CO-PRECIPITATION OF CERAMIC POWDERS-FACT OR FICTION

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ABSTRACT

Co-precipitation of several metal oxide precursors from solution is possible only when a double salt of a specific stoichiometry is the most insoluble species in a solution. In all other cases, co-precipitation is really the simultaneous precipitation of two or more insoluble species. Precipitated ceramic powder precursors are discussed in relation to the types of chemical segregation that is caused by "co-precipitation".

INTRODUCTION

Historically precipitation has been used as a separation process. When a salt solution with impurities is precipitated, the impurities are concentrated in the mother liquor and only a trace of these impurities reports to the precipitated crystal. These impurities are found in the voids and defects of the crystals and are typically low in concentration(i.e. ppm levels). The recent ceramic literature is filled with examples of ceramic powders produced by "co-precipitation" of a precursor salt then thermal decomposition to the oxide. The benefit of "co-precipitation" most often stated in this literature is "atomistic mixing" in the resulting ceramic powders. But if precipitation is truly a separation process how then can "co-precipitation" take place in the true sense of the word (i.e. crystals with all the metals in it atomistically mixed)?

In the ceramic literature the "co-precipitation" process is described as follows; a solution of metal salts often nitrates is mixed with a precipitating agent common for all of the metals. Oxalic, citric or other organic acids or ammonium hydroxide are frequently used as the precipitating agent since many metal oxalates or citrates or hydroxides have a low solubility. What happens during this "co-precipitation" process is discussed further in this paper. Basically there are two possibilities: 1) precipitation of a mixed metal precursor crystal (i.e. a double (or triple) salt) with a specific stoichiometric ratio of the metals or 2) segregative precipitation of individual particles of the different metal oxalates for example which are colloidally unstable and hetero-coagulate together into a mixed aggregate particle. Which possibility takes place depends on the thermodynamics of the solution.

THERMODYNAMICS

For ionic crystal precipitation, the equilibrium solubility is given by the solubility product as shown in the following example.

$$A^{+2} + 2X^{-} \text{-----}> AX_2(s) \qquad (1)$$

$$K_{sp} = [A^{+2}]_o\,[X^{-}]_o^{\,2} \qquad (2)$$

where $[A^{+2}]_o$ and $[X^{-}]_o$ are the ionic concentrations of A and X respectivly at equilibrium. For conditions not at equilibrium the molar Gibbs free energy is used. The molar Gibbs free energy for the above precipitation can be expressed as

$$\Delta\hat{G} = -RT\ln(S) \qquad (3)$$

where R is the gas constant, T is the absoluted temperature, and S is the saturation ratio defined as:

$$S = \frac{[A^{+2}]\,[X^{-}]^2}{K_{sp}} \qquad (4)$$

where $[A^{+2}]$ and $[X^{-}]$ are the actual ionic concentrations of A and X respectively. The saturation ratio is the driving force for both nucleation and growth of the resulting crystal.

In complex cases where there are several salts which can precipitate from the solution this simple thermodynamic picture is changed. Depending on the equilibria of the solution, two distinct precipitation possibilities exhist. One is true co-precipitation and the other is simultanteous precipitation and co-aggregation.

TRUE CO-PRECIPITATION

Consider for a minute a solution with two metals A and B in solution with a precipitating agent X added. With true co-precipitation only one equilibria is responsible for the formation of a solid phase as follows;

$$A^{+2} + nB^{+3} + mX^{-} \text{-----}> AB_nX_m(s) \qquad (5)$$

with only one solubility product $K_{sp}^{AB_nX_m}$. Examples of this type of precipitation are; hydrated metal arsenate, selenates, permanganates, chromates and dichromates and ferrocynates (e.g.$Co_3(AsO_4)_2.8H_2O$, $CdSeO_4.2H_2O$, $LiMnO_4.3H_2O$, $ZnCr_2O_4.2H_2O$, $Co_2Fe(CN)_6.xH_2O$). These examples can be referred to as double metal hydroxides or double salts. There is little information in the chemical literature on the subject of multi-metal carboxylate solubility products. The only mixed metal carboxalate example that I could find in the literature is that of copper acetate meta arsenate[1], Cu $(C_2H_3O_2)_2.3Cu(AsO_2)_2$, which is an insoluble pigment called Paris green.

