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RESEARCH AND DEVELOPMENT ON THE EFFECTS OF HIGH PRESSURE AND TEMPERATURE ON VARIOUS ELEMENTS AND BINARY ALLOYS

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FOREWORD

This report was prepared by GE Metallurgical Products Department and General Electric Research Laboratory, under USAF Contract No. AF 33(616)-5995. This contract was initiated under Project No. 7351, "Metallic Materials", Task No. 73517, "Unique Metallic Materials and Techniques. " The work was administered under the direction of the Materials Central, Directorate of Advanced Systems Technology, Wright Air Development Division, with Mr. S. A. Worcester acting as project engineer.

This report covers work conducted from June 1958 to October 1959.

This report is divided into three parts. Part A is an account of the study made by E. W. Goliber and K. H. McKee at the GE Metallurgical Products Department, Detroit, Michigan, on the possibility of using high pressure and temperatures to create new types of alloys, and to modify the properties of existing ones.

Part B describes the use of x-ray diffraction analysis at pressure to following the transformations occurring in metals and metallic compounds. This phase of the program was carried out by J. S. Kasper and R. H. Lewinski at the GE Research Laboratory, Schenectady, New York.

In addition to these structural studies, an exploratory survey has been made at the GE Research Laboratory by J. E. Hilliard, J. W. Cahn, and V. A. Phillips on the effects of high pressure on the kinetics of phase transformation in steel and alloys of copper-beryllium, lead-tin, gold-nickel, and aluminum-copper. This work is described in Part C together with a summary of a theoretical study of the effect of pressure on phase equilibria in binary systems.

ABSTRACT

An investigation has been made of the effect of pressure on the properties and kinetics of transformation in various alloy systems. Many of the experiments were exploratory and yielded no evidence for irreversible changes with pressures of up to 100,000 atm at elevated temperatures. However, a shift was observed in the gamma loop of the iron-chromium system from 12.5 to about 20 per cent chromium. Evidence for a similar shift in the gamma loop of the iron-aluminum system was also found. Pressure heat treatment of a tool steel gave a refinement of the austenite grain size and an improvement in the distribution of carbides.

An apparatus for x-ray diffraction analysis at pressures up to 35,000 atm has been constructed, and observations have been made on the bismuth I to II transition.

In the kinetic experiments it has been found that pressure markedly decreases the transformation rate of austenite to pearlite and the precipitation rate in the systems: aluminum-copper, copper-beryllium, lead-tin, and gold-nickel.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

I. Perlmutter

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Chief, Physical Metallurgy Branch
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RESEARCH AND DEVELOPMENT ON THE EFFECTS OF HIGH PRESSURE AND TEMPERATURE ON VARIOUS ELEMENTS AND BINARY ALLOYS*

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PART A

INTRODUCTION

The purpose of this project was to study the effects of the application of high pressures and temperatures on selected elements and binary alloys to determine whether new metallic structures of existing alloys or wholly new alloys can be produced. The program was designed to be exploratory in nature. Some of the studies dealt with metals and alloys that were of interest as structural materials whereas other studies dealt primarily with mechanisms and the alloys involved were of secondary interest.

The more important conditions and mechanisms which were considered in selecting alloy systems for study under pressure are given below. In some cases there was little-known theoretical basis for expecting that these desired changes would occur.

1. Lattice transformations which are likely to occur under pressure such as the transformation from body-centered cubic to the denser face-centered cubic structure.
2. Changes in solubility which might occur under pressure.
3. Suppression of undesirable phases and the favoring of desirable phases under pressure.
4. Systems in which alloying is predicated by relationships such as atomic sizes, crystal structures, etc., but where alloying is difficult to effect at atmospheric pressure because of the volatility of one component. In these systems extremely high pressures may not be necessary to contain the components.

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5. Atom compressibility as indicated from considerations of atomic structure and/or experimental work of P. W. Bridgman.(1)

This phase of the program was designed to uncover primarily nonreversible changes, but it should be noted that the products of some reversible changes would have been detected by the studies made. Thus, increased solubility under pressure, even though reversible, might be indicated by the presence of a fine dispersion or precipitate. Such a result, of course, might prove quite valuable. Furthermore, the compressing of an atom itself would appear to be almost certainly reversible, but nonreversible structural modifications might have been attained by temporarily compressing atoms of one variety.

The high pressure equipment employed had been in use in the High Pressure Laboratories of the Metallurgical Products Department and in the Research Laboratory of General Electric Company, and no effort was expended as a part of this contract in modifying the basic design of the apparatus. Experiments were conducted up to pressures of 100,000 atmospheres and temperatures to 2500°C.

The experimental results are grouped according to the nature of the changes anticipated and not in the order in which the experiments were conducted. Because of the availability of materials and special equipment required and because of the limited time for the program it was considered advisable to run many of the experiments simultaneously. It was felt that this would not detract seriously from the results obtained since the individual studies were exploratory in nature and relatively brief. By so proceeding it was possible to explore a larger number of systems in minimum time, but it should be recognized that some obvious refinements should have been made and would have been made had the runs been made sequentially.

EXPERIMENTAL PROCEDURE

As previously noted, the pressure apparatus employed is capable of attaining at least 100,000 atm and temperatures in excess of 2000°C. Originally, it was planned to carry out experiments at 50,000 atm pressure at a suitable temperature, and at holding times of up to 5 minutes so as not to cause undue strain on the pressure apparatus. Sample size was 0.375 inch in diameter x 0.500 inch long. However, as early experiments proceeded, several pressure vessel failures occurred, and in an attempt to remedy the situation the sample diameter was reduced to 0.200 inch and the thickness of the liner material correspondingly increased. This modification proved so successful that later experiments were extended to 100,000 atm and time at temperature was frequently extended to 30 minutes with no difficulty. In an effort to retain products of high pressure-temperature treatments all specimens were quenched under pressure by removing power under pressure and utilizing the apparatus as a heat sink. In most cases, specimens had cooled to less than 200°C within 60 seconds after power removal.

Al_2O_3 was the principal ceramic liner material used. In cases where extensive reaction occurred between the specimen and the liner material, such as occurred in alloys containing titanium, MgO was employed with good success.

Sample temperature during a pressure run was measured by means of a Pt/Pt-Rh thermocouple encased in a fired alumina tube which was carefully inserted in a 1/16-inch-diameter hole drilled perpendicular to the long axis of the specimen. Temperature was then measured by means of a manually recorded potentiometer. In the beginning, it was hoped that thermocouples would only be employed initially to calibrate a system under study and that subsequent runs could be made without thermocouples using power input as a measure of temperature. Such a procedure would shorten the time necessary in performing an experiment and would remove possible sources of contamination. This technique worked well early in the program, but as experiments progressed it was found that some variation existed in the plot of temperature vs power input from sample to sample in some systems. Where this condition was encountered, thermocouples were used in all runs on that system.

Although the program was planned to uncover nonreversible changes, it was hoped that by plotting thermocouple data, some added information might be gained as to allotropic transformations, reactions etc., occurring during the course of a run. However, a careful study of the temperature data obtained indicated that the method used was insensitive to such changes.

The highest purity starting materials obtainable were used in all systems studied. In the initial experiments solid samples were used. However, when pressure vessel failures were encountered with these materials, prepressed powder samples were substituted in an effort to correct the problem. As the program progressed with no further difficulty, solid samples were once again used with good success.

Powder samples were weighed, blended for 4 hours at 60 rpm under argon, pressed to the correct size at 15 tsi, and stored under argon prior to use. Solid samples were pre-cast in a multihearth arc furnace. The "buttons" were melted at least twice under argon to ensure homogeneity, and dummy titanium samples were included in each run as getters during melting.

The results of the experiments were analyzed by x-ray diffraction, light and electron microscopy, Rockwell hardness, microhardness, etc., with x-ray diffraction and metallography being the principal tools of analysis.

A General Electric XRD-3 diffractometer and a 14.32 cm Debye-Scherrer powder camera were employed for x-ray diffraction analysis, with the selection of the target material depending on the system under study. Where possible, the specimens were analyzed in the same condition as they came from the pressure cell, with only light grinding and etching necessary to remove reaction products at the specimen surfaces. Chemical analyses were usually not made, the analysis being taken as that of the sample as mixed. Since the high pressure runs frequently resulted in laminated specimens, a fresh surface could be easily examined with a minimum of specimen preparation. Typical specimens before and after pressure treatment are shown in Fig. 1.

Because of the nature of the pressure equipment used it was impossible to conduct experiments in the pressure vessel at atmospheric pressure. Therefore, where control specimens made at atmospheric pressure were deemed necessary for comparison purposes, these were heat treated in a muffle furnace at the required temperature and water quenched. In cases where powder samples were used in the high pressure runs, control experiments were made with high-purity cast alloys of the same compositions. These controls were considered valid for detecting gross changes in the pressure-treated specimens, but it was apparent that they would not be suitable for detecting slight changes in solubility, etc., because of the different starting materials used.

In all, more than 200 runs were made and analyzed at the Metallurgical Products Department during the course of the project, with 150 of these at high pressures and temperatures.

In some systems, only a few runs were necessary to draw a conclusion, whereas with others many runs were needed.

EXPERIMENTAL RESULTS

Investigations on the Formation or Stabilization of Phases

Chromium

Chromium has commanded considerable attention in recent years because of its resistance to oxidation and because of its relatively high melting point. In its usual body-centered cubic form, however, it is extremely brittle at room temperature and it is therefore limited in its use as a structural material. There is some evidence for a transformation from body-centered cubic to the face-centered cubic structure just below the melting point,(2) and in this form it should be considerably more ductile. Chromium is of particular interest as a subject for high-pressure research because the transition from body-centered cubic to the denser face-centered cubic form is favored by pressure.

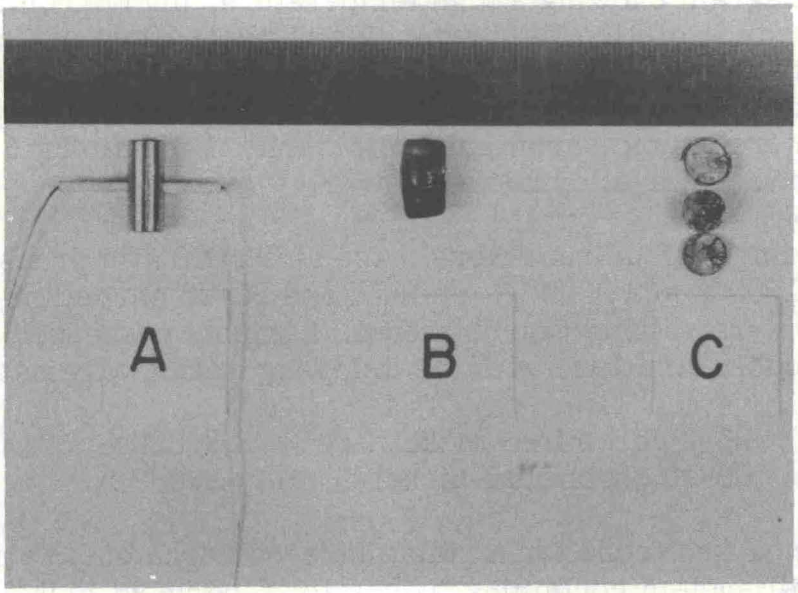

Fig. 1 Pressure samples. (A) Specimen ready for pressure run with Pt/Pt-Rh thermocouple and alumina insulating tube, but without other cell components. (B) Specimen after pressure run. Severely deformed but intact. (C) A specimen which was severely laminated during pressure run.

Seven runs were made at 50,000 atm pressure and temperatures of 1800° to 2400°C on a sample of high-purity chromium containing 0.019 per cent nitrogen as the principal impurity.

Analysis by x-ray diffraction showed that no nonreversible transformations had occurred. All patterns showed the typical reflections for body-centered cubic chromium. The lattice parameter was found to be 2.884 A, in good agreement with that reported by Swanson and Tatge (2.8839 A).(3) In the sample heated to 2400°C, extensive reaction with the Al_2O_3 liner occurred and metallographic examination of this sample showed three or more phases present with acicular platelets and globular oxides predominating in a chromium matrix.

Nothing was observed which would indicate that a transformation from body-centered cubic to the face-centered cubic structure had occurred.

Chromium-Nickel

It has been reported that a chromium base face-centered cubic alloy can be stabilized by the addition of 30 per cent nickel and 1 per cent molybdenum.(4) Moreover, Stein and Grant(5) have proposed a binary chromium-nickel constitutional diagram showing a high temperature, high chromium face-centered cubic solid solution field extending to about 30 wt per cent nickel. Efforts to stabilize such a phase without alloy additions have been unsuccessful. It was thought that applications of pressure and temperature might produce a stable face-centered cubic chromium solid solution containing 5 to 20 wt per cent nickel without other alloy additions.

Accordingly, four runs were made at 50,000 atm pressure at 1650°, 1750°, 1850°, 1900°, and 2000° C on 95-5 and 80-20 chromium-nickel alloys. Examination by x-ray diffraction showed all samples possessed a single-phase body-centered cubic structure with the following lattice parameters:

95-5 chromium-nickel = 2.882 A
80-20 chromium-nickel = 2.887 A

Thus, no evidence was found for a stable face-centered cubic structure in the chromium-nickel system containing from 0 to 20 per cent nickel.

Iron-Chromium

In the iron-chromium system, a face-centered cubic phase known as the gamma phase reportedly extends into a body-centered cubic region up to 12.5 per cent chromium between temperatures of about 900° to 1400°C. This is known as the gamma loop. Thus, iron-chromium represents a system in which both the face-centered cubic and the body-centered cubic phases are known to exist. Moreover, in the phase diagram, the two phases border upon one another. If pressure has any appreciable effect on the transformation from body-centered cubic to the denser face-centered cubic structure, the gamma loop should be displaced to compositions above 12.5 per cent chromium under the influence of pressure.

Samples of composition 10, 12.5, 15, and 20 wt per cent chromium were cast. Sections were submitted for carbon analysis and found to contain 0.03 per cent carbon.

Specimens were heated to 1000°, 1100°, and 1200°C at atmospheric pressure and at 100,000 atm and were subsequently quenched.

Microscopic examination of the specimens treated at atmospheric pressure revealed a refined pseudo-martensitic structure (Fig. 2) for the 10 per cent chromium composition, whereas examination of the 12.5, 15, and 20 per cent chromium compositions showed a coarse-grained, single-phase structure (Fig. 3). This may be taken as an indication of the formation of the gamma loop up to about 10 to 12.5 per cent chromium which is in agreement with that reported by Adcock(6) in his work on determining the position of the gamma loop in the iron-chromium system.

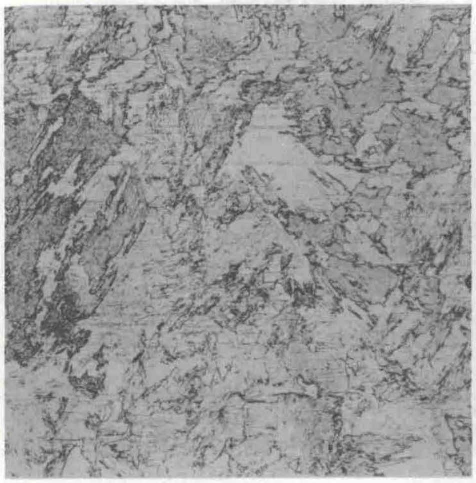

Fig. 2 Iron-(10 wt per cent chromium). Quenched after holding for 30 minutes at 1100°C, atmospheric pressure. 100X

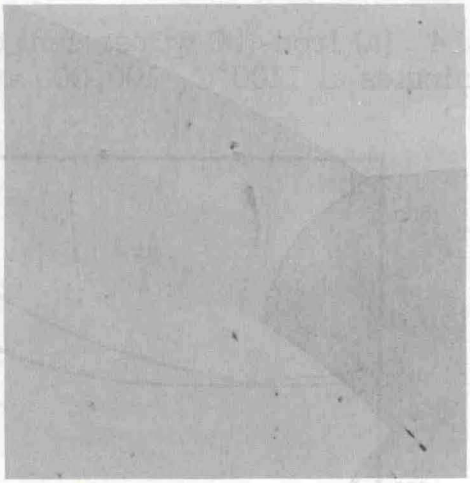

Fig. 3 Iron-(12.5 wt per cent chromium). Quenched after holding for 30 minutes at 1100°C, atmospheric pressure. 100X

In the specimens treated at 100,000 atm, the pseudo-martensitic structure was observed in all specimens except the 20 per cent chromium composition and this had a two-phase structure (see Fig. 4). To determine if the coarse-grained, single-phase structure would be obtained above 20 per cent chromium under pressure, 22.5 and 25 per cent chromium compositions were prepared. Subsequent analysis indicated that these contained 0.02 per cent carbon and as such were essentially comparable to the 10 to 20 per cent compositions prepared previously. The specimens were treated at 1200°C under atmospheric and under 100,000 atm pressure. Microscopic examination revealed that all these specimens had the coarse-grained, single-phase structure similar to that shown in Fig. 3. Thus, on the basis of the observed microstructural changes with pressure described above and summarized in the following table, it can be concluded that the application of pressure had shifted the gamma loop from about 12 to about 20 per cent chromium and that the two-phase structure noted at 20 per cent chromium probably represented the $\alpha + \gamma$ region. (This is illustrated in the phase diagram shown in Fig. 5.)

