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Effect of Water Suspension pH on Thermomechanical Properties of Al_2O_3–10 wt% ZrO_2 Ceramics

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Abstract

The influence of suspension pH on the thermomechanical properties of Al_2O_3–10 wt% ZrO_2 ceramics was studied. It was observed that the pH of water suspensions strongly influences the agglomerate size of oxide powders. The maximum agglomerate size corresponds to the isoelectric point of the suspensions. Alumina ceramics prepared in such a way are characterized by an increase in monoclinic zirconia content and a decrease in resistance to fracture. Increases in the acidity or alkalinity of the suspension, equivalent to an increase in the surface grain charge, leads to an increase in tetragonal zirconia content and improvement of the properties of the ceramics.

Die Rolle des pH-Werts der bei der Herstellung von Al_2O_3–10 Gew.% ZrO_2-Keramiken auftretenden Suspension auf die thermomechanischen Eigenschaften wurde untersucht. Der pH-Wert der wässrigen Suspension ist ausschlaggebend für die Größe der Agglomerate der oxidischen Pulver. Die größten Agglomerate bilden sich am isoelektrischen Punkt der Lösung. Derartig hergestellte Verbundwerkstoffe weisen einen erhöhten Anteil monoklinen ZrO_2 auf und zeigen eine Festigkeitsabnahme. Eine Erhöhung oder Erniedrigung des pH-Werts der Suspension bewirkt eine Erhöhung der Oberflächenladung der Pulver und führt zu einem erhöhten Anteil an tetragonalem ZrO_2 und zu verbesserten keramischen Eigenschaften.

On a étudié l'influence du pH de suspension sur les propriétés thermomécaniques de céramiques Al_2O_3–10% masse ZrO_2. On a observé que le pH des suspensions aqueuses influence considérablement la taille des agglomérats de ces poudres oxydes. Le maximum de taille d'agglomérat correspond au point isoéléctrique des suspensions. Les céramiques alumines préparées de cette façon se caractérisent par un accroîssement de la teneur en zircone monoclinique et par une diminution de la résistance à la fracture. L'augmentation de l'acidité ou de la basicité des suspensions, correspondant à l'accroîssement de charge surfacique des grains, conduit à une augmentation de la teneur en zircone tétragonale et à une amélioration des propriétés de ces céramiques.

1 Introduction

The toughening of ceramics by inducing a martensitic transformation in the stress field of the dominant crack has aroused much interest in recent years.[1–7] It has been clearly proven that the toughening agent of ceramics is metastable tetragonal or cubic zirconia.[6,7] The critical size of tetragonal zirconia inclusions is $D_{ct} = 1{\cdot}4\,\mu m$ and of the cubic form $D_{cc} = 3{\cdot}0\,\mu m$. This means that all zirconia grains of sizes below this value, due to the constraints of the alumina matrix, can be retained in metastable form at room temperature and contribute to toughening of the ceramics. The larger ones transform spontaneously to the monoclinic form during cooling from the sintering temperature to the room temperature, with accompanying microcracking of the matrix.

Accordingly, in the technology of transformation-strengthened alumina ceramics only ultrafine powders are used. Because of the reagglomeration of very fine ceramic powders during storage, ball milling of these fine powders before processing is necessary.

In compliance with the hydroxo-complex systems theory of Derjagin, Landau and Vervey, Overbeck,[8] a deagglomeration process is possible, when repulsive forces attributed to the surface electric charge of grains will be greater than Van der Vaals attractive forces.

As observed directly from electrophoretic experiments, the charge of solid oxides in aqueous suspensions depends on pH and surface composition due to aging processes or preparation routes, respectively, and some value of pH exists at which an immersed solid oxide has zero net charge. This point is usually called the isoelectric point (IEP) or zero point of charge (ZPC).

A change of water suspension pH below or above the isoelectric point should be favourable to powder dispersion and, since reagglomeration to form particles $> D_{ct}$ is prevented by repulsive forces due to the high surface charging, this results in an increase of metastable tetragonal zirconia content and an improvement in the mechanical properties of alumina ceramics. The present work aims to check this hypothesis.

