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THE COMPATIBILITIES OF BORON AND GERMANIUM

LAWRENCE R. BIDWELL

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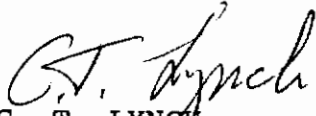
FOREWORD

This program was conducted under Project 7353, "Characterization of Solid Phase and Interphase Phenomena in Crystalline Substances", during the period August 1968 to May 1969.

The research was performed in the Advanced Metallurgical Studies Branch of the Metals and Ceramics Division, AFML, Wright-Patterson Air Force Base, Ohio 45433. The able assistance of Mr. C. Underwood of AFML and Messrs. J. Lincoln and M. Rosenblum of the University of Cincinnati in various phases of the experimental work and the helpful comments of Dr. S. Lyon are gratefully acknowledged.

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This technical report has been reviewed and is approved.


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ABSTRACT

The salient features of the boron-germanium phase equilibrium diagram have been deduced from X-ray diffraction, metallographic, thermal analysis, and electron microprobe studies on both sintered and melted alloys. The system can be characterized as a classical monotectic-eutectic with no intermediate phases. The occurrence of hypomonotectic boron crystals and boron crystals grown from a germanium melt indicates a slight solubility of germanium in solid boron and of boron in liquid germanium at the monotectic temperature. X-ray diffraction, thermal analysis, and metallographic studies indicate that the germanium-rich liquid freezes as essentially pure germanium and that the solid solubility of germanium in boron and of boron in germanium is virtually nil at the eutectic temperature. The minute quantity of boron that does dissolve in solid germanium does so substitutionally with a 0.01 to 0.02 volume percent contraction of the germanium lattice. These results indicate that germanium may have utility as a boron diffusion barrier for boron fiber-reinforced metal-matrix composites.

(Distribution of this abstract is unlimited.)

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SECTION I

INTRODUCTION

Fiber reinforced composites have received a great deal of attention in the past several years as a class of materials offering almost endless possibilities for achieving outstanding combinations of desired engineering properties--especially when normalized on a weight basis. While the earlier work in the field of composite technology was primarily devoted to the study and evaluation of plastic-matrix composites, more recently the rate of effort has been greatly expanded by the inclusion of an exploration for metal-matrix materials.

Fibers of elemental boron on a tungsten substrate and of various inorganic borides represent one of the most attractive classes of reinforcing materials for both plastic and metal-matrix composites due to their light weights, high strengths and high moduli of elasticity. Their great thermal stability is an additional characteristic that makes them particularly well-suited for use in metal-matrix composites formulated for application at elevated temperatures. It is no small disappointment therefore, that these materials are generally chemically incompatible with the metals upon which most of our conventional engineering alloys are based. Snide,¹ for one, has shown that both boron and titanium diboride are subject to serious deleterious filament-matrix interactions in iron, cobalt and nickel in the

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temperature range (900°C) in which they are used as the basis for the superalloys. In a more complete evaluation of the compatibility of these filaments with titanium and titanium alloy matrices he found similar deleterious interactions and furthermore was able to demonstrate that they occurred largely by the one-way diffusion of boron into the matrix.

In a relatively recent analytical review of the technical potential of metal-matrix composites, Burte and Lynch² identify filament-matrix compatibility as the major problem area in the development of composites for use at elevated temperatures. Snide, Lynch and Whipple³ have noted several approaches that can be used to attack this problem, namely, (1) develop new filamentary materials that are stable with respect to the matrix; (2) employ matrix alloying additions that reduce the chemical activities of the diffusing species; and (3) develop coatings that act as a diffusion-barrier with respect to filament-matrix interactions. For the effective utilization of boron or boron compounds in the more conventional intermediate temperature metal-matrices, approach (3), possibly with minor alterations of the matrix through (2), would appear to be the most promising.

In previous work on the formation of borides of the Group IV B elements^{4,5} aimed at providing crystallographic information for the purpose of characterizing the atomic bonds in pure boron and in the non-transition metal inorganic borides, solid germanium and boron appeared to be relatively insoluble in each other and

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did not appear to form any intermetallic compounds. The possibility that germanium might provide a suitable boron diffusion-barrier in metal-matrix composites prompted the present, more detailed, study of these questions. The observations that have been made in this investigation are sufficient to permit the classification of the boron-germanium phase equilibrium diagram and to characterize its significant features.

