Acknowledgements

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Preparation of copper-coated titania particles for composites

In recent years, various methods for production of metal ceramic particulate composites have been developed based on powder and liquid metallurgy techniques [1–5]. Frequently, non-wettability between oxide particles and metals results in segregation of metal and ceramic phases and poor interfacial bonding in metal–ceramic particulate composites [6–7]. To improve the wettability, the ceramic particles are frequently coated with metals. Various coating techniques have been developed [8] of which electroless deposition is the method most commonly used [9]. Deonath and Rohatgi [10] have used this procedure to coat copper on mica particles. The major steps involved in the electroless method are: (a) activation of the surface of the ceramic particles by deposition of a noble metal such as Pd, Pt and Ag; (b) deposition of metal on the activated surface from a reducing bath containing metal ions.

Owing to the large surface area of ceramic particles, uniform activation throughout the surfaces can be achieved only with a large amount of activator. As a result, the process frequently becomes uneconomical with conventional activators. In this communication, we report a new method for coating titania (TiO_2) particles with copper (thickness range 2 to 15 μm) employing a relatively inexpensive activator – copper tartrate (CuT). Experiments were also carried out to coat copper onto TiO_2 particles using conventional activator $SnCl_2/PdCl_2$ solution [6]. The results obtained from both techniques are compared.

TiO_2 powder of particle size 1 to 20 μm was supplied by M/s Travancore Titanium Products Ltd, Trivandrum. Copper tartrate (CuT) solution was prepared by mixing sodium potassium tartrate

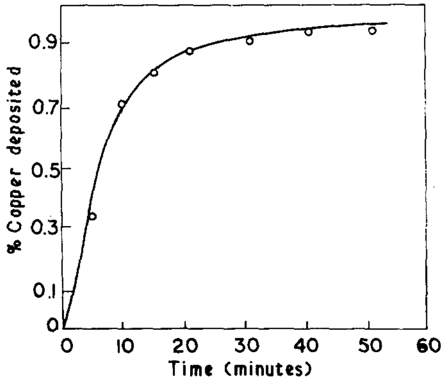

Figure 1 Copper tartrate adsorption on TiO_2 particles as a function of time.

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and copper sulphate solutions in 2:1 mole ratio. TiO_2 particles, preheated at 600° C for 3 h and cooled at room temperature in a desiccator, were immersed in CuT solution and stirred for varying times. Fig. 1 shows that the rate of adsorption of CuT is a maximum during the first 30 min. The rate was determined by analysing the copper content in samples of powder periodically removed from solution. The particles were separated from the solution by centrifuging and then washed free of non-adsorbed CuT complex with distilled water. The CuT adsorbed on TiO_2 particles was reduced to copper by treating with alkaline formaldehyde solution (30%) at pH 8.5 to 9.5. This reaction was monitored by observing the colour of the particles (the blue colour due to CuT changes to the pale brown colour of copper). Further coating of copper on activated surfaces was carried out for different time intervals from Fehling–formaldehyde solution, with the following compositions: $CuSO_4.5H_2O$ – 10 g litre^{-1}, sodium potassium tartrate – 25 g litre^{-1}, sodium hydroxide 7 g litre^{-1}, and formaldehyde – 10 m litre^{-1}. Using an electric stirrer of variable speed, the TiO_2 particles were kept in suspension in the solution by stirring at the rate of 120 rpm. After the experiment was completed, the particles were washed free of alkali with distilled water followed by ethanol, and dried in vacuum at room temperature for 4 h. Fig. 2 shows the amount of copper deposited on the particles as a function of time.

TiO_2 particles were also coated with copper after activating with $SnCl_2/PdCl_2$ solutions [9, 11] of two concentrations of $PdCl_2$ (0.1 and 0.01 g litre^{-1}). Fig. 2b and c show the amount of copper deposited at various intervals using these activation procedures. The copper coating solution remained the same in all cases.

