Boron phosphide coatings on molybdenum by chemical vapour deposition, and their composition and microhardness

Boron monophosphide (BP) is of interest because of its semiconducting properties [1], high melting point (3000° C), high hardness (~4700 kg mm^{-2}) [2] and high stability in chemicals. In contrast, molydenum has an inferior resistance to erosion and oxidation, which a surface layer of boron phosphide could improve. Boron phosphide has been deposited on silicon [3–8], cemented carbide and graphite [9] substrates by chemical vapour deposition. However, no reports have been published on the composition of the deposits, because of the difficulty of complete dissolution. In the present work, the relation between the deposition conditions and the deposit's structure, microhardness oxidation resistance, and B/P ratio were examined.

Boron phosphide was deposited on a molybdenum plate (0.1 mm × 5 mm) from a gaseous mixture of boron trichloride, phosphorous trichloride, hydrogen and argon in the temperature range 880 to 1020° C.

In Fig. 1, the surface appearance and cross-section of the deposits obtained after 30 min at 980° C are shown. An interlayer, 1 μm thick, (Fig. 1b) was identified as molybdenum monophosphide (MoP) using X-ray diffraction. The adherence between three phases was excellent, and cracks or exfoliation were not observed even when a diamond indenter was applied to the boundaries of BP/MoP and BoP/Mo. The molybdenum phosphide layer was formed in the initial 5 min period, after which the boron phosphide layer thickened linearly with deposition time (Fig. 2).

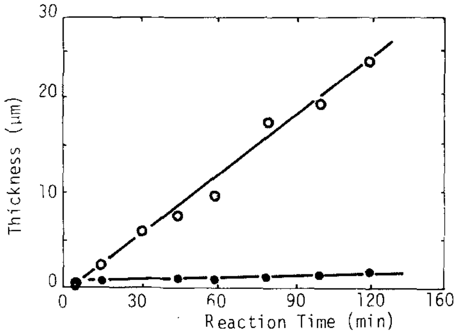

Figure 2 Effect of reaction time on deposit thickness. Deposition conditions: 980° C, $BCl_3/(BCl_3 + PCl_3)$: 0.5, total gas flow rate: 4.0 ml sec^{-1}. (○) BP, (●) MoP.

The lowest deposition temperature was found to be about 880° C, and fine-grained deposits were obtained below 1000° C. The atomic ratio of B/P in the deposits was determined as follows. Boron phosphide was deposited onto a quartz substrate

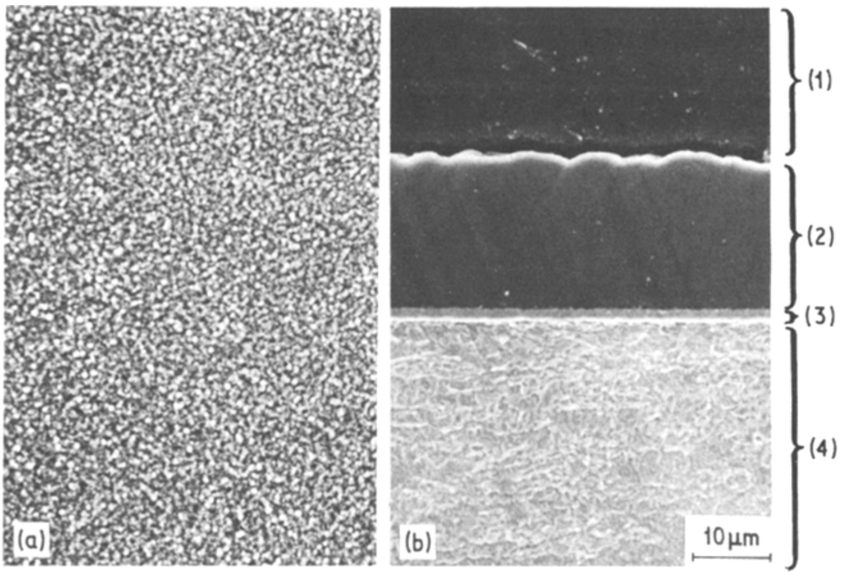

Figure 1 The appearance of the surface and a cross-section of BP layers deposited onto an Mo plate. Deposition conditions: 900° C, $BCl_3/(BCl_3 + PCl_3)$: 0.67. (a) Surface, (b) cross-section; (1) Mo substrate, (2) MoP, (3) BP, (4) resin.

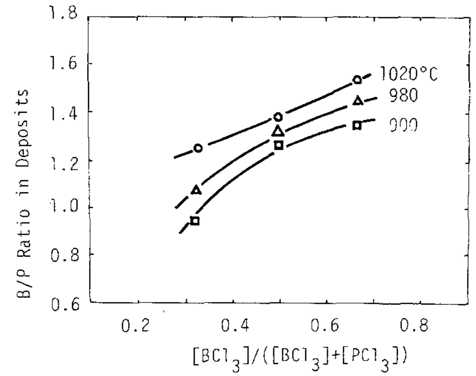

Figure 3 Effect of gas flow ratio $[BCl_3/(BCl_3 + PCl_3)]$ on the atomic ratio of B/P in the deposits. Growth temperatures: (○) 1020° C; (△) 980° C; (□) 900° C.