SECTION II EXPERIMENTAL PROCEDURE

A. Alloy Preparation

The alloys used in this work⁵ were prepared from -325 mesh, 99.2% purity boron obtained from the U.S. Borax and Chemical Corp. and from semiconductor grade germanium donated by the General Electric Research Laboratory. The germanium was crushed and ground in a boron carbide mortar, mechanically blended with amounts of boron varying from 2 to 95 at.% and cold-pressed into 10g powder compacts in a hardened steel die. In the initial experiments, the compacts were heated in boron nitride crucibles under a variety of conditions that had proven adequate for the formation of silicon borides. These included--solid-state reaction in a purified helium atmosphere for 48 hrs at 900°C, i.e., just below the 937°C melting point of germanium--and solid-liquid reaction in both helium and vacuum for periods of up to 24 hrs and at temperatures ranging from 1000° to 1400°C. In the subsequent experiments, a series of samples was heated above the melting point of boron, i.e., ~2075°C.⁶ Since the vapor pressure of germanium reaches 10 torr or greater at temperatures above 2000°C, all of these samples were induction heated with a graphite susceptor in a helium purged atmosphere. Soaking times were of the order of 10-15 min. With this procedure material losses could generally

be kept to less than 10%. In all cases the boron nitride crucibles were treated to remove the B_2O_3 binder, introduced as an aid in manufacture, before they were used as containers for the boron-germanium alloys. This treatment involved either heating in a hydrogen atmosphere to $1700^\circ C$ or firing in vacuum to temperatures significantly higher than the crucibles were subsequently to be used.

Several ternary boron-germanium-silicon compositions were prepared from the above materials and semiconductor grade silicon and subsequently subjected to solid-liquid reaction at $1600^\circ C$ for periods up to 8 hrs. These alloys were in some cases made by firing mixtures of the three components and in others by use of a previously melted silicon-germanium master alloy.

B. X-ray and Metallographic Methods

One or more portions of each sample was investigated by X-ray diffraction using a flat, powder-specimen and either $Cu-K_\alpha$ or $Co-K_\alpha$ radiation and an X-ray diffractometer. In those instances where precision comparative lattice parameters were desired a scanning rate of 0.2 deg/min was employed.

Specimens were prepared for metallographic examination by grinding on silicon carbide papers through 600 grit and then mechanical polishing with Al_2O_3 , CeO or diamond abrasives. Although numerous polishing techniques were tried, none was

completely satisfactory due to the very large difference in the hardnesses of boron and germanium. Excessive surface relief in the high-boron content alloys was especially difficult to avoid.

C. Thermal and Electron Microprobe Analysis

The reaction horizontal of a 2 at.% boron alloy was determined by differential thermal analysis. Temperatures were measured with a calibrated chromel-alumel thermocouple and the differential e.m.f. between the sample and an Al_2O_3 standard was measured with an L&N K-3 potentiometer. Several determinations of the melting point of pure germanium were made as a calibration of the apparatus. A value of $937 \pm 1^\circ\text{C}$ was obtained in these measurements.

A 70 and a 90 at.% boron alloy were examined by electron microprobe analysis using both Ge-L_α X-rays and back-scattered electrons at 20 KV. The specimens were coated with a vapor-deposited layer of graphite in order to obtain an electrically conducting surface.

SECTION III

RESULTS AND DISCUSSION

In the previous investigation,⁵ which was aimed at synthesizing possible germanium-boron compounds, X-ray diffraction patterns on the initial series of samples (solid-solid and solid-liquid reaction at 900° to 1400°C) gave no indication of the formation of a boride phase, nor were there any obvious shifts in d-spacings indicating the formation of either a boron or germanium solid solution. Germanium borides were considered most likely to be formed in the samples with a high boron content. However, the germanium in these samples tended to coalesce into spheres as though the boron particles were not being wet by the liquid germanium. In order to eliminate the possibility that wetting action was being inhibited by a boron suboxide film, such as B_6O , a second series of samples was heated above the melting point of boron. An X-ray diffraction examination of these alloys gave results similar to those prepared at lower temperatures in that no germanium-boron compounds or significant solid solutions were detected.

Metallographic studies made in the present investigation give substantial insight into the nature of the boron-germanium system. Figures 1 and 2 show the attack of solid boron particles that have been in contact with liquid germanium for 2 hrs at 1400°C,

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indicating that boron has at least some solubility in liquid germanium. The results of heating a 70 at.% boron alloy to 2150°C are shown in Figure 3. Nearly complete gravity segregation of the lighter boron and the more dense germanium has occurred, revealing a liquid immiscibility typical of a monotectic reaction. Entrapped, interdendritic germanium can easily be seen in the upper, boron-rich, layer. The lower, germanium-rich layer, however, contains little evidence of boron except for the many small equiaxed crystals located near the outside surfaces. These crystals were probably nucleated and grew within globules of boron liquid that had attached themselves to the walls of the crucible. A small number of elongated crystals also appear in the upper portion of the layer, which are difficult to rationalize as having grown from entrapped boron liquid. A more likely explanation is that they were nucleated at some preferred site, such as the crucible wall, but were grown from boron in solution as they floated upward in the germanium liquid.

