The role of glass in alumina-based engineering ceramics

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Nearly all types of engineering polycrystalline ceramics produced and studied today contain certain portion of glass located at boundaries between the microcrystals of a ceramic material (grain boundaries), or in triple grain boundary junctions. The glass is formed at sintering temperature from raw material's impurities, or from substances added intentionally to assist sintering or to modify the properties of polycrystalline material. The paper gives a brief review on the role of glass in the most widely used engineering ceramics today, Al_2O_3. The most recent results of our study of the influence of small amounts of glass (up to 10 vol. %) and of glass-forming additives SiO_2-MgO and SiO_2-CaO on sintering, microstructure, microstructure development, and room-temperature mechanical properties including wear, of polycrystalline alumina-based engineering ceramics are presented for illustration.

Introduction

Except of extremely pure materials prepared by special (and expensive) processing routes from high purity raw materials, virtually all industrially produced polycrystalline ceramics contain certain amount of glass. A marginal example of glass-containing ceramics is porcelain, which typically consists of between 50 and 80 % of glass with dispersed needles of mullite and larger grains of silica. [1] However, such ceramics are beyond the scope of this paper. This will be focused on engineering ceramics containing typically less then 10 vol. % of glass and used primarily for applications where good mechanical properties are required, both at room and high temperatures. As will be shown below, glass plays a crucial role in such materials, influencing significantly both the microstructure and the mechanical properties.

Glass in engineering ceramics is usually present in the form of a film at grain boundaries with thickness of several nanometres, or cumulates in multiple grain boundary junctions, so called triple pockets. Direct high-resolution transmission electron microscopy measurements revealed that grain boundaries of alumina ceramics sintered with addition of CaO and SiO_2 were covered with a continuous layer of amorphous calcium aluminosilicate. [2] The thickness of such layer was independent on the amount of impurities or sintering aids, but varied with the composition of the amorphous phase (CaO content in this case). Calculations based on the simplified geometrical model of the polycrystalline material microstructure assuming constant equilibrium thickness of the glass layer at all grain boundaries, suggested that as little as 0.15 vol. % of impurities are sufficient to form a continuous glassy film at all grain boundaries. [3] The equilibrium thickness is achieved for respective grain boundary glass composition and excess glass is cumulated in the triple pockets. [4, 5] The size of triple pockets then increase with increasing amount of glass in the material.

One of the important features of glassy phase in ceramics is its tendency to crystallization. Crystallization changes the composition of glass, depleting it of components, which then become the building stones of crystalline phases. Crystallization then results in changes of structure, thermal properties (thermal expansion, for example) and temperature dependence of viscosity of the glass. Interestingly, as shown by Raj and Lange [6], the crystallization of small quantities of glass segregated at grain boundaries is more difficult than crystallization of bulk glass of the same composition. The reason is that the fluid at grain boundaries is constrained. Any volume change during the phase transformation rises the strain energy, which opposes the transformation. Under such circumstances, glass at grain boundaries may not crystallize at all, or may crystallize only partially. The crystallization occurs therefore primarily in triple pockets. The direct consequence is that the gradient of composition exists between the grain boundary and the adjoining triple pocket where crystallization occurs.

Grain boundary glasses influence the properties of ceramics in many ways. Firstly, the presence of the amorphous phase (or glass forming melt at the processing temperature) promotes densification by improving the particle reorganization by viscous flow, and by additional mechanisms, like solution-reprecipitation of matrix grains and diffusion of the ceramic matrix phase through the melt. [7] Secondly, the presence of the liquid results in formation of markedly different microstructure compared to that of the materials sintered without the presence of the melt. In some cases the consequence of liquid phase sintering is microstructure refinement due to more moderate conditions required to obtain the fully dense material. However, in most cases the abnormal grain growth is observed in LPS ceramics as a consequence of so called Ostwald ripening. In this case larger grains grow on expense of smaller ones due to the concentration gradient of the dissolved matrix phase in the melt between the convex outer faces of large grains and concave faces of the smaller ones. Often the presence of plate-like, or needle-like grains is observed in ceramic microstructures as a consequence of Ostwald ripening.

