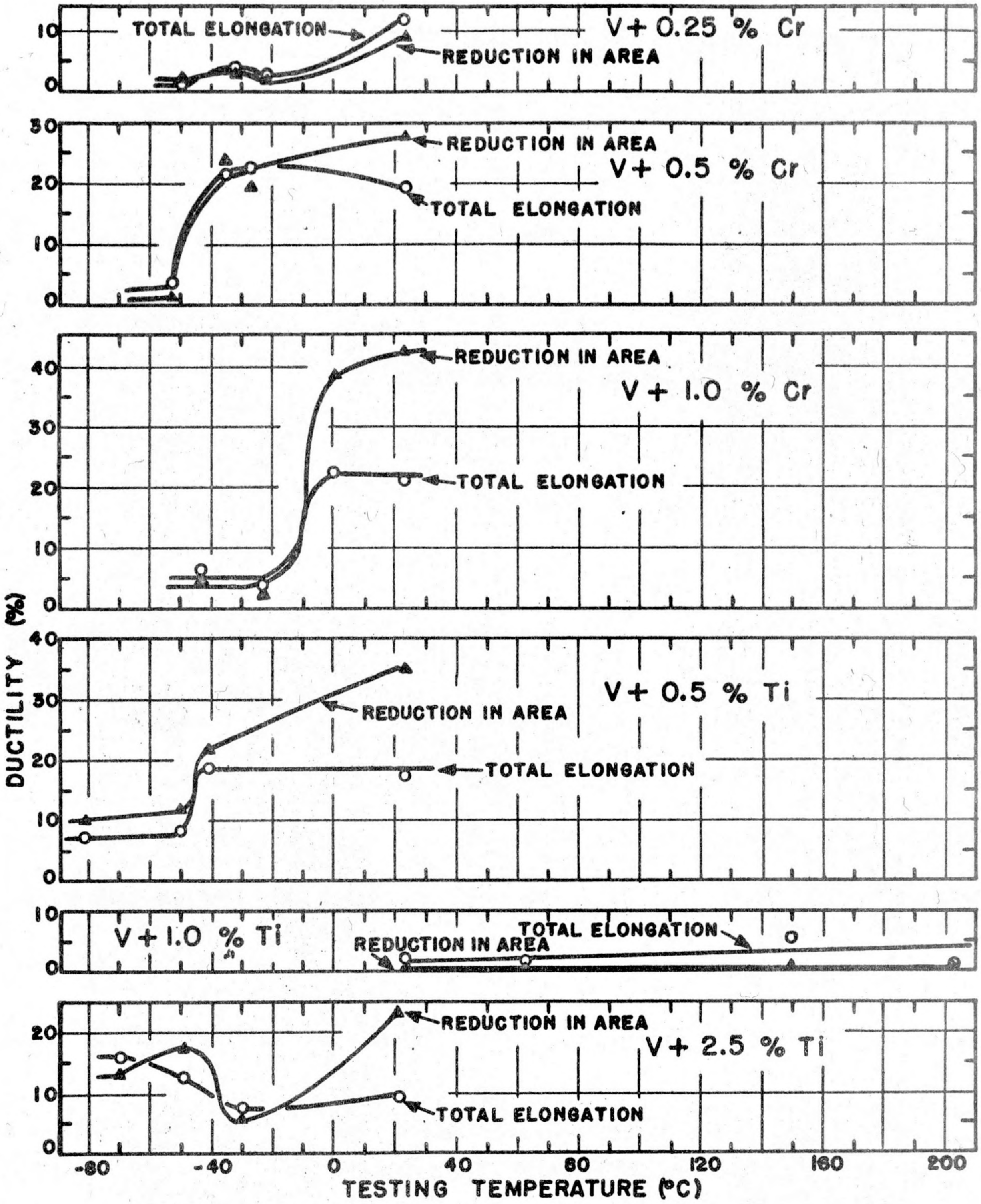

Figure 19. Ductility of vanadium containing small amounts of chromium and titanium

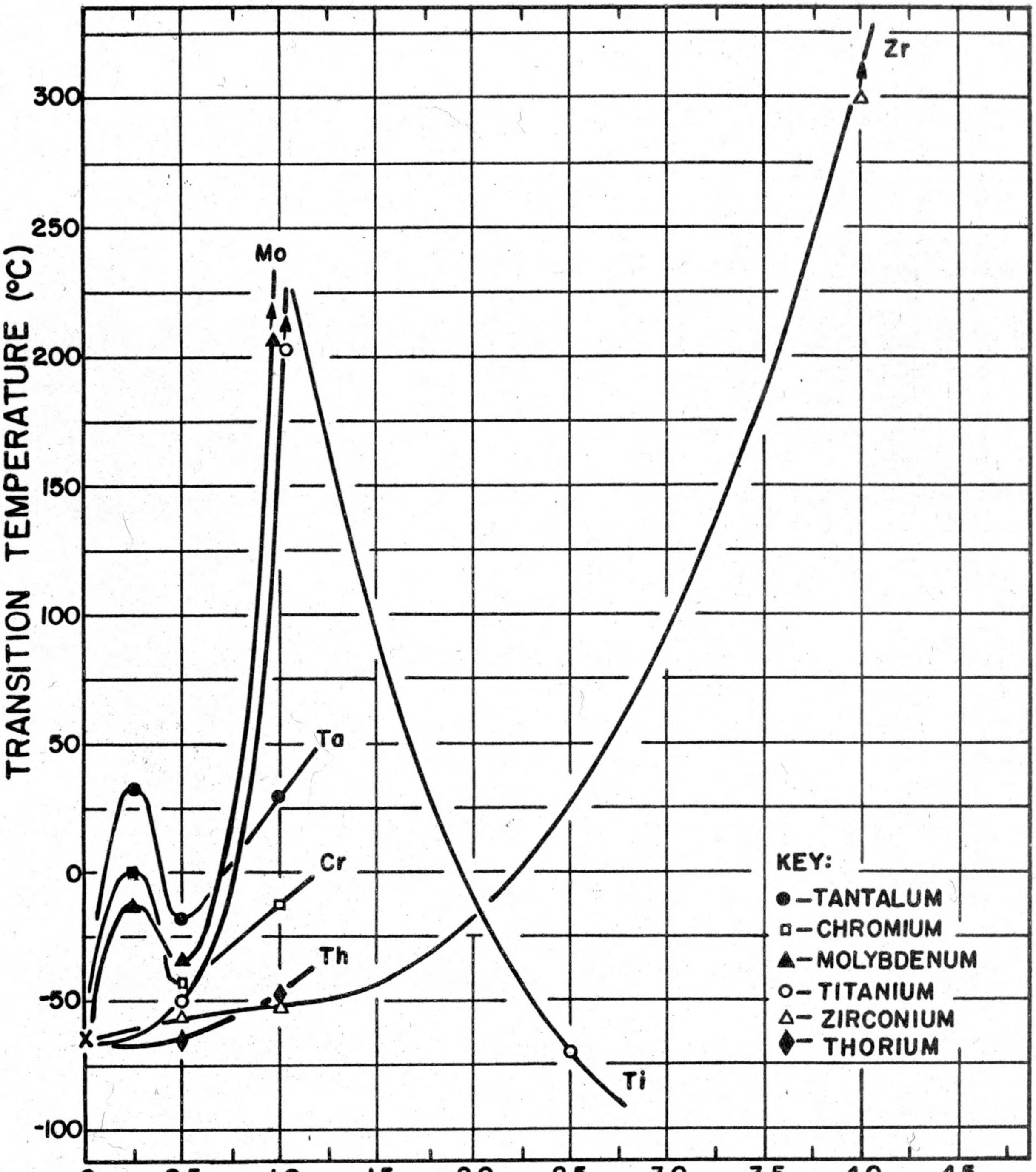

Figure 20. Effect of small amounts of metallic elements on the transition temperature of vanadium

2.5 per cent and possibly thorium when present in amounts less than .5 per cent. Also, it will be observed in Figure 20 that the metallic additions have anomalous maxima and minima effects.

Microstructures which are representative of the substitutional alloys, i.e., metallic additions to vanadium, investigated are shown in Figures 22 through 32. The microstructure of unalloyed vanadium is shown in Figure 21. An interpretation of each microstructure is given with the appropriate figure. All of the samples were etched in a solution containing 20 parts nitric acid, 20 parts hydrofluoric acid, and 60 parts glycerine.

