

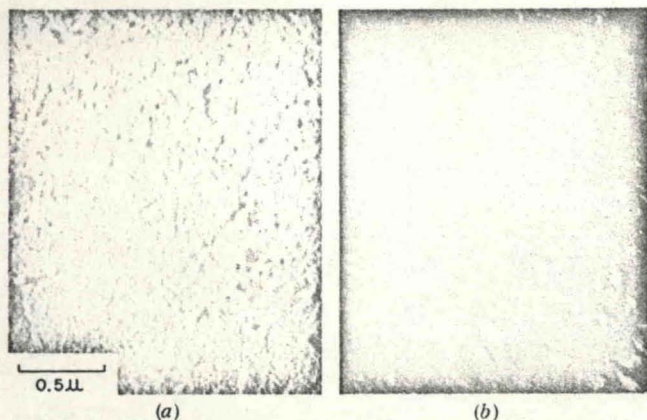


Fig. 4—Rene 41, solution heat-treated at 1230°C, water-quenched; heat-treated 18 hr at 650°C: (a) not pressurized; (b) pressurized 1 hr at 31 kbar and 260°C prior to heat treatment.

group III specimens, the total volume fraction of γ' precipitates has decreased by a factor of two. One would be tempted to attribute this observation to a decrease in concentration of precipitation sites, probably due to the collapse of voids during pressurization.

Fig. 3 shows that precipitation heat treatment of specimens pressurized at 260°C results in a fine dispersion of γ' without any loss in the total volume fraction of precipitates, which suggests that pressurization at elevated temperature provides additional nucleation sites for γ' .

Hagel and Beattie² observed the evolution of carbides in superalloys. They have shown that carbide structure progressively changes with aging time and temperature from simple hexagonal MC to M_4C_3 to $M_{23}C_6$ to the final M_6C structure. Wolff³ has noticed unidentified subcarbides preceding the precipitation of $M_{23}C_6$ in a high-nickel austenite. Harrington⁴ observed up to 10 pct increase in strength in stainless steel stress aged below the proportional limit at temperatures between 400° and 500°C and the increase in strength was attributed to "internal pressure" induced precipitation. A strong tendency for formation of stable carbides of chromium, iron, or molybdenum was observed in nickel at high pressure and temperatures⁵ despite the increased solubility of carbon in pure nickel under pressure.⁶ It is thus possible⁵ that pressurization of the fully solution heat-treated alloy (treatments IV and V, Table I) will cause the rejection of fine clusters of simple carbides which in turn will act as favorable nucleation sites.

One should now refer to Fig. 4 wherein pressurized and nonpressurized specimens are compared after 18 hr heat treatment at 650°C. In the case of the nonpressurized specimen, particles are not resolved, whereas in the pressurized specimen, fine clusters of particles are clearly detected.

The above arguments rely heavily on circumstantial evidence, and more direct observations are required to clarify the experimental observations. Towards this end, we are now proceeding with transmission-microscopy work, the results of which we hope to report in the near future.

⁶C. M. Hammond and G. S. Ansell: *Trans. Am. Soc. Metals*, 1964, vol. 57, pp. 727-38.

²W. C. Hagel and H. J. Beattie: *Trans. Am. Soc. Metals*, 1964, pp. 978-85.

³Ursual E. Wolff: *Trans. Met. Soc. AIME*, 1966, vol. 236, pp. 19-27.

⁴R. H. Harrington: *Trans. Am. Soc. Metals*, 1965, vol. 58, pp. 119-59.

⁵H. M. Strong: General Electric Research Center, Schenectady, N. Y., private communication.

⁶H. M. Strong: *Trans. Met. Soc. AIME*, 1965, vol. 233, pp. 643-51.

Observations of the Bi III-IV and Bi IV-V Transitions by Resistivity Measurements

R. Kossowsky

BRIDGMAN¹ has listed five possible transitions in bismuth at 25°C which were observed as volume changes. He was unable however to detect the last three transitions by electrical-resistivity changes. Kennedy and LaMori² have verified the pressures at the Bi I-II and Bi II-III transitions. They suggested however that the 125-kbar transition previously reported by Bundy³ actually corresponds to the 90,000 kg per sq cm transition observed by Bridgman.¹ Jura⁴ reported a well-defined drop in resistivity at 92 kbar obtained by a four-lead method.