2 Experimental Methods

The starting materials were alumina powder of 4N purity (99·99 wt%) and average grain size below 0·5 μm, and ultrafine zirconia powder obtained by chemical methods. For this purpose, a solution of $ZrOCl_2$ in water was introduced at room temperature into a stirred NH_4OH solution. The precipitated gel was washed several times with distilled water and decanted, and then heated under hydrothermal conditions at 230°C for 6 h in an autoclave. The product of crystallization was rewashed in distilled water to completely eliminate chloride ions. The crystallite size, determined by means of X-ray diffraction, was below 0·1 μm.

According to the main thesis of the present work, the variation of electrophoretic mobility with suspension pH for alumina and zirconia powders were determined. Microelectrophoretic measurements were made in an apparatus equipped with a rectangular flat-type quartz cell (100 × 25 × 1·3 mm), Pd electrodes, electric support and microscope type BTU-1. Twenty readings at each stationary level were taken. The concentration of solid powder in all cases was maintained at a constant value of 0·1 g/dm^3, while pH was regulated using HCl or NH_4OH. According to the Smoluchowski[8] relation, electrophoretic mobility values were counted to the zeta potential:

$$U = \frac{D . \zeta}{4 . \pi . \eta} \quad (1)$$

where U = electrophoretic mobility as a relation of the velocity of the particle under an electric field to the intensity of this field; D = the dielectric constant of the suspension; η = the viscosity of suspension; and, ζ = the zeta potential.

For selected pH values, particle/agglomerate size distribution of alumina and zirconia powders was determined using apparatus Sedigraph 5000 ET (SY-LAB).

At the same pH values, the composition of Al_2O_3–10 wt% ZrO_2 ceramics were prepared. The components of the alumina matrix having the chemical composition: alumina, 99·55 wt %; magnesia, 0·20 wt%; yttria, 0·25 wt%, were homogenized for 48 h in a ball mill in distilled water. Then 10 wt% zirconia was added and the mixture homogenized for a further 48 h. The samples of the ceramics were cold pressed under 140 MPa and sintered at 1710°C in a gas furnace.

The critical stress–intensity factor, K_{Ic}, of ceramics was determined after Evans[9] on notch-beam specimens of configuration described earlier[6] and an Instron TTDM testing machine. The bearing spacing was 36 mm and rate of loading 0·1 mm min^{-1}.

The bending strength was determined on bars 5 × 5 × 50 mm and the same testing machine with the same rate of loading and bearing spacing.

The thermal shock resistance of ceramics was estimated following the method proposed by Hasselman.[10] For this purpose, bars of 5 × 5 × 50 mm were heated in a tubular furnace up to temperatures in the range 200–700°C and then dropped into boiling water, cooled in the water, dried and subjected to the bending tests.

The phase composition of zirconia in alumina ceramics was determined from the X-ray diffraction profiles recorded from free surfaces (as received) within 26–32° 2θ angles range (Cu Kα) by means of a Dron-2 X-ray diffractometer. On the basis of X-ray diffraction patterns, after Garvie *et al.*,[11] the amount of monoclinic and tetragonal phase of zirconia was calculated.

3 Results and Discussion

As can be seen from the data presented in Fig. 1, the isoelectric point of zirconia lies at pH 6·2, but that of alumina lies at pH 5·2. According to the theory mentioned in Section 1, the agglomerate size of zirconia and alumina should decrease for pH values lower or higher than that of the isoelectric point.

The determination of zirconia and alumina

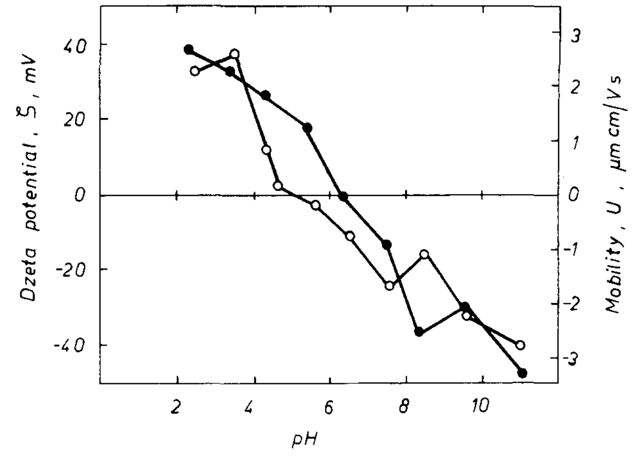


Fig. 1. Zeta potential of zirconia (●) and alumina (○) as a function of suspension pH.

agglomerate size distribution illustrated in Figs 2 and 3 confirm this thesis. The maximum of zirconia agglomerate size is observed for a pH value equal to the isoelectric point, while the minimum occurs for pH values lower and higher than that of the isoelectric point. The above results are similar to observations of time and inclination to sedimentation of zirconia suspensions.