C. Effect of Non-Metallic Additions

The effect of nitrogen, oxygen, and carbon on the brittle-ductile transition in vanadium was investigated by means of the bend test as mentioned in a previous section. Data similar to that shown in Figures 15 and 16 were taken for each of the alloys examined. Likewise, the transition temperature was recorded as that temperature at which there was a pronounced increase in the amount of deflection the specimen could be given before it fractured. The specimens to which these elements had been added could, in general, not be bent as much as pure vanadium, but the transition

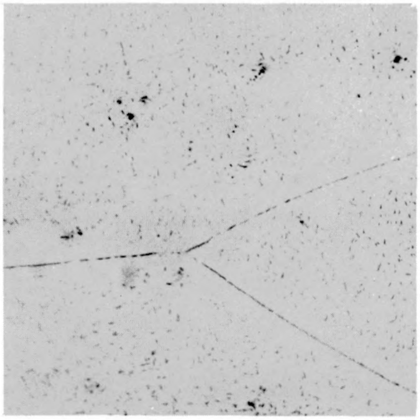

Figure 21

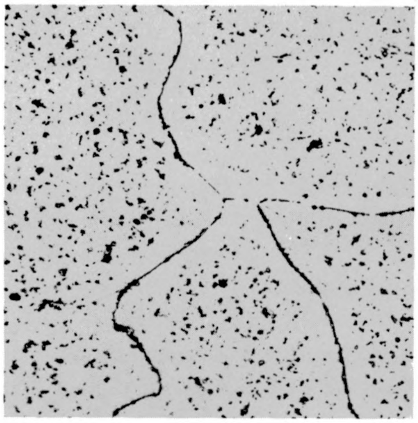

Figure 22

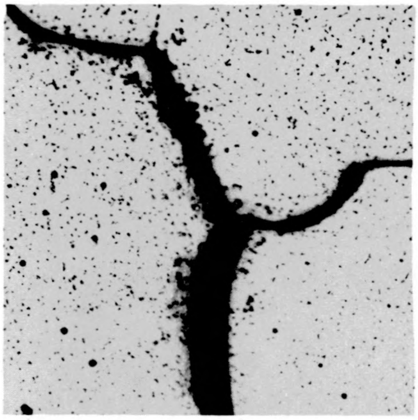

Figure 23

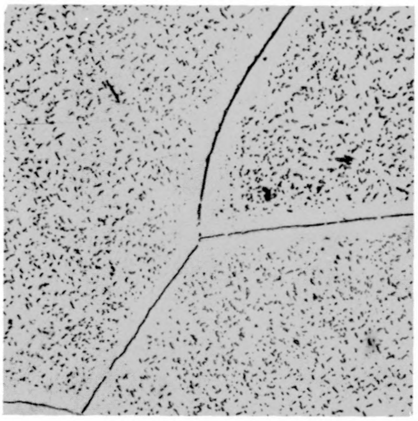

Figure 24

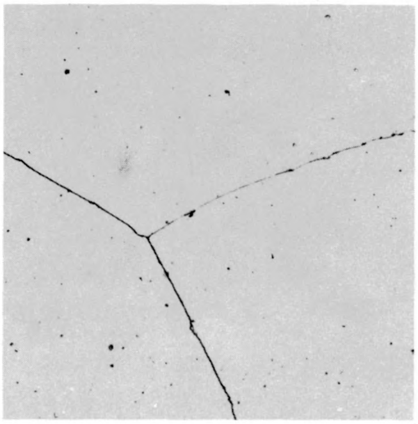

Figure 25

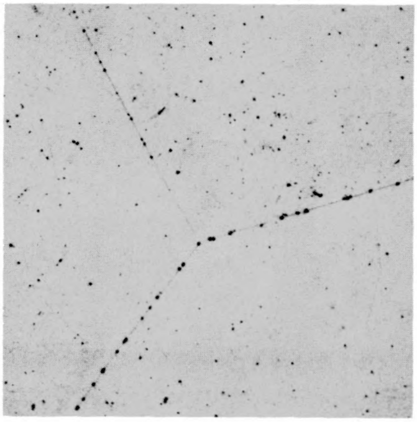

Figure 26

Figure 21. Bomb-reduced vanadium

As-annealed. Impurity phase in the grains. (X250).

Figure 22. Vanadium containing .5 per cent thorium

As-annealed. Impurity phase in the grains. (X250).

Figure 23. Vanadium containing 1.0 per cent thorium

As-annealed. Crack propagating along grain boundary which contains essentially pure thorium. Impurity phase in the grains. (X250).

Figure 24. Vanadium containing .5 per cent titanium

As-annealed. Impurity phase in grains and along grain boundaries. (X250).

Figure 25. Vanadium containing 1.0 per cent titanium

As-annealed. Small amount of impurity phase in the grains. (X250).

Figure 26. Vanadium containing 2.5 per cent titanium

As-annealed. Small amount of impurity phase in the grains and along the grain boundaries. (X250).

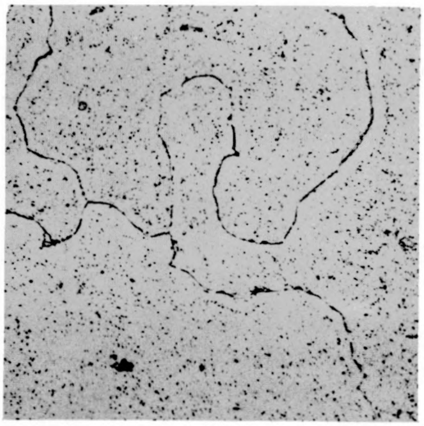

Figure 27

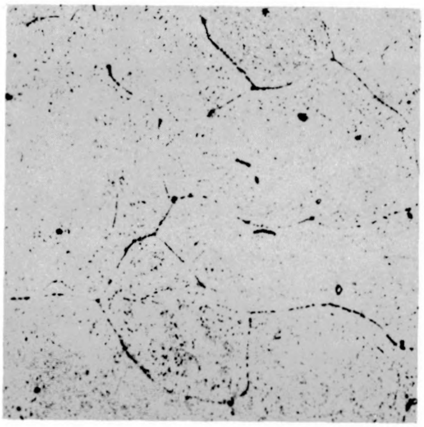

Figure 28

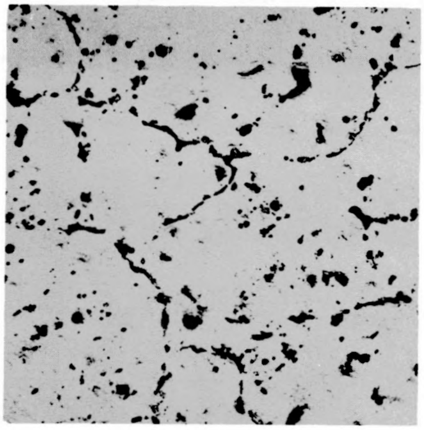

Figure 29

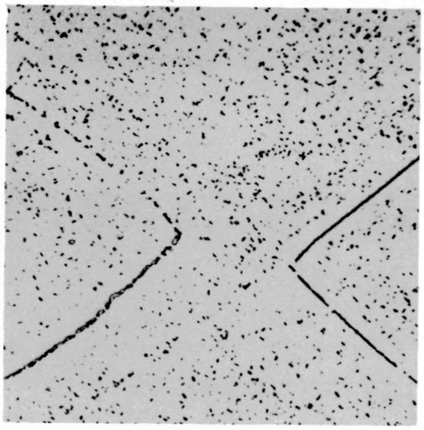

Figure 30

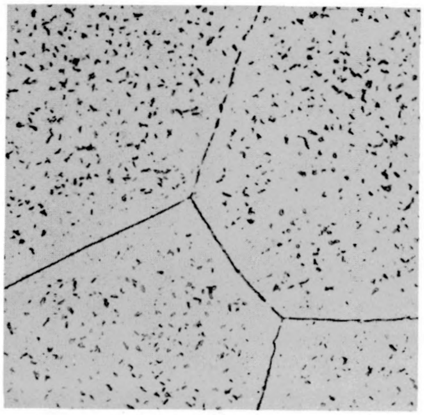

Figure 31

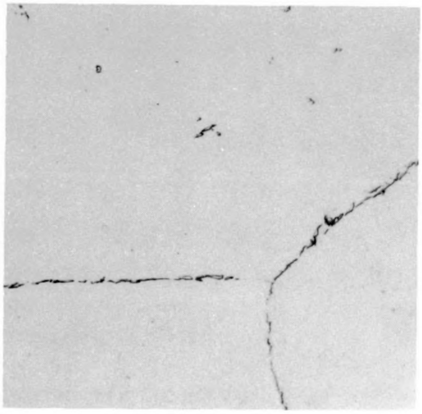

Figure 32

Figure 27. Vanadium containing .5 per cent zirconium

As-annealed. Impurity phase in the grains and along the grain boundaries. (X250).

Figure 28. Vanadium containing 1.0 per cent zirconium

As-annealed. Impurity phase in the grains and along the grain boundaries.. (X250).