During our investigation on metal coating, we found that titania particles adsorb water-soluble metal complexes. It has also been noted that the nature of adsorption depends on the stereochemistry of the complexes. Metal complexes with planar configuration are adsorbed on the surface of TiO_2 particles more rapidly and they are not washed away when stirred in water. As a contrast, while the metal complexes with octahedral configuration are also adsorbed on the surface of the TiO_2 particles, they are washed away when stirred in distilled water. It was also found that the size of the metal complex molecule also plays a prominent role. Our experiments show that large complex molecules (CuT) are adsorbed to a lesser extent than smaller molecules (copper ammonia complex) within a prescribed time interval. The adsorbed complex can be reduced to metallic copper which, in turn, will activate the surface of the particles for deposition of copper from a reducing bath. Owing to the higher stability of copper ammonia complex to reduction by NaOH–HCHO solution compared to reduction by copper tartrate, the latter has been employed in this study. Since the rate of reduction of copper ions present at low concentrations is very slow [9], use of 30% HCHO is essential to reduce the adsorbed complex. The deposition of copper from the reducing bath is catalysed by the initially deposited activating agent and the rate of deposition is dependent upon the catalytic surface area. Fig. 2 shows that the rate of deposition of copper on titania particles by the CuT method is higher than that of the $SnCl_2/PdCl_2$ method. A comparison of the theory and processes of activation of TiO_2 particles by these two methods may be useful in explaining this phenomenon. Fig. 1 shows that 0.91% copper can be deposited as CuT on TiO_2 particles from CuT solution. It was observed that this amount is independent of the concentration of the CuT solution [12]. Therefore, it may possibly be assumed that deposition is more or less uniform in nature. The amounts of palladium chloride (0.10 and 0.01 g litre^{-1}) used in our experiments are much lower then 0.91%. The dependence of the amount of

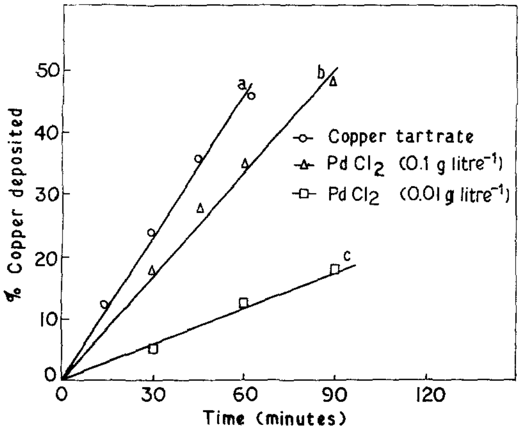

Figure 2 Copper deposition on TiO_2 particles as a function of time for different activation conditions.