The Bi III-IV and Bi IV-V transitions have not been reported in any of the above-mentioned references.²⁻⁴ Bundy³ observed a small dent in the low-temperature boundary of the Bi VII region which is consistent with the presence of a III-IV boundary. Zeitlin and Brayman⁵ were the only ones to report small but well-defined drops in resistance of bismuth at 44.0 and 63.8 kbar, corresponding to Bridgman's III-IV and IV-V transitions, respectively.

High-purity (99.99 pct) 0.020-in.-diam 0.5-in.-long bismuth wire was used to calibrate the Uniram tetrahedral high-pressure apparatus used in the present work. The bismuth phase changes at 25°C were correlated with changes in electrical resistance as a function of pressure. The output of a sensitive bridge constructed of carbon resistors and kept at a constant temperature of $\pm 1^\circ\text{C}$ during the measurements was fed to the Y axis of a Moseley X-Y recorder and the X axis was used for time scans.

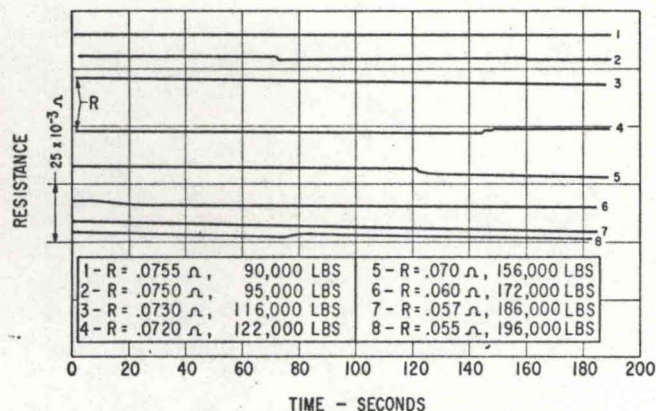
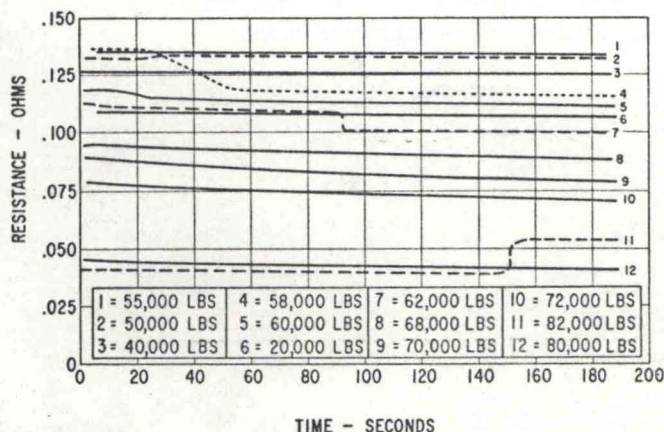
Specimens were pressurized using a hydraulic press with maximum capacity of 200,000 lb. Load was applied in increments of 2000 lb and held for about 3 min. The resistance was recorded at the end of this time period. Good contact was established below 20,000 lb. Typical recorder charts are reproduced in Figs. 1 and 2 which show that resistance fluctuations were practically nil during each time scan. Well-defined discontinuities in resistance were observed at 58,000 and 82,000 lb, Fig. 1. Two small but definite "blips" are noticed at 92,000 and 122,000 lb, Fig. 2. At 156,000 lb another drop is observed which

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continues with increasing load up to 190,000 lb.

The dependence of resistance on load during the loading cycle is plotted in Fig. 3. The sluggishness of the I-II and II-III transitions is not surprising.



Davidson and Lee⁶ have shown that for polycrystalline bismuth and very slow loading rates more than 15 min elapsed between the start and end of the I-II transition with close to 3 min incubation time. The II-III transitions took 200 sec to complete with more than a minute incubation time.⁶ The start of I-II transition is taken as the first drop in resistance and the start of II-III is taken as the rise in resistance after a short plateau. The correct II-III transition point is obtained by subtracting the difference in load between the start and end of the I-II transition from the load of start of II-III. The experimental results are summarized in Table I.