Figure 29. Vanadium containing 4.0 per cent zirconium

As-annealed. V_2Zr compound in the grains and along the grain boundaries. (X250).

Figure 30. Vanadium containing .25 per cent molybdenum

As-annealed. Impurity phase in the grains and along the grain boundaries. (X250).

Figure 31. Vanadium containing .50 per cent molybdenum

Impurity phase in the grains and along the grain boundaries. (X250).

Figure 32. Vanadium containing 1.0 per cent molybdenum

Small amount of impurity phase in the grains and along the grain boundaries. (X250).

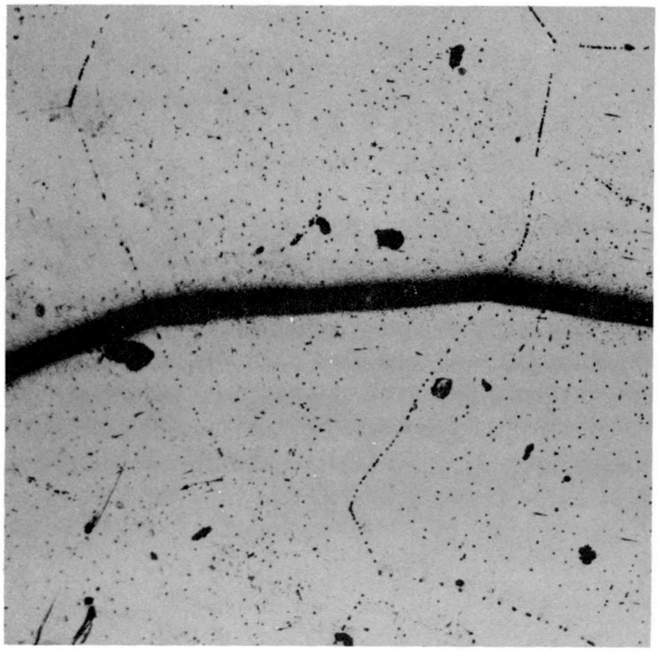

Figure 33. Transgranular fracture in vanadium containing .215 per cent oxygen (X250)

was still apparent. Also, all the fractures were observed to be of a brittle transgranular nature (Figure 33).

The transition temperature of each of the alloys investigated is tabulated in Table 5 along with their respective hardness values. Also, the transition temperature of these alloys appears as plotted points in Figure 34. It will be observed that, of the interstitials hydrogen, nitrogen, oxygen, and carbon, hydrogen has the most pronounced effect on the transition temperature of vanadium. Carbon affects the transition temperature only slightly whereas nitrogen and oxygen have an effect intermediate to that of

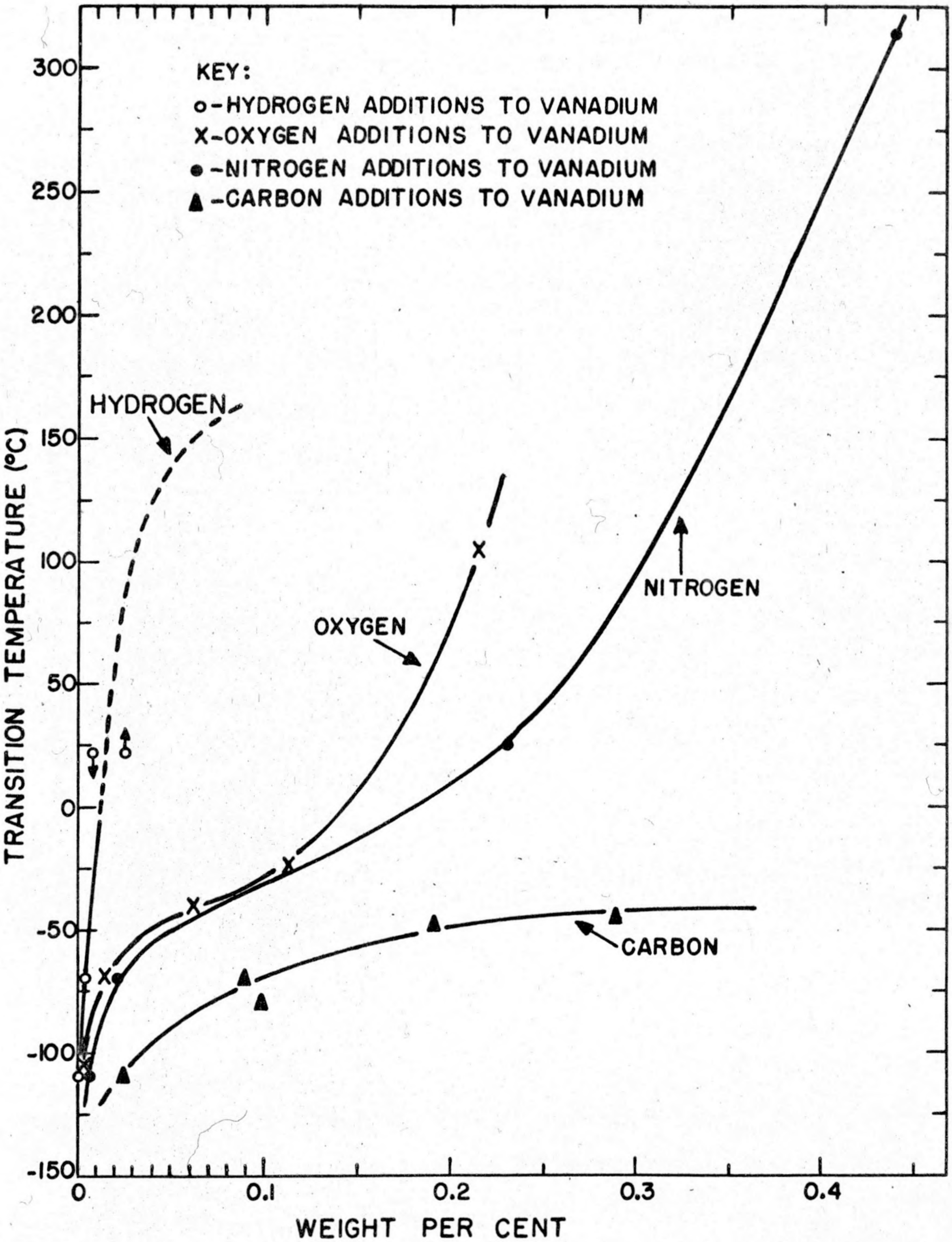

Figure 34. Effect of hydrogen, oxygen, nitrogen, and carbon on the brittle-ductile transition in vanadium

Table 5. Transition temperature and hardness values of vanadium containing various amounts of oxygen, nitrogen, carbon, and hydrogen

Composition	Transition tempera-ture(°C)	Test Procedure	Rockwell "A" Hardness
Crystal-Bar Vanadium + .001%H	-110	Tensile	21
Bomb-Reduced Vanadium + .006%H	- 70	Bend	38
Crystal-Bar Vanadium + .010%H	23	Bend	
Crystal-Bar Vanadium + .027%H	23	Bend	
Crystal-Bar Vanadium + .010%O	-110	Tensile	21
Bomb-Reduced Vanadium + .015%O	- 70	Bend	38
Bomb-Reduced Vanadium + .065%O[a]	- 40	Bend	45
Bomb-Reduced Vanadium + .115%O[a]	- 25	Bend	46
Bomb-Reduced Vanadium + .215%O[a]	105	Bend	55
Crystal-Bar Vanadium + .005%N	-110	Tensile	21
Bomb-Reduced Vanadium + .021%N	- 70	Bend	38
Bomb-Reduced Vanadium + .23 %N	25	Bend	58
Bomb-Reduced Vanadium + .44 %N	315	Bend	68
Crystal-Bar Vanadium + .024%C	-110	Tensile	21
Bomb-Reduced Vanadium + .09 %C	- 70	Bend	38
Bomb-Reduced Vanadium + .10 %C	- 80	Bend	43
Bomb-Reduced Vanadium + .19 %C	- 47	Bend	44
Bomb-Reduced Vanadium + .29 %C	- 45	Bend	42

[a] The composition of this alloy is the nominal composition.

hydrogen and carbon. The portion of the curve shown for hydrogen additions at room temperature and above was derived by bending vanadium wires by hand. Although, this manner of testing was not considered reliable for accurately determining the transition temperature of vanadium to which hydrogen had been added, it did serve to isolate the effect of hydrogen on vanadium at room temperature. The wire which contained .027 per cent hydrogen could not be bent at room temperature without fracturing, whereas a wire containing .01 per cent hydrogen could be bent in a 180° arc at room temperature without fracturing. The slope of the curve for hydrogen additions was decreased at temperatures above 150°C on the basis of the studies by Roberts and Rogers (10a). They observed that a vanadium wire which contained about .05 per cent hydrogen was quite ductile at 150°C. The microstructures of the alloys which contained various amounts of hydrogen, oxygen, nitrogen, and carbon were all very similar to the one shown in Figure 33.