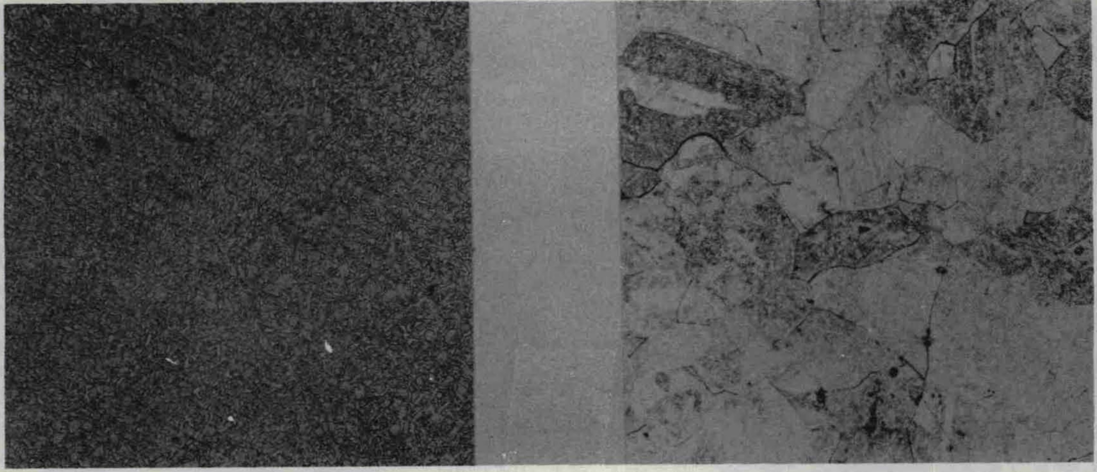

Fig. 4 (a) Iron-(20 wt per cent chromium). Quenched after holding for 30 minutes at 1100°C, 100,000 atm. (b) Iron-(10 wt per cent chromium). 100X

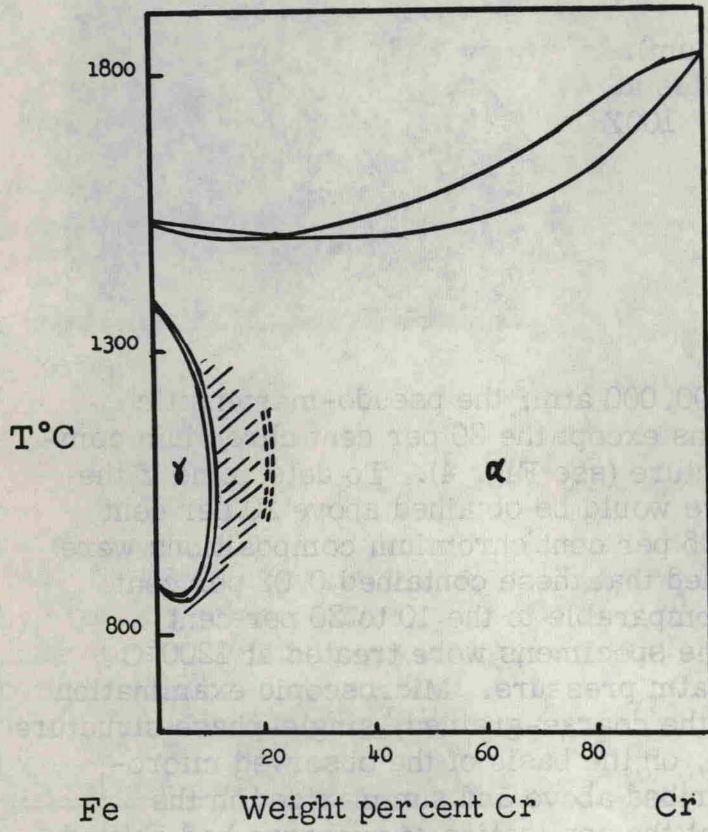

Fig. 5 Phase diagram of the iron-chromium system. Shaded area indicates the gamma-loop shift at 100,000 atm.

Wt % Chromium	Treated at Atmospheric Pressure	Treated at 100,000 Atm Pressure
10	Pseudo-martensitic structure	Pseudo-martensitic structure
12.5	Coarse-grained, single-phase	Pseudo-martensitic structure
15	Coarse-grained, single-phase	Pseudo-martensitic structure
20	Coarse-grained, single-phase	Two-phase structure
22.5	Coarse-grained, single-phase	Coarse-grained, single-phase
25	Coarse-grained, single-phase	Coarse-grained, single-phase

This conclusion is substantiated by the hardness data given below which show higher hardness values for the pressure-treated specimens in the range from about 12 to about 20 per cent chromium which represents the gamma loop shift indicated above.

Rockwell "A" Hardness Values of Specimens Prepared at Atmospheric Pressures and at 100,000 Atm

			100,000 Atm	Atmospheric Pressure
90	Fe--10	Cr	58 R_A	54.5
87.5	Fe--12.5	Cr	61	35.5
85	Fe--15	Cr	61	37.0
80	Fe--20	Cr	64.5	44.0
77.5	Fe--22.5	Cr	52	45.0
75	Fe--25	Cr	52	53.0

Although it is known that both cold-work and nitrogen additions could result in grain refinement in alloys of this type, lack of an appreciable hardness difference in the 10 per cent chromium composition indicates that the effects of cold-work or nitrogen do not account for the differences in the higher chromium compositions.

Since the pressure-treated specimens were not analyzed for carbon and since graphite was employed in the pressure cell, one might suspect that a change in carbon content might have occurred during the pressure treatment and that this might possibly account in some way for the observed differences. However, the specimens were not in direct contact with carbon, and a careful examination of the microstructures revealed no evidence whatsoever for carbon diffusion.

Thus, it appears very probable that the gamma loop has been shifted to higher chromium compositions by the application of pressure. A practical application of such a shift in the gamma loop lies in the possibility of utilizing alloy additions together with pressure to produce a hardenable high-chromium alloy.

Iron-Aluminum

The iron-aluminum system is analogous to the iron-chromium system in that it possesses a gamma loop region reportedly extending into the body-centered cubic portion of the phase diagram to about 0.6 per cent aluminum.(7) Application of pressure at temperature could be expected to extend the gamma loop region to higher aluminum contents, and thus provide the basis for hardenable iron-aluminum alloys containing more than 0.6 per cent aluminum.

Samples of 0.5, 1.0, and 2 wt per cent aluminum in iron were prepared from cast buttons containing 0.03 per cent carbon and heat treated at 1150° and 1250°C for 30 minutes under 100,000 atm pressure and quenched. Control samples were also prepared from the same material and heat treated as above at atmospheric pressure and water quenched.

Metallographic examination of all specimens of this series subjected to pressure showed a refined spiky, pseudo-martensitic structure (Fig. 6), which could be regarded as indicative of the presence of the gamma phase at higher temperatures as noted in the previous work on the iron-chromium system. Examination of control specimens heat treated at atmospheric pressure showed a single-phase structure of very large grain size, but with some slight grain refinement noted in the 0.5 per cent aluminum sample. Fine spots were noted in the structures of all samples. These were identified as etch pits. Some inclusions were also detected in the pressure-treated samples which might have been the result of reaction of the specimen with the Al_2O_3 liner materials.

Since a pseudo-martensitic structure was detected in all pressure-treated samples, it was thought that a gamma loop shift to aluminum contents of above 2 per cent was probable under pressure. However, the data were considered inconclusive because the 0.5 per cent aluminum control did not exhibit a pseudo-martensitic structure as expected on the basis of the reported phase diagram. Moreover, more conclusive evidence for the gamma loop shift would have been obtained if compositions had also been selected beyond the gamma loop region where a single-phase structure would have been observed. Consequently, additional compositions of 0.25, 2.25, 2.50, and 3.0 wt per cent aluminum in iron were prepared and heat treated at 1150°C under 100,000 atm and atmospheric pressure to further investigate the system. Chemical analysis of these compositions showed them to contain 0.01 per cent carbon, which is lower than the 0.03 per cent carbon materials previously employed.

Metallographic examination of these compositions showed essentially the same structures noted in the previous compositions. All the pressure-treated samples exhibited a pseudo-martensitic structure, and the conventionally treated samples showed a large-grained, single-phase structure, although the 0.25 per cent aluminum control did possess the more refined grain size as previously noted in the 0.5 per cent aluminum control. However, the 0.25 per cent aluminum control (Fig. 7) still did not have the martensitic structure that is believed to be indicative of the austenite to ferrite transformation.

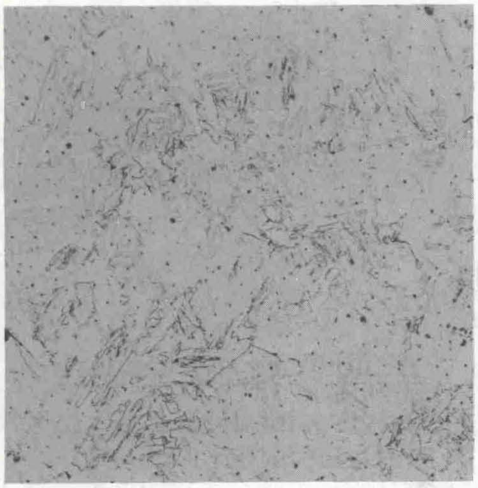

Fig. 6 Iron-(2 wt per cent aluminum). Quenched after holding at 1150°C, 100,000 atm. Etch: 2 per cent Nital. 100X

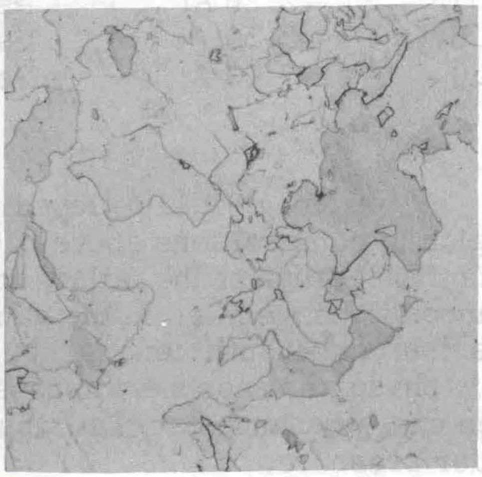

Fig. 7 Iron-(0.25 wt per cent aluminum). Quenched after holding for 30 minutes at 1150°C, atmospheric pressure. Etch: 2 per cent Nital. 100X

Hardness measurements, as listed below, indicated a consistently higher hardness in all pressure-treated specimens, which might be taken as an indication of the formation of a martensite-type phase. Moreover, the hardness of the 0.25 per cent aluminum control was higher than the other control compositions which might be an indication of incipient martensite formation.

Rockwell "A" Hardness Values of Iron-Aluminum Specimens
Prepared at Atmospheric Pressure and at 100,000 Atm

		100,000 Atm	Atmospheric Pressure
99.75	Fe--0.25 Al	56.0 R_A	37.0 R_A
99.5	Fe--0.5 Al	56.0	27.8
99.0	Fe--1.0 Al	55.5	29.0
98.0	Fe--2.0 Al	56.0	31.5
97.75	Fe--2.25 Al	57.0	35.0
97.5	Fe--2.50 Al	56.0	36.0
97.0	Fe--3.00 Al	56.0	38.0

Observed Microstructures
Iron-Aluminum System

Composition (wt %)		100,000 Atm	Atmospheric Pressure
99.75	Fe--0.25 Al	Pseudo-martensitic	Very refined, single-phase
99.50	Fe--0.5 Al	Pseudo-martensitic	Refined, single-phase
99.0	Fe--1.0 Al	Pseudo-martensitic	Coarse-grained, single-phase
98.0	Fe--2.0 Al	Pseudo-martensitic	Coarse-grained, single-phase
97.75	Fe--2.25 Al	Pseudo-martensitic	Coarse-grained, single-phase
97.5	Fe--2.50 Al	Pseudo-martensitic	Coarse-grained, single-phase
97.0	Fe--3.00 Al	Pseudo-martensitic	Coarse-grained, single-phase

Although it is believed that pressure has shifted the gamma loop region to compositions above 3.0 per cent aluminum, conclusions may be doubtful because of the failure to produce the pseudo-martensitic phase in compositions well within the gamma loop at atmospheric pressures. It is possible that insufficient carbon was present to retain the metastable martensitic phase at atmospheric pressure, and that pressure had some effect on free energy changes so that a pseudo-martensitic phase could be stabilized under pressure.

Because of the indications obtained in these experiments and the more positive data obtained in the iron-chromium system, it is felt that the gamma loop region of the iron-aluminum system at higher carbon contents should be examined using the martensite retention technique, or low-carbon alloys should be investigated by directly determining gamma phase formation under pressures and at temperatures using resistivity or other forms of measurement.

Investigations of Phase Stabilization

Chromium-Nickel (sigma phase)

The sigma phase has been detected in several binary systems including iron-chromium, cobalt-chromium, iron-vanadium, etc. Sully$^{(8)}$ and others have postulated an "excessive electron-atom ratio" theory to predict its occurrence in transition series alloys. To date, the sigma phase has been found at the approximately predicted composition in all systems except chromium-nickel.

Beck and Manly,$^{(9)}$ in work on the cobalt-chromium-nickel ternary phase system, reported that the sigma phase approaches the chromium-nickel binary system at approximately 33 atom per cent nickel at 1200°C. While there is reason to suspect the formation of sigma phase in chromium-nickel under some conditions, there is no known reason for expecting that pressure would favor its formation. However, it was hoped that application of high pressure with temperature would provide the conditions required to form the sigma phase in the chromium-nickel system.

Compositions of 60-40, 62-38, 65-35, 67-33, and 70-30 wt per cent chromium-nickel were run at 100,000 atm and the following temperatures:

1600°C for 10 minutes
1600°C for 10 minutes, followed by 20 minutes at 1200°C
1600°C for 10 minutes, followed by 20 minutes at 600°C

Metallographic examination showed the presence of two phases. X-ray diffraction studies indicated that these phases were chromium and nickel solid solutions. Sigma phase was not detected by those methods in any of the samples analyzed.

Nickel-Copper

The ordered compounds Ni_3Fe, Ni_3Mn and Ni_3Co have been reported in their respective systems.$^{(10)}$ The ordered compound Ni_3Cu has never been reported. It was felt that this compound might be stabilized under high pressures and temperatures. Two samples of composition Ni_3Cu were melted at 1600°C under 100,000 atm pressure, cooled to 1000°C, held isothermally for 30 minutes and quenched under pressure. Metallographic and x-ray diffraction studies indicated that both specimens had the typical face-centered cubic solid solution structure with a lattice parameter of 3.557 A. No evidence was found for the presence of the ordered compound, Ni_3Cu.

There are also indications of incipient formation of nickel-copper under ordinary pressures up to 450°C.(11) It was hoped that the application of pressure would cause the formation and stabilization of this compound. Accordingly, cast samples of composition nickel-copper were heat treated at 450°C for 30 minutes at 100,000 atm pressure. Examination of these specimens also indicated that a typical face-centered cubic solid solution structure ($a_o = 3.569$ A) was present.

Cobalt-Aluminum

The compound Co_3Al is not known in the cobalt-aluminum system, although Hansen(12) reports some indication that it may occur as a transition phase. The ordered body-centered cubic cobalt-aluminum is known, and the isomorphic compound nickel-aluminum and Ni_3Al are recognized in the nickel-aluminum system. Co_3Al should possess utility in cobalt base alloys. The counterpart of Co_3Al, Ni_3Al, is recognized as the most important single compound in nickel base high-temperature alloys because (1) Ni_3Al is the major dispersed phase, (2) it possesses the dense ordered face-centered cubic structure, and (3) it is coherent with the matrix. For the same reasons, cobalt alloys could be rendered more useful if the dense compound Co_3Al were formed under pressure.

The stoichiometric composition Co_3Al was prepared from high-purity powders and melted by holding at 1600°C for 20 minutes at pressures of 50,000 and 100,000 atm. In addition, samples were cast under the above pressures and then isothermally held at 1200° and 1250°C to ascertain the effects of heat treatment under pressure. These materials were compared with samples heat treated at atmospheric pressure.

Metallography showed identical structures for both modes of treatment indicating that pressure had no beneficial effect in synthesizing the Co_3Al. X-ray diffraction showed the presence of two phases, identified as cobalt-aluminum and beta-cobalt (Table I).

