THE STRUCTURE OF PLASMA SPHEROIDISED REFRACTORY MATERIALS

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ABSTRACT

Plasma spheroidisation results in the formation of liquid droplets which undercool considerably below the equilibrium melting point before crystallisation. This tends to produce materials with a variety of unusual microstructures which may be of industrial interest. The mechanisms by which such structures are formed in some oxide and nitride systems is discussed using the examples of Al_2O_3, Al_2O_3-SiO_2, SiO_2-Al_2O_3-Si_3N_4, SiO_2-ZrO_2 and Al_2O_3-ZrO_2.

1. INTRODUCTION

When refractory powders are passed through a plasma they rapidly melt, deform to spherical shape under the action of surface tension, and remain spherical after solidification so that the process has generally been referred to as spheroidisation. In many cases the aim is simply to form spherical particles from an irregularly shaped feed material, however microstructural changes also occur which may result in the formation of unique materials of technological significance. The most widely discussed process of this sort is the plasma dissociation of the mineral zircon ($ZrSiO_4$) which does not crystallise to the same structure on cooling but forms a dispersion of monoclinic ZrO_2 crystallites in SiO_2 glass[1-4]. The glass matrix may be dissolved by caustic soda providing a convenient means of extracting ZrO_2. Plasma dissociated zircon also has potential ceramic applications[5].

The spheroidisation process produces a stream of liquid particles isolated from each other within a gas and this results in solidification conditions unlike those occurring in conventional processes. Thus crystallisation, if it occurs at all, is nucleated at a large undercooling below the equilibrium melting point. The combination of large undercooling and rapid cooling rate may result in the formation of metastable phases or very finely dispersed multiphase microstructures. The present paper discusses the structure of several laboratory prepared plasma spheroidised refractory materials and examines the factors controlling their development.

2. EXPERIMENTAL PROCEDURE

Spheroidisation was carried out in the small scale apparatus illustrated in Fig. 1. This consists of a d.c. plasma torch operating within a closed, water cooled system. Powders were injected radially into the torch effluent in a stream of Ar. Additional gas, usually He, could be injected radially into the chamber 150 mm downstream from the anode orifice. The gas-particle stream was then directed through a conical section into a water cooled cyclone which allowed collection of the powder. The plasma torch was operated on nitrogen at a d-c input of ≈16 Kw.

Powders to be treated were prepared by grinding and separated into various size fractions by screening or the use of a 'Cyclosizer' elutriation apparatus. Some

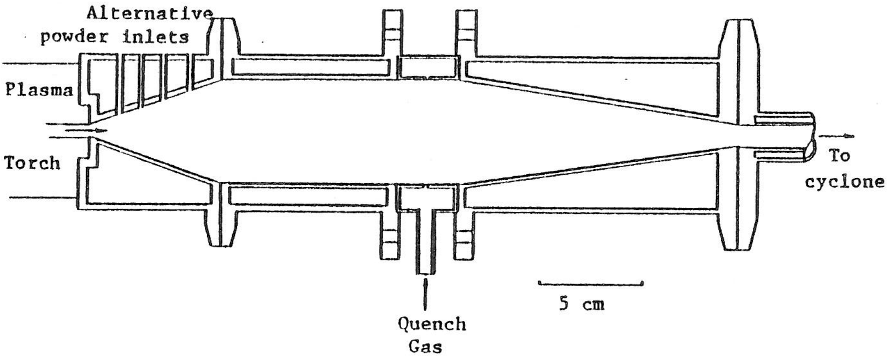

Figure 1. Plasma spheroidisation apparatus

of the starting materials (SiAlON, Al_2O_3-ZrO_2, mullite) were prepared by reaction of suitable powder mixture compacts at temperatures in the range 1500-1800°C in alumina crucibles within an induction heated graphite susceptor.

The structures of the spheroidised materials were examined by X-ray diffraction, optical microscopy, and transmission electron microscopy of ion beam thinned specimens or fragments produced by crushing. Differential thermal analysis was used in some cases to determine transformation temperatures.