D. Results of the X-ray Investigations

The lattice constant, a_o, was determined for massive poly-crystalline samples of crystal-bar and bomb-reduced vanadium over a wide range of temperature. The crystal-bar vanadium had been given a 70 per cent reduction in thickness by rolling. The increase in hardness associated with this deformation was only about three points on the Rockwell "A" scale. Hence, the material, although plastically deformed, had been work-hardened only a slight amount. The bomb-reduced vanadium had been annealed at 900°C for five hours. The results of this investigation are tabulated in Table 6 and appear as plotted points in Figure 35. In the case of bomb-reduced vanadium, seven reflections were used in determining the lattice constant at a given temperature, whereas only six reflections were used in the case of crystal-bar vanadium. The accuracy of the lattice constant for a given temperature was enhanced by the application of the Nelson-Riley function and least-squares treatments. Between room temperature and -124°C the lattice constant of bomb-reduced vanadium decreased in accordance with the normal thermal contraction of the lattice. However, in the case of the crystal-bar vanadium the lattice constant decreased in the normal manner only down to -75°C. Between -75°C and -155°C, the lattice constant of crystal-bar vanadium was essentially constant, and below -155°C there was a significant decrease in the lattice constant. There was no indication of an allotropic transformation in vanadium at low temperatures since the same body-centered cubic reflections were observed at all temperatures.

In addition to determining the temperature dependence of the lattice constant of vanadium, the intensity of the various x-ray reflections was examined for a temperature dependence by two different approaches. The first approach involved an attempt to determine the temperature factor, B, in the equation:

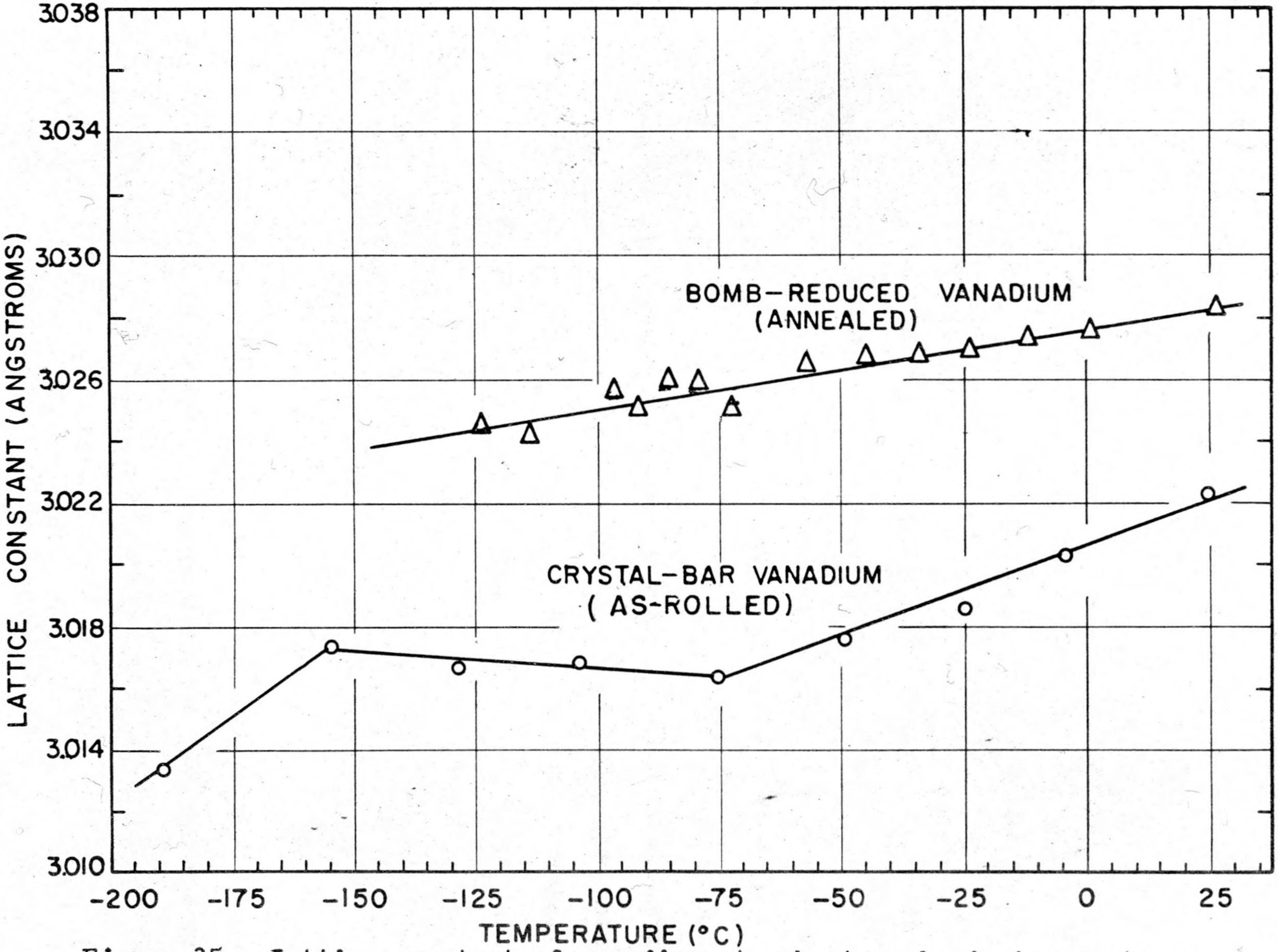

Figure 35. Lattice constant of vanadium at sub-atmospheric temperatures

$$\frac{|F_x|}{|F_c|} = e^{-B\left(\frac{\sin^2 \theta}{\lambda^2}\right)}$$

where F_x is the observed structure factor, and F_c is the calculated structure factor. However, the values of the ratio $\frac{|F_x|}{|F_c|}$ as determined at a given temperature were so erratic that no reliable temperature factor could be obtained. The second approach to determining the temperature dependence of the diffracted x-ray intensity was by considering the relationship between $\mathrm{Log}_e I$ and the function $\frac{\phi(x)}{x}$. The intensity of each x-ray reflection was obtained by graphically integrating the area under the peak with a planimeter. The relationship between $\mathrm{Log}_e I$ and $\frac{\phi(x)}{x}$ should be linear according to the following derivation of the temperature dependence of intensity for a given (hkl) reflection (23, p. 557):

$$I(hkl) \propto |F|^2 = |F_o|^2 \, e^{-2B\left(\frac{\sin^2 \theta}{\lambda^2}\right)} = |F_o|^2 \, e^{-2M}$$

where F is the structure factor at temperature $T^{\circ}K$ and F_o is the structure factor when the atoms in the unit cell are at rest. Debye has deduced the value

$$M = \frac{6h^2}{m_a k \Theta} \left[\frac{\phi(x)}{x} + \frac{1}{4}\right] \frac{\sin^2 \theta}{\lambda^2}$$

Table 6. Lattice constant, a_o, of vanadium between 26°C and -189°C

Bomb-reduced vanadium		Crystal-bar vanadium	
Temperature (°C)	Lattice constant, a_o (Angstroms)	Temperature (°C)	Lattice constant, a_o (Angstroms)
26	3.0281	23	3.0218
1	3.0276	-4	3.0203
-12	3.0272	-25	3.0186
-24	3.0269	-51	3.0176
-35	3.0268	-75	3.0164
-45	3.0266	-103	3.0169
-58	3.0266	-127	3.0166
-73	3.0254	-155	3.0174
-80	3.0258	-189	3.0134
-86	3.0258		
-91	3.0251		
-96	3.0256		
-114	3.0245		
-124	3.0245		

where Θ is the characteristic temperature of the crystal, h is Planck's constant, k is Boltzmann's constant, and m_a is the mean mass of the atoms in the crystal.

$$x = \frac{\Theta}{T} \quad \text{and} \quad \phi(x) = \frac{1}{x}\int_0^x \frac{\epsilon}{e^{\epsilon} - 1}\, d\epsilon$$

Values of $\phi(x)$ in terms of x are given in the International Tabellen (23, p. 574). Hence, using the above formulas the following relationship is obtained:

$$\log_e I \propto \log_e |F_o|^2 - 2M$$

$$\log_e I \propto \left[\log_e |F_o|^2 - \left(\frac{3h^2}{m_a k \Theta} - \frac{\sin^2 \theta}{\lambda^2} \right) \right]$$

$$- \left[\left(\frac{12h^2}{m_a k \Theta} \right) \left(\frac{\sin^2 \theta}{\lambda^2} \right) \right] \quad \frac{\phi(x)}{x}$$

or

$$\log_e I \propto k_1 - k_2 \left(\frac{\phi(x)}{x} \right).$$

The results of plotting $\log_e I$ versus $\frac{\phi(x)}{x}$ for crystal-bar and bomb-reduced vanadium are shown in Figure 36. For crystal-bar vanadium the slope of the line relating $\log_e I$ and $\frac{\phi(x)}{x}$ changed at about -60°C for all reflections. However, in the case of bomb-reduced vanadium the change in slope, when observed, occurred over the range -15°C to -50°C.

