

Figure 1 A crystal axial relation between  $\alpha$ - $\text{Al}_4\text{SiC}_4$  and  $\text{Al}_4\text{Si}_2\text{C}_5$  of aluminium silicon carbide. The lattice points of  $\text{Al}_4\text{SiC}_4$  are shown with white circles and those of  $\text{Al}_4\text{Si}_2\text{C}_5$  with black dots. The hexagonal lattice points of the latter corresponding rhombohedral are also given. Suffixes 1 and 2 indicate the lattice of  $\alpha$ - $\text{Al}_4\text{SiC}_4$  and  $\text{Al}_4\text{Si}_2\text{C}_5$ , respectively.

from  $1970^\circ\text{C}$  to room temperature. If the compound  $\text{Al}_4\text{Si}_2\text{C}_5$  is cooled slowly from  $1970^\circ\text{C}$  to  $1900^\circ\text{C}$ , the  $\text{Al}_4\text{Si}_2\text{C}_5$  phase does not appear at all, but  $\alpha$ - $\text{Al}_4\text{SiC}_4$  phase and silicon carbide are formed. Therefore, this new compound may be considered to be a stable phase at temperatures above  $1900^\circ\text{C}$ . Other experimental results showed that at temperatures below  $1900^\circ\text{C}$ ,  $\alpha$ - $\text{Al}_4\text{SiC}_4$  is more stable than the  $\text{Al}_4\text{Si}_2\text{C}_5$ .

The X-ray diffraction profiles of  $\text{Al}_4\text{Si}_2\text{C}_5$  are quite different from those of  $\alpha$ - and  $\beta$ -aluminium silicon carbide reported by Barczak [1] and

Schneider [2]. The axial relation of the crystal lattices between  $\text{Al}_4\text{SiC}_4$  and  $\text{Al}_4\text{Si}_2\text{C}_5$  is shown in Fig. 1. The  $a$ -axis dimension in the hexagonal lattice of  $\text{Al}_4\text{Si}_2\text{C}_5$  is very similar to that of  $\alpha$ - $\text{Al}_4\text{SiC}_4$  and the  $c$ -axis dimension of the former is nearly twice as long as the latter.

The intensity distribution of X-ray diffraction and the unit cell dimension of  $\text{Al}_4\text{Si}_2\text{C}_5$  are very similar to those of aluminium carbonitride,  $\text{Al}_6\text{C}_3\text{N}_2$  reported by Jefferey and Wu [4]. Therefore, the crystal structure of the former may be similar to that of the latter. It can be postulated that the layer structure of  $\text{Al}_4\text{Si}_2\text{C}_5$  is formed by substituting the two SiC layers for two AlN layers in the  $\text{Al}_6\text{C}_3\text{N}_2$  structure.

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### The preparation and properties of single crystal copper phosphide

Copper-phosphorus alloys are used in the metal industry instead of pure phosphorus for deoxidizing brass and bronze alloys and in the preparation of phosphor bronze. As a result there have been several studies of the copper-phosphorus phase

diagram [1-3]. All of the diagrams indicate the presence of a compound with the formula  $\text{Cu}_3\text{P}$ , tricopper phosphide or, more commonly, copper phosphide. The crystal structure and some of the properties have been investigated [4, 5]. This compound has analogues in copper arsenide ( $\text{Cu}_3\text{As}$ ) and copper antimonide ( $\text{Cu}_3\text{Sb}$ ) and the former has been shown to have semiconducting

properties [6]. All of these compounds obey the Mooser–Pearson selection rule [7] which defines the nature of a compound likely to exhibit semiconducting properties. It was hence of interest to prepare copper phosphide in single crystal form and examine its properties.

From the phase diagrams, the melting point of copper phosphide was given as being approximately  $1000^{\circ}\text{C}$ . It was estimated that the phosphorus pressure over a melt of copper phosphide at this temperature would be of the order of  $3.1\text{ MN m}^{-2}$ . Thus crystal growth was performed in a pressurized Czochralski vertical lift growth system using molten boric oxide as a liquid encapsulant [8]. Copper phosphide was obtained from the manufacturer's [9] as-prepared bars formed by direct reaction of copper and phosphorus in a sealed silica glass system. This was melted in silica-lined carbon crucibles by means of radio frequency heating. The liquid boric oxide effectively prevented any phosphorus loss. The first single crystal was grown by using a hollow tantalum tube to initiate growth and subsequent crystals were grown using seed crystals cut from this and other crystals.

Sample slices of the crystals were used to measure electrical, crystallographic and mechanical properties. The electrical properties were measured by means of the Van de Pauw method using clover leaf samples sand-abraded from slices of crystals. Various metal contacts were investigated. The crystallographic properties were measured by Laue back-reflection, Debye–Scherrer powder and Bueger precessional X-ray techniques and the mechanical properties by standard metallurgical methods.

An example of a single crystal of copper phosphide is shown in Fig. 1. The crystals are blue-black in colour. It was found that the inert gas pressure in the growing system could be progressively lowered to  $1.0\text{ MN m}^{-2}$  before phosphorus escaped from the melt. This indicates that the compound is reasonably thermally stable. Measurements of melting point proved difficult to make but such measurements indicated a melting point of  $1025 \pm 10^{\circ}\text{C}$ . This is in reasonable agreement with the literature [3].