A calibration curve of specimen pressure vs press load is plotted in Fig. 4. Because of the two different values of 87 and 92 kbar obtained by Bridgman¹ and Jura,⁴ respectively, two lines are drawn through the Bi I-II, Bi II-III, Tl II-III, and Bi V-VI.

On the lower calibration line the two intermediate points are then plotted at 92,000 and 122,000 lb which correspond to 44 (± 0.5) and 64 (± 0.5) kbar, respectively. These results are in good agreement with the Bi III-IV and Bi IV-V transitions at 44.1 and 63.7 kbar, respectively.¹

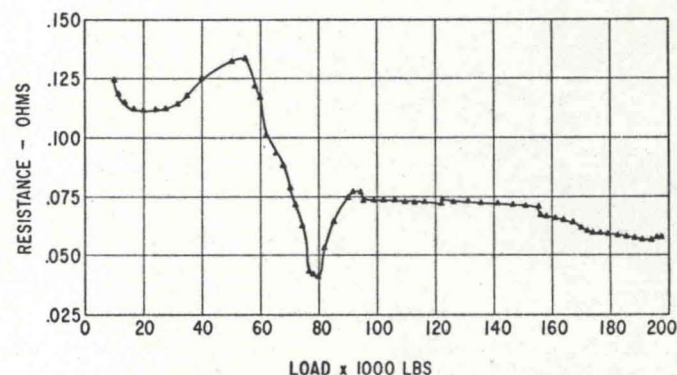


Table I. Bismuth Transitions (in 10,000 lb) and Relative Resistance Changes

		Test Number					$\Delta V/V_0$ (Bridgman)
		315	297	286	282	318*	
I-II	Start	57	58	58	58	58	0.0460
	End	76	77	78	80	64	
	$\Delta R/R_0$	-0.741	-0.752	-0.741	-0.749	-0.754	
II-III	Start	80	81	82	84	68	0.0295
	Start (Corr.)	63	62	62	62	62	
	End	92	91	80	92	72	
	$\Delta R/R_0$	+0.188	+0.190	+0.201	+0.187	+0.172	
III-IV	Start	92	93	—	—	92	0.0060
	End	95	94	—	—	93	
	$\Delta R/R_0$	-0.020	-0.025	—	—	-0.024	
IV-V	Start	122	124	122	122	—	0.0050
	End	123	124	124	124	—	
	$\Delta R/R_0$	+0.027	+0.025	+0.022	+0.020	—	
V-VI	Start	156	157	158	159	158	0.0120
	End	194	192	Interrupted at 180,000	190	193	
	$\Delta R/R_0$	-0.116	-0.115	—	-0.114	-0.115	

*See text and Figure 5.

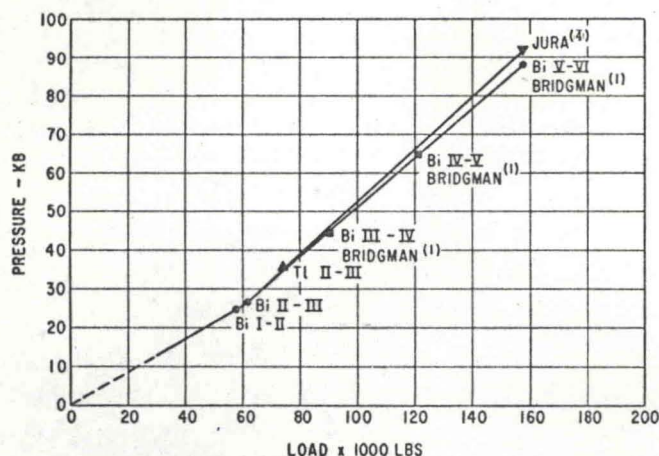


Fig. 4—Calibration curve for uniram tetrahedral high-pressure apparatus.