Even more complicated examples of three mixed metal precipitates exists for example $CsGa(SeO_4)_2.2H_2O$. In this case and in the case of double salt precipitation, a mixed metal complex is likely to form in solution which is then precipitated out of solution. For that reason knowing what mixed metal complexes form in solution is a way of predicitng what mixed metal precipitates can be produced. There are a number of mixed metal alkoxides that can be produced in alcohol solution. These mixed metal hydroxides can be hydrolyzed to give a mixed metal hydroxide which may be insoluble or may further react via a condensation polymerization to form the mixed metal oxide. A large list of the possible mixed metal alkoxide complexes in alcohol solution is given in Bradley's book[2] on metal alkoxides. A Sr $Ti(O\text{-}i\text{-}Pr)_6$ complex[3] in solution is responsible for the production of $SrTiO_3$ after hydrolysis and calcination and a $ZrTi(O\text{-}i\text{-}Pr)_6$ complex is responsible for the production of $ZrTiO_3$. Some thorough experiments with mixed metal alkoxide complexes have been performed by a group at the University of New Mexico at Albuquerque lead by Prof. Mark Hampden-Smith. His group has produced $MTi(O\text{-}i\text{-}Pr)_5$ complexes[4] (where M = Li, Na or K) and $MSn(OEt)_6$ complexes[5] where M = Tl_2 or Zn.

While these mixed metal alkoxide complexes are a means of obtaining atomic mixing of the various metals the stociometry ratio of metals, n in equation 5, may or may not be that desired for the ceramic powder. A different stociometric ratio, n, for the same two metals is not likely to be precipitated out just because the initial solution contains a different stocihiometric ratio. Also for many electronic ceramic compositions it is desirable to have many other metals incorportated at the ppm level into the ceramic powder as sintering aids, grain growth inhibitors and crystal phase stabilizers. Adding these other metals is very difficult with true co-precipitation since only the one double salt, $AB_nX_m(s)$, is insoluble.

SIMULTANTEOUS PRECIPITATION AND CO-AGGREGATION

The other precipitation possibility is the simultaneous precipitation of two insoluble species controled by two separate precipitation reactions as follows.

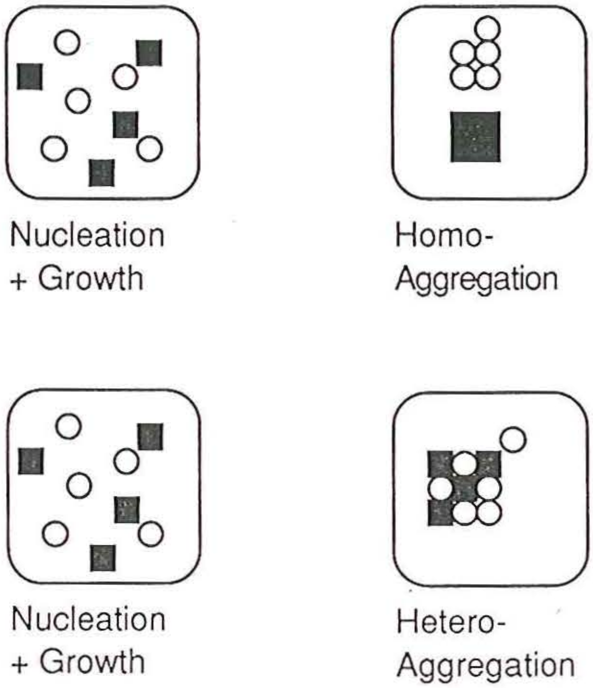

Figure 1 Segregation of $AX_2(s)$ (black squares) and $BX_3(s)$ (open circles) during simultaneous precipitation and co-aggregation.