TABLE I

X-RAY DIFFRACTION ANALYSIS

Cobalt-Aluminum System--Co_3Al Composition

Molybdenum K Radiation

d/n	I/I_0	Identification
2.17	VW	β -Cobalt
2.03	S	β -Cobalt
1.92	MS	β -Cobalt
1.46	VW	β -Cobalt
1.275	W	Aluminum-Cobalt
1.265	W	β -Cobalt
1.170	MS	Aluminum-Cobalt
1.07	W	β -Cobalt
1.05	VVW	β -Cobalt
1.01	M	Aluminum-Cobalt

Chromium-Aluminum

The intermetallic compound chromium-aluminum is not found in the chromium-aluminum system. However, the high melting compounds cobalt-aluminum and nickel-aluminum are present in their respective systems. It is postulated that chromium-aluminum might be formed under high pressures, and that this compound should possess a melting point substantially above either of its constituents.

Stoichiometric proportions of chromium and aluminum were heated to 1900°C under pressures of 50,000 and 100,000 atm. The resulting cast specimens were so friable that they could not be prepared for metallographic examination. However, the major reflections in the x-ray diffraction patterns (Table II) were found to be the same as those given by samples of the same composition melted at atmospheric pressure.

TABLE II

X-RAY DIFFRACTION ANALYSIS

Chromium-Aluminum System--CrAl Composition

Molybdenum K Radiation

Cast at Atmospheric Pressure		Cast--100,000 Atm Pressure	
d/n	I/I_0	d/n	I/I_0
--	--	2.58	VVW
2.42	M	2.42	W
2.16	S	2.16	S
1.98	VW	1.98	W
1.95	VVW	1.94	VVW
1.86	VW	1.84	VVW
1.64	VVW	--	--
1.52	W	1.54	VW
1.47	VW	1.46	VVW
1.40	VW	--	--
1.35	VW	--	--
1.32	M	1.33	M

A further effort was made to clarify the chromium-aluminum system by studying compositions of 80-20, 85-15, and 70-30 chromium-aluminum under pressure, but because of the complexity and quality of the diffraction patterns obtained it was decided that the specimens did not warrant the extended study that would be required.

Investigations of Intermediate Phase Suppression

Nickel-Aluminum

The phase diagram for nickel-aluminum shows that the ordered compound Ni_3Al forms as the result of the peritectic reaction between nickel-aluminum and the melt. Consequently, in synthesizing this compound, severe peritectic segregation usually occurs, which necessitates long-time, high-temperature annealing treatments for homogenization. Such treatment normally results in large grain size which is detrimental to physical properties. It is postulated that since the peritectic occurs so close to the liquidus, casting under pressure may modify the mode of nucleation and cause Ni_3Al to form congruently from the melt, thus avoiding peritectic segregation.

Experiments were run in which melts of composition Ni_3Al were cooled quickly from 1600°C under pressures of 50,000 and 100,000 atm. Metallographic examination of the specimens so obtained showed a two-phase structure indicating that the peritectic reaction had still occurred (Fig. 8) A third experiment was run in which the melt was cooled to 1300°C and held isothermally for 30 minutes to cause homogenization of the Ni_3Al. Metallographic examination indicated that although homogenization was not complete, the usual very large grains were substantially formed. It seems likely, though the evidence is meager, that the application of pressure up to 100,000 atm under these conditions will not cause Ni_3Al to form congruently from the melt.

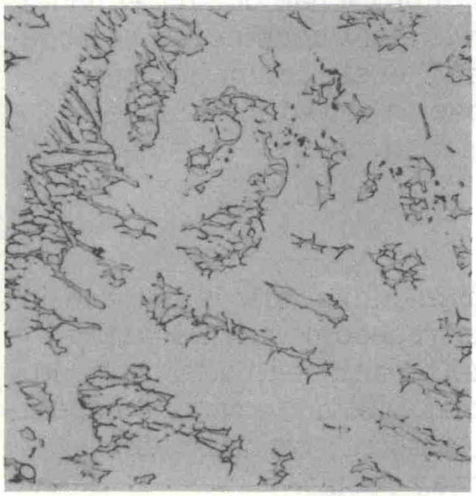

Fig. 8 Ni_3Al compound. Melted at 1600°C, 100,000 atm and cooled under pressure. (The white field is Ni_3Al and the dark etching minor phase is nickel-aluminum.) 500X

Nickel-Titanium

Nickel alloys with additions of 15 wt per cent titanium or less are not forgeable. An examination of this region in the phase diagram shows the presence of the hexagonal intermetallic Ni_3Ti and a solid solution of titanium in nickel. This alloy was to be prepared under pressure in the hope that the solubility of titanium may be increased and that the formation of Ni_3Ti might either be suppressed or that it might be precipitated in a cubic form analogous to Ni_3Al rather than in its usual form of hexagonal needles.

Runs were made on powder samples of 80-20, 85-15, and 90-10 wt per cent nickel-titanium alloys at 50,000 atm pressure and at temperatures of 1300°, 1350°, 1400°, and 1450°C. The samples were held at temperature for 10 minutes and quenched. These temperatures were below the melting point, and diffusion was not sufficient to produce equilibrium structures. The experiments were therefore repeated at 1600°C to produce cast structures.

Metallographic comparison of the high pressure runs with duplicating runs made at atmospheric pressure showed no detectable changes. X-ray examination showed that Ni_3Ti had precipitated in its normal hexagonal structure.

To ascertain if solubility changes could be produced by heat treatment under pressure, samples of a cast 90-10 wt per cent nickel-titanium alloy were heat treated at 1000°C at atmospheric pressure and under 50,000 atm pressure for 30 minutes, which was the maximum holding time permissible for satisfactory operation of the pressure equipment. Metallographic examination showed no apparent differences in amounts of eutectic and nickel solid solution present, indicating that no significant changes in solubility had occurred under these conditions. However, the above structures were not considered homogenous,(indeed, eutectic should not have been present if equilibrium had been attained) and if sufficient holding time could have been allowed to achieve equilibrium, a change in solubility might have been observed.

Nickel-Molybdenum

The inferior properties of some molybdenum-nickel alloys are due in part to the formation of the intermetallic nickel-molybdenum which sharply decreases the ductility of the alloy. In conventional techniques, this phase is suppressed by aluminum additions. It was hoped that casting various compositions of this alloy under pressure would collapse, dissolve, or otherwise suppress this intermetallic so that a ductile alloy may result.

Runs were made at 50,000 and 100,000 atm pressure and a temperature of 1600°C on 62-38 and 40-60 wt per cent molybdenum-nickel alloys. Metallographic comparison of samples with those melted at atmospheric pressure indicated that the alloys had not been affected in any way by pressure application.

GENERAL STUDIES

Titanium-Magnesium

This system has been difficult to investigate by conventional techniques because of the great difference in volatility of the components. Because of this there is little known about the phase diagram. Aust and Pidgeon(13) reported the solubility of titanium in magnesium to be 0.0025 per cent at 650°C and 0.15 per cent at 850°C. Fredrickson(14) managed to dissolve 1.5 per cent magnesium in titanium by sheath-rolling compressed compacts. In a previous study by the General Electric Company, Oriani and Strong(15) dissolved approximately 1 per cent magnesium in titanium using high pressures (about 70,000 atm) and temperatures.

It was decided to survey the entire titanium-magnesium system using high pressures in order to ascertain the solubility of the components and to search for any intermediate phases in the system. Accordingly, powder compositions of 90-10, 70-30, 50-50, 30-70, and 10-90 wt per cent titanium and magnesium were prepared using high-purity atomized magnesium and sodium reduced titanium powders.

Initially, runs were made at 50,000 atm pressure and temperatures of 800°, 1200°, and 1400°C for 10 minutes. In addition, samples of the 90-10 wt per cent titanium-magnesium composition were held at 1850° to 1900°C for 10 minutes.

In the higher magnesium alloys some difficulty was initially encountered in holding the volatile component, but subsequent runs resulted in satisfactory samples.

Analysis of specimens by metallography and x-ray diffraction indicated that there were no intermediate phases in the system, and that mutual solubility of the components is very limited. X-ray diffraction examination of all compositions showed a two-phase alloy. Lattice parameter determinations on 90-10 and 10-90 wt per cent titanium-magnesium compositions indicated no change up to 1400°C where both components then showed slightly enlarged unit cells, probably indicating slight mutual solubility.

Titanium a = 2.96 A
c = 4.72 A

Magnesium a = 3.215 A
c = 5.23 A

Lattice parameters of the starting powders were as follows:

Titanium a = 2.95 A
c = 4.69 A

Magnesium a = 3.21 A
c = 5.21 A

Metallographic examination of 90 titanium and 10 magnesium melted at 1900°C showed globular magnesium areas in an acicular titanium matrix (Fig. 9). As this microstructure did not agree with that found by Oriani and Strong, who worked with solid starting materials, it was decided to attempt to duplicate their work, since powders could conceivably suffer from adsorbed gases which would affect the results.

Accordingly, three cylinders of high-purity titanium were machined with 0.070-inch holes drilled in each end to receive 0.070-inch diameter extruded magnesium rod so that the final product would contain 2 per cent magnesium. The samples were then melted at 1900°C under 50,000 and 100,000 atm pressure. Examination (Fig. 10) showed all samples possessed the acicular matrix noted in the powder samples, and, moreover, the titanium and magnesium alloy exhibited a fine globular dispersion of magnesium which indicated that solubility was much less than the 2 per cent introduced. Unless one assumes the melting temperature was sufficiently high for gaseous impurities to be absorbed even in the solid sample, there is no apparent explanation for the different structures obtained in the two investigations.

As the application of high pressures in this study was primarily to contain the volatile component, it was decided to attempt to use an available vacuum hot press to make larger specimens in order to ascertain physical properties. This apparatus is capable of 200 atm pressure and temperatures of 2000°C, and possesses the advantage of more positive control of variables, particularly atmosphere.

Fig. 9 Titanium-(10 wt per cent magnesium). Prepared by melting powdered components at 1900°C, 100,000 atm and cooled under pressure. (Globules of magnesium in an acicular titanium matrix.)
500X

Fig. 10 Titanium-(2 wt per cent magnesium). Prepared by melting bulk components at 1900°C, 100,000 atm and cooling under pressure.
500X

Two cylinders 1 inch in diameter x 2 1/2 inches long of a titanium and 2 per cent magnesium composition were hot-pressed from powders at 1000°C and 200 atm pressure for 2 hours. The cylinders were then machined into tensile bars and tested. Tests were compared with pure titanium specimens prepared from the same powder batch under the same conditions. Results are as follows:

	Titanium-2% Magnesium (avg of 2)	Titanium (avg of 4)
Density	4.397 g/cm^3	4.50 g/cm^3
Tensile strength	70,000 psi	79,000 psi
Yield strength	50,800 psi	53,000 psi
Elongation	18.9 per cent	18.0 per cent
R.A.	21.9 per cent	23.3 per cent

Metallographic examination showed a fine globular dispersion of magnesium in a dense, essentially porous free, equiaxed titanium matrix (Fig. 11). Physical properties show a slight degeneration of properties from those of pure titanium. It is unknown whether changes in temperature or holding time would have improved the physical properties of this alloy. It is interesting to note, however, that the microstructure obtained was closer to that described by Oriani and Strong, so that gas absorption may have affected the results obtained in the high pressure equipment.

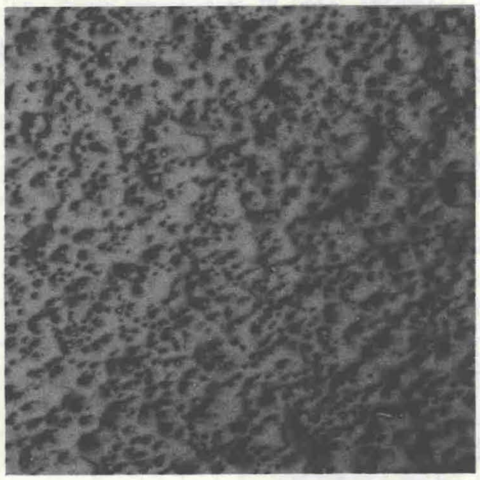

Fig. 11 Titanium-(2 wt per cent magnesium). Hot pressed from powders at 1000°C, 200 atm. Unetched, polarized light. 100X

Nickel-Aluminum Oxide

Dispersion hardened alloys have been recognized as being of great importance in high-temperature applications. Unfortunately, most particles used as hardeners in present high-temperature alloys either dissolve or coarsen at service temperatures. The resulting softening and structural changes limit the useful life of the alloy. Al_2O_3 exhibits virtually no solubility in nickel. [Cochardt(16) has calculated from thermodynamic data a solubility of 1×10^{-14} at 1000°K.] One of the major obstacles in the use of Al_2O_3 as an alloy hardener has been the problem of producing fine, uniform particle dispersions. By employing the internal oxidation method of reacting nickel oxygen, aluminum, and nickel at elevated temperatures under pressure, it was thought that a fine dispersion of Al_2O_3 in nickel might be produced.

A powder mixture was made of nickel oxide, a 50-50 aluminum-nickel alloy, and pure nickel containing stoichiometric proportions of nickel oxide and aluminum such that the reacted mixture would contain 5 mol per cent aluminum oxide in nickel. Several runs were made in the temperature range 1200° to 1700°C at pressures of 50,000 atm. Metallographic and x-ray diffraction examination indicated that complete reaction did not occur until a temperature of about 1650°C was reached. The aluminum oxide thus formed appeared in chains and ringlets which were mostly agglomerated in the grain boundaries of the nickel matrix and at the interfaces of the former nickel-oxygen - nickel-aluminum boundaries (see Fig. 12). Lattice parameter measurements of the nickel matrix showed a lattice constant of 3.524 A which indicates the matrix is essentially impurity free.

The dispersion of aluminum oxide was not nearly as fine as was desired. The particles were of the order of one micron in size and considerably agglomerated. Although it is realized that refinements in technique, such as reducing the particle size of the starting materials and employing extended milling for better blending, would offer some improvements, it was not seen that application of pressure offered any advantages and no additional work was performed.

High-speed Tool Steel

Presently, high-speed tool steels are very difficult to homogenize because of the relative insolubility of alloy carbides in the gamma phase. Efforts to homogenize in the gamma region at higher temperatures result in grain growth which is more detrimental than any improvement gained by increased carbide solubility. It was felt that austenitizing under pressure might result in increased homogeneity at equivalent or lower temperature and that tempering under pressure might retain this advantage in the final product.

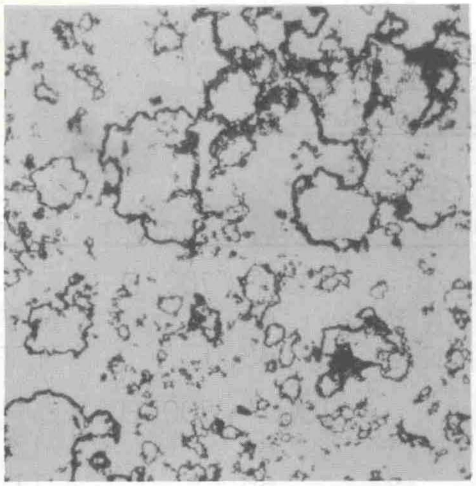

Fig. 12 Mixture of nickel oxide, 50-50 aluminum-nickel alloy, and pure nickel powders heated at 50,000 atm. Unetched. 200X

A sample of super high-speed steel was obtained with the following typical analysis:

Carbon	0.77%
Tungsten	18.5 %
Chromium	4.50%
Vanadium	2.00%
Molybdenum	1.00%
Cobalt	9.00%

Specimens were preheated at 1500°F for 10 minutes and then austenitized at 2000°, 2300°, and 2400°F for 10 minutes at atmospheric pressure and under 100,000 atm and quenched. In addition, some of the quenched samples were tempered at 900°F and others were double tempered at 1000° and 700°F for 30 minutes at each temperature at atmospheric pressure and under 100,000 atm.

Rockwell "C" hardness determinations and metallography were the principal tools of analysis. Austenitic grain size was delineated by Villela's reagent in all samples except those austenitized at 2000°F. Efforts to etch the 2000°F specimens with other etchants were unsuccessful. Grain size was determined by the standard intercept method at 1000X magnification.(17) Results of these studies are summarized in the following Table III.

TABLE III

Comparison of Grain Size and Hardness of Pressure Treated and Conventionally Treated Tool Steel

	As Quenched	Grain Size	Tempered	Grain Size	Double Temper	Grain Size
Temperature	2000°F		900°F		1000° + 700°F	
Hardness R_C (exp)	61.5	N.V.*	63.0	N.V.	62.0	N.V.
Hardness R_C (std)	61.5	N.V.*	63.0	N.V.	63.0	N.V.
Temperature	2300°F		900°F		1000° + 700°F	
Hardness R_C (exp)	64.0	11	66	11	65	12
Hardness R_C (std)	65.5	11	66	12	66	11
Temperature	2400°F		900°F		1000° + 700°F	
Hardness R_C (exp)	66.0	11	63.5	8	62	5
Hardness R_C (std)	62.0	3	64.0	3	62	3
Temperature	2500°C					
Hardness R_C (exp)	60.0	5				
Temperature	2600°C					
Hardness R_C (exp)	60.0	3				

*Not Visible

Metallographic examination revealed that the average particle size of the alloy carbides was generally finer and their distribution was somewhat more uniform in pressure-treated specimens at all austenitizing temperatures as compared to those treated at atmospheric pressure. Moreover, a cursory examination by electron microscopy of samples quenched from 2300°F and tempered at 900°F indicated that the pressure-treated sample possesses a finer martensitic structure with some indication of a fine acicular precipitate which could not be identified (Figs. 13 and 14). Comparison of pressure-treated and conventionally treated specimens austenitized at 2300°F indicated the same average grain size, although the conventionally treated specimen was 1.5 R_C harder in the as-quenched condition. However, this advantage was not retained during tempering.