Finally, to verify the dependence of Bi I-II and Bi II-III transformation rates on loading rate and to ascertain that the drop at 92,000 lb is not an "over-shooting" aftereffect, another test was run. The load was continuously increased to 58,000 lb and the resistance was monitored until equilibrium was reached. Load was increased by increments of 1000 lb and held for long periods of time, see Fig. 5. It should be noted that the I-II transition under full equilibrium conditions starts at 58,000 lb with a short incubation time

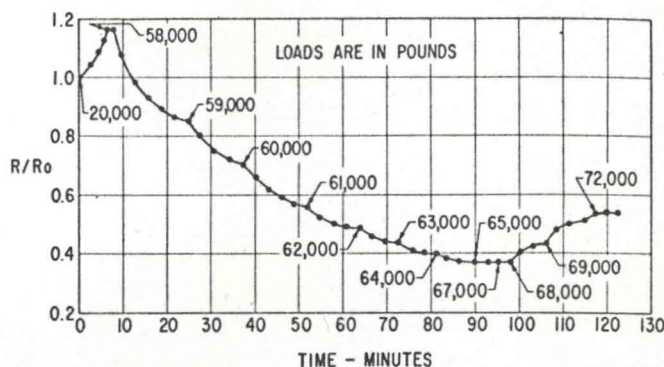


Fig. 5—Dependence of relative resistance on time at various press loads.

and ends at 64,000 lb. This corresponds to about 27 kbar and is in good agreement with the results of other investigators.^{2,4}

¹P. W. Bridgman: *Proc. Am. Acad. Arts Sci.*, 1952, vol. 4, pp. 165-251.

²G. C. Kennedy and P. N. LaMori: *Progress in Very High Pressure Research*, Hibbard and Strong, eds., p. 304, John Wiley and Sons, New York, 1961.

³F. P. Bundy: *Phys. Rev.*, 1957, vol. 110, p. 314.

⁴G. Jura: *Metallurgy at High Pressures and Temperatures*, Gschneider, Hepworth, and Parlee, eds., p. 246, Gordon and Breach, New York, 1964.

⁵A. Zeitlin and J. Brayman: *High Pressure Measurements*, A. A. Giardini and E. C. Lloyd, eds., pp. 301-09, Butterworths, Washington, 1963.

⁶T. E. Davidson and A. P. Lee: *Trans. Met. Soc. AIME*, 1964, vol. 230, pp. 1035-38.

Properties of Pyrolytically Produced Boron Fibers

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IN recent years, a great deal of research has been directed toward the production of continuous low-density, high-strength, high-modulus boron fibers for aerospace applications. A technique which has proven to be quite successful for forming these fibers involves the reaction of boron trichloride and hydrogen on a hot tungsten wire. In this process, a boron fiber is produced which consists of a tungsten boride core¹ covered with amorphous or crystalline boron depending on the temperature of the preparation.^{2,3} The purpose of this paper is to present the properties which have been obtained to date from measurements and observations on these fibers.

Selected samples of boron filament produced by reacting boron trichloride and hydrogen on a 0.5 by 10⁻³ in. diam tungsten wire substrate using different reacting temperatures were cross-sectioned, polished,

and photomicrographed with cross-polarized light. The temperature of the wire was measured using a two-color optical pyrometer. Photomicrographs of these samples are shown in Fig. 1. Three general types of boron, in addition to the tungsten borides, have been identified by means of X-ray powder diffraction techniques: a) at low temperatures (below 1400°C) the boron is deposited in the amorphous form; b) at temperatures between 1400° and 1500°C the boron is deposited in the β tetragonal form; and, c) above 1500°C the boron is deposited in the β rhombohedral form. In the depositing range of 1400° to 1500°C the boron initially deposits as amorphous and becomes crystalline as evidenced by the large equiaxed grains which then merge into columnar grains in later stages of boron deposition. This can be seen in Fig. 1 and has been observed in the X-ray patterns of these fibers, which contain both halos from the amorphous boron and lines from the β tetragonal form. Above 1500°C the only boron reflections observed in the X-ray patterns were those of the β rhombohedral form and only columnar grains are seen in the photomicrographs. Photomicrographs of the surface in Fig. 2 show the smooth-surface kernal-type deposition which corresponds to the amorphous form and the rougher surfaces which correspond to the crystalline form.

Mechanical measurements were made on amorphous boron produced at 1300°C rather than the crystalline boron because the strengths of these filaments were greater and were more consistent. A tensile tester consisting of a fixed crosshead containing a double

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