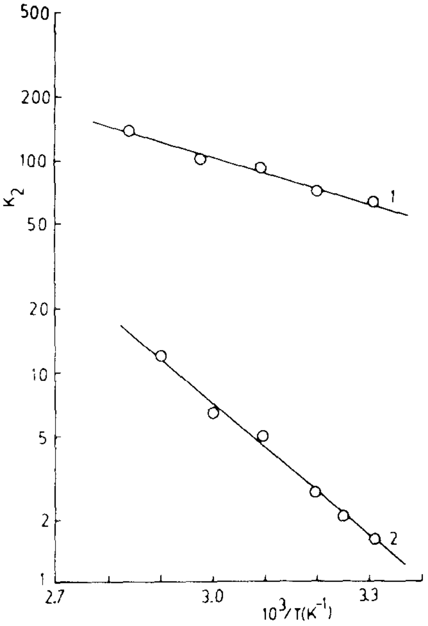

Figure 4 Plots of the dependence of $\log K_2$ on $1/T$ for (1) MgO and (2) CaF_2.

TABLE II Energies of adsorption of a pair of H^+ and Cl^- ions and of the complex, and the entropy change in the etching of MgO and CaF_2 crystals

Crystal	$E_1' + E_2'^*$ (eV)	E_4' (eV)	ΔS^0 (kcal mol^{-1} K^{-1})
MgO	0.68	0.15	6.8
CaF_2	0.92	0.42	4.1

* Assuming that $E_3 \approx 0$.

Assuming that the energy of the formation of the complex molecule and the energy of the migration of H^+ and An^- on a surface are negligible, $\frac{1}{2}(E_1' + E_2')$ may be taken as the energy of adsorption of a pair of each H^+ and An^- ions on the surface. Now the heat of physical adsorption is usually below 0.4 eV [8]. Therefore, it may be concluded that for MgO and CaF_2 in the region where peaks in the rate versus concentration curves develop, adsorption of an individual H^+ and Cl^- and of the intermediate complex is physical. The process is also associated with an increase in entropy (Table II).

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Electron microscopic examination of splat-cooled foils of Sn–Sb–Ag Alloy

By very rapidly cooling from the melt (so-called liquisol quenching) Klement *et al.* [1] were able to solidify Au–Si alloys near the eutectic composition in an amorphous state. This discovery has since been followed by the production of large number of amorphous phases in a variety of binary and ternary alloy systems using liquid quenching [2–6]. Added to these exciting results, researchers in this field have also observed unusual properties in materials prepared by liquisol quenching, such as striking improvements in the mechanical properties and unexpected semiconducting and superconducting properties. One should note the works

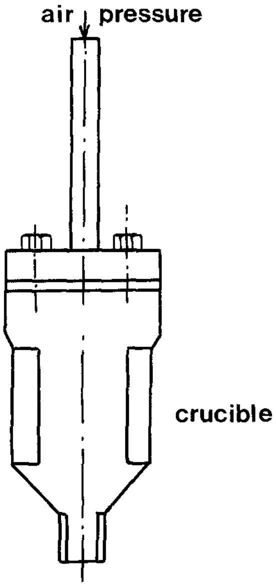

Figure 1 Schematic representation of the apparatus used in the splat-quenching technique.

of Buckel *et al.* [7–9] who have published the results for the different Zn based alloys, prepared by fast condensation upon cold substrates.

The purpose of this paper is to report the formation of an amorphous phase in a ternary Sn–Sb–Ag alloy by the splat-cooled method. To freeze-in the disorder characteristic of the liquid state required employment of an ultra-fast quenching technique (Fig. 1). This method relied on propelling small globules, at high velocity, onto a cold surface, a technique known as "splat-quenching" capable of achieving cooling rates of several million degrees per second. A specimen, weighing about 25 mg, was melted in a vertical steel crucible which had a 0.5 mm diameter orifice in its base and was heated by a resistance furance. Because of the relatively high surface tension of molten alloys, the liquid was retained in the cavity and had no tendency to flow through the small opening at the end of the steel crucible. A fast flowing jet of molten alloy through this orifice was easily obtained by applying suitable air pressure above the crucible. The splats thus obtained were bright and thin but of non-uniform thickness. Some of the foils were thin enough for direct examination in a JEOL electron microscope at 80 kV [10].

The transmission electron microscope observations on parts of an as-splat-cooled sample (Fig. 2) revealed a lack of diffraction contrast. The diffraction pattern of the selected area showed only a few diffuse rings, indicating that the region had an amorphous structure. Such amorphous constitution has not previously been reported in the literature for Sb–Sn alloys [2].

In conclusion, by increasing the rate of solidification it has been proved that a near-peritectic Sn–10.4 wt % Sb–1 wt % Ag ternary alloy can be solidified into an amorphous structure.