As can be expected, the materials with qualitatively different microstructures show a wide range of mechanical, electrical and thermal properties. Presence of glass, for example, reduces the thermal conductivity of polycrystalline alumina.[1] Room temperature mechanical properties (fracture toughness, bend strength, wear resistance) are related to presence of glass via microstructure characteristics of the material. Although not proved experimentally, the molecular dynamic simulations performed by Blonski and Garofalini[8] suggest, that silicate glasses strengthen the alumina-alumina grain boundaries, increase fracture energy, change the fracture mode from inter- to transgranular and, as a consequence, may increase the fracture toughness of the material. The grain boundary strength is also influenced by residual stresses generated in the material in the course of cooling from processing temperature due to thermal expansion mismatch between glass and crystalline ceramic matrix. If the thermal expansion of glass in triple pockets is lower than that of matrix, the grain boundaries are at room temperature “wedged” or weakened by the presence of glass. The glass with higher thermal expansion than the thermal expansion of matrix “clamps” the grain boundaries thus making them stronger. Thus, even if the microstructures of polycrystalline materials are qualitatively identical, markedly different mechanical properties can be obtained due to various thermal expansions of glasses in the matrix. This demonstrated in case of Si_3N_4 Peterson and Tien[9], who prepared a set of materials with practically identical microstructures, but with fracture toughness varying between 4 and 6 $MPa.m^{1/2}$.

Extremely important is the influence of glass on high temperature mechanical properties. Softening of the glassy phase at high temperatures impairs especially flexural strength and creep resistance.[10]

As seen from the previous text, the presence or absence of glass in technical ceramics influences virtually all aspects of a ceramic material, ranging from processing conditions through microstructure characteristics to properties of the final material. Some of the results acquired in the course of our study of liquid-phase sintered alumina-based polycrystalline ceramic materials are presented in the following sections.

Sintering and Microstructure

Most commercial aluminas contain intentional additions of SiO_2, CaO or MgO, together with small amounts of alkaline oxides. From this point of view the typical glass in polycrystalline alumina ceramics resembles by its composition usual silicate industrially produced glasses. The principal difference is high content of aluminium oxide, which is transferred to the melt by dissolution of the alumina matrix grains. Among the systems mentioned, the alumina-calcia-silica system is of considerable importance, because the eutectic temperatures of the system range between 1140 and 1400 °C facilitating the formation of a liquid at relatively low temperatures and therefore fast densification. Addition of SiO_2 and CaO to the alumina powder generates several volume percent of a liquid and the process involving solution-recrystallization of alumina particles in the liquid accelerates the sintering of alumina, as illustrated by Figure 1. Unlike the alumina sintered without the presence of liquid whose microstructure is shown in Figure 2, a material containing large, platelike or rodlike α-alumina grains is usually formed as a consequence of the silica and/or calcia addition. The development of the elongated grains with increasing temperature is illustrated by figures 3a-d. The abnormal grain growth in alumina is observed when the additives are present above critical concentrations roughly corresponding to their solubility limits in the alumina crystals.[11] The driving force of formation of the platelike grains is the uneven dissolution of various crystallographic faces of α-alumina crystals due to anisotropy of the solid-liquid interfacial energies. [12]