The results of the investigation of single crystals of vanadium at low temperatures by means of the Weissenberg camera, in general, complement the results obtained on polycrystalline samples of vanadium. The crystals were examined for only one orientation, that being a rotation about the $[110]$ axis. It was observed that between room temperature and -115°C the symmetry of the crystal was unchanged. However, below about -70°C the $(22\bar{2})$ reflection seemed to disappear. It was possible to regain this reflection by realigning the crystal at low temperatures.

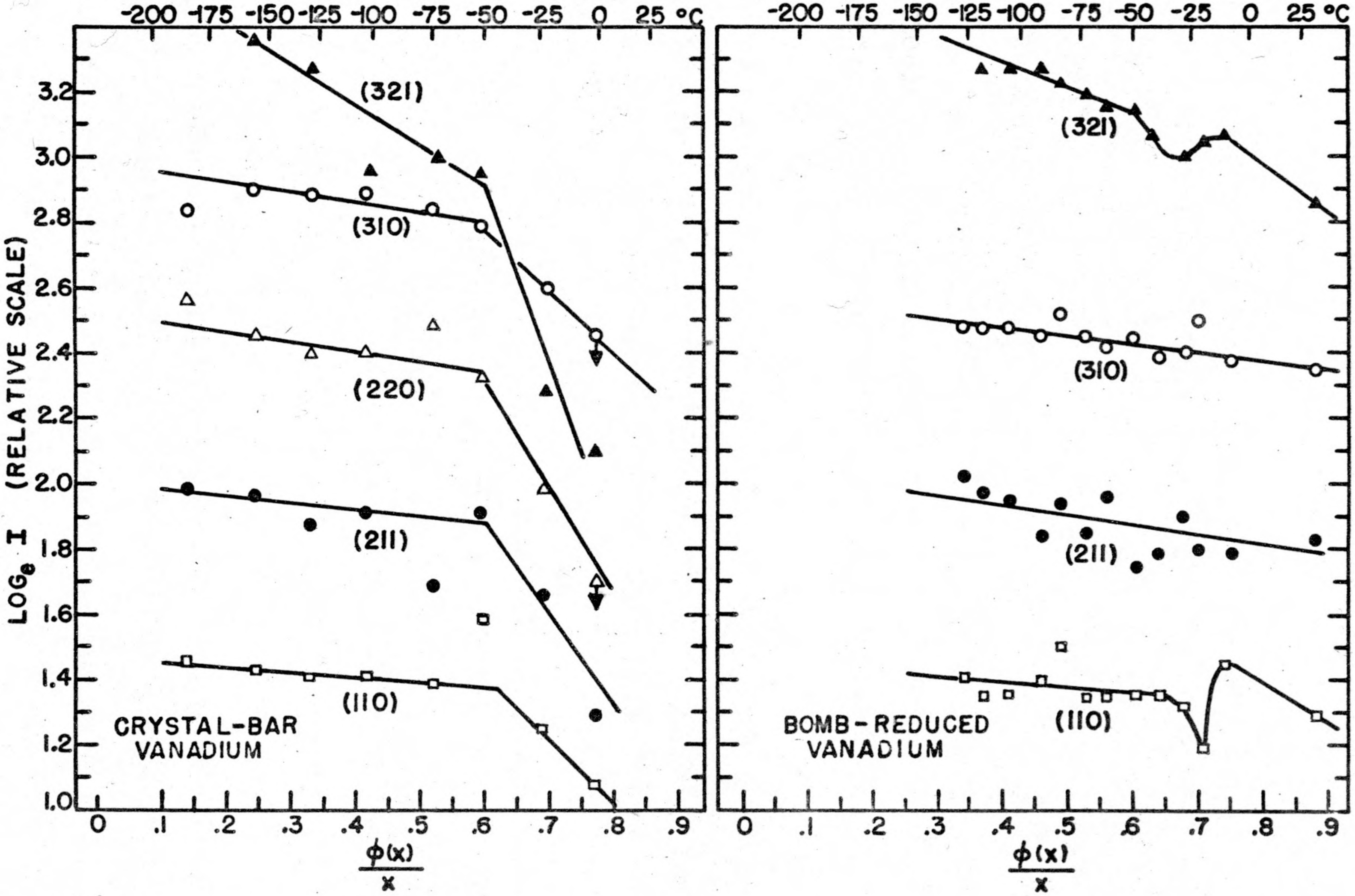

Figure 36. Temperature dependence of the intensity of x-ray reflections

The validity of the observed x-ray diffraction effects is substantiated by dilatometric and electrical resistance measurements on poly-crystalline samples of vanadium. The data obtainable from these two studies were, in general, irreproducible with regard to temperature from sample to sample and indicated that the observed effects were dependent upon the specimen composition and metallurgical history. However, the dilatometric studies indicated that there was an abnormal increase in specimen dimensions between -160°C and -140°C. Between -140°C and -80°C the sample dimensions remained practically constant and this in turn was followed by a normal expansion of the sample upon warming to room temperature. The electrical resistance studies on bomb-reduced vanadium samples between -180°C and room temperature showed a large increase in electrical resistance at about -70°C (Figure 37).

E. Internal Friction Data

The results of the low temperature internal friction investigations are shown in Figure 38. The internal friction peaks in the annealed vanadium samples were observed to be independent of the amplitude of oscillation. The peak centered about -70°C was due to the presence of hydrogen since hydrogen had been intentionally added to the wire specimen. There was some evidence for a shift of this peak

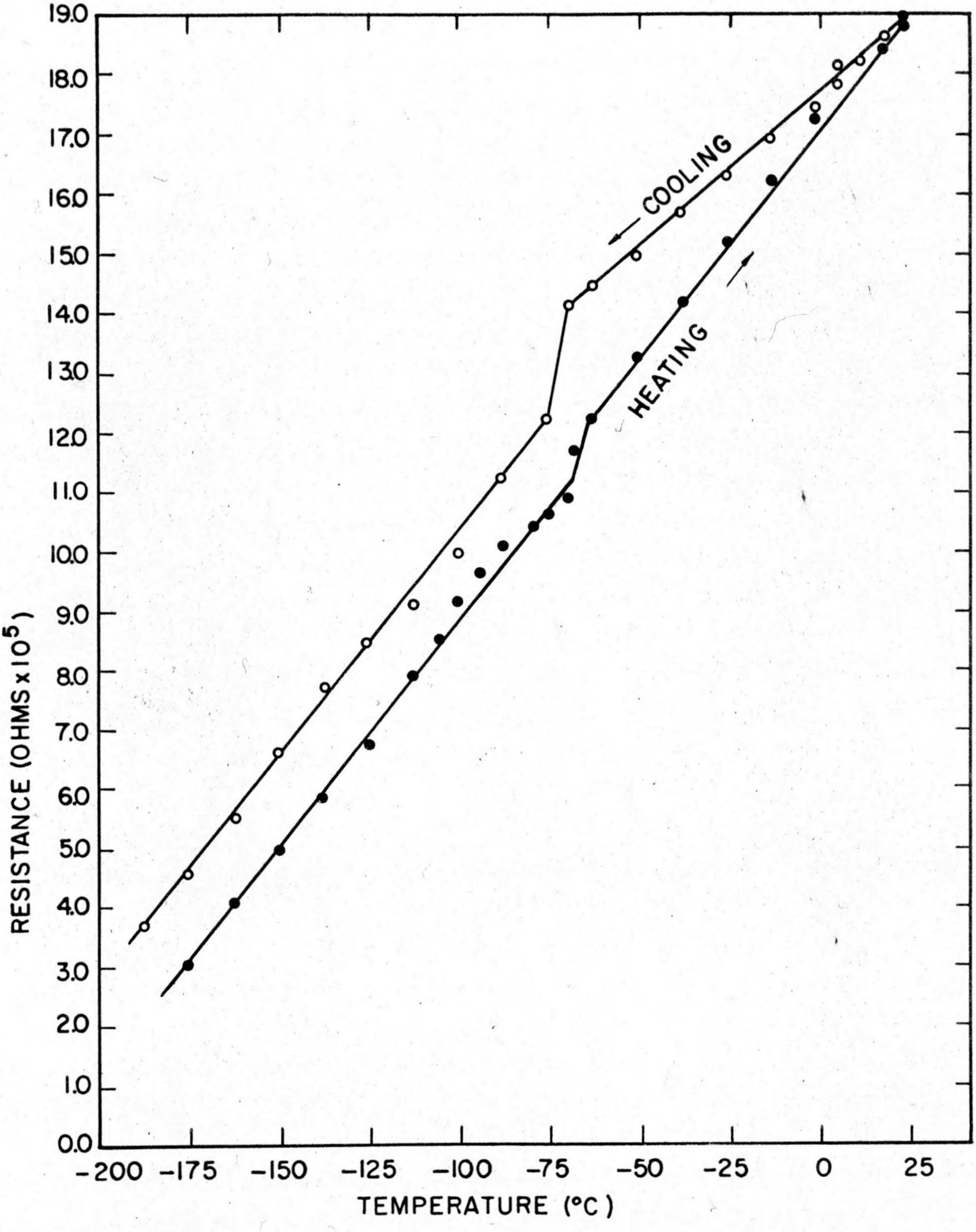

Figure 37. Electrical resistance of bomb-reduced vanadium at sub-atmospheric temperatures