Comparison of 2400°F treated samples is interesting as the manufacturer recommended 2350° to 2400°F as the normal austenitizing temperature for this material. The grain size of the pressure-treated specimen remained fine (ASM No. 11), whereas the grain size of the conventionally treated sample had coarsened to ASM No. 3, giving a grain size difference of about a factor of 4. Further examination showed the carbides had remained spherical and

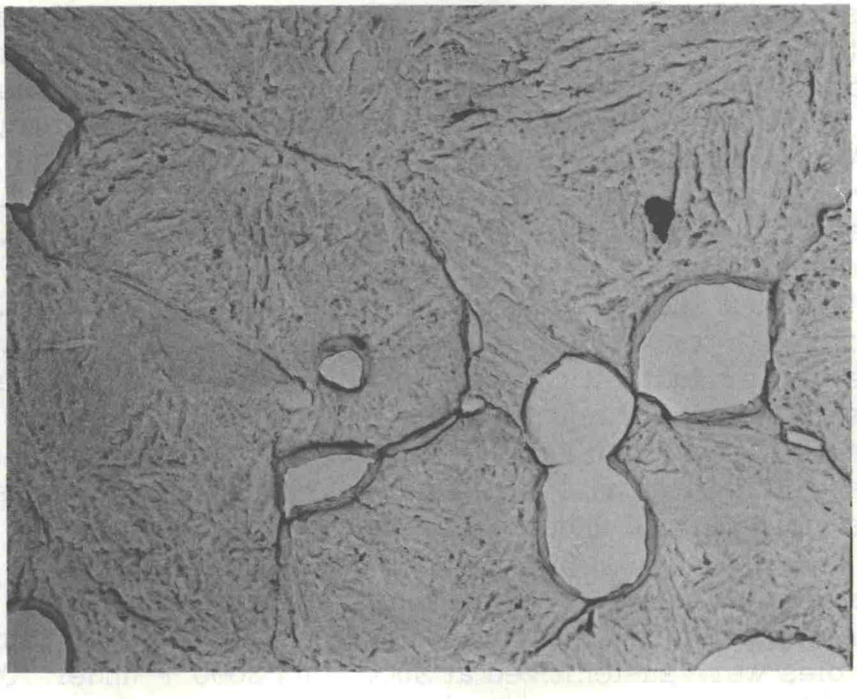

Fig. 13 High-speed tool steel. Heat treated at atmospheric pressure. Austenitized at 2300°F, quenched and tempered at 900°F for 10 minutes. Etch: Villela's reagent. Electron micrograph. 5000X

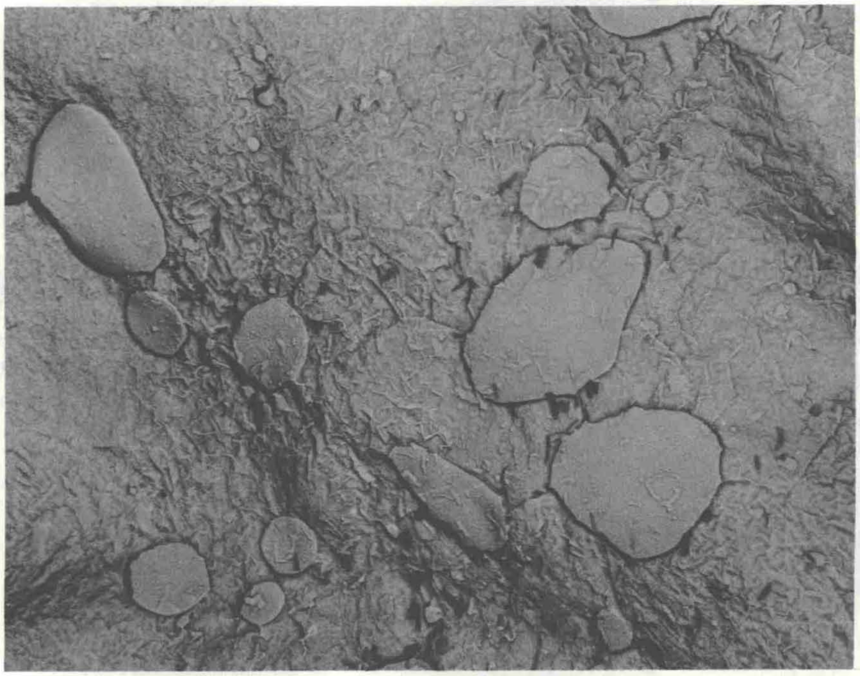

Fig. 14 High-speed tool steel. Heat treated at 100,000 atm pressure. Austenitized at 2300°F, quenched and tempered at 900°F for 10 minutes. Etch: Villela's reagent. Electron micrograph. 5000X

uniformly distributed under pressure, whereas, when normally treated, severe growth and coalescence of the alloy carbides at the grain boundaries had occurred. Moreover, the hardness of the pressure-treated sample had increased to 66 R_C while the control dropped to 62 R_C in the as-quenched condition. A single tempering at 900°F showed the standard had regained some hardness through secondary hardness effects, whereas the pressure-tempered specimen displayed no secondary effects as its hardness declined to 63.5 R_C. However, the grain size of the samples tempered under pressure did not remain constant, but showed increases to ASM No. 8 and ASM No. 5 for single and double drawing, respectively. As one would not expect a drawing operation to change the former austenitic grain size, the austenitic treatment of these samples must be considered questionable. However, a comparison of the largest grain sized specimen austenitized at 2400°F under pressure with normally austenitized material at the same temperature indicates that grain size remains more refined under pressure.

In order to determine the austenitizing temperature that is required under pressure to produce the structure noted in the controls austenitized at 2400°C, samples were austenitized at 2500° and 2600°F under 100,000 atm pressure for 10 minutes and quenched under pressure. Hardness of both samples fell to 60 R_C and austenitic grain size increased to ASM No. 5 and ASM No. 3 at 2500° and 2600°F, respectively. Metallographic examination of the alloy carbide phase in these samples indicated that a severe "chinese script" like coalescence of the carbides had occurred at the grain boundaries at both temperatures (Fig. 15).

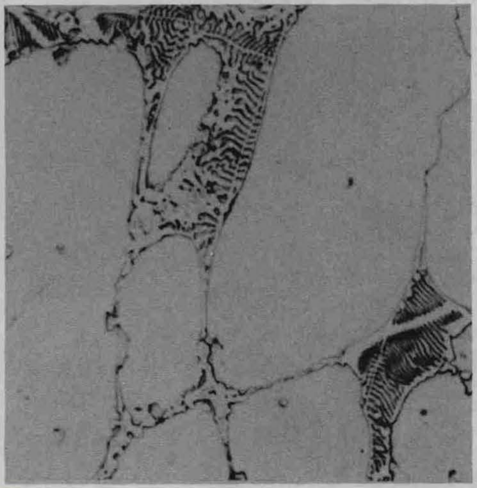

Fig. 15 High-speed tool steel. Heat treated at 100,000 atm pressure. Preheated at 1500°F for 10 minutes. Austenitized at 2600°F for 10 minutes and then quenched.

In summary, austenitizing under pressure has apparently raised the grain growth threshold at least 100°F. Furthermore, it appears that pressure has resulted in more positive control of particle size and distribution of complex carbides up to the grain growth temperature. Tempering under pressure has probably affected the rate of nucleation and precipitation from martensite, and the precipitate formed could be of a different nature. Pressure treatments seem to have little effect on hardness. The pressure treated samples do tend to be a little lower in hardness, however, and this may be an indication that the rate of solution of the alloy carbides has been adversely affected by pressure.

The more important variables governing the properties of tool steels include austenitic grain size and carbide distribution. In view of the effects of pressure on these variables as noted above it may be concluded that pressure treatment should have a beneficial effect on the properties of tool steel. Unfortunately, due to limitations imposed by the specimen size employed, these probable improvements could not be directly measured.

DISCUSSION OF RESULTS

The large volume change occurring in the transformation from graphite to diamond is extremely rare, if not unique, in metal as well as in nonmetal systems. The results of this exploratory project indicate that metal systems in general are not likely to reveal highly sensational irreversible changes as a result of the application of pressure. This is in agreement with that expected in view of the elastic nature of the metallic bond and of the fact that metallic systems generally already exist as closely packed structures because of the nondirectional nature of the bond.

However, reversible, more moderate structural changes such as the transformation from body-centered cubic to the face-centered cubic structure, would be expected to occur as a result of the application of pressure, since these transformations often involve at least some volume change and they occur rather readily in metal systems with moderate changes in conditions even without the application of pressure. Thus, strong evidence was found in the iron-chromium and iron-aluminum systems to indicate that the face-centered cubic (gamma) region was extended to higher alloy contents by the application of pressure. The fact that a similar reversible transformation was not detected in pure chromium or chromium-nickel alloys does not indicate, of course, that it has not occurred since in these cases transformation products may not have been produced or retained. The effects of pressure noted on high-speed steel may have been due more to the effects of pressure on the kinetics of the system rather than on phase transformations directly.

Although these transformations may not involve vastly different structures, it should be recognized that they may be the basis for significant property improvements. Unfortunately, interest in the practical aspects of these findings may be somewhat dampened by the inability to produce sufficiently large quantities of the alloys for more extended testing or for actual structural application. However, a continued, more careful, and more theoretical study of pressure effects may contribute significantly to our understanding of the fundamental nature of metal systems and may indirectly lead to improvements in alloys made by more conventional techniques.

ACKNOWLEDGMENTS

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The General Electric Research Laboratory contributed very heavily in the way of consultation, and extensively reviewed the reported results. The authors wish to gratefully acknowledge the help of J.W. Cahn, R.W. Guard, W.R. Hibbard, J.E. Hilliard, J.H. Keeler, G.D. Oxx, T.A. Prater, A.U. Seybolt, W.H. Smith, E.R. Stover, D.A. Vermilyea, and J.H. Westbrook. The breadth of this study would not have been possible without the specialized experiences of these scientists in specific metal systems.

The pressure treatments were conducted by the Diamond Section of the Metallurgical Products Department, and J.E. Cheney of this section contributed the high-pressure technology required in the program.

PART B

INTRODUCTION

The broad objective of this project is to obtain structural information by means of x-ray diffraction for materials at high pressures, especially in systems where reversible phase transformations occur. Since the high-pressure phase in such systems cannot be retained and examined at ordinary conditions (1 atm pressure), it is imperative that diffraction data be obtained while the material is above the transformation pressure. This, of course, is not feasible with the massive equipment used in conventional high-pressure studies. The technique we are employing consists of utilizing a miniature pressure cell (specifically diamond) which is transparent to x-rays of short wavelength and for which only modest forces are required to produce high pressures. It is basically the technique developed by Lawson and co-workers(18) at the University of Chicago.

The substances which could be most profitably studied would appear to be metals since their pressure transformations are generally reversible. The alkali and ammonium halides also transform reversibly, but they have already been studied and the structural change--from sodium-chloride structure type to cesium-chloride structure type--is well known. Unfortunately, in the case of metals, many of the reported transformation pressures are somewhat higher than the limits to which the technique has been used previously, or else there are special difficulties such as high absorption of x-rays (bismuth) or problems of containment (cesium). Accordingly, it has been our goal to improve on the known technique to allow the attainment of higher pressures and to develop special procedures for coping with highly absorbing substances.

The element bismuth is of central interest in our program. It is known to undergo several polymorphic transitions above 25,000 atm,(19) but no successful recording of the diffraction patterns of the high-pressure polymorphs has been reported. There is intrinsic value in knowing the crystal structure of the high-pressure forms of bismuth, and in addition the solution of the problems presented by bismuth should aid considerably in the further study of other metals.

In brief, then, the major activities have been the continual development of general techniques and a concentration on the bismuth problem, culminating in the successful repeated recordings of diffraction patterns of bismuth in the high-pressure form above 25,000 atm.

APPARATUS

Since no detailed description of the apparatus has been given previously, it is presented now.

The most important feature is the diamond cell, produced from highest quality industrial diamonds of 2 1/2 to 3 carats. These were well-developed rhombic dodecahedra free of strains and with only a slight yellow color. After grinding off two opposite corners to produce two parallel (100) faces, a cylindrical hole of 0.015-inch diameter was drilled through the center of the diamond and normal to the (100) faces, i.e., in a [100] direction, which is presumed to be the "hardest" direction. Except for a 0.030-inch length in the center the hole was given a 60° taper to the flat surfaces. The design and dimensions of the diamond cell are shown in Fig. 16, and the actual diamond in place for an experiment may be seen in Fig. 19. The cutting and drilling operations were performed satisfactorily by a commercial diamond die manufacturer, the Wayne Die Company, Hillside, New Jersey.

The sample to be compressed almost fills the cylindrical hole of 0.015-inch diameter and 0.030-inch height. Pistons of hardened steel (for pressures below 30,000 atm) or of carboloy have been used. These are shaped to give an extremely close fit in the hole of the diamond. They are made with the 60° taper and with the small cylinder of 0.015-inch diameter for a length of 0.010 to 0.020 inch.

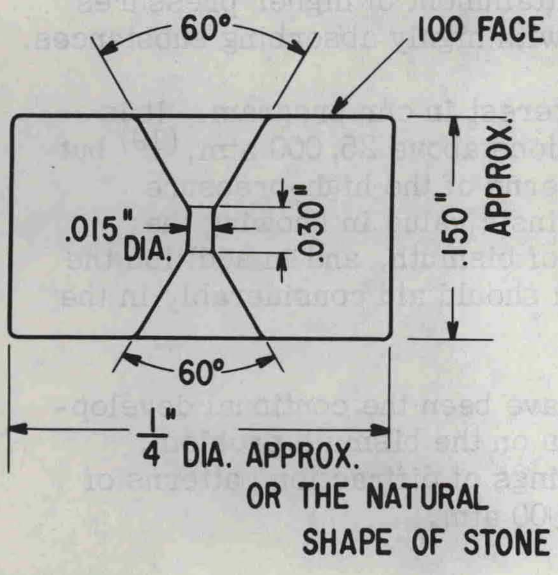


Fig. 16 Diamond die (GE Research Lab.)

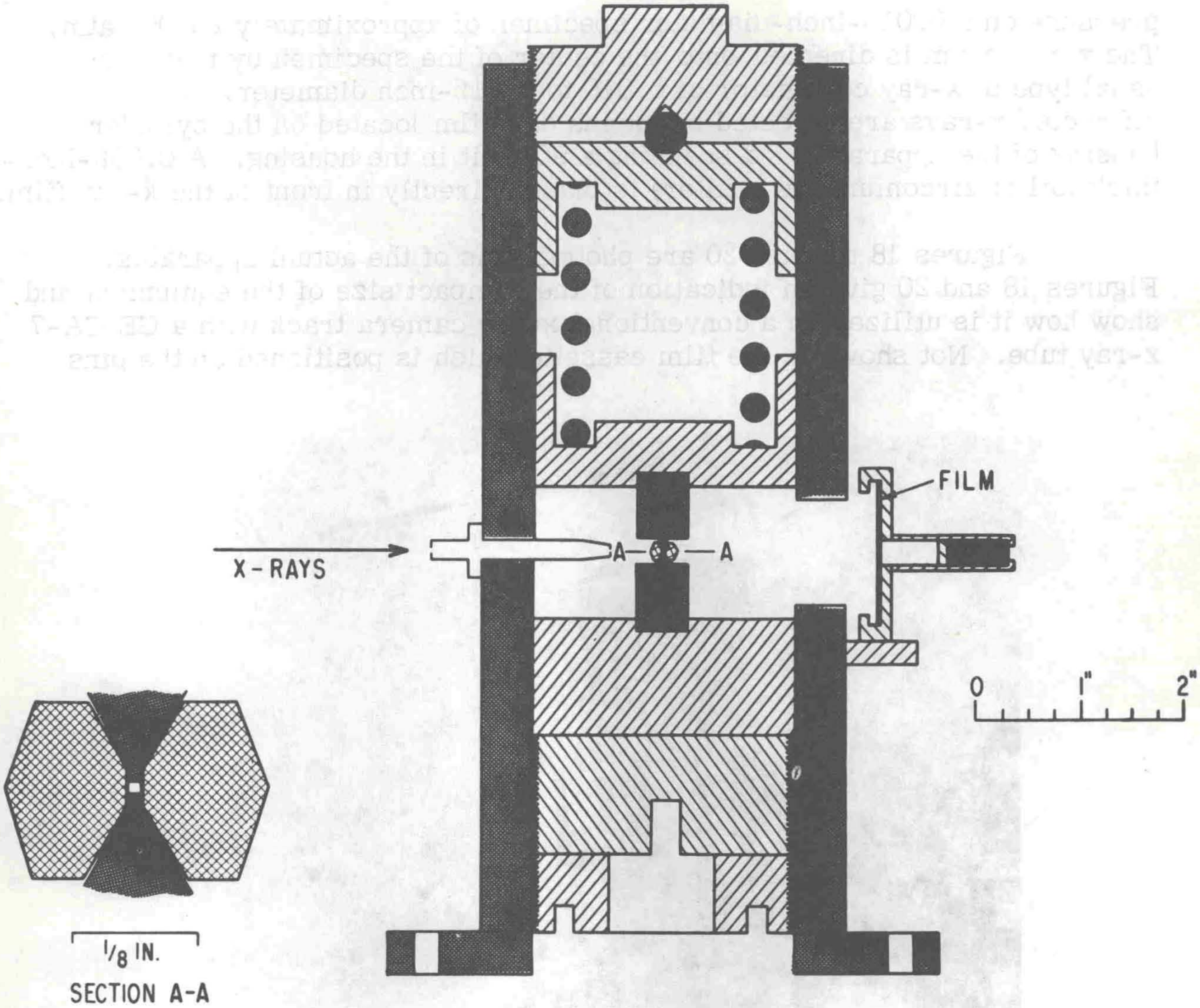


Fig. 17 Sketch of high-pressure apparatus.