$$A^{+2} + 2X^{-} \text{----->} AX_2(s) \text{ with } K_{sp}^{AX_2} \tag{6}$$

$$B^{+3} + 2X^{-} \text{----->} BX_3(s) \text{ with } K_{sp}^{BX_3} \tag{7}$$

In order to precipitate a particular bulk stoichiometric ratio, it is necessary to note the different solubility of the two salts and compensate for the extra solubility of one of the the salts with a higher initial concentration of the metal ion. Once this is done the solid produced will have the desired bulk stoichiometry. But how well mixed will these metals in the solid be? Certainly not at an atomic level. The scale of chemical segregation depends on the relative rates of nulceation, growth and aggregation in precipitation. Specifically the rate of hetero-aggregation is the most important factor that will determine if the individual particles are of a single solid $AX_2(s)$ or $BX_3(s)$ or a mixture of the two. The rates of nucleation, growth and homo-aggregation of each solid will determine the size of the particles either $AX_2(s)$ or $BX_3(s)$ separately. The extremes of this process are shown schematically in Figure 1. In this figure, we see nucleation and atomistic growth taking place separately and then either homo-aggregation or hetero-aggregation. With homo-aggregation, we have chemical segregation on the aggregate size scale. With hetero-aggregation, we have chemical segregation on the individual particle size scale. The size of the individual particles is controled by the rates of nucleation and atomistic growth of each of the solids $AX_2(s)$ and $BX_3(s)$. To decrease the size of the chemical segregation, the individual particles should be the smallest possible. This can be done by using precipitation conditions of high supersaturation above the critical value for nucleation. This gives high rates of nucleation which will deplete the supersaturation in solution faster than the similarly high rate of atomistic growth. To promote hetero-aggregation in preference to homo-aggregation the system must be completely colloidally unstable. This is frequently easily done by a large concentration of inert salt left in solution after the precipitation reaction which decreases the double layer thickness and causes fast electrostatic coagulation of all particles in the suspension. In other cases, polymeric flocculants can be used for this purpose.

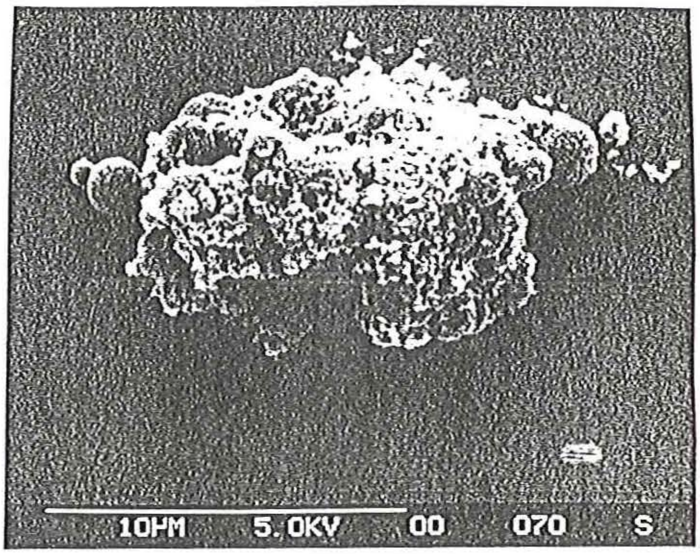

Figure 2 Precipitation of YBa_2Cu_3 oxalate, a precursor of the super-conducting $YBa_2Cu_3O_7$. Sample taken 5 minutes after mixing two solutions as described in the text. By EDAX large spheres are copper oxalate and the small particles cementing the spheres together are a yttrium bartium oxalate mixture. Bar = 10 µm.