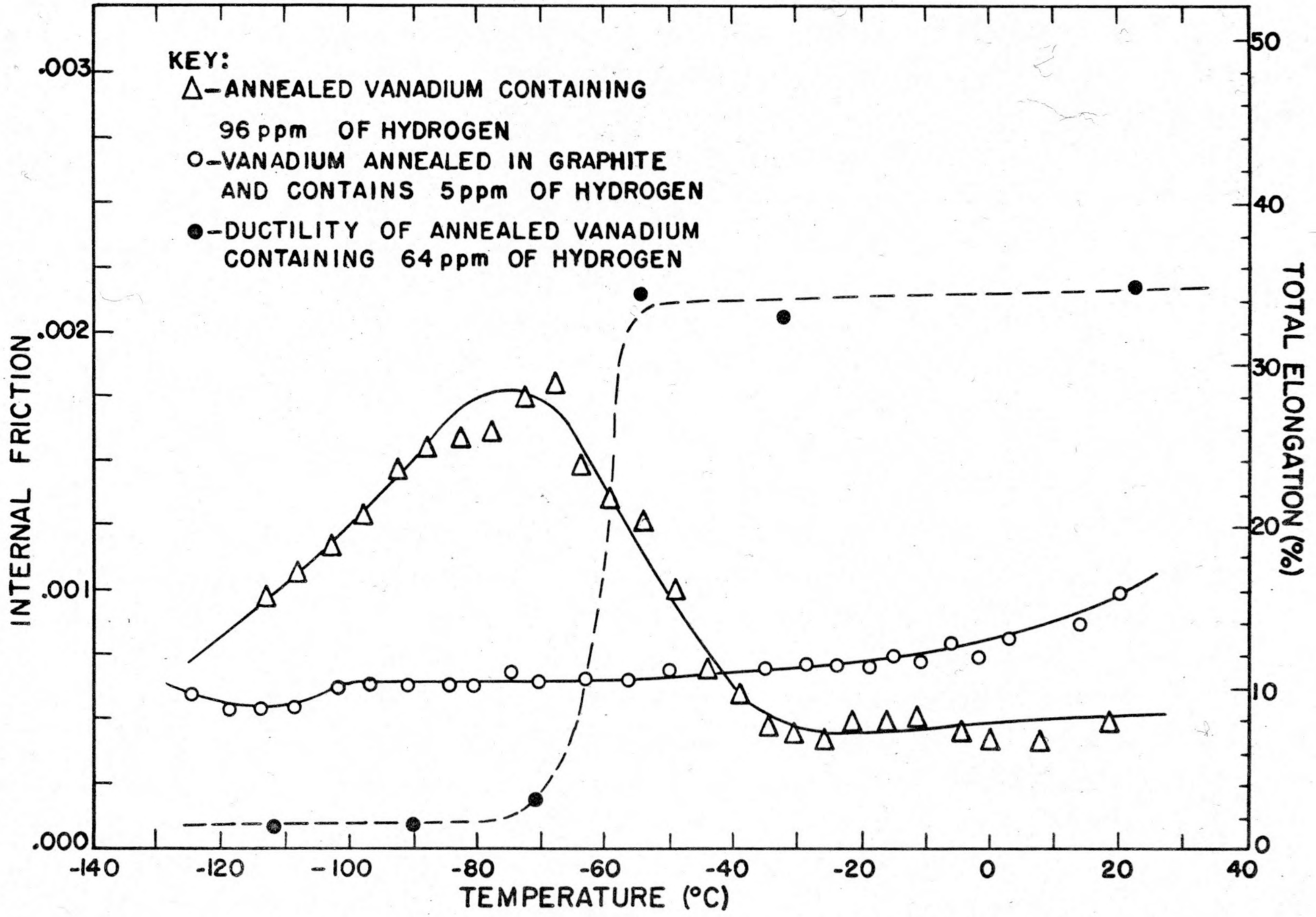

Figure 38. Internal friction of annealed vanadium

to higher temperatures when the internal friction was determined for wires containing smaller amounts of hydrogen.

The effect of annealing vanadium in graphite was to eliminate the internal friction peak at sub-zero temperatures and presumably this was due to the presence of only .0005 per cent hydrogen in the vanadium wire. Although not shown in Figure 38, internal friction peaks were observed at 173°C and 264°C. These peaks were associated with the stress-induced ordering of oxygen and nitrogen interstitials, respectively, since each of them occurred within 10°C of the oxygen and nitrogen internal friction peaks observed by Powers (15). All of the internal friction investigations were made at a frequency of oscillation of .5 cycle per second.

Superimposed upon the plot in Figure 38 is the ductility of bomb-reduced vanadium as a function of temperature. This material contained .0064 per cent hydrogen.

VI. DISCUSSION OF RESULTS

A. Presence of a Brittle-Ductile Transition

The tensile properties of vanadium conformed to the general pattern observed in body-centered cubic metals by other investigators. With decreasing test temperature, the yield strength and proportional limit of bomb-reduced vanadium were observed to increase sharply at about -65°C. Also, at about this temperature, the ductility was greatly reduced and the nature of the fractured surface of the test specimen changed from a ductile to a brittle cleavage type of failure. However, in the higher purity crystal-bar vanadium, a similar transition in tensile properties occurred at about -110°C. Hence, it can be concluded that a brittle-ductile transition occurs in bomb-reduced and crystal-bar vanadium at -65° ± 10°C and -110° ± 10°C, respectively.

The results of the bend tests on bomb-reduced vanadium likewise indicated the existence of a brittle-ductile transition in bomb-reduced vanadium. At temperatures above -65°C, the vanadium test specimens could be bent fifteen degrees with respect to the horizontal without fracturing, whereas below this temperature the specimens could be bent only a slight amount before fracture occurred.

In both bomb-reduced and crystal-bar vanadium there was evidence to indicate that vanadium could regain some ductility below -140°C. This was shown by the curves of ductility versus temperature for crystal-bar vanadium (Figure 12) and the curve of deflection versus temperature for bomb-reduced vanadium (Figure 16). However, the degree of ductility regained below -140°C was small.

B. Effect of Metallic and Non-Metallic Elements on the Brittle-Ductile Transition

The results of the investigation on the effects of metallic additions to vanadium show maximum and minimum effects. Similar anomalous effects were observed by Olds and Rengstorff (24) in their investigation on the effects of small amounts of alloying elements on the transition temperature in molybdenum. Likewise, Abrahamson and Grant (25) reported similar effects of small amounts of alloying elements on the transition temperature in chromium.

An indication of the reliability of the data obtained in this investigation is shown in Table 7. In this tabulation, the results obtained by Rostoker, Yamamoto, and Riley (26) in an investigation of the room temperature ductility of binary vanadium-base alloys are compared with the room temperature results of this investigation.

Table 7. Room temperature ductility of vanadium-base alloys

Alloy composition	Classification of alloy[a]	
	Rostoker, et al.	This investigation
V + 1.0%Zr	Ductile	Ductile
V + 3.0%Zr	Brittle	Brittle
V + 1.0%Ti	Brittle	Brittle
V + 2.5%Ti	Ductile	Ductile
V + 1.0%Mo	Brittle	Brittle
V + 1.0%Cr	Brittle	Ductile

[a] In this tabulation, an alloy was classed as ductile if it underwent 10 per cent or greater elongation.

As can be seen in Table 7, comparable results were obtained in both investigations with the exception of the chromium alloy. However, this exception is probably due to the fact that the vanadium used by Rostoker, et al. in their investigation contained more impurities than the vanadium used in this investigation since the room temperature ductility of the vanadium used by Rostoker, et al. was only six per cent elongation and the corresponding ductility of the vanadium used in this investigation was about 35 per cent elongation. Hence, it can be concluded that some significance can be attached to the curves shown in Figure 20, at least for metallic additions greater than .5 per cent.