The crystals are very hard, the hardness being measured as 260 VPN or 26 Rockwell "C". This is comparable with commercial grade mild steel. They are also brittle. Tensile tests gave a breaking

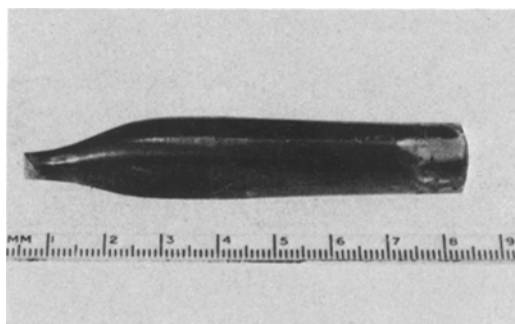


Figure 1 A single crystal of copper phosphide ( $\text{Cu}_3\text{P}$ ).

pressure of  $6.9\text{ MN m}^{-2}$  and they have a low coefficient of friction and poor wear resistance.

The compound in single crystal form is relatively inert chemically, showing no change in air after several months exposure. It is also resistant to attack by mineral acids, only concentrated nitric acid producing any real effect. Slices can be mechanically polished to a high-quality mirror finish.

The electrical measurements gave the material a low resistivity of  $5 \times 10^{-5}\ \Omega\text{cm}$ . There were no indications of any semiconductor properties. X-ray examination of the crystals confirmed the structure as being hexagonal with the  $a$  and  $c$  lattice parameters as  $7.11 \pm 0.05\ \text{\AA}$  and  $6.96 \pm 0.5\ \text{\AA}$ , respectively. Previous values are  $7.098\ \text{\AA}$  and  $6.942\ \text{\AA}$ , respectively [4].

It has been shown that copper phosphide ( $\text{Cu}_3\text{P}$ ) can be grown in single crystal form from the melt. The properties defined make it of little interest for any mechanical applications. However, the very low resistivity and the hardness may make it useful in some electrical applications.

### Acknowledgement

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### *Observation of shear bands in crystalline, spherulitic polypropylene under compression at low temperatures*

When glassy polymers are stretched or compressed, local zones of concentrated strain (crazes or shear bands) are often obtained. Their formation depends on strain rate, temperature, and sign of the stresses (tensile or compressive). The process of craze formation which mainly occurs under tension, and their influence on crack propagation and fracture have been elaborated to a large extent in recent years [1–3]. A few reports indicated, however, that crazing can occur as well in crystalline polymers [4–7]. This was shown, in particular, for crystalline polypropylene by Olf and Peterlin [8]. Crazes form at low temperatures, in the range between  $-210$  and  $0^{\circ}\text{C}$ .

Shear band formation is commonly associated only with glassy polymers [9–11]. The shear bands are formed by highly localized shearing of the randomly oriented material. This plastic deformation yields high molecular orientation of the material in the shear bands. They possess a thickness of less than  $1\ \mu\text{m}$  perpendicular to the direction of the applied shear stress, which has to be induced by compression. They can grow laterally as long as the local stress concentration at the sharp tip of the shear band is sufficient for propagation. When a certain degree of local deformation is exceeded, coarse shear bands can induce final fracture of the material [12].

In contrast to investigations on crazes in crystalline polymers, there are no studies which deal with the formation of shear bands in such materials. There are only some papers which treat the mode of deformation of oriented polymers in compression at low temperatures [13, 14].

In an attempt to check this effect with an un-

oriented crystalline polymer, spherulitic isotactic polypropylene was studied in the temperature range  $-196$  to  $-50^{\circ}\text{C}$ . At these temperatures the testing material is below its glass transition temperature. Shear band formation is expected to be easy, if this process is analogous to the well known shear band formation of some amorphous polymers under compression below their glass transition temperatures.

The experiments described here were made with polypropylene specimens having the following dimensions:  $10\ \text{mm} \times 10\ \text{mm} \times 20\ \text{mm}$ . The notched specimens were loaded under compression at  $-196^{\circ}\text{C}$  and at  $-50^{\circ}\text{C}$  with a strain rate of  $\epsilon = 4 \times 10^{-4}\ \text{sec}^{-1}$ . Before notching, the test pieces were subjected to different heat-treatments which are described elsewhere [15]. Thus different spherulite diameters could be produced. Two types of polypropylene with various atactic content were used: PP 1120LX,  $\sim 5\%$  atactic and PP 1320,  $\sim 20\%$  atactic, both obtained from the BASF. AG, Ludwigshafen, Germany.

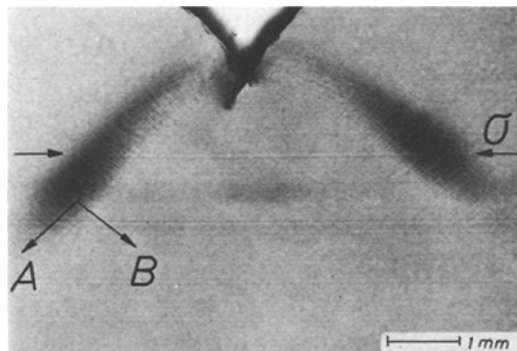


Figure 1 Two sets of shear bands (A, B) formed under compression in the vicinity of a notch in crystalline, isotactic polypropylene. Scratches produced after the test indicate the compression axis.