3. SOLIDIFICATION OF ONE-COMPONENT SYSTEMS

The classical work of Turnbull and co-workers[6] demonstrated that, if a liquid metal is subdivided into isolated droplets, most of them crystallise at a considerable undercooling below the equilibrium melting point, an effect ascribed to homogeneous nucleation because of elimination of pre-existing nuclei. These studies suggested that an undercooling of $0.2T_m$ (T_m = equilibrium melting point, K) was required for homogeneous nucleation, however more recent work has cast some doubt on this value and there is evidence[7] that the undercooling required is perhaps 0.3 to $0.4T_m$.

A problem with attempts at obtaining homogeneous nucleation in metals is the catalytic effect of the oxide or other high melting point contaminants. This would not be expected to be significant in plasma spheroidised high melting point compounds such as oxides if they were completely melted, thus liquid particles could cool to 0.6 to $0.8T_m$ before crystallising. Growth of the first nuclei into such a highly cooled melt would not be limited by heat flow considerations and growth would therefore occur at a very high rate determined by interface processes. The crystallisation pattern would depend upon the rate of release of the heat of fusion, determined by the crystal growth rate, and the rate of heat removal. If the heat of fusion was released faster than it could be removed by heat transfer from the particle surface, the liquid temperature would rise, suppressing further nucleation so that one or a few crystals would be formed in each particle. On the other hand, if the rate of heat removal was greater than the rate of generation, cooling would continue and, because of the extremely large temperature dependence of nucleation rate, the nucleation rate would increase to give a very fine polycrystalline structure. The thermal history of a droplet during crystallisation will therefore depend upon crystal growth rate, surface heat transfer coefficient and droplet diameter[8].

The large undercooling possible during spheroidisation can result in nucleation of a metastable phase because the energy barrier to nucleation of this phase is lower than the equilibrium phase, as occurs for example in Al_2O_3 where the metastable γ-Al_2O_3 is nucleated (transformation to the ordered δ-Al_2O_3 form usually occurs during cooling). If the cooling rate after crystallisation is sufficiently rapid the metastable form will be retained to room temperature. In the case of Al_2O_3 a particle size effect is observed, namely, particles larger than ≈20 μm consist of α-Al_2O_3 because the thermal history during solidification is such that the original nucleus can transform to α-Al_2O_3 whereas the metastable phase is retained in smaller particles[8].

4. GLASS FORMATION

Under certain circumstances crystal nucleation can be completely suppressed during cooling of a liquid droplet so that crystallisation does not occur and an amorphous solid or glass is formed. Glass formation is aided by a glass transition temperature close to the crystal nucleation temperature so that the glass transition will be reached before the nucleation rate becomes sufficiently large for significant crystallisation to occur[9].

Glasses may be formed relatively easily during spheroidisation of silicates because of their high viscosity but the glass forming composition range will be extended beyond that possible by normal processing. Glass formation in plasma prepared powders has been discussed in detail for the Al_2O_3-SiO_2 system[10] in which the glass formation range may be extended sufficiently for a glass of the mullite composition ($3Al_2O_3.2SiO_2$) to be formed if the particle size is less than ∿20 μm[11]. The mullite glass crystallises rapidly to very fine mullite crystals on heating to 1000°C. The minerals sillimanite and kyanite may also transform to a glass by plasma treatment and these materials could find applications in the ceramic industry. Experiments aimed at forming mullite ceramics by low temperature compaction and transformation of mullite composition glass have proved partly successful and further developments along these lines could be useful.