A sketch of the apparatus, to scale, is given in Fig. 17. The diamond cell is at A and shown magnified in the separate diagram to the left. The lower piston is seated in a massive steel block which is held stationary by a locking arrangement. The moving parts are above and consist of the upper piston, a calibrated steel spring between two guides, a ball bearing, and a screw. The upper piston is seated in the lower portion of the metal guide. A given rotation of the screw compresses the spring which exerts a known force on the top piston and compresses the sample between the pistons. A full rotation of the screw corresponds to a 50-lb force, and this corresponds to a pressure on a 0.015-inch-diameter specimen of approximately 20,000 atm. The x-ray beam is directed onto the center of the specimen by means of a usual type of x-ray collimator of 0.010 to 0.015-inch diameter. The diffracted x-rays are detected by means of a film located on the cylinder housing of the apparatus and spanning a 90° slit in the housing. A 0.002-inch-thick foil of zirconium (as a filter) is placed directly in front of the x-ray film.

Figures 18 through 20 are photographs of the actual apparatus. Figures 18 and 20 give an indication of the compact size of the equipment and show how it is utilized on a conventional x-ray camera track with a GE CA-7 x-ray tube. Not shown is the film cassette which is positioned on the pins

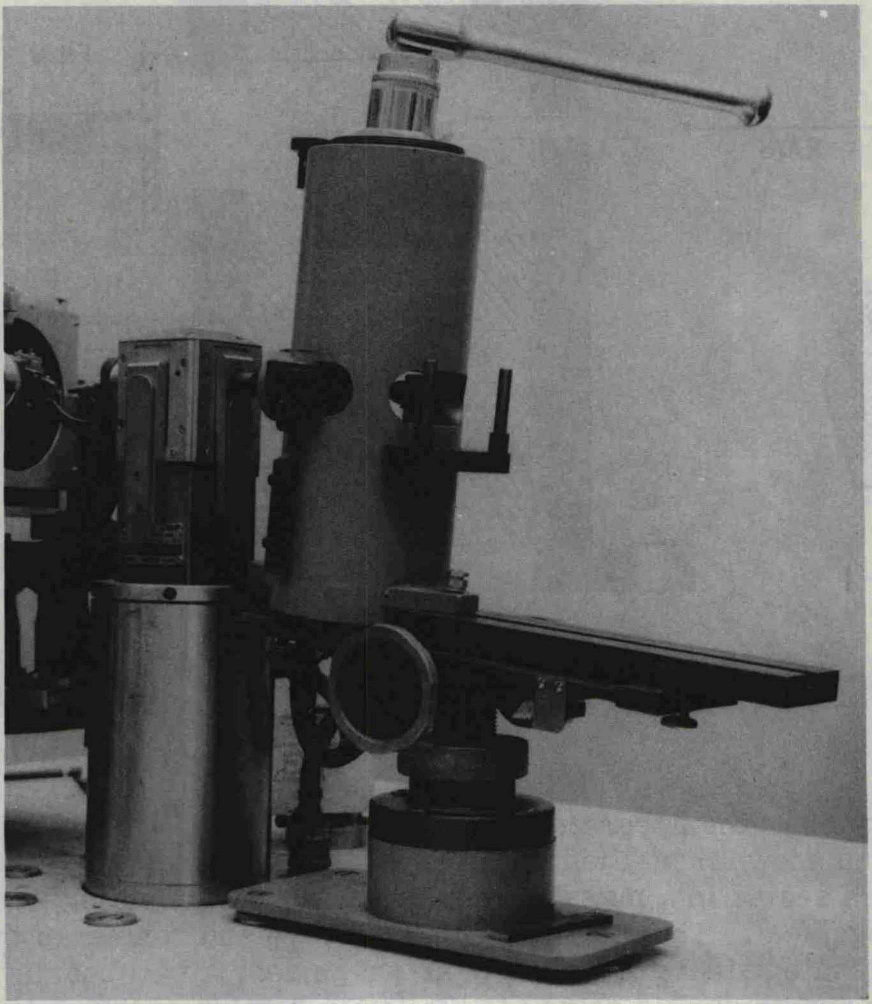


Fig. 18 High-pressure diffraction apparatus in usual position for diffraction experiment.

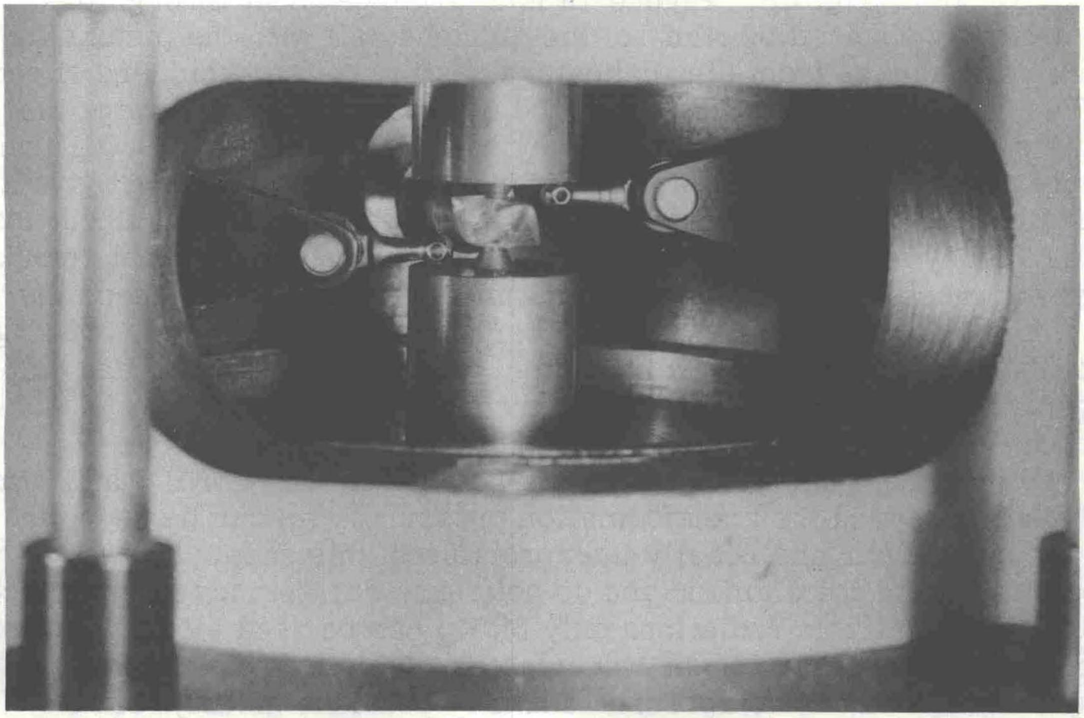


Fig. 19 View of diamond cell through exit normally covered by x-ray film cassette.

Fig. 20 High-pressure diffraction apparatus being adjusted for high-pressure experiment.

seen most clearly in Fig. 18. Figure 19 is an enlarged shot through the opening, normally covered by film, of the diamond cell with the pistons in position and with levers from dial indicators resting on the shoulders of each piston. The dial indicators have been found of great value in following the course of a compression experiment. They read reproducibly to 0.001 inch and not only make possible the detection of large volume changes but give a reliable indication that the sample is being compressed properly without loss of material. They also insure that contacting of the pistons does not occur. Not shown anywhere in the photographs is a metal sleeve, which keeps the pistons centered accurately and which appears to be necessary to avoid slight cocking of the pistons. The sleeve is slotted to allow the entrance and exit of the x-rays and the insertion of the levers from the dial gages.

The insert in Fig. 20 contains diffraction patterns of NH_4I at 1 atm and at 5000 atm, beyond the transformation pressure. As can be seen, the patterns are quite clear and readily interpretable in this case. The few bright spots are from the diamond and do not cause any serious interference. Of the commonly available radiations only MoK_α can be used effectively; the absorption is too severe for longer wavelengths. This is a disadvantage in producing a pattern that is compressed and may preclude getting reliable information from complicated structures with large unit cells, but it is not a severe limitation for simple structures of high symmetry.

A compression curve for rubidium-bromide (Fig. 21) illustrates typical behavior exhibited by the dial gages. The transformation with its large volume change of 17 per cent is associated with the high slopes of the curve. It is to be noted that considerable hysteresis is present. The reported transformation pressure should be at about 6000 atm. Such hysteresis effects are to be expected with the type of pressure device being used, but it appears especially large in this case. Actually, the curve of Fig. 21 was obtained at an earlier date. Since then, with a cell where the hole in the diamond and the pistons were made with closer tolerances and a better fit was obtained, the amount of hysteresis appears to be reduced substantially. Also, the use of zinc stearate as a lubricant, as suggested by previous workers,(21, 22) seems to be beneficial in this respect.

Some other points of technique may be mentioned since they have been found helpful for successful operation. In loading the diamond cell, optical examination with a low-power microscope is made. It is convenient that the specimen and pistons on either end are visible through the diamond. It is well to always utilize the same length of specimen (after preliminary compression) and to check on the fit of the pistons. The length of specimen is best determined by micrometer measurements with pistons inserted. Care is taken in

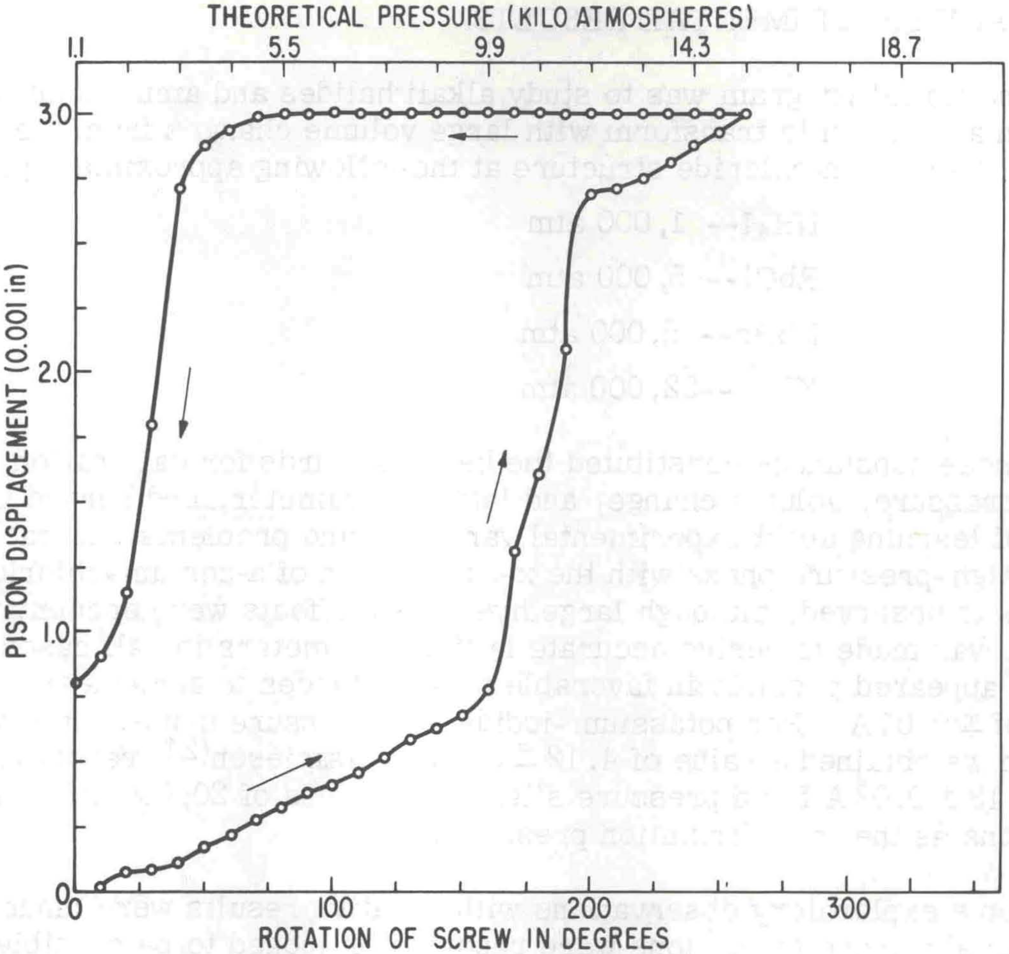


Fig. 21 Compression curve for rubidium-bromine.

positioning the diamond cell before application of pressure that the position is optimum with respect to thickness of diamond and the occurrence of the fewest diamond spots in the least objectionable regions of the film.

Once the sample is compressed, a radiograph of the pressure cell is taken before starting the x-ray exposure. The radiograph gives a good indication of the centering of the beam on the sample and is particularly helpful in insuring that the pistons will not be in the beam. Hardly any difficulty with piston interference has been experienced since this practice was started.

PRELIMINARY EXPERIMENTAL RESULTS

The initial program was to study alkali halides and ammonium iodide, all of which are known to transform with large volume changes from the sodium-chloride to the cesium-chloride structure at the following approximate pressures:

NH_4I-- 1,000 atm
RbCl-- 5,000 atm
RbBr-- 5,000 atm
KI --22,000 atm

These substances constituted the best standards for calibration with regard to pressure, volume change, and lattice parameter, and served the purposes of learning about experimental variables and problems. In each case, the high-pressure phase with the x-ray pattern of a cesium-chloride structure was observed, although large hysteresis effects were encountered. No attempt was made to derive accurate lattice parameters for all cases, although it appeared possible in favorable circumstances to achieve an accuracy of ± 0.01 A. For potassium-iodide at a pressure somewhat above 22,000 atm we obtained a value of 4.12 ± 0.02 A. Jamieson(21) reports a value of 4.13 ± 0.02 A for a pressure slightly in excess of 20,000 atm which he ascertains as the transformation pressure.

Some exploratory observations with negative results were made on a few materials where transitions were reported or judged to be possible. Thus, no structural change up to 20,000 atm was observed for silver-chloride or for V_2O_3. Also, preliminary experiments were made with silver-iodide, but these were abandoned because of uncertainties as to the nature of the material, since the diffraction patterns were anomalous even before application of pressure.

The preliminary results were achieved with an inferior diamond, in which flaws were visible and in which the cylindrical hole was along the undesirable [111] direction. Also, hardened steel pistons were used at first. This diamond was eventually cleaved in going to pressures in the neighborhood of 30,000 atm. It is our feeling that use of steel pistons may have been largely responsible for the resulting cleavage. This experience was, on the whole, encouraging in suggesting that with high-quality diamonds more carefully ground with the axis of the hole along [100] and with carboloy pistons, it would be possible to achieve pressures in excess of 30,000 atm. Accordingly, subsequent work was done with new diamond stones of higher quality shaped as described previously and with carboloy pistons.

EXPERIMENTS WITH BISMUTH

The major effort of the later portion of the project has been the attempt to observe the diffraction pattern of bismuth in the state after the first transformation at about 25,000 atm and to deduce the structure of the new phase. The successful recording of diffraction data after transformation has been accomplished many times in a reproducible fashion, but the structure has not been deduced at the time of writing.