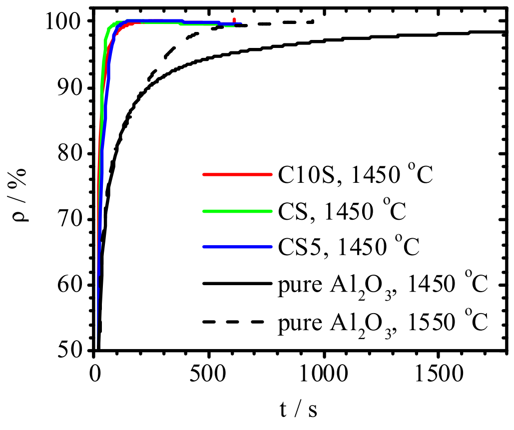

Fig. 1 The influence of sintering additives on densification of alumina ceramics

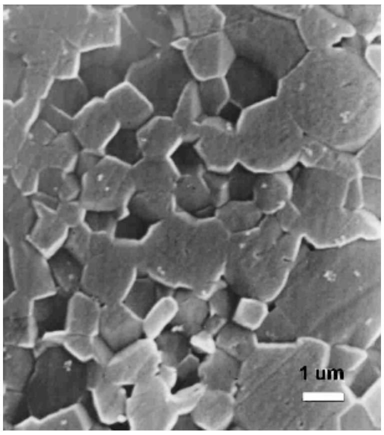

Fig. 2 Microstructure of alumina densified without additives

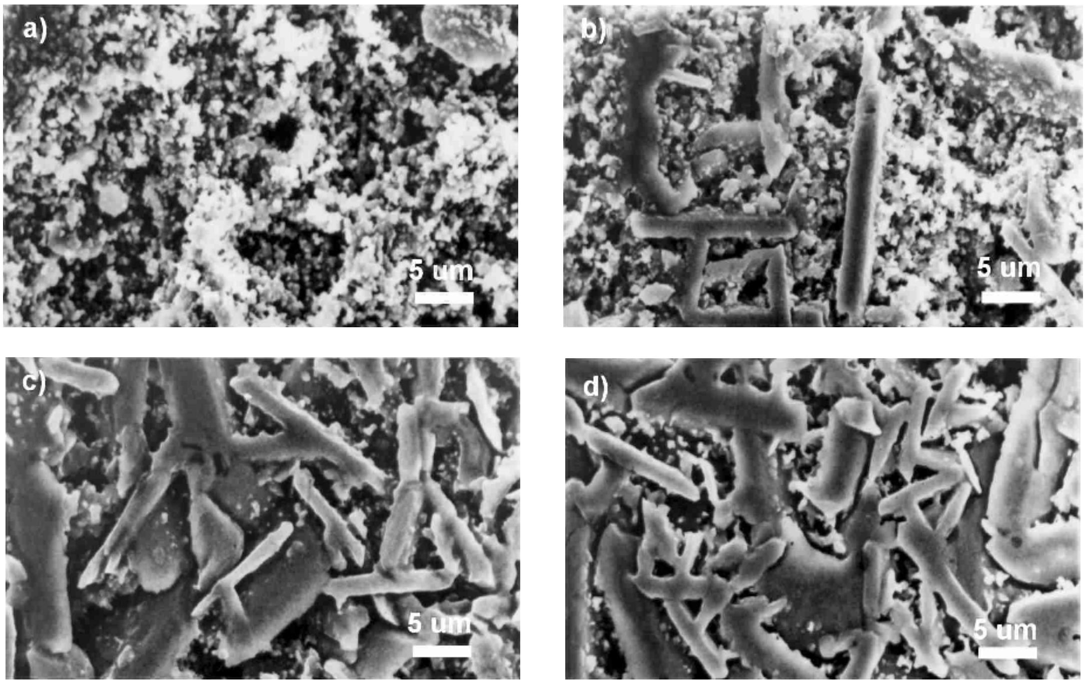

Fig. 3 The microstructure developmentt of CaO.5SiO_2-sintered alumina. The platelets are developed by Ostwald ripening – dissolution and reprecipitation of the alumina matrix grains. The sintering temperatures: a – 1470 °C, b – 1490 °C, c – 1510 °C, d – 1530 °C.

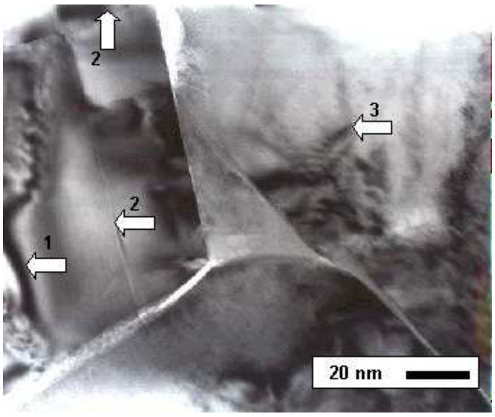

Fig. 4 The TEM micrograph of the glass-containing triple pocket and the adjoining grain boundaries of the MgSiO_3-sintered polycrystalline alumina. The arrows mark the matrix defects formed as a consequence of thermal expansion mismatch between alumina and the glass. 1 – strain fringe, 2 – subgrain boundary, 3 – array of dislocations.