Nitrogen containing glasses could be significant because their devitrification temperatures are higher than similar oxide glasses. Some nitrogen containing glasses can be formed by relatively slow cooling[12] but plasma processing offers the possibility of extending the glass forming range. A difficulty arises with Al-Si-O-N however because of decomposition and attempts to prepare glasses with the composition of phase X in this system ($3Al_2O_3.2SiO_2.{}^2/_3\,Si_3N_4$) proved disappointing[13] because the reaction $3SiO_2+Si_3N_4 \rightarrow 6SiO+2N_2$ resulted in elimination of Si, O and N from small particles with a composition in which the ratio $SiO_2:Si_2N_4 = 3$, to give a product consisting largely of Al_2O_3. Larger particle size material only partly decomposed and there was some evidence for formation of a glass with devitrification temperature of 1100°C compared with 1000°C for mullite. Glass formation has proved to be easier in composition containing MgO.

5. PHASE SEPARATION IN SILICATES

The phase diagrams of most silicate systems show a region of liquid-liquid phase separation, the extent of which increases with increasing cationic field strength[14]. In some systems, for example Al_2O_3-SiO_2, the miscibility gap is metastable[15]. There are two possible mechanisms for phase separation within a miscibility gap, spinodal decomposition in which random compositional fluctuations increase in amplitude to give an interconnected distribution of the two phases, or homogeneous nucleation of droplets of one phase in another may take place. The degree of undercooling necessary for homogeneous nucleation of one liquid from another will be much less than for a crystalline phase from liquid because of the lower interfacial energy between liquid compared with crystals and liquid[16].

Spinodal decomposition will occur at an extremely fast rate because there is no nucleation barrier and extremely rapid cooling is necessary to suppress phase separation for compositions lying within the spinodal region of the miscibility gap[17]. Thus spheroidisation of silicates with compositions in the miscibility gap region could be expected to result in suppression of crystallisation of the primary phase but phase separation of the liquid, either by spinodal decomposition or droplet formation, with considerable influence on the final microstructure obtained. Examples of these effects are observed in the Al_2O_3-SiO_2 and ZrO_2-SiO_2 systems.

(i) Al_2O_3-SiO_2

A metastable miscibility gap with consolute point of approximately 40 wt% Al_2O_3 was proposed by McDowell and Beall[15]. Transmission electron microscopy of fine SiO_2- 37 wt% Al_2O_3 powders prepared by plasma condensation showed that phase separation had occurred during cooling to give an extremely fine interconnected structure of an Al_2O_3 rich and a SiO_2 rich glass with a scale of ≈5 nm[18]. On reheating this material the Al_2O_3 rich glass crystallised to mullite at 1000°C to give a fine dispersion of mullite crystallites in SiO_2 glass. Heating to higher temperatures resulted in coarsening of the mullite and eventually crystallisation of the SiO_2 glass to cristobalite. Sintering studies showed that dense ceramics consisting of a fine dispersion of mullite in SiO_2 glass could be prepared from this material.

(ii) ZrO_2-SiO_2

The ZrO_2-SiO_2 phase diagram shows a miscibility gap with a wide composition range in the metastable region (Fig. 2) and zircon, which dissociates into ZrO_2 and a SiO_2 rich liquid above 1700°C, lies within this gap. The temperature range for homogeneous nucleation of ZrO_2 from the liquid (i.e. 0.6-0.8 T_m) is also shown in Fig. 3 and this suggests that either homogeneous nucleation of ZrO_2 or phase separation into a ZrO_2 rich and SiO_2 rich liquid may be possible during spheroidisation. These conclusions seem to be borne out by microstructural studies.

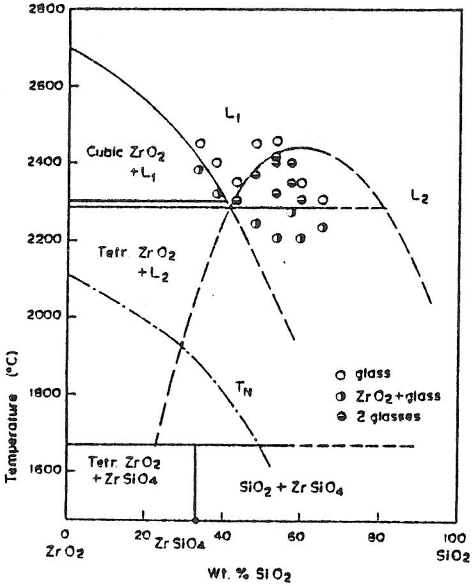

Fig. 2 Part of ZrO_2-SiO_2 phase diagram showing metastable miscibility gap region and estimated homogeneous nucleation temperature of ZrO_2 (T_N = 80% liquidus temperature).