Figure 4 shows a typical hypomonotectic composition (95 at.% boron) consisting of a boron matrix containing both pro-monotectic and monotectic crystals, which are indistinguishable in this view, and monotectic germanium rejected during freezing at the monotectic temperature. Figure 5 shows a rather rare example of a boron crystal apparently growing within the monotectic germanium. Presumably this crystal was nucleated at the liquid-

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matrix interface and grew from boron in liquid solution during cooling below the monotectic temperature. If this is in fact the case, it would support the prior indication (Figure 1) that boron has at least a moderate solubility in liquid germanium. It would also indicate, however, that this solubility decreases significantly with decreasing temperature. Differential thermal analyses of several germanium and germanium-2 at.% boron samples confirm this viewpoint in that within an uncertainty of less than 1°C, the freezing temperatures of the pure germanium and the alloys were identical. It is likely, therefore, that the terminus of the germanium liquidus curve occurs at essentially pure germanium.

The earlier indication of the apparent lack of a germanium solid solution was unexpected. Germanium has many characteristics in common with silicon, e.g., both have diamond cubic structures, form similar types of compounds, form a complete series of nearly ideal solid solutions and differ in atomic diameter by only 3 1/2%. Since silicon can accommodate more than three atomic percent boron in substitutional solid solution, it was anticipated that boron might have a similar solubility in germanium. Consequently, the question of the extent to which boron is soluble in solid germanium was further examined by conducting comparative lattice parameter measurements on the alloys prepared both by melting and by solid-state reaction (900°C) and on germanium that had been melted with the same procedures used

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for the alloys. The lattice parameters for the germanium in all samples fell within the range $5.6566 \pm 0.0005 \text{ \AA}$. While a higher degree of accuracy cannot be assigned these measurements, their relative precision was sufficient to consistently show a contraction of the alloy lattice of 0.01 to 0.02 volume percent compared to the pure germanium samples. This would appear to indicate the presence of a very minute quantity of boron in substitutional solid solution.

Metallographic examination of the melted boron-rich alloys revealed what appeared to be a third phase in many of the samples with the highest boron contents. Typical examples of these idiomorphs are shown in Figures 6 and 7. The crystals shown in these photomicrographs are seen in light surface relief as the result of excessive polishing. The high contrast photography used is misleading in that the crystals are actually quite difficult to see under normal microscope viewing. Their identity was rather perplexing in that the X-ray diffraction data indicated that only germanium and boron were present. The possibility that the crystals were boron carbide, formed as a result of carbon contamination from the graphite susceptor, could be eliminated by virtue of the fact that they did not occur in samples of pure boron melted under similar circumstances. In addition, the degree of surface relief obtained was much less than would be expected for boron carbide in a boron matrix.

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An electron microprobe analysis was conducted on several samples in a further effort to establish the crystal's identity. A back-scattered electron image of one of these crystals is shown in Figure 8. This image has been electronically reversed so that the light areas indicate less scattering and hence, a lower atomic number. The black regions are essentially pure germanium. Unfortunately a direct analysis for boron was beyond the capabilities of the instrument. However, an area scan for germanium-L_α X-rays, shown in Figure 9, clearly shows that the germanium content of the crystal is much lower than the matrix, thus eliminating the possibility that the particle is a germanium boride phase. These crystals are unquestionably boron and while the possibility that they represent material that was unmelted during the preparation of the alloys cannot be excluded, their morphology is much more characteristic of primary hypomonotectic crystals that grew from a supercooled melt on cooling below the liquidus temperature and thus contained less than the equilibrium amount of germanium. At the monotectic temperature the monotectic liquid then decomposed into a germanium-rich liquid and solid boron with a much higher germanium content than the previously solidified material. A comparison of the germanium X-ray intensity from boron particles imbedded in a germanium matrix in a 70 at.% boron alloy, against the intensity from the matrix indicates that less than 3 at.% germanium is soluble in boron at elevated temperatures.

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The above results are quite conclusive in showing that, in contrast with the Group IV B elements carbon and silicon, which form boron compounds quite readily, no germanium-boron compounds are formed. This conclusion is in agreement with the findings of Samsonov et al.⁷, who could find no evidence for the formation of a germanium boride either by the direct reaction of solid boron and liquid germanium or by the reduction of germanium oxide with boron carbide. These investigators also conducted similar experiments with tin and lead and likewise, could find no evidence for the existence of either tin or lead borides. The present opinion regarding the interaction between boron and the Group IV B elements considers that the three outer electrons of boron are too localized--or tightly bound--to participate in metallic bonding but yet are too few in number to form simple covalent bonds. The difficulty in forming silicon borides in comparison with the ease with which boron carbide is formed, and the apparent lack of germanium, tin and lead borides is thought to be consistent with the increasing metallic character of the IV B elements in the order carbon, silicon, germanium, tin and lead.