In the case of alumina powder, the isoelectric point is at pH 5·2. Similarly, the maximum of the agglomerate size corresponds closely to the isoelectric point and minimums are found at pH 1·5 and 11·0.

In the case of a suspension pH close to the isoelectric point of zirconia the process of grain agglomeration results in the formation of particles $> D_{ct}$, which leads to a decrease in the metastable tetragonal zirconia content. Therefore the mechanical properties of zirconia-toughened alumina ceramics also become worse.

As can be seen from Fig. 4, the mechanical properties of Al_2O_3–10 wt% ZrO_2 ceramics are strongly dependent on the pH of the suspensions.

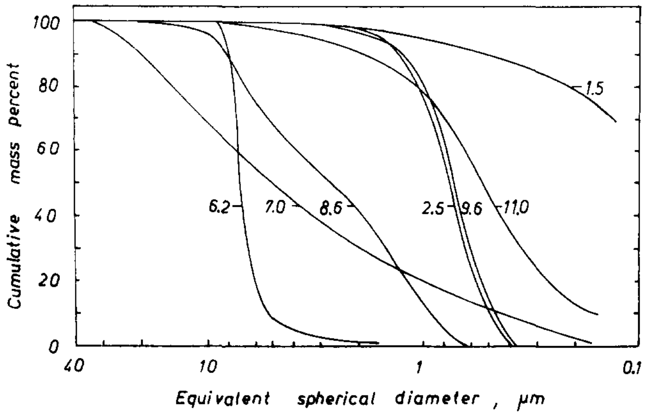


Fig. 2. Particle/agglomerate size distribution of zirconia in aqueous suspensions at pH levels indicated.

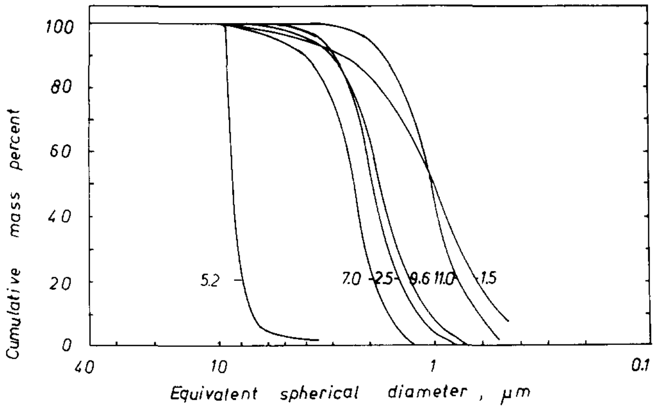


Fig. 3. Particle/agglomerate size distribution of alumina in aqueous suspensions at pH levels indicated.

The minimum of the critical stress–intensity factor of ceramics (3·80 MN $m^{-3/2}$) corresponds to the isoelectric point of zirconia (pH 6·2). Enhancing the alkalinity or acidity of suspensions results in an increase of K_{Ic} to the value 7·06 MN $m^{-3/2}$. The bending strength of ceramics also changes in the same way.

The observed changes could be correlated with the phase composition of zirconia in alumina ceramics (Fig. 4). X-ray analysis of samples prepared from suspensions close to the isoelectric point indicate a content of only 41·7% tetragonal zirconia, in contrast to extreme pH values, where it is close to 100%. So, such low value of tetragonal zirconia content for the IP point is equivalent to a content of 58·3% monoclinic zirconia in alumina ceramics and leads to the appearance of microcracks.

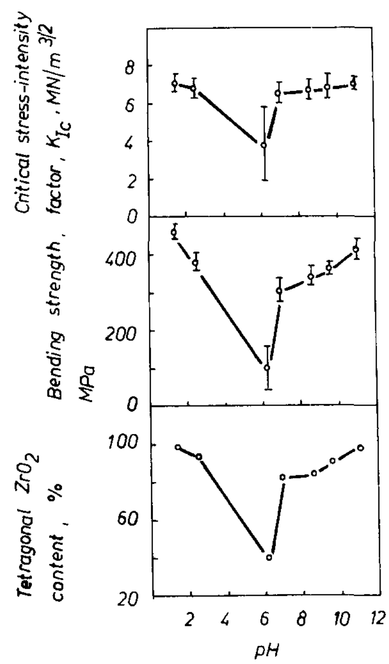


Fig. 4. Changes of mechanical properties and phase composition of Al_2O_3–10 wt% ZrO_2 ceramics as a function of suspension pH.