The experimental problems with bismuth are especially difficult and special techniques had to be developed before the present success could be achieved. For one thing, the extremely high x-ray absorption of bismuth precludes the possibilty of obtaining x-ray patterns in the usual manner--a 0.015-inch-diameter specimen is much too large for transmission of sufficient x-rays. This problem was overcome by using 0.001 to 0.002-inch foil whereby satisfactory patterns for the untransformed bismuth were possible. In order to achieve pressure, the foil was imbedded in zinc stearate, but then problems of containment were encountered. It was found necessary at this stage to have the extremely good fit of piston into cylinder. Once this was accomplished, the desired high pressure could be attained and the first observations of transformation via diffraction effects could be made. Due to an unanticipated phenomenon, these effects could not be interpreted structurally. It was found that upon transformation the specimen became much coarser grained. In fact, the photographs suggest that only a few large grains (in some cases possibly a single crystal) are responsible for the observed diffraction data. It is very difficult if not hopeless to deduce a structure under these circumstances. It was clear, however, that the pattern of diffraction spots was not compatible with the structure of untransformed bismuth. From a variety of such photographs it was possible to decide on values of several prominent interplanar spacings, although not with high accuracy and not as well as could be done for a finely polycrystalline specimen. It is evident, also, that the pressure on the foil specimen is not generally uniform. In a single photograph there may appear sharp spots as well as grossly streaked ones associated with high strains. The hope of deciding on the symmetry of the new crystalline modification from a study of many such films with different orientations of crystallites was not realized. No substantial improvement of the situation resulted from varying the thickness of bismuth foil.

The next approach was to produce flat specimens of 0.001 to 0.005-inch thickness but consisting of very fine discrete bismuth particles in the hope that they would produce the usual type of "powder photograph" with continuous Debye-Scherrer arcs. The particles were spread uniformly on some glyptal on a microscope slide. After drying, the glyptal could be stripped and imbedded in zinc stearate in the same manner as the foil. Debye-Scherrer patterns were thus obtained but not of very high quality. The specimens with the finest particles ($<< 30\mu$) gave patterns that, while not too spotty, were very faint; and in order to get stronger patterns it was necessary to use particles of $\sim 30\mu$ and to tolerate more spottiness. While the quality of these films was not of the best and no further improvement seemed possible with further experimentation, a representative list of "d values" could be obtained and this is given in Table IV. Generous error limits are given not only because of difficulties of accurate measurement, but also because of seemingly real variations probably due to differences in pressure for the different experiments. Most important was the fact that, within the given limits, the spacings from the polycrystalline specimens corresponded to values obtained from the spots given by the foil specimens. There were, however, additional spots in the latter case.

With regard to interpretation of the given pattern, it is clear that the structure of the new phase is not a simple one, such as face-centered cubic, or any other common structure typical of metallic elements. Considerable effort has been expended in the attempt to obtain the unit cell and the atomic arrangement, but without success. Several possible cells have been deduced and one of these appears particularly attractive because of its relationship to the ordinary bismuth cell, but no satisfactory atomic arrangement could be found. The problem is made difficult by the largeness of the unit cell that appears to be called for. There is another source of uncertainty that should be mentioned. A second phase transformation occurs about 2000 atm beyond the pressure required for the first. It is possible, then, that the observed patterns are for two new phases rather than one. This possibility has been borne in mind in the attempts at interpretation but has not led to any fruitful conclusion. Experimentally, the pressures finally employed were only slightly beyond the point of no transformation, but this cannot guarantee that only one phase is present.

The resolution of the problem appears to depend on better experimental results, although the possibility of a deduction of a structure from existing data cannot be ruled out. In principle the simplest approach would be to exceed considerably the pressures used so far to insure that only phase III (beyond the second transformation point) was present. This means at present utilizing forces beyond the limits we have tried with the risk of cleaving the diamond. We have been reluctant to do this until we have exploited more the possibilities of our experimental arrangement which functions so well within the present limits. Another possibility is to devise means of obtaining rotation patterns for the "single crystal" situation present in the foil specimens. This may be feasible, but only with elaborate arrangements. The approach which seems

TABLE IV

Representative Diffraction Pattern from Polycrystalline Specimens of Transformed Bismuth (pressure > 25,000 atm)

Interplanar Spacing--"d" in Å	Intensity
3.14 ± 0.03	W^+
2.88 ± .03	M
2.72 ± .02	W
2.48 ± .02	VW
2.16 ± .02	W
1.90 ± .02	W
1.68 ± .02	VW
1.53 ± .02	VW
1.45 ± .02	VW

There are additional very weak lines beyond this point but whose certainty is questionable.

most attractive to us is to use temperature as a further variable. With increase of temperature both of the first two bismuth transformations occur at substantially lower pressures, but with a wider separation in pressure between them. Thus, there would be the advantage of operating at lower pressures, the higher certainty of separation of the two phases, and the ability to produce only phase III with pressures within our present limits. At room temperature the transformation pressures for phase I to II and phase II to III are approximately 25,000 and 27,000 atm respectively. At 150°C the corresponding pressures are 18,000 and 23,000 atm. In addition, there is the possibility that a foil would not give the coarse-grained patterns but rather polycrystalline ones. There is also the general desirability of having temperature as another variable. Accordingly, we have designed a furnace which should give temperatures of at least 200°C, and it is planned to continue the experiments with bismuth in the vicinity of 150° to 200°C. If results can be obtained at these temperatures they should provide useful information and aid materially in the solution of structure for the two new bismuth phases.

While the furnace is being constructed, other materials such as cesium, graphite, and boron will be examined at room temperature within our present pressure limitations.

ACKNOWLEDGMENTS

We happily acknowledge the advice and assistance of H.M. Strong and F.P. Bundy, who have contributed greatly to the successful operation of the apparatus.

We are especially indebted to O. Brusdal and E.H. Hull, since they designed the pressure apparatus and supervised its construction and were generous with their expert advice.

PART C

INTRODUCTION

The kinetic experiments undertaken at the Research Laboratory have included a study of the effect of pressure on the austenite to pearlite transformation in steels and precipitation in the four binary systems: aluminum-copper, copper-beryllium, gold-nickel, and lead-tin.

In order to interpret the kinetic data it is necessary to allow for the purely thermodynamic effects of pressure on phase equilibria. A theoretical investigation was therefore made to derive the thermodynamic relationships required for calculating the shift with pressure of the boundaries of a phase diagram. A summary of the results for a binary system is presented in the next section. Although the thermodynamic relationships are perfectly rigorous, they can only be applied approximately because of the lack of high-temperature compressibility data at the present time. The calculated changes in a phase diagram are therefore subject to an uncertainty which is difficult to estimate without resort to experiment. For this reason an experimental determination of the eutectoid region of the iron-carbon system has been started and preliminary results are presented in this report. This particular system was chosen not only for its scientific and practical interest, but also because of its relevance to the kinetic work on the pearlite transformation.

THERMODYNAMIC EXPRESSIONS FOR THE EFFECT OF PRESSURE ON PHASE EQUILIBRIA

When planning and interpreting experiments at high pressures, it is often necessary to estimate the direction and extent of the displacement in phase equilibria. The appropriate thermodynamic relationships have therefore been derived for multiphase equilibria in multicomponent systems. Since these derivations are rather lengthy they will be given in a separate report at a later date; for the present we will only list the relationships that are specifically applicable to a binary system.

Univariant Equilibria

In a two-component system, three phases can coexist only at one particular temperature (say, T_e), which is a function of the applied pressure P. The variation of T_e with P is given by Clapeyron's relationship

$$\frac{d\,T_e}{dP} = \Delta V/\Delta S \quad , \qquad (C1)$$

$$= \Delta V\, T_e/\Delta H \quad , \qquad (C2)$$

in which ΔV, ΔH, and ΔS are the total change in volume, enthalpy, and entropy of the system as it undergoes the transformation at the temperature T_e and pressure P. The individual values of ΔV, ΔH, and ΔS will depend on the size and average composition of the system, but the ratios $(\Delta V/\Delta S)$ or $(\Delta V/\Delta H)$ will be invariant.

Equation (C2) can be rewritten in terms of the molar properties of the three phases as follows:

$$\frac{d\,T_e}{d\,P} = \left\{ \frac{(c^\beta - c^\gamma)\,V^\alpha + (c^\gamma - c^\alpha)\,V^\beta + (c^\alpha - c^\beta)\,V^\gamma}{(c^\beta - c^\gamma)\,H^\alpha + (c^\gamma - c^\alpha)\,H^\beta + (c^\alpha - c^\beta)\,H^\gamma} \right\} T_e \quad , \tag{C3}$$

where c is the atomic fraction of component 2, and the superscripts α, β, and γ are used to denote the molar properties of the three phases.

Bivariant Equilibria

For two-phase equilibria in a two-component system, the pressure and temperature can be varied independently. If at a temperature T_e the atomic compositions of the two coexisting phases are c^α and c^β, then

$$\left(\frac{\partial\,T_e}{\partial\,P}\right)_{c^\alpha} = \left\{ \frac{V^\beta - (1-c^\beta)\,\overline{V}_1^\alpha - c^\beta\,\overline{V}_2^\alpha}{H^\beta - (1-c^\beta)\,\overline{H}_1^\alpha - c^\beta\,\overline{H}_2^\alpha} \right\} T_e \quad , \tag{C4}$$

in which the $\overline{V}$'s and $\overline{H}$'s are the partial molar volumes and enthalpies of the components in the two phases at the temperature T_e and pressure P. The corresponding expression for the β phase is obtained by interchanging the superscripts.

The compositional displacement of a point on the phase boundary is given by any one of the following expressions:

$$R\,T_e \left(\frac{\partial\,c^\alpha}{\partial\,P}\right)_T \left[1 + \frac{\partial\,\ln f_2^\alpha}{\partial\,\ln c} \right]_{P,T} =$$

$$\frac{c^\alpha\,(1-c^\alpha)}{c^\beta - c^\alpha} \left\{ V^\beta - (1-c^\beta)\,\overline{V}_1^\alpha - c^\beta\,\overline{V}_2^\alpha \right\} , \tag{C5}$$

$$RT_e \left(\frac{\partial \ln c^{\alpha}}{\partial P}\right)_T \left[1 + \frac{\partial \ln f_2^{\alpha}}{\partial \ln c}\right]_{P,T} = \frac{(1-c^{\alpha})}{c^{\beta}-c^{\alpha}} \left\{ V^{\beta} - (1-c^{\beta})\,\overline{V}_1^{\alpha} - c^{\beta}\,\overline{V}_2^{\alpha} \right\}, \tag{C6}$$

or

$$RT_e \left[\frac{\partial \ln (1-c^{\alpha})}{\partial P}\right]_T \left[1 + \frac{\partial \ln f_2^{\alpha}}{\partial \ln c}\right]_{P,T} = \frac{c^{\alpha}}{c^{\beta}-c^{\alpha}} \left\{ V^{\beta} - (1-c^{\beta})\,\overline{V}_1^{\alpha} - c^{\beta}\,\overline{V}_2^{\alpha} \right\}, \tag{C7}$$

in which f_2^{α} is the activity coefficient of component 2 in the coexisting α-phase. (It should be noted that the thermodynamic factor

$$\left[1 + \frac{\partial \ln f_2^{\alpha}}{\partial \ln c}\right]_{P,T}$$

is unity if the α-phase is sufficiently dilute for Henry's law to be obeyed.) The choice between Eqs. (C5) through (C7) is determined by the requirement that, for convenience in calculation, the derivative used should be relatively insensitive to small changes in c^{α} and c^{β}. Equation (C5) satisfies this condition if $(c_{\beta} - c_{\alpha}) << 1$ and c_{α}/c_{β} is approximately constant. However, for the cases $c^{\alpha} << 1$ and $c^{\alpha} \approx 1$, Eqs. (C6) and (C7) respectively should be used.

Equations (C6) and (C7) have a simple graphical interpretation which is demonstrated in Fig. 22 on a plot of the g atomic volume vs atomic composition. (Although the figure has been drawn with α and β as terminal phases, the construction holds for any disposition of the phase regions.) A tangent (hbfg) is drawn to the curve for the α-phase at the composition c^{α} and the line bc is extended to i and e. Then

$$RT_e \left(\frac{\partial \ln c^{\alpha}}{\partial P}\right)_T \left[1 + \frac{\partial \ln f_2^{\alpha}}{\partial \ln c}\right]_{P,T} = \text{the distance ge} \quad ,$$

and

$$- RT_e \left[\frac{\partial \ln(1-c^{\alpha})}{\partial P} \right]_T \left[1 + \frac{\partial \ln f_2^{\alpha}}{\partial \ln c} \right]_{P,T} = \text{the distance ih}$$

The sign to be attached to these distances is positive if g lies below e, or if h lies below i.

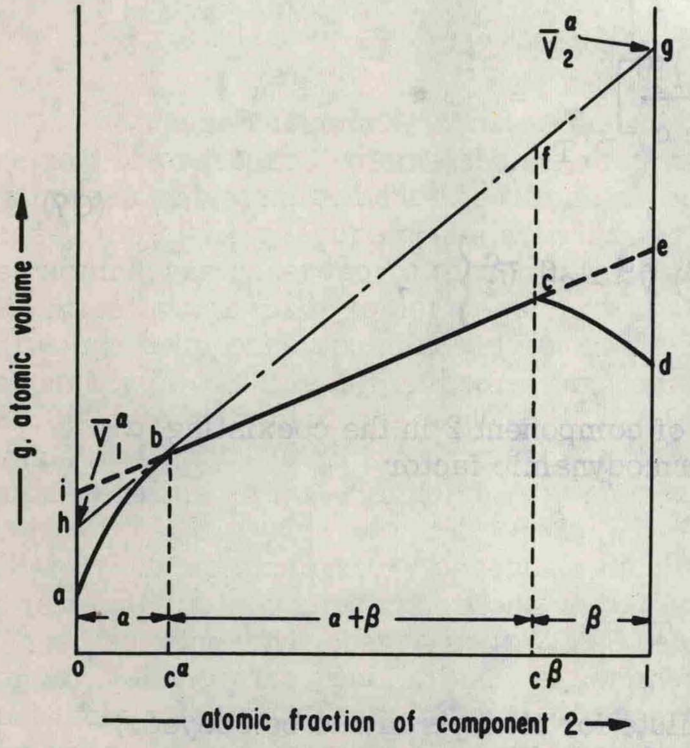


Fig. 22 Graphical construction to determine the pressure dependence of the equilibrium compositions in a binary system.

EFFECT OF PRESSURE ON THE AUSTENITE-PEARLITE TRANSFORMATION

Experimental Procedure

A study has been made of the pearlite transformation in two steels of approximately eutectoid composition, one being a commercial 1080 and the other a high-purity alloy.

For the runs made in the high-pressure apparatus the specimens were in the form of pills, 0.150 inch in diameter by 0.050 inch high. Two such pills (of the same composition) were packed in sodium chloride and sealed in a cylindrical stainless steel capsule. The purpose of the sodium chloride was to reduce the extent of the nonhydrostatic deformation during loading of the high-pressure cell. The samples were heated by passing current through the walls of the stainless steel capsule. The power supply was well stabilized, and it was possible to maintain the temperature constant to within ± 1°C. The temperature was measured with a calibrated chromel-alumel thermocouple, the hot junction of which was located at the center of the capsule between the two specimens. By switching the heating power off, the specimens could be rapidly cooled to room temperature. (The initial rate of cooling at 800°C was about 200°C/sec.)

The following pressure-temperature cycle was employed. The samples were first austenitized at temperatures between 800°C and 900°C for 20 minutes at the minimum pressure (less than 500 atm) required to establish electrical contact with the capsule. After austenitizing, the pressure was increased isothermally to 34,000 atm. The samples were then rapidly cooled to the transformation temperature (usually 600°C) and held for periods from 4 seconds to 3 hours. This was followed by a "quench" to room temperature, after which the pressure was released.

In addition to the runs made in the high-pressure apparatus, samples of the 1080 steel were also transformed in a salt pot to establish the pearlite growth rate at atmospheric pressure.

Experimental Results

1080 Steel

The commercial 1080 steel used was of the following composition: carbon 0.75; manganese 1.00; phosphorus 0.03; and silicon 0.17 wt per cent. When transformed at 600°C at atmospheric pressure, this steel displayed (Fig. 23) a fine pearlite structure with no pro-eutectoid constituent present whereas all samples transformed at 34,000 atm displayed (Figs. 24 and 25) an appreciable amount of pro-eutectoid cementite at the grain boundaries. This observation is in agreement with a calculation (described in the next section) which indicates that, with increasing pressure, the eutectoid composition is shifted to a lower carbon content. Thus a steel which is of eutectoid composition at atmospheric pressure will become hypereutectoid under pressure.

The most dramatic effect of pressure, however, was the decrease in the pearlite growth rate. This is illustrated by a comparison of Figs. 25 and 26. The latter is for a sample transformed at 600°C for 16 seconds at atmospheric pressure. It will be noted that the transformation is about half completed, whereas for a sample held under 34,000 atm at the same temperature for 15 minutes, only one small patch of pearlite is visible at the top center of Fig. 24.