The observations made in this investigation are sufficient to permit a characterization of the significant features of the boron-germanium phase equilibrium diagram. These features are illustrated schematically in Figure 10 and include: (1) a monotectic reaction-isotherm that occurs at some unknown temper-

Conclusions

ature below the melting point of boron (2075°C) and (2) a limiting eutectic reaction-isotherm that occurs at essentially the melting point of germanium (937°C). The composition of the monotectic liquid is presumed to lie between 70 and 90 at.% boron based on the absence of primary boron crystals in the former composition and their presence in the latter composition. The solubility of germanium in solid boron and of boron in liquid germanium is restricted but nevertheless significant at the monotectic temperature. The composition of the germanium eutectic is essentially pure germanium and the solid solubilities of boron and germanium are negligibly small at the eutectic temperature.

All of the above observations indicate that germanium should provide an efficient boron diffusion-barrier. Parallel experiments conducted on ternary alloys containing silicon revealed that the solid solubility of germanium in both silicon borides and boron-rich silicon-boron solid solutions is undetectably small. Consequently, germanium would also appear to be an equally efficient barrier coating for silicon boride filaments.

While the ability to inhibit the outward diffusion of boron may prevent the type of degradation observed by Snide¹ in titanium-boron composites, much more is required of a viable and effective coating. Burte and Lynch² have noted that although extensive filament-matrix interactions are usually undesirable, more than a simple interlocking effect is needed to provide adequate load transmission normal to the filament axis. Thus, "--controlled

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reaction, rather than no reaction is the goal." The boron-rich samples prepared at low temperatures (900°C) strongly suggest that wetting action between boron and germanium may be difficult to achieve. This possibility is given support by the observations of Hough,⁸ who was unable to vapor deposit an adherent germanium coating on a boron filament at 800° to 900°C. This problem could be simply resolved, however, by doping the germanium with silicon. Silicon and germanium form a complete series of solid solutions⁹ and a germanium-rich solution should readily wet boron without serious interactions. The final judgement as to the applicability of germanium as a protective coating for either boron or silicon boride filaments must be based upon an evaluation of the compatibility of germanium with each matrix material that is under consideration.

SECTION IV

CONCLUSIONS

1. Germanium, unlike the similar Group IV B elements carbon and silicon, does not form a boride.

2. The boron-germanium system can be classified as a monotectic-eutectic system in which a boron-rich liquid undergoes a monotectic decomposition into solid boron and a germanium-rich liquid that, in turn, freezes as a limiting eutectic.

3. The solubility of germanium in solid boron and of boron in liquid germanium is restricted, though significant at the monotectic temperature.

4. The solid solubilities of germanium and boron in each other at the eutectic temperature are negligible. The minute quantity of boron that can be dissolved in solid germanium does so substitutionally with a contraction of the germanium lattice of from 0.01 to 0.02 volume percent.

5. The solid solubility of germanium in silicon borides or boron-rich silicon-boron alloys is negligibly small.

6. Germanium should provide an efficient boron diffusion-barrier coating for either boron or silicon borides. Its utility for this purpose, however, must be evaluated from the standpoint of the compatibility of germanium and the specific matrix material that is under consideration.

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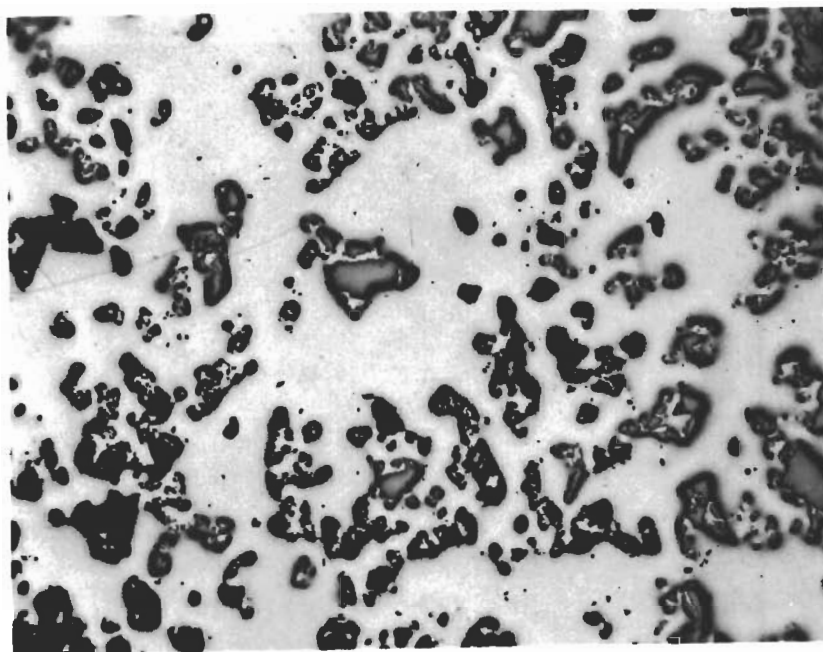


