Letters

A Ceramic Crucible for Barium Titanate Melts

It is particularly difficult to find a satisfactory crucible material in which to melt barium titanate. Solid barium titanate reacts rapidly with alumina, and liquid barium titanate with zirconia. The two refractory metals relatively stable in air, platinum and rhodium, are both attacked [1, 2]. Small multi-crystal boules have been pulled from a melt of barium titanate in iridium crucibles. They contained from 0.01 to 0.02wt% of iridium [1, 2]. However, in each case, careful control of the atmosphere was required to avoid oxidation of the iridium, and presumably heavier contamination of the melt. With a readily reduced material like barium titanate, this restriction on atmosphere is probably undesirable for optimum crystal growth [3].

An examination of the phase diagram in the system $BaTiO_3$-$SrTiO_3$ suggests a new approach to the problem. It is seen from fig. 1 (after Basmajian and de Vries [4]) that there is a melting point minimum of 1585° C at a composition of 2.5% $SrTiO_3$. Consider a melt of this composition in a strontium titanate crucible at 1585° C. If some of the strontium titanate crucible dissolves in the melt at the interface, some of the liquid will freeze out. The result is a solid lining of the crucible with a barium-strontium titanate, of strontium content slightly greater than that of the melt. Further reaction will be limited by the relatively slow processes of diffusion in the solid barium-strontium titanate. At higher temperatures, the melt composition will be close to the upper curve. "Freezing out" of solid solution will again inhibit further reaction.

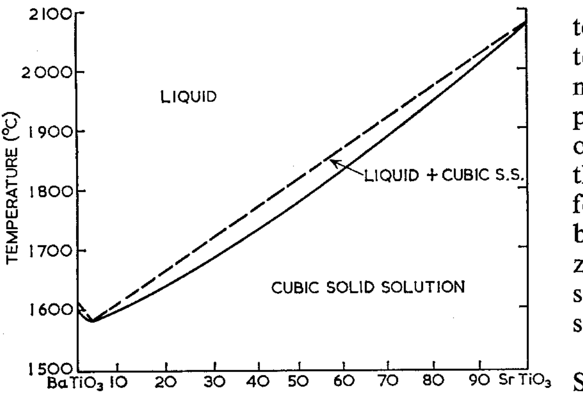

Figure 1 Simplified phase diagram of the system $BaTiO_3$-$SrTiO_3$ (after Basmajian and de Vries [4]).

To test these ideas, a number of experiments were carried out. The strontium titanate used was Associated Lead CP grade, and the barium titanate was National Lead high purity grade. The strontium titanate for the crucibles was prefired to 1500° C for 1 h, ground, and pressed either directly into crucible shape or as a simple cylinder. 7% water as binder and 3 ton/in.^{2} (470 kg/cm^2) were used. The prefiring minimised shrinkage on firing. After pressing, the cylindrical block of strontium titanate could be easily carved into a required crucible shape. A preliminary light firing can be used if any further shaping work is required. The crucibles were fired to 1750° C for 1 h on zirconia plates. A shape suitable for the Bridgman method of crystal growth could readily be made.

When working with barium titanate at temperatures above 1460° C, it is convenient to have a few % strontium titanate in the material, to avoid formation of the hexagonal phase [4]. Its effect on properties of interest is often unimportant. Brown and Todt [5] found that 1.5 ± 0.5% strontium titanate was essential for satisfactory growth in their production of barium titanate single crystals by a floating-zone technique. Basmajian and de Vries [4] show a melting point minimum at 2.5 ± 0.5% strontium titanate.

For this work, a composition of 2 mol % $SrTiO_3$, 98 mol % $BaTiO_3$ was used. The mixed powder was prefired to 1200° C for 30 min, and ground. A pressed pellet was raised to its melting point (1590 ± 5° C) in a strontium titanate crucible, and held at that temperature for ½ to 2 h. There was no evidence of reaction. The molten barium titanate could be poured cleanly from the crucible, with little evidence of the crucible having been wetted.

Working at the melting point minimum of the $BaTiO_3$-$SrTiO_3$ system means that solid state diffusion in the crucible walls is as low as possible. If the temperature is raised, the strontium titanate content of the melt will increase, to an equilibrium value dependent upon the temperature. The maximum temperature used was 1700° C (for 1 h), when the crucible appeared to be perfectly satisfactory.

This technique can, of course, be used for any materials with a suitable phase diagram, i.e. with substantially different melting points and which form solid solutions of interest. A minimum is not essential. For single crystal growth, a simple liquid-to-solid boundary in the diagram can be desirable.

Acknowledgements

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Quantitative Size-Factors for Gold-Manganese Solid Solutions

King [1] has shown the need to have an accurate knowledge of the quantitative size-factors involved in alloy systems.

Lattice parameters have been measured, at 18° C, for a number of Au-Mn alloys. The alloys were prepared by melting together, in an evacuated silica phial, accurately weighed amounts of assay Au wire and 99.99% pure Mn, supplied by Johnson, Matthey and Co Ltd. Each ingot was homogenised for approximately 100 h at 950° C, to remove any coring which might have occurred in the initial rapid cooling from the molten state. The final weight of an alloy was checked against the initial weight of pure metals used, and in no case was the loss in weight greater than 0.05%. To check the degree of homogeneity, lattice parameters were determined from filings taken from each end of the ingots. For any one alloy, the lattice parameters were required to agree to within 0.0002 Å.

Filings, from each alloy, were annealed, in vacuo, for 100 h at 400° C, and then quenched in cold water. Lattice parameters, of these filings, were determined by the Debye-Scherrer technique using X-rays emitted from a copper target. The X-ray camera had a diameter of 11.483 cm, with the film mounted in the Straumanis manner. The X-ray wavelengths assumed were: $CuK\alpha_1$, 1.54050; $CuK\alpha_2$, 1.54434 Å. The results are listed in table I.

Linear extrapolation of these figures gives the effective atomic volume for Mn as 16.03 Å^3.

TABLE I

Composition (at. % Mn)	Lattice parameter (Å)	Atomic volume (Å^3)
00.0	4.0781	16.956
3.7	4.0759	16.927
12.3	4.0686	16.840
15.8	4.0667	16.815
17.9	4.0649	16.793
18.9	4.0636	16.776

The volume size-factor, for the Au-Mn system, is thus −5.46%, the linear size-factor is −1.86%, and the Vegard's law factor is 31.29%. These values are in general agreement with the earlier results quoted by King [1].

The lattice parameter/temperature curve for a β-phase alloy, containing 49.75 at. % Mn, shows a cubic/tetragonal transformation at 125° C [2]. Extrapolation of the cubic lattice parameters down to 18° C gives a parameter of 3.208 Å for the ordered bcc lattice, indicating, a value of 16.50 Å^3 for the atomic volume. This point lies on the linear curve of atomic volume/composition as determined for the α-phase alloys (fig. 1). Such a result is in agreement with the general findings for β-intermediate phases in alloys of Cu, Ag, and Au [3, 4].

The behaviour of this alloy appears to confirm the theory of Warlimont [5], which suggests that, when the volume size-factor is less than 20%, the ordered cubic lattice decomposes martensitically at lower temperatures. Later work [6] has shown that the temperature at