The thermal expansion mismatch between the amorphous (glassy) grain boundary phase and the alumina matrix grains phase generates in the course of cooling from the processing (sintering) temperature significant fluctuating residual stresses, which can achieve as much as 500 MPa both in compression and tension. The TEM micrograph of the MgSiO_3-sintered alumina shown on Figure 4 indicates that the alumina grains adjoining the triple pocket are heavily stressed and strained. The stress state of the material has then direct consequences for the mechanical properties, including bending strength, fracture toughness and wear resistance.

Mechanical Properties and Wear

The addition of silicate sintering additives generally tends to decrease the density, Young's modulus, strength, hardness and refractoriness of alumina ceramics. Powell-Dogan and Heuer[13] studied in detail a set of 96 % LPS aluminas containing various additives including CaO, MgO, SiO_2 and Na_2O. The mechanical properties (especially the fracture strength) were seriously affected by thermal expansion of glass and the extent of its crystallistaion due to volume changes and associated microcrack formation in the ceramic body in the course of devitrification.[14] The presence of grain boundary glass is not, however, necessarily deleterious. The anisotropic microstructure with elongated or platelike grains is more likely to display so-called R-curve behaviour (the increase of fracture energy with increasing length of the crack) as a consequence of toughening by grain bridging, grain pull-out and crack deflection, with corresponding increase of fracture toughness of the material.[15] However, our results indicate, that in case of the LPS alumina is the toughening effect relatively modest.

The use of silicate based sintering additives leads also to significant improvement of the wear resistance of alumina, and this is well recognized industrially. Recent laboratory studies using model high purity aluminas of controlled composition have shown the generally beneficial effects of Group II metal silicate additions on the wear resistance of alumina materials.[16] Several models have been proposed for the mechanism of action of the amorphous silicate during wear, but its exact function has not been conclusively established. As concluded in our previous work[17] in the $MgSiO_3$ liquid phase sintered aluminas the intergranular silicate films appear to have the main function of strengthening the grain boundaries, and material loss in these materials occurs at much reduced rates. High fluctuating stresses in the $MgSiO_3$ and $CaSiO_3$ sintered materials result from the thermal expansion coefficient differences between the alumina, and the grain boundary magnesium aluminosilicate glass. These stresses appear to influence microcrack propagation rate by causing slowing the rate at which a transgranular crack can propagate across the boundary. Depending on the composition and amount of the grain boundary phases, the wear resistance of the LPS aluminas is 3 to 10 times higher than the wear resistance of the pure alumina with the equivalent mean grain size (Figure 5 and 6).

Conclusion

The presence of glass in polycrystalline ceramic materials is an important factor strongly influencing all aspects of the material, from the processing conditions through microstructure characteristic to the mechanical properties. However, especially in case of the alumina-based materials the detailed understanding of the mechanisms responsible for action of the additives is scarce, and further work is required.

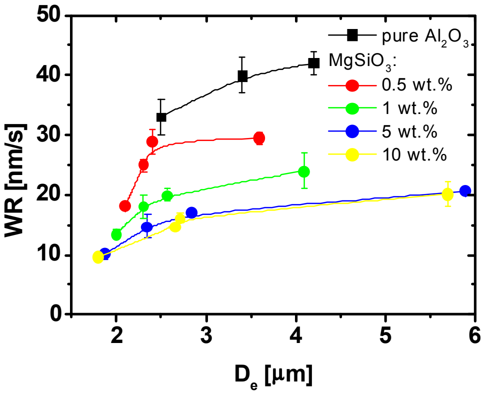

Fig. 5 The dependence of wear on the overall amount of the added $MgSiO_3$ sintering additive.

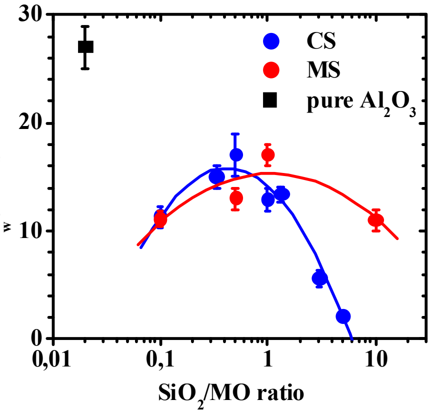

Fig. 6 The influence of the chemical composition of the sintering additives (system CaO-SiO_2 and MgO-SiO_2) on wear of alumina.

Acknowledgement

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