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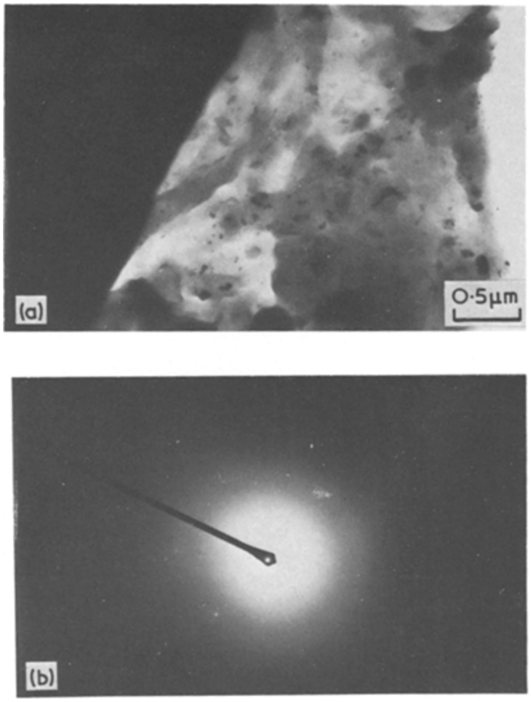

Figure 2 (a) Bright-field micrograph illustrating the microstructure of splat-cooled Sn–10.4 wt % Sb–1 % wt Ag. (b) Selected-area electron diffraction pattern corresponding to the region of the specimen shown in (a).

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Alloy pre-form preparation through the reduction of sintered oxides

A commonly used method of producing various forms (sheet, wire, etc.) of metals and alloys is by the technique of powder metallurgy. Typically, powder metallurgical techniques involve [1]:

(a) Preparation of starting metal powders, usually by reduction of the oxides.

(b) Preparation of the alloy powder, usually by atomization of the molten mixture yielding powders in the 10 to 50 μm range or by mixing of elemental powders.

(c) Compaction of the powder into pre-forms by pressure (cold) followed by sintering or by hot-pressing.

(d) Secondary working of the sintered piece or machining the final form.

A major problem which arises is the ability to work with and store the metal or alloy powders under conditions where extensive surface oxidation could be avoided. If hot-pressing is necessary to prepare the pre-form, it must be done in vacuum or neutral atmosphere to avoid oxidation of the alloy. In general, the process would be considerably simplified and possibly made less expensive if the metal or alloy pre-form could be prepared directly from the oxides.

In this work we have prepared a number of alloys in various shapes directly from the mixed and sintered oxides, which were prepared by chemical means and subsequently formed by standard ceramic methods. The formation of bars (Fig. 2), discs (Figs. 1 and 2) and rods (Fig. 2) of Ni–Fe, Cu–Ni–Fe and Cu–Ni–Co alloys is described.

Fe 33 wt% Ni. An appropriate mixture of 1 g $NiSO_4 \cdot 6H_2O$ to 2.26 g $FeSO_4 \cdot 7H_2O$ was dissolved in water, freeze dried and decomposed in air at ~ 850° C to yield the mixed metal oxides. The mixed oxide ($NiFe_2O_4$) powder was then mixed with a binder (10 wt% halowax dissolved in CCl_4) and pressed at 10 000 p.s.i. (~ 70 MPa) into disc form. The binder was burned off at ~ 500° C in air and the oxide disc sintered at 1200° C in air. The sintered oxide disc was then reduced in a hydrogen atmosphere at 1300° C for 6 h, resulting in the formation of Fe 33 wt% Ni alloy disc of ~ 95% density. Chemical analysis of the alloy indicated that the Ni and Fe were present in the correct amounts with respect to the mixed oxide. The impurities present were in agreement with those present in the reagent grade sulphates. The extent of shrinkage is shown in Fig. 1, where the oxide disc pressed with binder is on the right, the sintered oxide disc is in the centre and the alloy disc is on the left. The number on the surface of the alloy disc was originally scribed on the green disc. The lack of serious distortion of the scribed number indicated that shrinkage during reduction was very uniform.

Cu 50 wt%–Ni 21 wt%–Co 29 wt% and Cu 60 wt%–Ni 20 wt%–Fe 20 wt%. Aqueous solutions of $CuSO_4 \cdot 5H_2O$, $NiSO_4 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$ (1/0.48/0.70 g respectively) and $CuSO_4 \cdot 5H_2O$ $NiSO_4 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$ (1/0.38/0.40 g respectively) were spray dried to give the mixed sulphate salts. The mixed sulphates were decomposed in air at ~ 850° C to yield the mixed oxides. These were mixed with 10% by weight of halowax in CCl_4, dried and pressed at 10 000 p.s.i. (~ 70 MPa). After burning off the halowax at ~ 500° C in air, the compacts were then sintered at 1000° C in air for ~ 14 h and subsequently reduced at 1000° C in a hydrogen atmosphere for

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