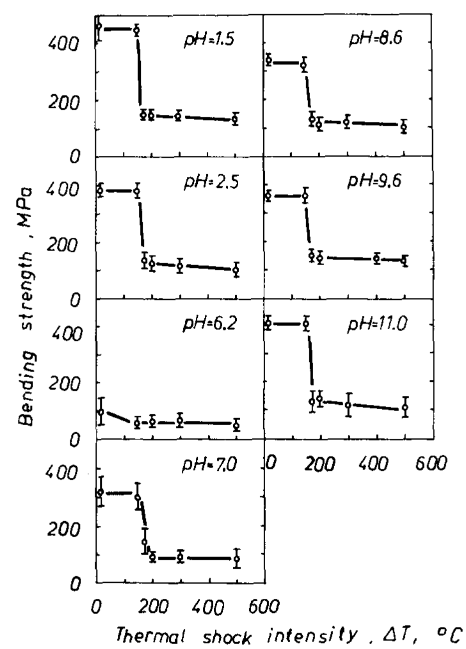


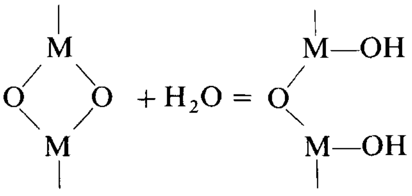
Fig. 5. Changes of bending strength of Al_2O_3–10 wt% ZrO_2 ceramics as a function of thermal shock intensity and suspension pH.

As it was shown earlier,[6] the character of crack propagation and therefore, the changes of ceramics strength versus thermal shock intensity depends indirectly on the content of the metastable form of zirconia in alumina ceramics, but directly on the crack density and initial crack length. According to Hasselman's theory,[10] the cracks shorter than length l_m from the minimum Hasselman's curve, $\Delta T = f(i_0)$, propagate kinetically due to thermal shock, with a corresponding catastrophic decrease in strength, but cracks of initial length $l_0 \geq l_m$ propagate quasi-statically.

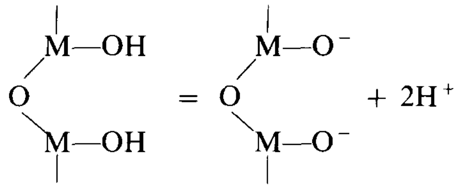
As follows from Fig. 5, quasistatic crack propagation is exhibited in ceramics prepared from suspensions with pH values close to that for the isoelectric point, but kinetic crack propagation is seen for other pH values.

4 Conclusions

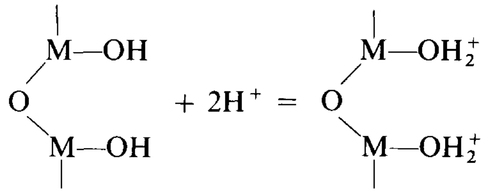
This study demonstrates that the pH of water suspensions strongly influences the agglomerate size of oxide powders. According to the theory of Derjagin, Landau and Overbeck, Vervey,[8] in water suspensions, an active surface oxide group absorbs a water molecule:



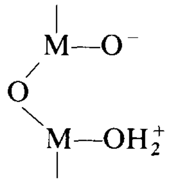
Because of amphoteric character, these groups dissociate with change of pH, forming a surface charge:



or



The state, when the surface of the grains has zero charge (equal to the IP point) is:



Therefore, the level of acidic–basic dissociation has an effect on the appearance of a surface charge (determined in this work as a zeta potential), increase of repulsive forces and observed deagglomeration of powders.

The maximum of agglomerate size corresponds to the isoelectric point of suspensions. Alumina ceramics prepared in such a way, namely at the isoelectric point, are characterized by an increase in the monoclinic zirconia content and a decrease in resistance to fracture. Increases of acidity or alkalinity of the suspensions are equivalent to an increase in the surface grain charge, lead to an increase in the tetragonal zirconia content and an improvement of the properties of the ceramics.

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