Figure 1. Ge-30 at.% B, heated in vacuum for 2 hrs at 1400°C; unetched. (X100)

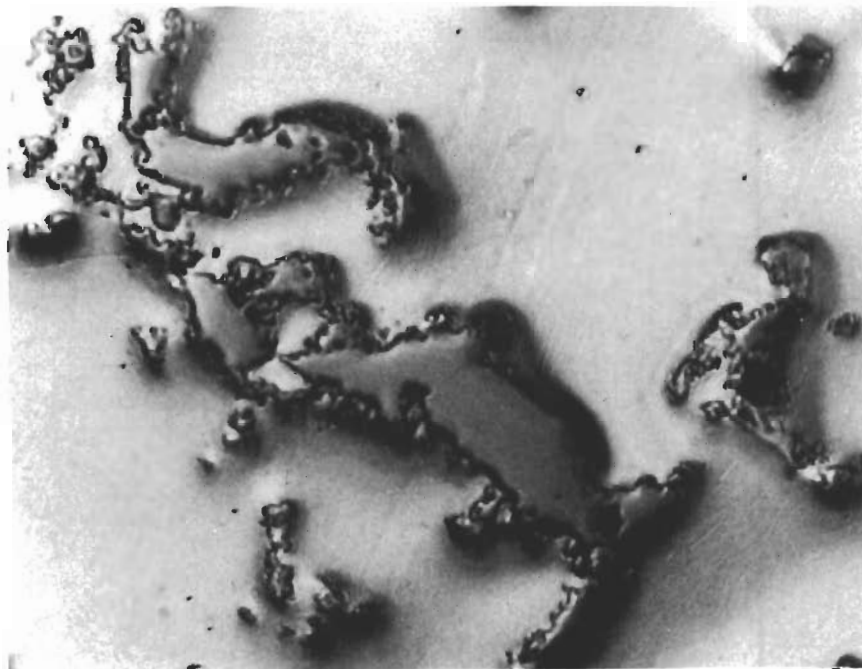


Figure 2. Ge-30 at.% B, heated in vacuum for 2 hrs at 1400°C; unetched. (X500).

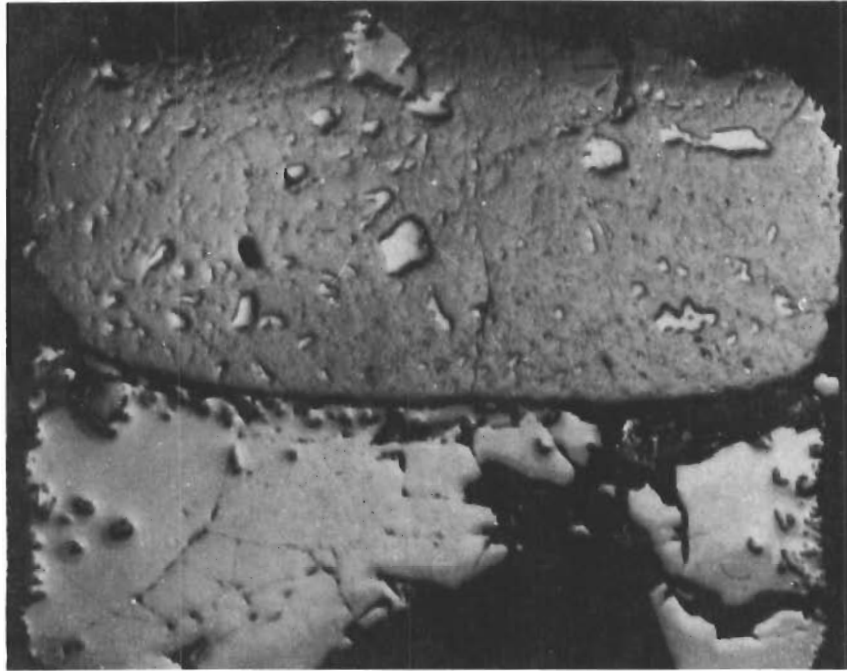


Figure 3. Ge-70 at.% B, heated in a helium purged atmosphere for 15 min at 2150°C; longitudinal section, unetched. (X16).