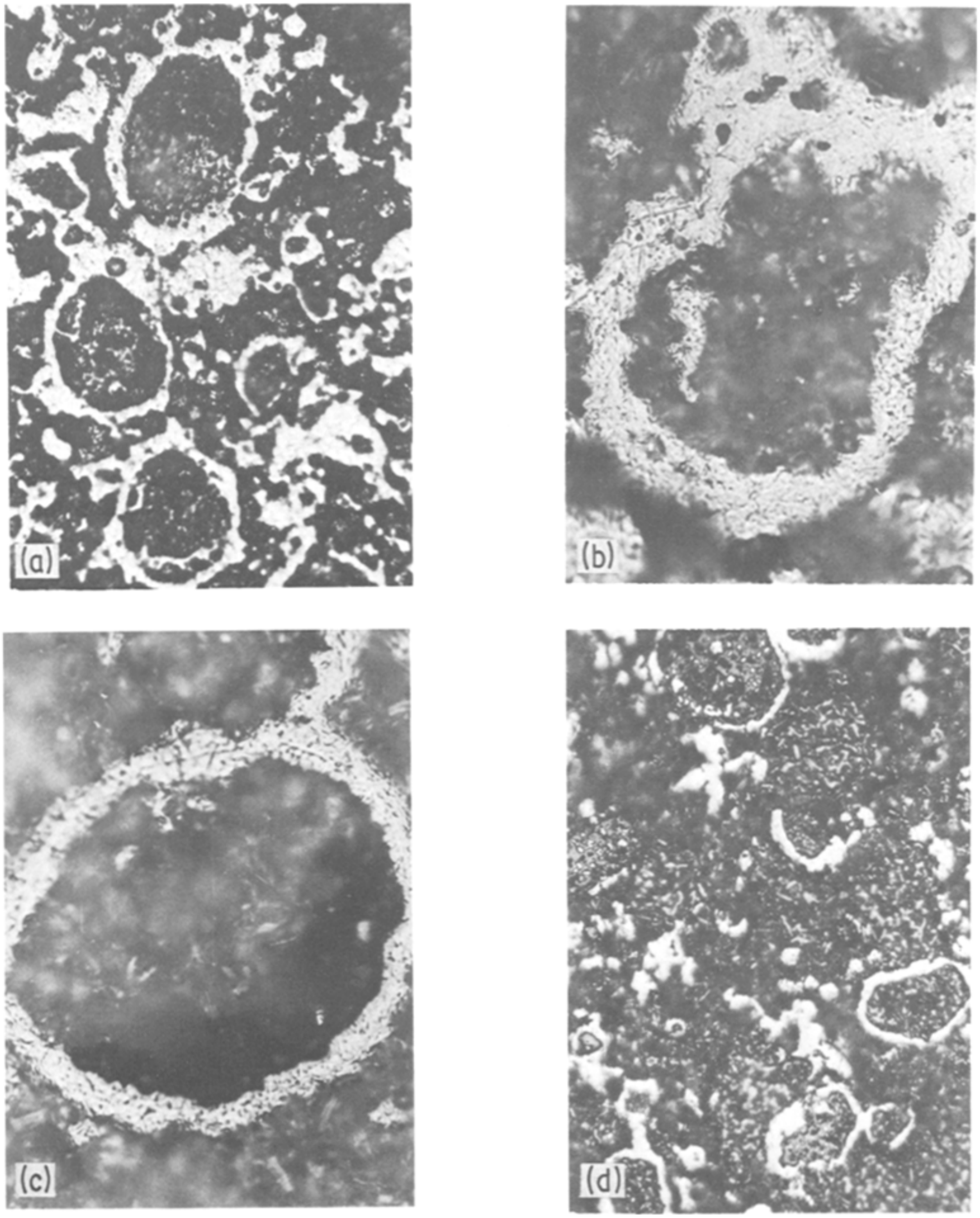

Figure 3 Photomicrographs of copper-coated TiO_2 particles partially sintered for observation: (a) × 900; (b) and (c) × 3000 (activated by CuT); (d) × 900 (activation by the $SnCl_2/PdCl_2$ method).

activating agent is demonstrated by Fig. 2b and c, where two different concentrations of $PdCl_2$ were used. Since the amount of copper deposited by the CuT adsorption method is always the same (even if the CuT is taken in excess), the rate of deposition of copper from Fehling–formaldehyde should not vary from experiment to experiment if all the other parameters are kept constant. This is found to be true in our experiments. In the $SnCl_2/PdCl_2$ method of activation, Pd is deposited from a colloidal solution of Pd and hence activation need not be uniform. It has been observed that the rate of deposition varied considerably from one experiment to another. Therefore, coatings with a controlled thickness and uniformity will be difficult to obtain using the $SnCl_2/PdCl_2$ method. On the other hand,

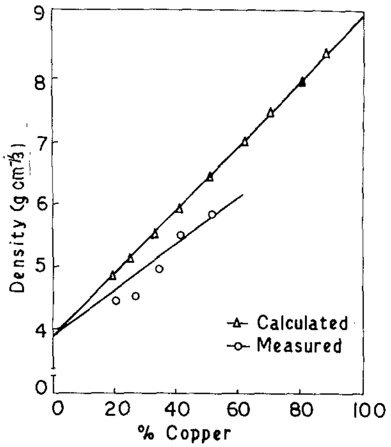

Figure 4 Variation of density of coated TiO_2 particles with copper content.

by the CuT activation method, uniform coatings have been achieved. Optical micrographs of partially sintered coated powders show that coatings after activation by the CuT method are fairly continuous and uniform (Fig. 3a, b and c). In the case of the $SnCl_2/PdCl_2$ activation method, coatings are not continuous on all particles (Fig. 3d) and the thickness of coatings is not uniform even when they are continuous.

The change in density of coated TiO_2 particles with varying copper content has been studied. The experimentally measured densities are reasonably close to the values (Fig. 4) calculated assuming perfectly dense coatings of uniform thickness.