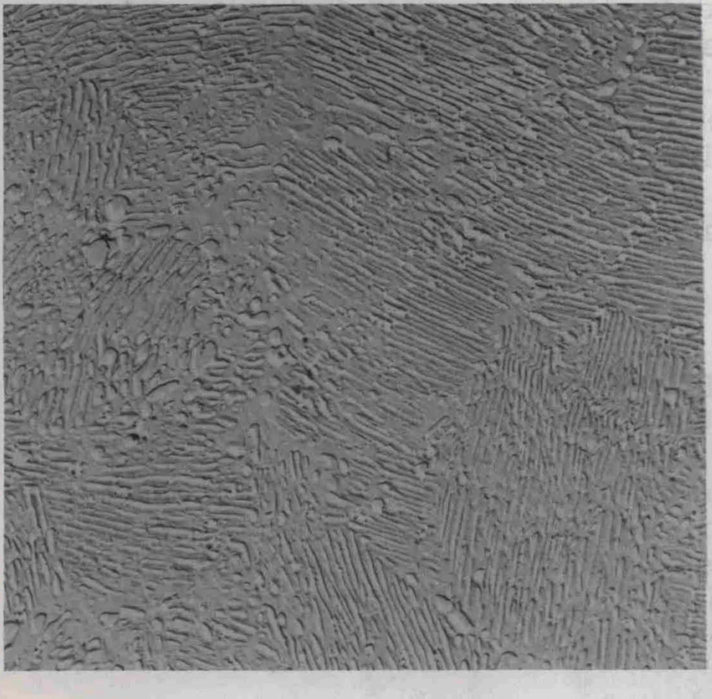


Fig. 23 1080 steel held for 15 minutes at 600°C at a pressure less than 500 atm, etched in picral. Electron micrograph, shadow-cast carbon replica. 10,000X

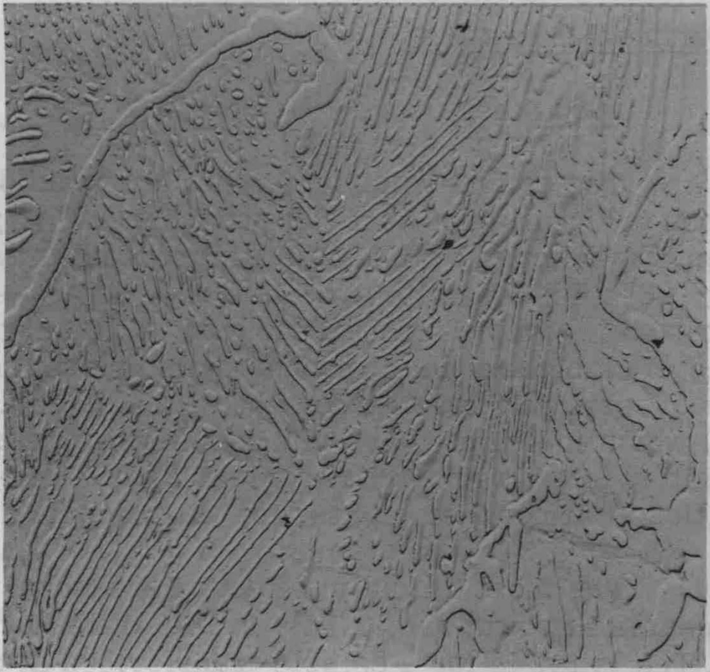


Fig. 24 1080 steel held for 3 hours at 600°C and 34,000 atm, etched in picral. Electron micrograph, shadow-cast carbon replica. 5000X

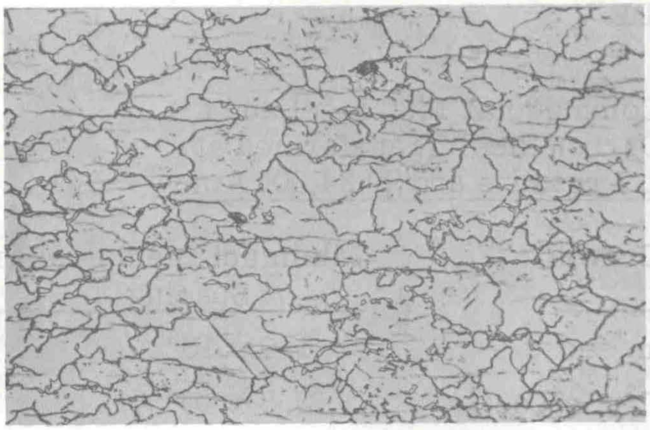


Fig. 25 1080 steel held for 15 minutes at 600°C and 34,000 atm, etched in picral. 500X

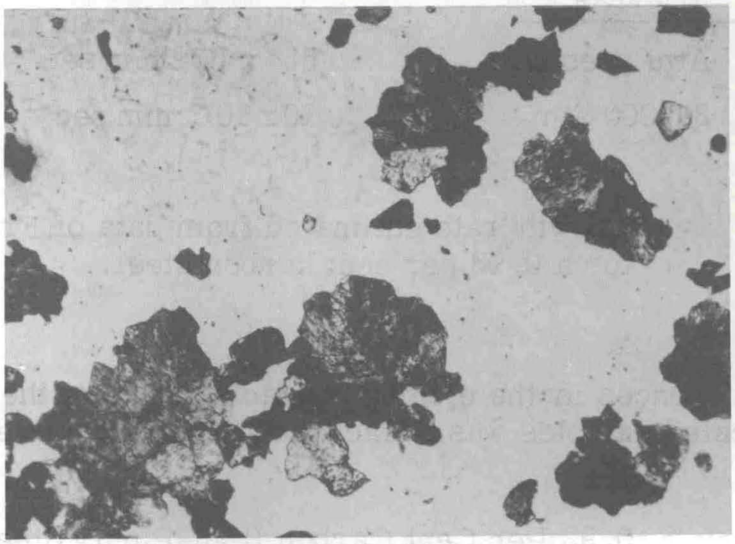


Fig. 26 1080 steel held for 16 seconds at 600°C at atmospheric pressure. Etched in picral. 500X

From measurements of maximum pearlite-nodule size, it was found (Table V) that pressure had decreased the pearlite growth rate by a factor of about 700.

Accompanying this decrease in growth rate was an increase in the minimum interlamellar spacing by a factor of about 2.3. The spacing measurements were made on electron micrographs, the magnification of which had been accurately determined.

Since hydrostatic pressure is known to decrease the M_S temperature, it is very probable that the M_S temperature for this steel is below room temperature at 34,000 atm. If this is true, then the martensitic structure observed in the untransformed regions of the pressure-treated specimens will have formed during the release of pressure at room temperature. Some

TABLE V

Properties of Pearlite in a Commercial 1080 Steel and a High-Purity 0.92 Per Cent Carbon Steel Transformed at 600°C Under (a) Atmospheric Pressure and (b) 34,000 Atm

1080	Pearlite Growth Rate	Minimum Interlamellar Spacing
(a) Atm pressure	5×10^{-3} mm sec^{-1}	1.0×10^3 A
(b) 34,000 atm	0.007×10^{-3} mm sec^{-1}	2.3×10^3 A
0.92 Per Cent Carbon		
(a) Atm pressure	$55^* \times 10^{-3}$ mm sec^{-1}	1.0×10^3 A
(b) 34,000 atm	10×10^{-3} mm sec^{-1}	1.4×10^3 A

*Growth rate estimated from data of Frye, Stansbury, and McElroy(23) for a 0.93 per cent carbon steel.

differences in the etching characteristics of the martensite in the pressure-treated samples was in fact observed, but this effect has not yet been followed up in detail.

0.92 Per Cent Carbon High-Purity Steel

For reasons to be mentioned later, it was believed that the drastic decrease in the pearlite growth observed in the 1080 steel might be due principally to the presence of manganese or one of the other impurities. Runs have therefore been made with a high-purity steel containing carbon 0.92; manganese 0.001; phosphorus 0.003; silicon 0.007; sulfur 0.009 wt per cent. (It would have been preferable to use a steel of the same carbon composition as the 1080, but at the time such a steel was not available. However, a set of high-purity steels has since been prepared and will be used for future work.)

The runs performed with this steel were similar to those described for the 1080 steel with the exception that the transformation rate at atmospheric pressure was not measured directly. At 600°C, the transformation in a pure steel is so rapid that special quenching techniques have to be employed. Since Frye, Stansbury, and McElroy(23) have made measurements on a steel whose composition (carbon 0.93; manganese 0.004; phosphorus 0.005; silicon 0.002; and sulfur 0.0001 wt per cent) is very close to that used in the pressure experiments, it was thought justifiable to use their data for the pearlite growth rate at atmospheric pressure.

With this steel the effect of pressure on the pearlite growth rate was far less than that observed in the 1080 steel. As will be seen from Table V the decrease in rate was only about a factor of five at 34,000 atm. In addition, the change in the interlamellar spacing was smaller.

It was also observed that the pro-eutectoid cementite was precipitated in the form of massive particles (Fig. 27) instead of as a film at the grain boundaries as seen in the atmospheric pressure treated high-purity steel (Fig. 28) and the pressure-treated 1080 steel (Fig. 25).

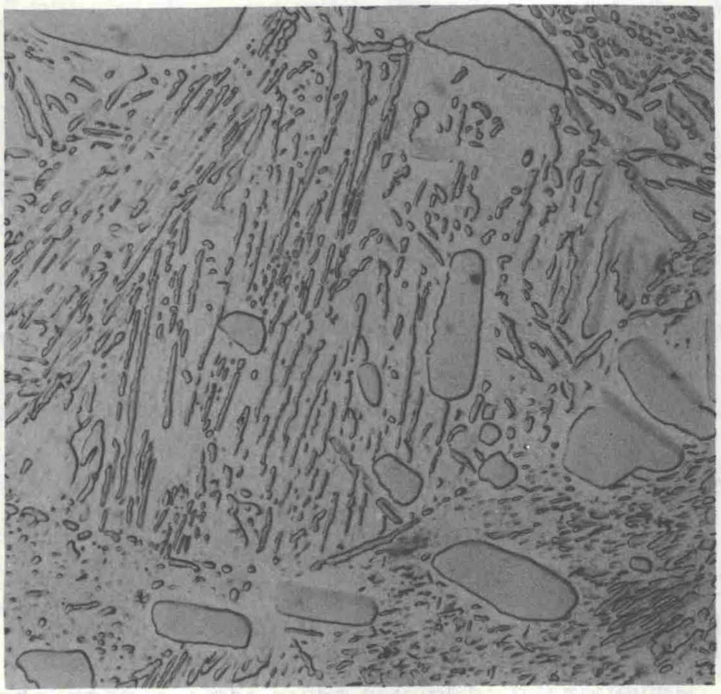


Fig. 27 0.92 per cent carbon high-purity steel held for 20 seconds at 600°C and 34,000 atm, etched in picral. Electron micrograph, shadow-cast carbon replica. 7000X

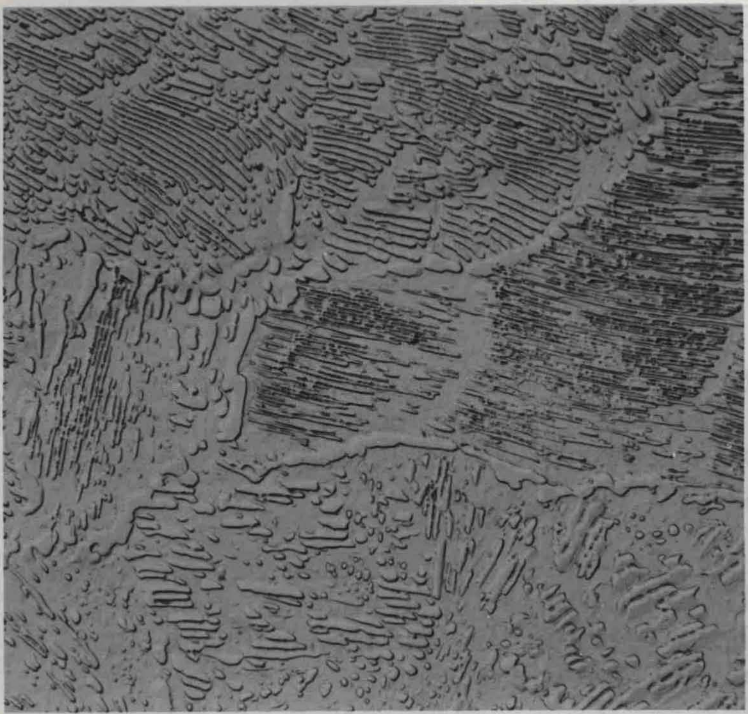


Fig. 28 0.92 per cent carbon high-purity steel held for 1 minute at 600°C at a pressure less than 500 atm, etched in picral. Electron micrograph, shadow-cast carbon replica. 7000X

DISCUSSION

The treatment of Zener and other workers leads to the following general expression for the pearlite growth rate, $\dot{G}$:

$$\dot{G} = \beta \Delta cD/(c^{\gamma} - c^{\alpha})\ S, \qquad \text{(C8)}$$

where β is a constant, Δ c is the difference in the carbon content of the austenite at the austenite-cementite and the austenite-ferrite boundaries, c^{γ} and c^{α} are the compositions of the bulk austenite and ferrite, S is the interlamellar spacing, and D the diffusion coefficient of carbon in austenite.

Let us now consider how each of these parameters varies as the pressure is increased from 1 to 34,000 atm. From the calculations and preliminary measurements on the shift with pressure of the phase boundaries of the iron-carbon system, it is estimated that Δ c changes by a factor of 0.5. If no pro-eutectoid cementite had precipitated prior to the transformation, c^{γ} would be the composition (0.92 per cent carbon) of the steel and would therefore be independent of pressure. However, it is known from the micrographs that at least a partial precipitation has occurred. We will therefore take c^{γ} as being approximately 0.6, which is about half way between the bulk composition and the estimated eutectoid composition of 0.4 per cent carbon. Thus at 34,000 atm, $(c^{\gamma} - c^{\alpha})$ changes by a factor of about 0.7 (since the variation of

c^{α} with pressure is negligible). Assuming that β remains constant, we thus have

$$(D_{34,000}/D_1) = 1.4\,(\dot{G}S)_{34,000}/(\dot{G}S)_1 \quad .$$

Substituting the ratios of the growth rates and the spacings measured for the high-purity steel (Table V), we obtain

$$(D_{34,000}/D_1) = 0.36 \quad .$$

If we define an activation volume, V^*, of diffusion by:

$$V^* = -RT \left(\frac{\partial \ln D}{\partial P}\right)_T \quad ,$$

and assume that it is independent of pressure, then a decrease of 0.36 in the diffusion coefficient at 600°C, corresponds to an activation volume of 2.1 cm^3/mole. This value does not appear to be unreasonable for the interstitial diffusion of carbon, since Lazarus(34) has recently reported an activation volume of about 2 cm^3/mole for the interstitial diffusion of oxygen in vanadium.

For the high-purity steel, therefore, the experimental observations are in accord with the Eq. (C1) for the growth rate of pearlite. If we make the same calculation for the 1080 steel we obtain

$$(D_{34,000}/D_1) = 0.0045 \quad ,$$

corresponding to an activation volume of 11.4 cm^3/mole. This seems impossibly high for interstitial diffusion and is even larger than would be expected for substitutional lattice diffusion. We therefore conclude that, in the 1080 steel, the diffusion of carbon was not the rate controlling step in the growth of pearlite, but that instead some other process associated with the presence of impurities dominated the transformation.

CALCULATIONS ON THE EFFECT OF PRESSURE ON PHASE EQUILIBRIA IN THE IRON-CARBON SYSTEM

Calculations have been made of the approximate shift to be expected in the iron-carbon eutectoid equilibria with pressure. These calculations were made using the thermodynamic expressions presented in an earlier section.

Change in Eutectoid Temperature

For the variation of the eutectoid temperature T_e with pressure P we have

$$(dT_e/dP) = \Delta V T_e/\Delta H \quad , \qquad \text{(C9)}$$

in which ΔV and ΔH are the total change in volume and enthalpy of an alloy as it undergoes a univariant transformation at the temperature T_e and pressure P. For ΔV a value of 0.059 cm^3/mole was calculated from dilational measurements of Mehl and Wells$^{(25)}$ on a 0.8 per cent carbon steel. According to the calorimetric measurements of Hagel, Pound, and Mehl,$^{(26)}$ ΔH is -1085 cal/mole. Substituting these values in Eq. (C9) we obtain

$$(dT_e/dP) = -\ 1.3 \times 10^{-3}\ ^\circ C\ atm^{-1}, \ (\text{at } T_e = 996^\circ K,\ P = 1\ atm)$$

If the derivative is assumed independent of temperature and pressure we find

$$\Delta T_e = -\ 44^\circ C,\ (\text{at } 34,000\ atm)\ .$$

Thus, at 34,000 atm, the eutectoid temperature will be at approximately 680°C as compared to 723°C at atmospheric pressure.