The effects of the metallic additions on the temperature of the brittle-ductile transition cannot be explained entirely. However, it is suggested that the observed effects are due to one or more of the following factors: interaction with dislocations by the atoms in substitutional solid solution in vanadium; formation of more stable oxides, nitrides, carbides, or hydrides by the metal added than the corresponding ones of vanadium; and impurity phases going into solid solution or exceeding the solubility limit of certain metals in vanadium. The impurity phases are oxides, nitrides, carbides, or hydrides which are initially present in vanadium or are formed as a result of adding a metal to vanadium.

As mentioned in a previous section, atoms forming dilute substitutional solid solutions can relieve the hydrostatic stress around an edge dislocation by diffusing to the regions around the dislocation where the lattice is locally compressed and expanded and thus anchor the dislocation. However, the shear stress around a screw dislocation is not relieved by this process. Zener (27) has suggested that in more concentrated substitutional solid solutions, where a solute atom may have another solute atom as a nearest neighbor, the shear stress around a screw dislocation may be relieved. Hence, it would be expected that the transition temperature of vanadium would be raised to higher temperatures upon adding increasing amounts of the substitutional alloying element since, with increasing solute concentration, the entire dislocation segment would be anchored more firmly. If the dislocation is anchored more firmly, then a higher temperature is necessary such that sufficient thermal energy is available to enable the dislocation to break away from its anchoring atmosphere. This factor may have been particularly responsible for the observed general increase in transition temperature of vanadium when chormium, molybdenum, and tantalum additions were made.

The second factor suggested as responsible for the observed effects of the metallic elements on the brittle-ductile transition in vanadium was the formation of more stable oxides, nitrides, carbides, or hydrides by the substitutional alloying elements. The free energies of formation of the most stable oxides of the metals added to vanadium are listed in Table 8. The oxides of the metals listed in Table 8 with free energy values larger than the one given for vanadium oxide, i.e., ThO_2, ZrO_2, and TiO, would be expected to form at the expense of the oxygen associated with vanadium upon adding either thorium, zirconium, or titanium. However, the oxides of tantalum, chromium, and molybdenum would not be expected to form upon adding either of these metals to vanadium since their oxides are less stable than vanadium oxide. Hence, it is suggested that when small amounts of zirconium, thorium, and titanium are added to

The effects of the metallic additions on the temperature of the brittle-ductile transition cannot be explained entirely. However, it is suggested that the observed effects are due to one or more of the following factors: interaction with dislocations by the atoms in substitutional solid solution in vanadium; formation of more stable oxides, nitrides, carbides, or hydrides by the metal added than the corresponding ones of vanadium; and impurity phases going into solid solution or exceeding the solubility limit of certain metals in vanadium. The impurity phases are oxides, nitrides, carbides, or hydrides which are initially present in vanadium or are formed as a result of adding a metal to vanadium.

As mentioned in a previous section, atoms forming dilute substitutional solid solutions can relieve the hydrostatic stress around an edge dislocation by diffusing to the regions around the dislocation where the lattice is locally compressed and expanded and thus anchor the dislocation. However, the shear stress around a screw dislocation is not relieved by this process. Zener (27) has suggested that in more concentrated substitutional solid solutions, where a solute atom may have another solute atom as a nearest neighbor, the shear stress around a screw dislocation may be relieved. Hence, it would be expected that the transition temperature of vanadium would be raised to higher temperatures upon adding increasing amounts of the substitutional alloying element since, with increasing solute concentration, the entire dislocation segment would be anchored more firmly. If the dislocation is anchored more firmly, then a higher temperature is necessary such that sufficient thermal energy is available to enable the dislocation to break away from its anchoring atmosphere. This factor may have been particularly responsible for the observed general increase in transition temperature of vanadium when chormium, molybdenum, and tantalum additions were made.

The second factor suggested as responsible for the observed effects of the metallic elements on the brittle-ductile transition in vanadium was the formation of more stable oxides, nitrides, carbides, or hydrides by the substitutional alloying elements. The free energies of formation of the most stable oxides of the metals added to vanadium are listed in Table 8. The oxides of the metals listed in Table 8 with free energy values larger than the one given for vanadium oxide, i.e., ThO_2, ZrO_2, and TiO, would be expected to form at the expense of the oxygen associated with vanadium upon adding either thorium, zirconium, or titanium. However, the oxides of tantalum, chromium, and molybdenum would not be expected to form upon adding either of these metals to vanadium since their oxides are less stable than vanadium oxide. Hence, it is suggested that when small amounts of zirconium, thorium, and titanium are added to

Table 8. Free energy of formation of metal oxides[a]

Metal oxide	$-\Delta F°$ per Oxygen atom at 298.16°K (Kilo calories)
ThO_2	139.6
ZrO_2	123.9
TiO	116.9
VO	93.5
Ta_2O_5	91.3
Cr_2O_3	84.3
MoO_2	60.7

[a] The free energies of formation were obtained from a tabulation prepared by Coughlin (28).

vanadium, these elements react with the oxygen in vanadium and form a second phase. The result of this action alone should be a lowering of the transition temperature of vanadium, since oxygen in vanadium solid solution raises the transition temperature. However, the lowering effect resulting from the formation of oxides is partially offset by the dislocation interaction factor, as described previously, which tends to raise the transition temperature. A similar affinity for the nitrogen, carbon, and hydrogen in vanadium by zirconium, thorium, and titanium is expected, however, adequate thermodynamic data were not available to substantiate this conclusion.

The increased solubility of impurity phases in the vanadium matrix at higher concentrations of a metallic addition is shown by Figures 30, 31, and 32 for molybdenum additions and Figures 24, 25, and 26 for titanium additions. The microstructures show that when one per cent of either molybdenum or titanium is added to vanadium, the solubility for the impurity phase present in .5 per cent alloys is increased. This increase in solubility for the impurity phase results in a brittle material with a high transition temperature as shown by Figure 20. Hence, it may be concluded that when oxides, nitrides, carbides or hydrides are in solution, their effect is to raise the transition temperature more than when present as a second phase in the vanadium matrix. The anomalous increase in solubility of the impurity phase in molybdenum-vanadium and in titanium-vanadium alloys which contain one per cent or greater amounts of molybdenum or titanium may be due to the shape of the corresponding ternary phase diagram surface.

When 2.5 per cent titanium was added to vanadium a finely dispersed second phase was formed which resulted in a material with a transition temperature lower than that of pure vanadium. This anomaly is not explainable on the basis of the present experimental evidence.

The transition temperature of vanadium was raised considerably upon adding 4.0 per cent zirconium. This effect is believed to be associated with the formation of the compound V_2Zr along the grain boundaries of vanadium (Figure 29). This hard brittle phase along the grain boundaries prevents the uniform distribution of the applied stress among the grains. Hence, the stress level within some grains may increase to such a point that the cleavage strength is exceeded and a brittle crack forms and propagates through the metal. A similar effect for thorium additions to vanadium might be expected since the solubility of thorium in vanadium is slight[a]. However, in this binary system, compounds are not formed and at the concentrations of thorium in vanadium investigated, a soft envelope of substantially pure thorium is formed at the grain boundaries. Thus, the vanadium alloys which contain small amounts of thorium rupture along the grain boundaries when the strength of the thorium is exceeded (Figure 23).

A comparison of the effects of hydrogen, nitrogen, carbon and oxygen on the brittle-ductile transition temperature in vanadium has been shown in Figure 34. As can be seen in this figure, the general effect of adding these interstitial elements was to raise the transition temperature of vanadium. On a weight per cent basis, hydrogen was the most effective in raising the transition temperature of vanadium, and carbon

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[a] Refer to Table 1, p. 9.

was the least effective. Oxygen and nitrogen had an effect intermediate to that of hydrogen and carbon. Oxygen and nitrogen are apparently equally effective in raising the transition temperature of vanadium. On the basis of limited experimental data, the amount of hydrogen necessary to cause room temperature embrittlement in vanadium is between .010 and .025 per cent hydrogen. Likewise, the amount of oxygen and nitrogen in vanadium necessary to cause room temperature embrittlement is approximately 0.2 per cent. The amount of carbon necessary to cause room temperature embrittlement of vanadium is greater than 0.4 per cent.