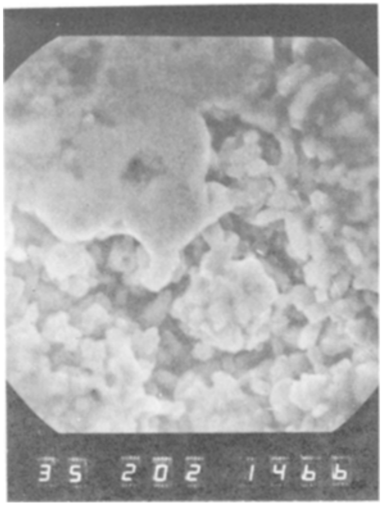

Figure 5 Microstructure of a pressed and partially sintered copper titania composite, × 2000.

The coated TiO_2 powder was compacted at various pressures and sintered in hydrogen atmosphere. Preliminary studies indicated that fairly strong green compacts could be prepared at as low a pressure as 76 MNm^{-2} and sintered to densities to about 85%. Fig. 5 shows microstructure of a compacted and partially sintered copper–titania composite.

In summary, a new, quick and more economic method than the conventional palladium chloride method has been developed to coat 2 to 15 μm thick layers of copper on TiO_2 particles. Weight percent of copper in the powders produced can be as high as 50. It has also been possible to control the thickness of the coating on TiO_2 particles with more certainty. The copper-coated TiO_2 particles produced by this method can be dispersed in molten alloys to produce cast metal ceramic particle composites. Alternatively, they can be pressed and sintered using powder metallurgy methods to produce metal ceramic particulate composites.

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Observations on the growth of thallium vanadium sulphide single crystals

The preparation and properties of single crystals of thallium vanadium sulphide for use in acoustic surface wave devices has been described by several groups of workers [1–3]. The crystals were grown by the Bridgman–Stockbarger technique in sealed silica glass ampoules at growth rates of 5 mm day^{-1}. This work records some observations made on the growth of crystals under similar conditions.

The starting material was received from the manufacturers* in three forms: First in the form of polycrystalline lumps prepared by sealed tube reaction of the elements, second, this same material which had been subjected to zone-refining at a refining rate of 2.0 cm h^{-1} in a sealed silica glass ampoule, which produced a polycrystalline bar and finally the same starting material which had been subjected to Bridgman–Stockbarger growth at a rate of 1 cm day^{-1}. This material contained large single-crystal pieces.

All of these materials were subjected to Bridgman-growth in which only a single furnace was used and the ampoules were lowered out of this furnace by means of a rack and pinion lowering mechanism situated beneath the furnace. This was driven by a multi-speed motor and this provided lowering rates of 1.0 to 30.0 mm day^{-1}. The temperature gradient used was 10° C mm^{-1} and the temperature was controlled by a Variac a.c. voltage controller only. The ampoules were cleaned prior to loading by immersion in aqua regia for at least 1 h followed by washing in distilled water and then iso-propyl alcohol. They were dried in an air oven at 80° C for at least 4 h. When dry they were loaded with the appropriate starting material, evacuated to 10^{-3} Torr, filled with pure argon to 0.3 atm pressure and sealed. The principal ampoule size was 20 mm diameter by 100 mm long sealed. This produced crystals of this diameter and about 50 mm long. Two seeding tips were used, first a 60° cone and second a bulb, 5 mm diameter connected to the main tube cone of about 90°, by a 10 mm long, 1.0 mm internal diameter capillary. Attempts to use seeds were not successful.

Table I lists a selection of results. From these it can be seen that most of the crystals started as a polycrystalline mass and the grain size gradually increased as growth proceeded. Occasionally a complete single crystal was obtained. This effect was not changed by the nature of the tip, the growth rate or the type of starting material. However, the extent of a second phase which appeared as particles made visible in the crystals by transmitted light, was markedly affected by the latter and zone refining or pre-growth of the starting material reduced the extent of this second phase. It was considered that the difficulty of obtaining complete single crystals every time might be a result of changes in stoichometry as growth proceeded. As a result sections along a boule were analysed. The mean of several analyses is given in Table II. It proved possible to obtain reproducible results for sulphur content, but the results for the thallium and vanadium showed a wide spread which did not allow meaningful conclusions to be drawn. Assuming the thallium is in a monovalent state and vanadium is in a pentavalent state a fomula for the samples is given in the table. These results indicate that if there is any change in composition as growth proceeds it is not extensive, but

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