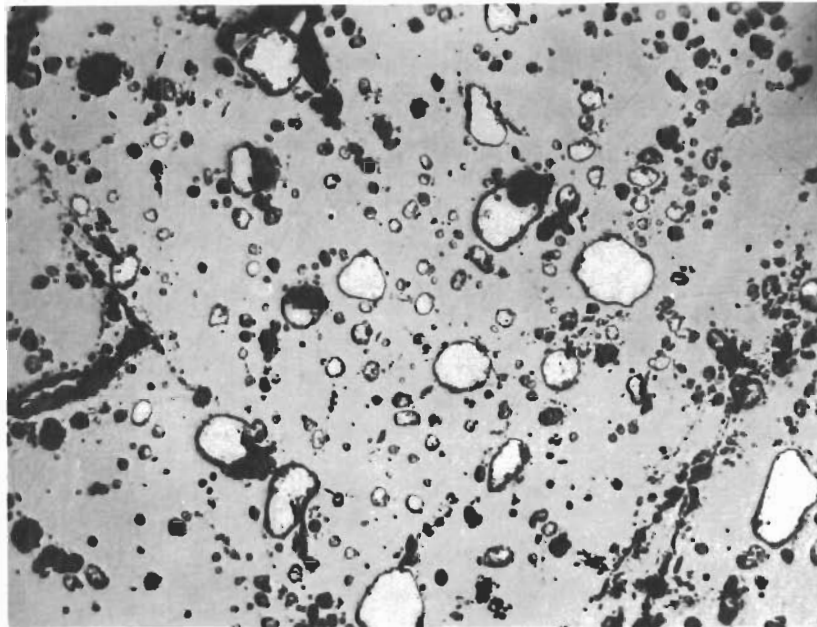


Figure 4. Ge-95 at.% B, heated in a helium purged atmosphere to 2095°C; unetched. (X100)

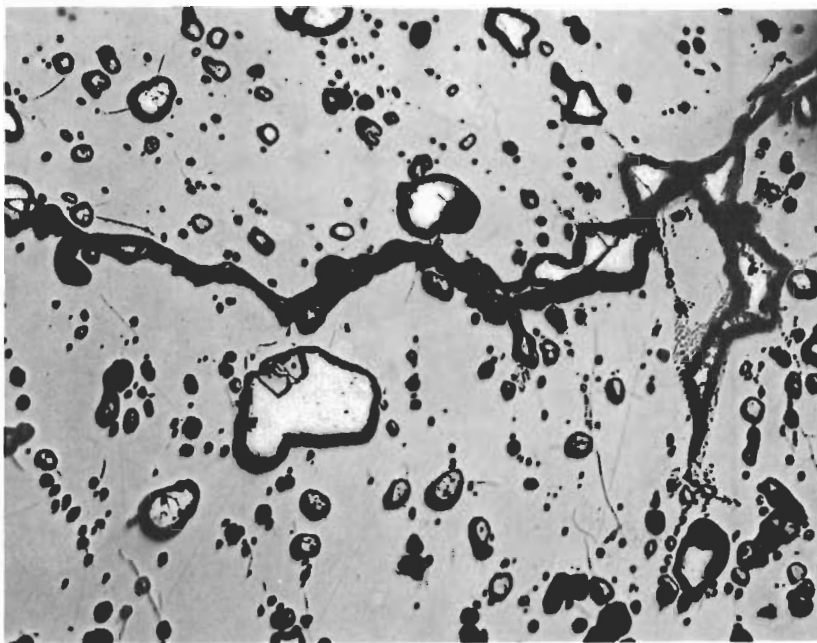


Figure 5. Ge-95 at.% B, heated in a helium purged atmosphere to 2095°C; unetched. (X100)