This type of behavior can be seen in the "co-precipitation" of BaY2Cu3(oxalate) as shown in Figure 2 and 3. These precipitated products were produced by quickly mixing equal volumes of two solutions one 0.4 M in oxalic acid and the other 4.8×10^{-2}M in $Ba(NO_3)_2$, 2.4×10^{-2}M in $Y(NO_3)_3$, and 6.8×10^{-2}M in $Cu(NO_3)_2$. Five minutes after mixing the two solutions three types of particles (i.e. Yittrium, Barium and Copper oxalate) are observed to be hetero-aggregated together. EDAX examination of the larger spherical particles shows that they are copper oxalate and the very fine particles are barium oxalate and yttrium oxalate. Due to their morphology the copper oxalate spheres appear to be formed by homo-aggregation. Figure 3 shows the same precipitation product after two days in the mother liquor. The particles have been reorganized into two types of particles; 1) a square sheet like crystal of a double salt of yttrium and barium oxalate 30 µm on a edge and 2) spheres of copper oxalate. At this time we know very little about this double salt of yttrium and barium oxalate. It is speculated that the square sheet yttrium and barium oxalate crystal has been formed by the dissolution and reprecipitation of the very fine barium and yttrium oxalate particles shown in figure 2. Were it not for the fact that 5 minutes after mixing a hetero-aggregated precipitation product was observed (Figure 2), the segregation shown in Figure 3 could have been interpreted to be the result of the separate nucleation, growth of YBa_n(oxalate) and homo-aggregation of Cu(oxalate) as shown in Figure 1.

The segregation observed in these precursor powders is often lost by calcining the powders where inter diffusion of the different metals takes place. If the segregation is large scale then it will take a long time for this interdiffusion to take place. For this reason an understanding of the reasons for and the kinetics of the the segregation processes in "co-precipitation" is important.

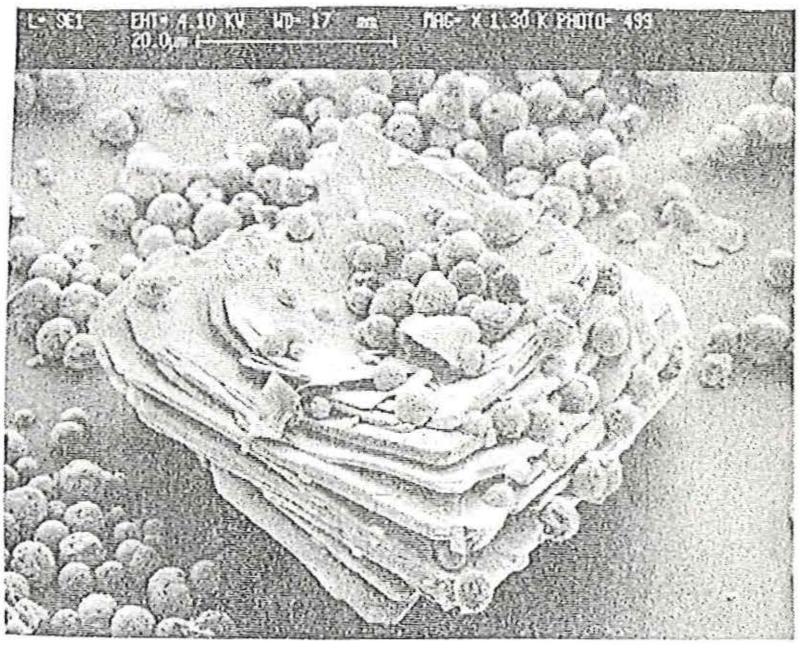

Figure 3 Precipitation of YBa_2Cu_3 oxalate, a precursor the the super-conducting $YBa_2Cu_3O_7$. Sample taken 2 days after mixing two solutions as described in the text. By EDAX spheres are copper oxalate and the crystal in the center of the picture is a yttrium bartium oxalate mixture co-aggregated with the copper oxalate spheres. Bar = 20 µm.

CONCLUSIONS

Since precipitation is generally a separation process the term co-precipitation used by most of the recent ceramic literature is a misnomer. True co-precipitation occurs when a mixed metal complex in solution is precipitated out as a double (or triple) salt. This only occurs when the double salt is the least soluble of the possible precipitation species. In all other cases co-precipitation is simple the simultaneous precipiation of two or more species which may or may not aggregate together. This aggregation leads to chemical segregation in the precipited powders The different types of chemical segregation observed in the "co-precipitation" of ceramic precursor powders has been shown with examples from the "co-precipitation" of YBa_2Cu_3 oxalate. Interdiffusion during calcination can remove fine scale segregation after simultaneous precipitation.

ACKNOWLEDGEMENT

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