Changes in the Compositions of the Coexisting Phases

For the variation of the composition, $C^{\gamma c}$, of austenite in equilibrium with Fe_3C we have from Eq. (C6)

$$RT \left(\frac{\partial \ln c^{\gamma c}}{\partial P} \right)_T \left[1 + \frac{\partial \ln f_C^{\gamma}}{\partial \ln c_C} \right]_{T,P}$$

$$= \frac{(1-c^{\gamma})}{c^{c} - c^{\gamma}} \left\{ V^{c} - (1-c^{c})\ \bar{V}_{Fe}^{\gamma} + c^{c}\ \bar{V}_{C}^{\gamma} \right\} , \qquad \text{(C10)}$$

in which c^{γ} and c^{c} are the atomic fractions of carbon in austenite and Fe_3C; V^c is the molar volume of Fe_3C; $\bar{V}_{Fe}^{\gamma}$ and $\bar{V}_{C}^{\gamma}$ are the partial molar volumes of iron and carbon in austenite; and f_C^{γ} is the activity coefficient of carbon in austenite. A similar equation can be obtained for the pressure derivative of $c^{\gamma\alpha}$ (the composition of austenite in equilibrium with ferrite) by making the appropriate substitutions in the superscripts.

The following values were used for the molar and partial molar volumes:

	723°C
V^{α}	7.32 cm^3 (c = 0.009)
V^{c}	5.98 cm^3 (c = 0.25)
$\bar{V}_{Fe}^{\gamma}$	7.17 cm^3 (c = 0.0362)
$\bar{V}_{C}^{\gamma}$	4.47 cm^3 (c = 0.0362)

The molar volume, V^{α}, of ferrite was derived from the lattice parameter measurements of Basinski, Hume-Rothery, and Sutton.(27) The partial molar volumes $\bar{V}_C$ and $\bar{V}_{Fe}^{\gamma}$ were calculated from the lattice parameter data of Essen and Müller(28) after correcting for the 0.15 per cent difference between their parameters for pure austenite and those (which we consider the more reliable) of Basinski et al.(27) Unfortunately, no high-temperature lattice parameters have apparently been determined for Fe_3C. Consequently, it was necessary to make an estimate from the measured values of V^{γ} and V^{α} and the volume change of 0.80 per cent reported by Mehl and Wells(25) for the formation of pearlite in a eutectoid steel. The value (5.98 cm^3 at 723°C) so obtained for V^c appears reasonable, since it corresponds to a molar volume given by the room temperature lattice parameter measurements of Jack(29) with a coefficient of thermal expansion about two-thirds that of ferrite.

The measurements of the carbon activity in austenite made by Smith(30) were used to derive the following value of the thermodynamic factor in Eq. (C10):

$$\left[1 + \frac{\partial \ln f_C^{\gamma}}{\partial \ln c}\right]_{T,P} = 1.29 \text{ (at } c^{\gamma} = 0.0362,\ T = 723°\text{C).}$$

Substituting the aforementioned values for the volumes and thermodynamic factor in Eq. (C10) (and the corresponding equation for the austenite-ferrite equilibrium) we obtain:

$$\left(\frac{\partial \log c^{\gamma\alpha}}{\partial P}\right)_T = -16 \times 10^{-6}\ \text{atm}^{-1} \text{ (at } c^{\gamma} = 3.62,\ T = 723°\text{C)}$$

$$\left(\frac{\partial \log c^{\gamma c}}{\partial P}\right)_T = -9.5 \times 10^{-6}\ \text{atm}^{-1} \text{ (at } c^{\gamma} = 3.62,\ T = 723°\text{C)}$$

If we assume that the derivatives are independent of pressure, then they can be integrated to give

$$c^{\gamma\alpha}(\text{at } 34,000 \text{ atm}) = 0.29\, c^{\gamma\alpha}(\text{at } 1 \text{ atm})$$

and

$$c^{\gamma c}(\text{at } 34,000 \text{ atm}) = 0.48\, c^{\gamma c}(\text{at } 1 \text{ atm})$$

We thus find that at 723°C, increasing the pressure to 34,000 atm shifts the ferrite-austenite boundary from 0.8 to 0.23 wt per cent carbon, and the austenite-Fe_3C boundary from 0.8 to 0.38 wt per cent carbon. Taking into account the 44°C calculated for the depression in the eutectoid temperature, these shifts correspond to a eutectoid composition of about 0.35 wt per cent carbon at 34,000 atm.

It must be emphasized that in the foregoing calculations we have neglected (because of the lack of data) the differential compressibility of the various phases. The results are therefore subject to an unknown error.

EXPERIMENTAL DETERMINATION OF THE IRON-CARBON DIAGRAM AT HIGH PRESSURES

An investigation has been started of the phase-diagram of the iron-carbon system at high pressures. The method being used is to determine the volume fractions of the coexisting phases in samples quenched after equilibration at a given temperature and pressure. The volume fractions are estimated by a systematic point count which a recent theoretical study(31) has shown to be the most efficient of the several metallographic procedures available.

So far two points on the austenite-cementite boundary at 34,000 atm have been determined. These are 0.47 (± 0.02 wt per cent carbon at 700°C and 0.60 (± 0.02 wt per cent carbon at 750°C. (The uncertainty limits are the standard deviations of the volume-fraction analysis.) These values indicate that the eutectoid composition will be at about 0.4 wt per cent carbon. They are therefore in reasonable agreement with the calculations described in the previous section. However, since a check has not yet been made that equilibrium was in fact attained in the specimens prior to quenching, the results cited must, for the time being, be considered provisional. In addition, no allowance has been made for the effect of pressure on the thermocouple emf.

EFFECT OF PRESSURE ON THE HIGH-TEMPERATURE PRECIPITATION IN ALUMINUM-COPPER ALLOYS

Experimental Procedure

Samples of a high-purity aluminum - (4 1/2 wt per cent copper) alloy in the form of six pills, each 0.080 inch in diameter by 0.025 inch high, were subjected to the following pressure-temperature cycle: (a) homogenization at 550°C for 30 minutes at a pressure of less than 500 atm; (b) an increase in pressure to 30,000 atm, the temperature being held steady at 550°C; (c) rapid cooling to a transformation temperature of 400°C at which the specimens were held for various times up to 2 hours; (d) rapid cooling to room temperature. A set of samples was also transformed at atmospheric pressure to provide a control.

Experimental Results

High pressure had little effect on the mode of transformation; in all specimens, precipitation of $CuAl_2$ occurred predominantly within the grains. (The identity of the precipitate was verified in all cases by x-ray diffraction analysis.) However, the rate of precipitation was much slower in the specimens transformed at 30,000 atm. This is illustrated by Figs. 29 through 31. The first is the structure of a specimen held at 400°C at a pressure of less than 500 atm for 20 minutes, by which time the precipitation of $CuAl_2$ was complete, whereas in samples (Figs. 30 and 31) transformed at 30,000 atm complete precipitation had not occurred even after 60 minutes. (The horizontal lines in Figs. 29 through 31 are the interfaces between the pills which constituted the specimen.) From a comparison of the microstructures of the pressure-treated specimens with those for specimens transformed at atmospheric pressure, it was visually estimated that the rate of transformation was about 40 times slower in the former.

Calculation of the Change in Solubility with Pressure

Unfortunately, no high-temperature density or lattice parameter measurements have apparently been made on the $CuAl_2$ phase. The calculation of the solubility change with pressure therefore had to be made on the basis of the molar values of the phases at room temperature. Using the lattice parameter data of Ellwood and Silcock(32) for the aluminum-rich solid solution and of Bradley and Jones(33) for $CuAl_2$ and assuming that the aluminum-rich solid solution obeys Henry's law, it was calculated that

$$T\left(\frac{\partial \log c}{\partial P}\right) = 8.2 \times 10^{-4}\ \text{atm}^{-1} \quad .$$

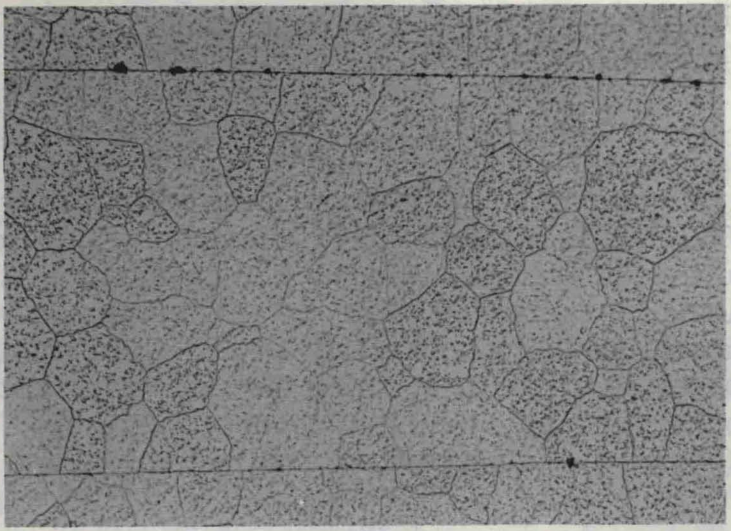
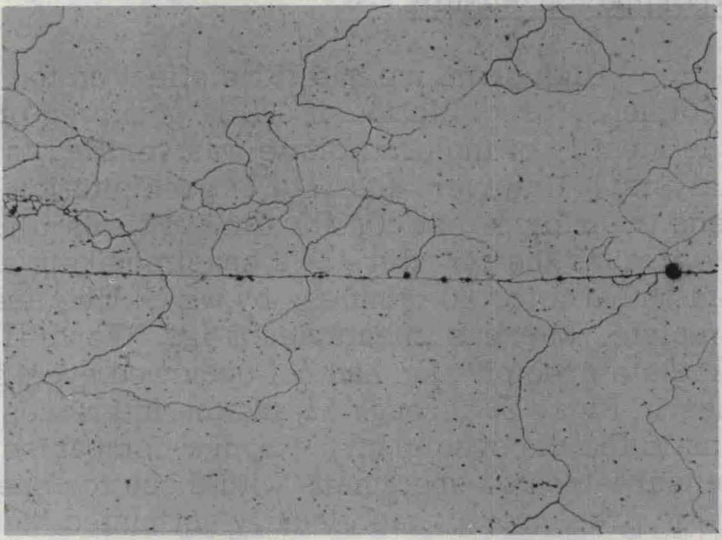


Fig. 29 Aluminum-(4 1/2 wt per cent copper) alloy homogenized at 550°C and transformed at 400°C for 20 minutes at a pressure less than 500 atm, etched in HF-HNO_3-HCl mixture. 100X

Fig. 30 Aluminum-(4 1/2 wt per cent copper) alloy homogenized at 550°C and transformed at 400°C for 20 minutes at 30,000 atm, etched in HF-HNO_3-HCl mixture. 100X



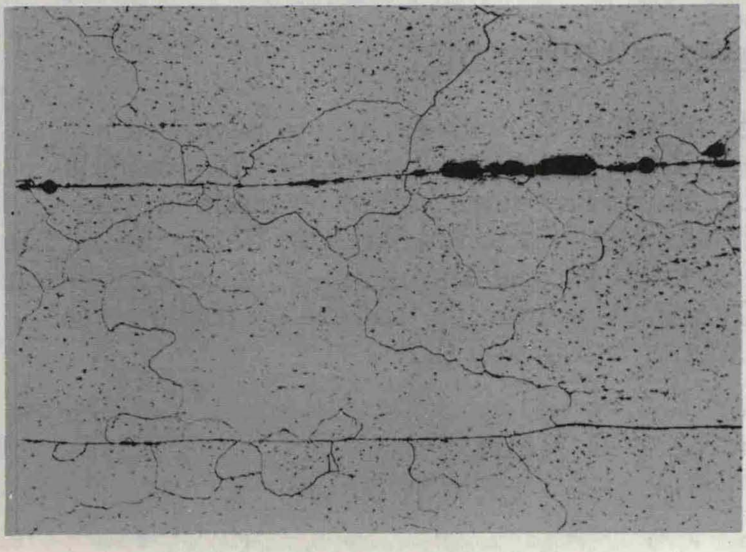


Fig. 31 Aluminum-(4 1/2 wt per cent copper) alloy homogenized at 550°C and transformed at 400°C for 60 minutes at 30,000 atm, etched in HF-HNO_3-HCl mixture. 100X

where c is the composition of the solid solution in equilibrium with $CuAl_2$.

If we assume that the derivative is independent of pressure, then on integration we obtain

$$c(400°C, 30,000 \text{ atm}) = 1.09\, c\, (400°C, 1 \text{ atm})$$

There is thus a 9 per cent (relative) increase in the solubility of aluminum for copper at 30,000 atm and 400°C. Since the solubility of copper at 400°C is about 1.4 wt per cent, the change in solubility at 30,000 atm corresponds to a decrease of about 14 per cent in the supersaturation ratio for an aluminum--(4 1/2 wt per cent) alloy.

DISCUSSION

If it is assumed that the precipitation of $CuAl_2$ is diffusion controlled, then the fortyfold decrease observed in the precipitation rate must be ascribed to the effect of pressure on the diffusion coefficient, because of the negligible change in the supersaturation ratio. Accordingly, if it is also assumed that the activation volume, V^*, for diffusion is independent of pressure, we can write

$$V^* = -RT\,\Delta(\ln D)/\Delta P = -RT\,\Delta(\ln \dot{G})/\Delta P\ ,$$

where $\dot{G}$ is the rate of precipitation. Substituting the experimental values: $-\Delta(\ln \dot{G}) = \ln 40 = 3.7$; $\Delta P = 30,000 \text{ atm} = 7.3 \times 10^2 \text{ cal cm}^{-3}$; and $T = 673°K$ we obtain

$$V^* = 6.8 \text{ cm}^3$$

This value is about the right magnitude for substitutional lattice diffusion. We can thus conclude that the assumption of diffusion being the rate controlling step is a reasonable one.

We intend to continue the study of this system in more detail, because the fortuitously small change in solubility greatly simplifies the interpretation of the effects of pressure on the kinetics of transformation.

EFFECT OF PRESSURE ON THE KINETICS OF TRANSFORMATION IN LEAD-TIN, GOLD-NICKEL AND COPPER-BERYLLIUM ALLOYS

The initial work on these alloy systems has now been completed and detailed reports will shortly be issued by J.W. Cahn on the lead-tin and gold-nickel work, and by V.A. Phillips on the copper-beryllium work. The following is a summary of their findings.

Copper-Beryllium

The effect of pressure during heat treatment on the optical microstructure and microhardness of a commercial copper-beryllium alloy has been studied. The application of 69 to 75,000 atm pressure during aging at 390°C decreased the growth rate of the discontinuous precipitate nodules greatly, and retarded the rate of general precipitation hardening to a lesser extent. Marked localized precipitation occurred on aging along slip bands formed during the initial application of the high pressure.

The application of 69 to 75,000 atm pressure during solution treatment at 825°C apparently substantially reduced the solubility of beryllium in copper in agreement with theoretical prediction and gave an unusually fine grained structure due to the inhibition of grain growth.

Gold-Nickel and Lead-Tin

Two cellular precipitating systems, gold-nickel and lead-tin, were examined under pressure. Available lattice parameter measurements for these systems indicate that only a small change in solubility (not exceeding 20 per cent of that at atmospheric pressure) is to be expected in the pressure range covered.

The effects of pressure on these two systems were quite different. A small decrease in cell growth rate was observed in gold-nickel (a factor of four for 50,000 atm at 420°C for a 30 per cent alloy), whereas in lead-tin the decrease was much larger (a factor of 400 for 40,000 atm for a 7.5 wt per cent tin alloy). The morphology was hardly affected: a small decrease in spacing with pressure for the gold-nickel alloy, and a small increase for the lead-tin alloy.

The magnitude of the change in diffusion rate implies a volume of activation smaller than that expected for bulk diffusion.

GENERAL DISCUSSION OF THE KINETIC EXPERIMENTS

The one effect of pressure that is common to all the systems studied is a decrease in transformation rate. This effect is certainly not due entirely (or even principally) to a pressure induced change in the phase equilibria, because for three of systems (copper-beryllium, lead-tin, and gold-nickel) we have estimated that the solubility of the precipitating phase decreases with increasing pressure; therefore, other things being equal, one would have expected an increase in the transformation rate. Instead, it appears that the predominating influence of pressure is a decrease in atomic mobility. For at least two of the systems (aluminum-copper and the pure eutectoid steel) the observed change in growth rates is quantitatively consistent with the expected dependence of the relevant diffusion coefficient on pressure.

In addition to the variation in transformation rate, changes were found in the morphologies and many of the other properties of the alloys. It would therefore be a considerable oversimplification to suggest that the data can be interpreted purely on the basis of diffusion. We know that the characteristics of any particular transformation are determined by a complex interplay of many factors, of which diffusion is but one. Not until the pressure dependences of these various factors have been isolated will we be able to account satisfactorily for all the property changes in pressure-treated metals and alloys. However, by the same token, the behavior of a transformation under high pressures will yield valuable information about the mechanisms prevailing at atmospheric pressure. We believe that this information may well prove to be an important outcome of this high-pressure research in kinetics.

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