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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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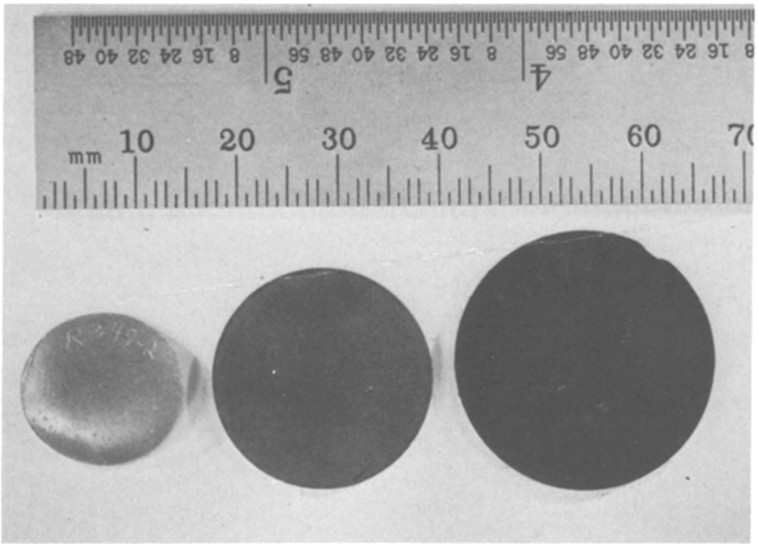

Figure 1 Shrinkage of pressed mixed oxide disc to reduced 33% Ni–67% Fe alloy disc. Green disc, right; sintered oxide, centre; alloy disc, left. Code number of alloy disc (R349-2) was scratched in green disc.

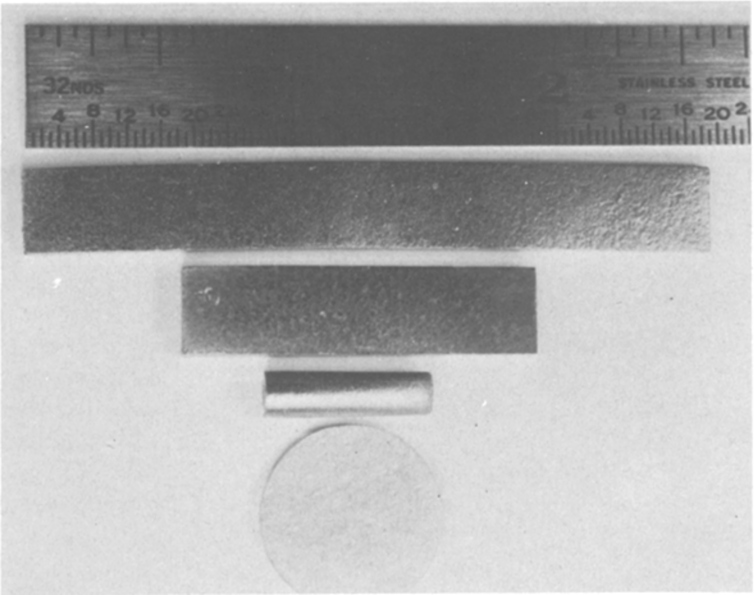

Figure 2 Examples of Cu–Ni–Fe alloy in various forms as reduced from the pre-formed oxides.

~ 2 h. Heating was then continued at 1150° C for an additional 4 h. The alloy compacts were quenched at room temperature under the hydrogen flow. Densities of ~ 98% were achieved.

In the process of going from a ceramic oxide to a preformed alloy a number of variables exist, all of which affect the final density, strength, shape and microstructure of the alloy parts thus formed.

Preliminary [2] experiments have indicated that an inverse relationship exists between the density of the alloy as reduced and sintered in hydrogen and the grain size and density of the oxide pre-form. Alloy sintering results on mixed oxide ceramics prepared from sulphates, citrates (in solution) and ball milled carbonates show [3, 4] that the alloy densification process is a function of the morphology and hence the surface area of the oxide grains. From our early experiment it seems that any experimental procedure which serves to yield larger available surface area (small particles, high porosity, etc.) leads to increased alloy density.

We have shown that metal and alloy pre-forms can be produced directly by the reduction of sintered oxides in a hydrogen atmosphere. This method has been used to obtains rods, discs and bars of various alloy compositions and shows promise as a means of preparation which avoids some of the existing problems in powder metallurgy.

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Observations of the reaction sintering of some β'-sialon compositions

The considerable interest in materials derived from the Al–Si–N–O system, and consisting principally of the β'-sialon phase ($Al_zSi_{6-z}N_{8-z}O_z$), arises in part because of their generally ready sinterability to full density. The early explanation suggested for the sintering behaviour of these materials was that vacant lattice sites enhanced atomic mobility [1]. However, it is now generally accepted that densification is the result of solution-reprecipitation processes involving oxygen-rich liquid phases at grain boundaries [2, 3]. Detailed attention has recently been paid to the solid–liquid equilibria existing in this system [4]. The importance of small amounts of liquid for the kinetics of reaction hot-pressing of β'-sialon materials has been noted [5], and it seems clear that compositions corresponding closely to β'-sialon itself will not densify, although important microstructural and chemical changes may occur [6]. These facts point to the likely importance of vapour phase or surface diffusion processes in this system at high temperature. We report here some results from studies of the reaction sintering behaviour of powder mixtures, corresponding to points spanning the β'-sialon phase line, at a z value in the region of 2, and which support conclusions drawn from the reaction hot-pressing studies.

The β'-sialon compositions are given in Table I, and are plotted on the $AlN–Al_2O_3–SiO_2–Si_3N_4$ diagram in Fig. 1. Contamination of the silicon nitride by silica (4 wt%) and the aluminium nitride by alumina (6 wt%) was allowed for. Powders were milled under propan-2-ol in an alumina charged polypropene vibro mill for 30 min. Corrections were also applied to take account of contamination of the powder by alumina (90 mg) during the milling process. Small pellets (10 mm long, 8 mm diameter, weighing ~ 800 mg) were pressed without binder at 200 MPa and embedded in either boron nitride powder or, more generally, one of a series of silicon nitride powders, in the cavity of a closed graphite crucible, and sintered

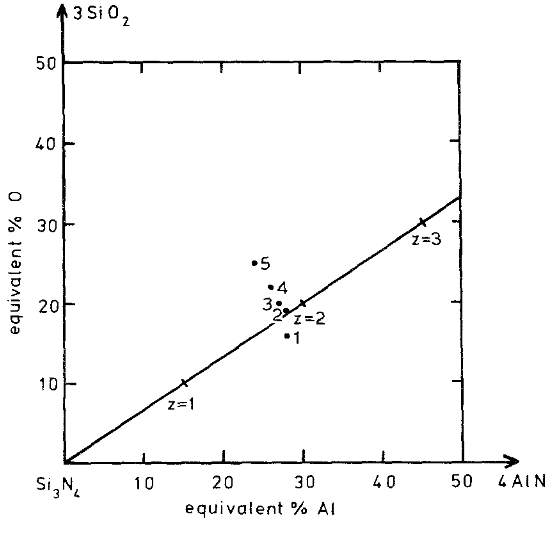

Figure 1 Points corresponding to the compositions studied, and their relationship to the β'-sialon phase line