PLASMA SYNTHESIS OF HOLLOW CERAMIC MICROSPHERES

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Abstract

Hollow spherical alumina particles were produced in an inductively coupled RF thermal plasma reactor. The main objective of present work was to investigate how the water content and porosity of raw materials and composition of gas phase influence the size of the holes. We concluded that the porous structure is highly responsible for hole formation and high initial water content is not prerequisite for holes.

1. Introduction

One application of thermal plasmas is spheroidization. The process involves the melting of the particles introduced into the plasma in part or entirely. Hence, their shape get spheroidized with the minimum surface area and surface energy. Plasma technology is especially suitable for melting ceramic particles of high melting point. Because of the extremely high temperatures and temperature gradients that provide rapid heat transfer, the particles can melt in a split second. Due to the heterogeneity of plasmas, fine adjustment of the plasma-particle momentum and heat transfer is of vital importance for the achievement of an effective heat transfer. For this reason several model has been developed [1-3], that calculate the temperature of a particle, the amount of the melted and the evaporated part of the particle in the function of time. These models differ in the method of calculation, in the calculation of heat transfer coefficients, the number of effects they take into consideration, etc., but one thing is common: none of them predicts rise in particles dimensions due to the accumulation and expansion of gas bubbles inside the particles.

We have carried out experiments to make spheroidized alumina particles in an RF inductively coupled thermal plasma from various starting materials. The conditions under which gas bubbles formed inside the particles were investigated. The effect of different gases both on the spheroidization and on the size of holes was studied, as well.

2. Experimental

The experimental apparatus consisted of a TEKNA-type induction plasma torch with a quartz confinement tube of 25 mm and a water cooled steel chamber connected to a cyclon. The plasma power of 21 kW was provided by a three turn, water cooled induction coil from an RF generator operating at an oscillator frequency of 3 MHz. High purity argon was used both as plasma and sheath gas with flow rates of 20 and 60 l min⁻¹, respectively. Hydrogen or oxygen were also mixed into the sheath gas with a proportion of 10%. The torch was connected to a water-cooled steel chamber and powder collector.
The powders were fed through an injection probe to the top of the plasma flame by argon carrier gas (3 l min⁻¹) with a constant feed rate of 10 g min⁻¹. One commercial gibbsite and two alumina powders were investigated. Main characteristics of particular powders are summarized in Table 1. Both the raw materials and the heat treated powders were characterized for water content, particle size distribution (by Malvern Master Particle Sizer), phase composition (XRD) and microstructure (SEM).

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Size</th>
<th>LOI (%)</th>
<th>Phase composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>&lt; 45 µm</td>
<td>0.44</td>
<td>γ-Al₂O₃</td>
</tr>
<tr>
<td></td>
<td>45-55 µm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>63-71 µm</td>
<td>0.02</td>
<td>α-Al₂O₃</td>
</tr>
<tr>
<td>Al(OH)₃</td>
<td>&lt; 45 µm</td>
<td>34.6</td>
<td>Gibbsite</td>
</tr>
<tr>
<td></td>
<td>1-71 µm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3. Results

Formation of a melted layer on the particle, that is crucial in terms of spheroidization is basically depends on the applied gases and it less depends on the starting materials. Once the heat transfer rate is improved by addition of hydrogen to the argon, spheroidization can be achieved even in case of Al(OH)₃, if the particle size is less than 45 µm. The non-agglomerated spheroidized particles are well perceptible under optical microscope. Under a magnification of 1000 times, several fractions of broken or damaged particles suggest the hollow products (Fig. 1.). SEM micrograph of particles embedded in resin and cut by diamond blade confirm this suggestion (Fig. 2.). This applies to experiments carried out in the presence of hydrogen in the sheath gas.

Fig. 1. SEM micrograph of a broken particle

Fig. 2. SEM micrograph of the cross section of a cutted particle

Holes were not typical in experiments where hydrogen was replaced with oxygen. In this case center of particles consisted of agglomerated polycrystalline prisms (Fig. 3.).
Spheroidization and formation of holes must imply some variation in the physical properties of particles. Table 2. shows the initial and final particle size and density. In contrast to some model calculations [3] the mean diameter of particles wasn’t reduced, it but increased in cases when $\text{Al}_2\text{O}_3$ was fed and hydrogen was also added. The relatively highest increase occurred at $\alpha$-$\text{Al}_2\text{O}_3$.

Table 2. Size-, density- and crystalline phase changes of powders in the set of experiments

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Gas in the sheath beside Ar</th>
<th>Crystalline phase before treatment</th>
<th>Crystalline phase after treatment</th>
<th>Particle size before treatment</th>
<th>Particle size after treatment</th>
<th>Powder density before treatment</th>
<th>Powder density after treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>$\text{H}_2$</td>
<td>$\gamma$</td>
<td>$\gamma$, $\delta$, $\theta$, $\alpha$</td>
<td>$30,3$</td>
<td>$38,3$</td>
<td>$3,4$</td>
<td>$3,2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$48,4$</td>
<td>$60,6$</td>
<td>$3,2$</td>
<td>$2,8$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$70,1$</td>
<td>$80,0$</td>
<td>$3,1$</td>
<td>$2,9$</td>
</tr>
<tr>
<td></td>
<td>$\text{O}_2$</td>
<td>$\alpha$</td>
<td>$\gamma$, $\delta$, $\theta$, $\alpha$</td>
<td>$45,2$</td>
<td>$66,5$</td>
<td>$3,7$</td>
<td>$3,2$</td>
</tr>
<tr>
<td>$\text{Al(OH)}_3$</td>
<td>$\text{H}_2$</td>
<td>Gibbsite</td>
<td>$\gamma$</td>
<td>$48,4$</td>
<td>$43,4$</td>
<td>$3,2$</td>
<td>$3,7$</td>
</tr>
</tbody>
</table>

Although hollow particles were typical in products from $\text{Al(OH)}_3$, as well, density increased significantly in this case. Quite obviously, changes in the particle size were inversely proportional to density changes. The latter, however, was not as high as it would be predicted from size changes by theoretical calculations. It could be attributed to the presence of broken and nanosized particles which would increase the overall density of the powder.