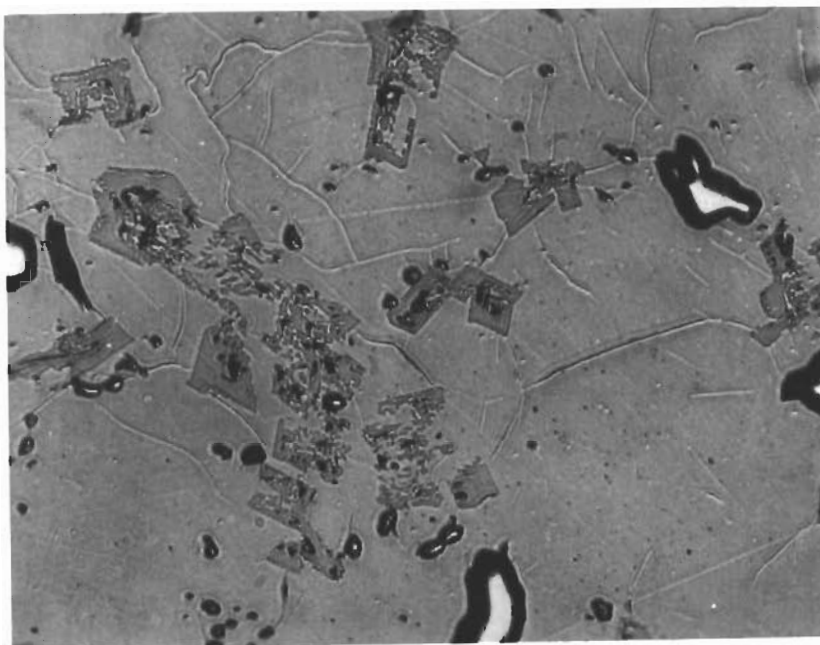


Figure 6. Ge-90 at.% B, heated in a helium purged atmosphere to 2100°C; unetched. (X200)

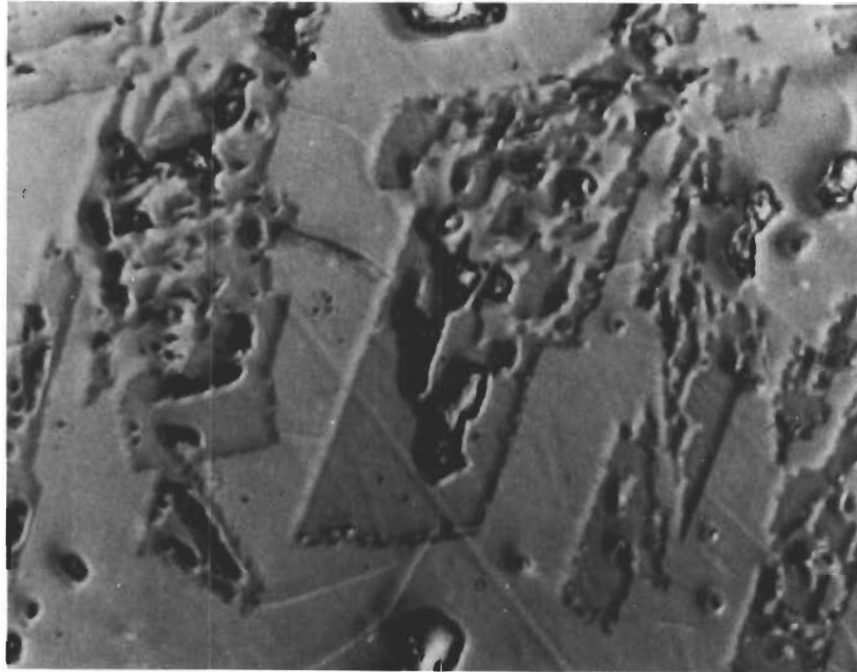


Figure 7. Ge-90 at.% B, heated in a helium purged atmosphere to 2100°C; unetched. (X500)

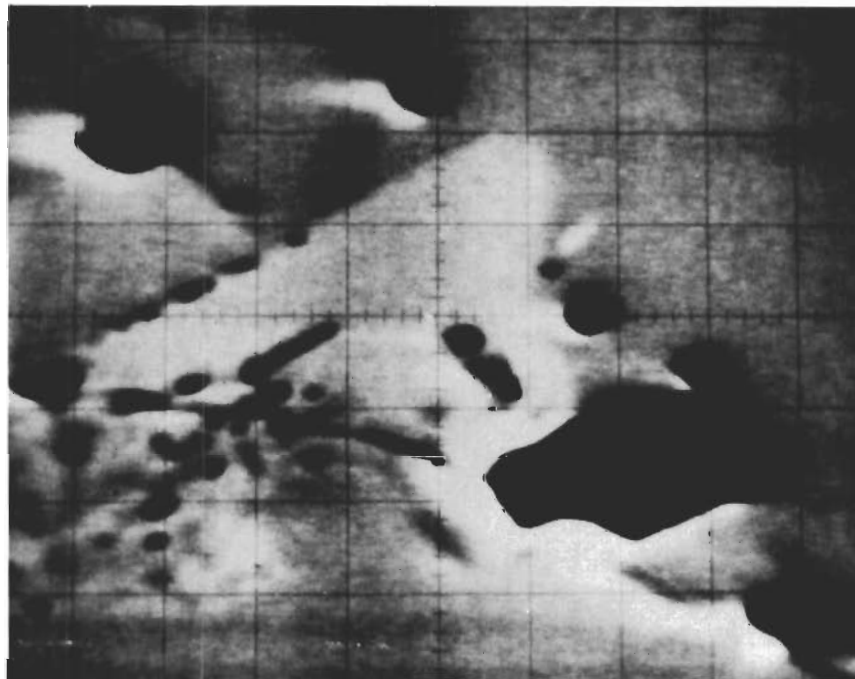


Figure 8. Ge-90 at.% B, heated in a helium purged atmosphere to 2100°C; electronically reversed back-scattered electron image. (X800)