The predominant structure observed in plasma dissociated zircon prepared from large particle size (100-200 µm) feed powders in a large scale reactor is of spherulitic crystals of monoclinic ZrO_2 in SiO_2 glass[24,19]. The spherulitic ZrO_2 pattern is consistent with branching growth controlled by diffusion in the surrounding viscous liquid. Some droplet type structures consistent with phase separation were also observed in this material[19].

The ZrO_2 present in commercial plasma dissociated zircon consists almost entirely of the monoclinic form (stable below ≈1100°C) together with a small proportion of the metastable tetragonal form, however laboratory prepared material of finer particle size contains a small amount of tetragonal ZrO_2 which increases in proportion as the particle size is decreased until it becomes the predominant form below ≈10 µm[20]. Transmission electron microscopy shows that the structure of 10 µm powder consists entirely of droplets of ZrO_2 with a wide range of particle sizes, dispersed in SiO_2 glass, in some cases suggesting two stage phase separation in the liquid, before crystallisation of ZrO_2 rich liquid to tetragonal ZrO_2. The tetragonal phase would normally transform to monoclinic on further cooling, however it is well known that tetragonal ZrO_2 may be stabilised to room temperature by surface energy and strain effects if they are smaller than a certain critical diameter of 10-40 nm[21]. The appearance of an increasing proportion of tetragonal ZrO_2 in finer particle size plasma dissociated zircon can readily be explained by the size distribution of spherical ZrO_2 particles formed by phase separation, that is the ZrO_2 particles less than a few tens of nm do not transform to monoclinic on cooling but larger particles do.

Sintering of these powders, after leaching to remove part of the SiO_2, results in the reaction of all of the SiO_2 with part of the ZrO_2 to form a zircon ceramic containing a dispersion of monoclinic and tetragonal ZrO_2. This type of structure shows promise of high fracture toughness because tetragonal ZrO_2 transforms in the region of a propagating crack with absorption of energy[22].

6. The Al_2O_3-ZrO_2 EUTECTIC SYSTEM

Glasses tend to be formed in the region of deep eutectics of rapidly quenched alloys and some experiments involving plasma spraying of Al_2O_3-ZrO_2 have shown that an amorphous phase is formed in the vicinity of the eutectic of this system[23]. Spheroidisation of -53 µm Al_2O_3-45 wt% ZrO_2 powders resulted in the formation of a structure consisting of a mixture of tetragonal ZrO_2, α-Al_2O_3 and δ-Al_2O_3 and transmission electron microscopy has revealed an extremely fine lamellar structure of ZrO_2 and Al_2O_3 with an interlamellar spacing of approximately 20 nm. Some regions showed an even more finely disseminated distribution of tetragonal ZrO_2 in Al_2O_3 ($\sim$10 nm) but the lamellae were broken up consistent with the "anomalous" structure observed in eutectics at fast growth rates when coupled growth of the two phases can no longer occur[24]. This system again illustrates the effect of small ZrO_2 particle size on stabilisation of the tetragonal form at room temperature and demonstrates the possibility of using a plasma prepared material as a basis for ceramics consisting of a fine dispersion of tetragonal ZrO_2 in a matrix of another phase.

7. CONCLUSIONS

Plasma spheroidisation of some refractory compounds may result in microstructures which cannot be produced in any other way. This opens up the possibility of plasma treatment of materials as a basis for the preparation of ceramics with unique properties.

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