Fig. 3. SEM micrograph of the cross section of a cutted particle subjected to plasma treatment with oxygen in the sheath

Fig. 4. SEM micrograph of $\alpha$-$\text{Al}_2\text{O}_3$ as the most porous starting material

4. Discussion

The application of different starting materials make it possible to investigate how the water content and porosity of the starting material can affect the hole size of the product particles. Both $\alpha$- and $\gamma$-$\text{Al}_2\text{O}_3$ are prepared by the calcination of aluminum-hydroxide. On the effect of heating, the hydroxide gradually loses the chemically bounded water content of 34.6%. The hexagonal prisms of gibbsite particles cracked on the cleavage planes leaving the particles porous. During calcination, the $\text{Al}_2\text{O}_3$ attains its thermodynamically most stable
phase of $\alpha$-Al$_2$O$_3$ over ~1200°C through several metastable phases $\gamma$, $\delta$, $\theta$, $\chi$, $\kappa$. As the transitional phases are heated, relatively few $\alpha$-Al$_2$O$_3$ nuclei are produced [4]. These nucleated grains undergo rapid growth through the porous transitional alumina phase, resulting in a more porous structure (Fig. 4.)

Water content of the starting material is assumed to play an important role in the formation of hollow particles [5]. Formation of holes can be explained by the expansion of gases – most probably water vapour – being present in the starting material in adsorbed or chemically bounded. Much of gases go off instantly from the porous structure of the particles. After having formed a melted layer, water vapour had no escaped from inside, but it has trapped within the molten shell because of the sluggish movement of the bubbles in the strongly viscous liquid alumina and the surface tension of the alumina/plasma interface.

In this way the final size of the holes is simply determined by the freezing temperature of liquid alumina, that is approximately 0.8 $\cdot$ $T_f$ in the case of quenching [6]. The amount of water vapour left in the holes can be estimated from the universal gas equation taking into consideration the liquid alumina/plasma interface. This calculations show, that the water content in the holes is less of two order of magnitude than the water content of the starting material. It indicates that a relatively high water content in the starting material is not prerequisite for the hole formation. Moreover, the biggest holes formed from the starting material with the less chemically bounded water content and with the highest porosity. In case of gibbsite as starting material, when water content was fairly high (34.6%), the spheroidized products were also hollow, but the size of them were similar to the products of $\gamma$-Al$_2$O$_3$.

Among the products several crater-shaped particles can be observed (Fig. 5). When one face of the melted particle solidified sooner or a part of the melted shell is thickened for some reason, the gases could escaped leaving behind this formation.

With the use of oxygen, heat conduction of which is inferior to that of hydrogen, the particle surface could melt only in thickness of some $\mu$m, while the bulk remained unchanged (Fig. 3). Formation of weird products (Fig. 6) can also be attributable to the inferior heat transfer. While the center of the particles remained solid, the gas bubbles were hindered from escaping and accumulated around it.

Fig. 5. SEM micrograph of a crater-shaped particle inside a bigger one

Fig. 6. SEM micrograph of a smaller particle particle

The resolidification of the melted particles take place rapidly because of the extremely high temperature gradients, that is concomitant of plasma. Several papers report [7] that liquid alumina solidifies not in the
most stable phase of $\alpha$-$\text{Al}_2\text{O}_3$, but rather in the form of $\gamma$-$\text{Al}_2\text{O}_3$. This is attributed to the fact that the solidified phase structure is basically determined by the relative critical free enthalpies of nucleation of alternative crystal structures. Not surprising, that considerable part of the spheroidized particles composed of the $\gamma$-$\text{Al}_2\text{O}_3$ and other metastable phases of alumina. The latter formed from the $\gamma$ phase according to the usual way of phase transformation on calcination if temperature history of the given particle makes it possible. In bigger particles (>30 $\mu$m) the heat effect of crystallization may promote additional phase changes. In the view of abovementioned it’s surprising that only $\alpha$-$\text{Al}_2\text{O}_3$ phase could be found in the XRD diffractograms of the products from gibsise. We suggest, that liquid alumina solidified in its $\gamma$ phase, but the $\gamma \rightarrow \alpha$ transformation were accelerated. This is confirmed by the experience [6] that the presence of water vapour increase the transformation rate of $\gamma$-$\text{Al}_2\text{O}_3$.

5. Summary

Experiments were carried out to form hollow, spheroidized $\text{Al}_2\text{O}_3$ particles from different starting materials. According to the results, spheroidization of particles is possible in wide size range if the heat transfer coefficient of the plasma is higher than that of pure argon. Formation of holes inside the spheroidized particles can be explained by the sluggish movement of bubbles in the highly viscous liquid alumina and the surface tension of the alumina/plasma interface. The size of holes is dependant of the chemically bound water content of the starting material. On the contrary, the biggest holes resulted from the starting material with the lowest bound water, but with highly porous structure. This shows the importance of porosity.

As the heat transfer conditions get inferior the melted part of particles restrain only to the outer shell, while the inner part remained solid. Hence, hole formation failed, the density increased.

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References