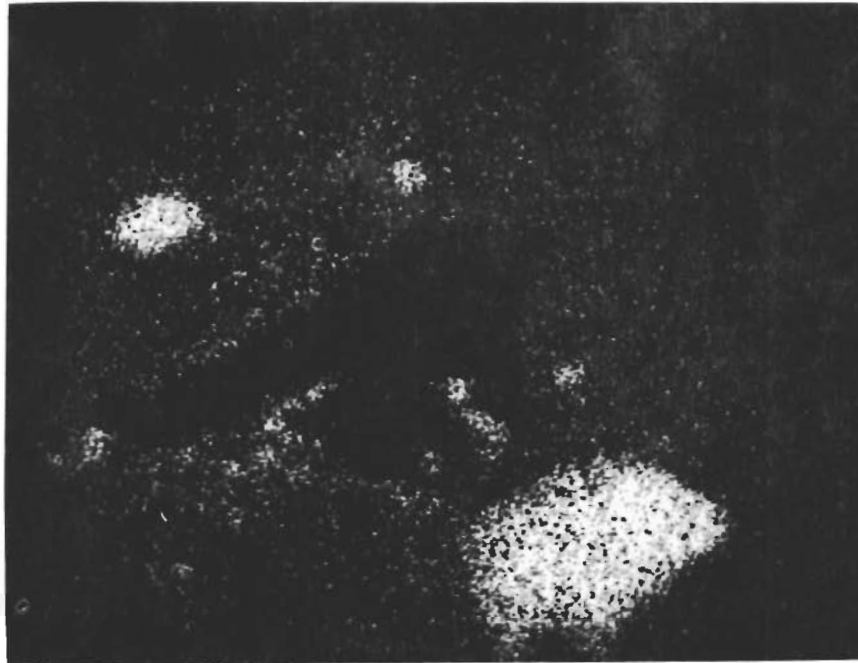


Figure 9. Ge-90 at.% B, identical area to Figure 8; Ge L_{α} characteristic X-ray image. (X800)

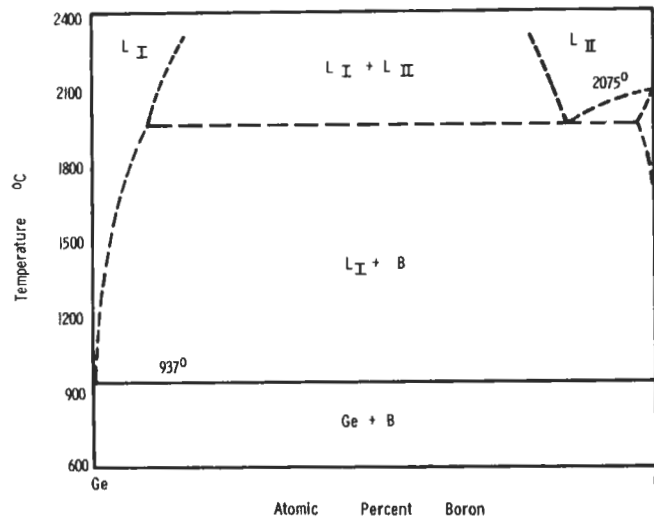


Figure 10. Schematic representation of the most probable significant features of the boron-germanium phase equilibrium diagram.

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13. ABSTRACT The salient features of the boron-germanium phase equilibrium diagram have been deduced from X-ray diffraction, metallographic, thermal analysis, and electron microprobe studies on both sintered and melted alloys. The system can be characterized as a classical monotectic-eutectic with no intermediate phases. The occurrence of hypomonotectic boron crystals and boron crystals grown from a germanium melt indicates a slight solubility of germanium in solid boron and of boron in liquid germanium at the monotectic temperature. X-ray diffraction, thermal analysis, and metallographic studies indicate that the germanium-rich liquid freezes as essentially pure germanium and that the solid solubility of germanium in boron and of boron in germanium is virtually nil at the eutectic temperature. The minute quantity of boron that does dissolve in solid germanium does so substitutionally with a 0.01 to 0.02 volume percent contraction of the germanium lattice. These results indicate that germanium may have utility as a boron diffusion barrier for boron fiber-reinforced metal-matrix composites.			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Boron						
Germanium						
Diffusion-Barrier						
Composites						
Phase Diagram						