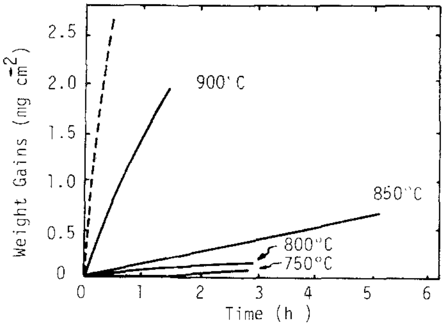

Figure 5 Oxidation resistance in the temperature range 750 to 900° C. Thickness of BP layer: 10 to 15 μm; $BCl_3/(BCl_3 + PCl_3)$: 0.5; growth temperature: 980° C. (– – – –) Untreated Mo plate.

under the same deposition conditions as for deposition onto molybdenum. The deposits on the quartz were weighed, sealed into a pyrex ampoule which contained concentrated nitric acid and heated to 200° C until the deposits had completely dissolved (> 10 h). The boron phosphide did not dissolve below 160° C. The boron content was determined by the barium borotartarate method [10].

The effect of the flow ratio of the chlorides $BCl_3/(BCl_3 + PCl_3)$ on the atomic ratio of B/P in the deposits is shown in Fig. 3, in which the sum of the flow rates of boron and phosphorous trichlorides was maintained at 0.15 ml sec^{-1}. The B/P ratio in most of the deposits exceeded unity, irrespective of preparation temperature.

From X-ray diffraction analysis, the whole peaks were determined to be solely boron monophosphide. Although the absence of any free boron inclusions cannot be excluded because of the weak X-ray diffractivity of boron, the high resistivity to nitric acid suggests that free boron was not contained in any appreciable amount.

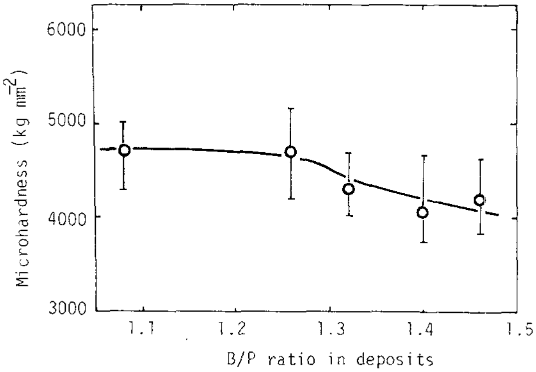

Figure 4 Effect of the atomic ratio (B/P) on microhardness.

The microhardness was measured using a microvickers tester (Akashi-MVK-C), and the effect of the B/P ratio on microhardness is shown in Fig. 4. The mean diagonal length of the indentations was roughly proportional to the square root of the load, as reported by Takigawa *et al.* [2] for loads of 25 to 1000 g. The microhardness gradually decreased from 4700 to 4100 kg mm^{-2} with an increase in B/P ratio from 1.08 to 1.47.

Oxidation resistance was measured using thermogravimeter in an air flow, and the increase in weight of the molybdenum plate coated with boron phosphide during oxidation is plotted against time in Fig 5. An untreated molybdenum plate became oxidized as shown by the broken line, even at 700° C, whereas the coated molybdenum plate is fairly resistant below 800° C, and above 850° C, oxidized to form a rough deposit of boron phosphate linearly with time.

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Quenching efficiency of some splat-cooling devices

The purpose of this communication is to summarize certain observations concerning the efficiency of quenching from the liquid state (splat-cooling) by four rapid cooling devices. These were designated according to the following, now widely used terminology: the "gun", the "two-piston", the "mill" and the "levitation" methods.

In the "gun" method a liquid drop is projected at high speed on to a copper substrate. An apparatus similar to the type designed by Duwez *et al.* [1], but with the copper target cooled with liquid nitrogen, was used.

In the "two-piston" method [2] a liquid globule is squeezed between two metallic flat surfaces activated by a high gas pressure. Pistons made of steel were used.

In the "mill" method [3] a molten alloy is injected between two counter-rotating brass cylinders with a hard chrome surface.

The "levitation" method [4] combines the advantages of melting without the use of a crucible with the "two-piston" technique [5, 6]. Our design [7] included both copper and hard-metal pistons.

As a test for the efficiency of quenching by splat-cooling devices the Ag–Cu system was used. The equilibrium diagram of this binary alloy exhibits a eutectic, although the Hume–Rothery conditions are satisfied. However, Duwez demonstrated [8] that in this binary alloy fast quenching from the melt, if efficacious, results in complete solubility. Depending on the cooling rate during quenching, different phases can be obtained. With optimum conditions, a single-phase, metastable fcc random solid solution will result over the entire Ag–Cu composition. This solid solution exhibits a slight, positive ($\sim 1\%$) deviation from Vegard's law and has been termed γ' [9]. Under less efficient quenching, a metastable fcc structure, marked by a $\sim 3\%$ deviation from Vegard's law, may occur. It was termed γ'' by Stoering and Conrad [10]. Deviating farther from γ', silver-rich and copper-rich metastable fcc solid solution phases may occur. These have been termed α' and β' to distinguish them from the equilibrium phases α (Ag-rich) and β (Cu-rich) [9]. A decrease in the cooling rate during quenching produces phases which depart from the ideal solid solutions given by Vegard's law. Thus the Ag–Cu system appears very convenient for testing the efficiency of splat-cooling.

Alloys were made using Ag and Cu of purity $\geqslant 99.99$ wt%. The components were weighed accurately to 0.1 mg. Initial melts were made in a graphite crucible under an argon atmosphere using induction heating. In the "gun", "two-piston" and "mill" methods samples in form of strips, weighing 150 to 200 mg, and in the levitation method samples of prismatic form, weighing 200 to 300 mg, were used.

Flakes quenched rapidly by the "gun" method were about 1 cm wide and 2 to 3 cm long and contained a large number of holes. As a result their thickness varied by up to 20 μm. The quenched flakes resulting from the "two-piston" method were approximately circular, about 1 to 5 mm in diameter, and 10 to 20 μm in thickness. In the "mill" method, the parameters were adjusted in order to obtain samples in the form of