C. Mechanism of the Brittle-Ductile Transition and Variation of Physical Properties through the Transition Temperature

The results of this investigation seem to substantiate the contention that the brittle-ductile transition is due to the interaction of dislocations with minute amounts of interstitial impurity atoms. In the case of vanadium these interstitials appear to be hydrogen, oxygen, and nitrogen and to a lesser extent carbon. Furthermore, the results indicated that the mechanism of the dislocation-solute atom interaction was not substantially different from that proposed by Cottrell (20) and extended by Nabarro (21). However, it is concluded on the basis of the variation of the physical properties through the transition temperature, which

Table 9. Mechanical and physical properties of vanadium

Property	Material	Temperature at which property changes	Explanatory remarks or manner determined
1. Brittle-ductile transition	Bomb-reduced vanadium	-65° ± 10°C	Tensile test
2. Brittle-ductile transition	Bomb-reduced vanadium	-70° ± 10°C	Bend test
3. Brittle-ductile transition	Crystal-bar vanadium	-110° ± 10°C	Tensile test
4. Young's Modulus	Bomb-reduced vanadium	-55° ± 10°C	Tensile test
5. Young's Modulus	Crystal-bar vanadium	-45° ± 10°C -130° ± 10°C	Tensile test
6. Brittle-ductile transition	Vanadium + metallic elements	-65°C	All elements raised the transition temperature
7. Brittle-ductile transition	Vanadium + non-metallic elements	-120°C	All elements raised the transition temperature
8. Lattice constant	As-annealed bomb-reduced vanadium	none	Normal thermal contraction of lattice
9. Lattice constant	As-rolled crystal-bar vanadium	-75°C, -155°C	Possibly due to ordering of interstitials

Table 9. (Continued)

Property	Material	Temperature at which property changes	Explanatory remarks or manner determined
10. Intensity of x-ray reflections	As-annealed bomb-reduced vanadium	-15°C to -50°C	
11. Intensity of x-ray reflections	As-rolled crystal-bar vanadium	- 60° ± 10°C	
12. Thermal expansion	As-arc-melted bomb-reduced vanadium	-140°C,-80°C	Possibly due to ordering of interstitials
13. Electrical resistance	As-arc-melted bomb-reduced vanadium	-70°C ± 10°C	Possibly due to ordering of interstitials
14. Internal friction	Annealed crystal-bar vanadium	-70°C	Possibly due to ordering of hydrogen atoms or ions

have been summarized in Table 9, that the transition in vanadium is possibly accentuated by the occurrence of ordering of the hydrogen atoms or ions in the vanadium lattice at about -65°C. The basis for this conclusion follows from the following experimental observations:

1. An internal friction peak centered about -70°C which is due to the presence of hydrogen.
2. The change in lattice constant at -75°C in as-rolled crystal-bar vanadium.
3. The change in electrical resistance of vanadium at about -70°C.
4. The change in the thermal expansion of vanadium at about -80°C.

Hence, the brittle-ductile transition in bomb-reduced vanadium at -65° ± 10°C is postulated to be due to the presence of oxygen, nitrogen, and carbon in the vanadium lattice and hydrogen atoms or ions assuming ordered positions in the lattice. The brittle-ductile transition in crystal-bar vanadium, however, occurs at the lower temperature of -110° ± 10°C probably because it contains less oxygen, nitrogen, and carbon.[a] The resulting effect on screw-dislocations of hydrogen atoms or ions assuming preferred ordered positions around the dislocations would not be unlike the stress-induced ordering

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[a] Refer to Table 1, p. 7.

of interstitials around screw dislocations as described by Nabarro (21).

The increase in ductility of vanadium at temperatures below -140°C cannot be explained on the basis of the present experimental evidence, but it is believed to be a valid experimental observation. Roberts and Rogers (10a) observed a similar effect in hydrogenated vanadium.

VII. SUMMARY AND CONCLUSIONS

Mechanical tests have been made on vanadium at sub-atmospheric temperatures to determine whether or not this metal undergoes a brittle-ductile transition. Also, the effect of small amounts of metallic and non-metallic additions on the brittle-ductile transition in vanadium has been investigated. Finally, some of the physical properties of vanadium have been investigated through the transition temperature for the purpose of determining the mechanism of the brittle-ductile transition in vanadium. A summary of the results and conclusions are as follows:

1. There is a brittle-ductile transition in bomb-reduced vanadium at -65° ± 10°C. The transition occurs at the lower temperature of -110° ± 10°C in crystal-bar vanadium probably because of its higher purity. Vanadium can regain some ductility at temperatures below -140°C and this is believed to be due to an ordering phenomenon.

2. Small amounts of chromium, molybdenum, tantalum, zirconium, titanium, and thorium, when added to vanadium, have anomalous maxima and minima effects on the transition temperature of vanadium. The only metallic additions which lower the transition temperature of vanadium are titanium when present in amounts of 2.5 weight per cent or greater and possibly thorium when present in amounts less than one weight per cent.

The effect of adding small amounts of either hydrogen, oxygen, nitrogen, or carbon to vanadium is to raise the transition temperature. Hydrogen is the most effective in raising the transition temperature and carbon is the least effective. Oxygen and nitrogen have an effect intermediate to that of hydrogen and carbon.

3. The brittle-ductile transition in vanadium is due to the interaction of dislocations with minute amounts of the interstitial solute atoms hydrogen, oxygen, nitrogen, or carbon. The transition in vanadium is believed to be accentuated by hydrogen atoms or ions assuming ordered positions in the vanadium lattice at temperatures below -65°C. This conclusion is based on the change of the physical properties of vanadium near the transition temperature. There was no evidence for a low-temperature allotropic transformation in vanadium.

VIII. LITERATURE CITED

1. Rostoker, W., *J. Metals*, *9*, 971 (1957).

2. Bechtold, J. H., and Shewmon, P. G., *Trans. Amer. Soc. Metals*, *46*, 397 (1954).

3. Bechtold, J. H., *J. Metals*, *5*, 1469 (1953).

4. Wessel, E. T., *J. Metals Trans.*, *9*, 930 (1957).

5. Geil, G. W., and Carwile, N. L., *J. Research Natl. Bur. Standards*, *45*, 129 (1950).

6. Sully, A. H., "Chromium", New York, N. Y., Academic Press, Inc., (1954).

7. Bechtold, J. H., *Acta Met.*, *3*, 249 (1955).

8. Wessel, E. T., *Trans. Amer. Soc. Metals*, *49*, 149 (1957).

9. Pugh, J. W., *J. Metals Trans.*, *9*, 1243 (1957).

10a. Roberts, B. W., and Rogers, H. C., *J. Metals Trans.*, *8*, 1213 (1956).

10b. Rostoker, W., and Yamamoto, A., *Trans. Amer. Soc. Metals*, *46*, (1954).

11a. Levingston, M. L., and Rogers, B. A., "The Thorium-Vanadium System", United States Atomic Energy Commission, Report No. AECD-3602, (1953).

11b. Allen, N. P., Kubaschewski, O., and von Goldbeck, O., *J. Electrochem. Soc.*, *98*, 417 (1951).

11c. K̂e, T. S., *Phys. Rev.*, *74*, 9 (1948).

12. Chang, Lo-Ching, and Gensamer, M., *Acta Met.*, *1*, 483 (1953).

13. Eldin, A. S., and Collins, S. C., *J. Appl. Phys.*, *22*, 1296 (1951).

14. Marx, J. W., Baker, G. S., and Sivertsen, J. M., *Acta Met.*, *1*, 193 (1953).

15. Powers, R. W., *Acta Met.*, *2*, 604 (1954).

16. Rostoker, W., and Yamamoto, A. S., Trans. Amer. Soc. Metals, 47, 1015 (1955).

17-18. Seybolt, A. U., and Sumsion, H. T., J. Metals Trans., 5, 292 (1953).

19. Roberts, B. W., Phys. Rev., 100, 1257 (1955).

20. Cottrell, A. H., Effect of Solute Atoms on the Behavior of Dislocations, in "Report of a Conference on Strength of Solids", p. 30, London, England, The Physical Society, (1948).

21. Nabarro, F. R. N., Mechanical Effects of Carbon in Iron, in "Report of a Conference on Strength of Solids", p. 38, London, England, The Physical Society, (1948).

22. Bruckner, W. H., J. Welding, 29, 467-s (1950).

23. "Internationale Tabellen zur Bestimmung von Kristallstrukturen", Vol. 2, Berlin, Germany, Gebruder Borntraeger, (1935).

24. Olds, L. E., and Rengstorff, G. W. P., J. Metals Trans., 9, 468 (1957).

25. Abrahamson, II, E. P., and Grant, N. J., Trans. Amer. Soc. Metals, 50, to be Published (1958).

26. Rostoker, W., Yamamoto, A. S., and Riley, R. E., Trans. Amer. Soc. Metals, 48, 565 (1956).

27. Zener, C., Phys. Rev., 71, 34 (1947).

28. Coughlin, J. P., "Contributions to the Data on Theoretical Metallurgy, XII. Heats and Free Energies of Formation of Inorganic Oxides", U. S. Dept. Int., Bur. Mines Bull. 542, (1954).