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Electrophoretic Deposition Behavior of Ceria-stabilized Zirconia/Alumina Powder

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The aim of this study was to evaluate the electrophoretic deposition (EPD) behavior of ceria-stabilized zirconia/alumina (Ce-TZP/Al_2O_3) granulated powder. Two types of slurry with powder-to-solvent ratios of 10 wt% and 20 wt% were used. Zeta potential of the slurries was measured using a spectrometer at different pH levels. Then, EPD was performed to measure the weight of the deposited particles at varying pH levels and at two voltages (50 V and 100 V). The isoelectric point of Ce-TZP/Al_2O_3 mixed powder was approximately at pH 8.5. When EPD was performed, deposition of ceramic particles was typically observed in the range of pH 3 to pH 7, with the greatest deposition found at around pH 7. Moreover, the deposition of ceramic particles increased with increase in slurry concentration and voltage.

Keywords: Electrophoretic deposition, Zirconia, Zeta potential

INTRODUCTION

The use of all-ceramic crowns and bridges, which provide good esthetics and biocompatibility, is becoming more and more popular in clinical dentistry. These ceramic restorations are usually fabricated by firing powdered porcelain manually onto a refractory model or by using a CAD/CAM system to mill a ceramic block mechanically[1-4]. However, with the hardness and brittleness of ceramic materials, there entails a high risk of fracture when these materials are used for crowns or fixed partial dentures in posterior teeth, which are subjected to great masticatory forces.

Recently, it has become possible to fabricate all-ceramic restorations that are highly resistant to breakage even when used in the posterior region, by using zirconia-based materials[5] for the framework of crowns or fixed partial dentures[6]. This is an effective strategy because the resultant materials are far stronger than conventional ceramics. In addition, a composite made of nanometer-sized ceria-stabilized zirconia/alumina has recently been developed by one of our coworkers. It was reported that this new material was comparable in strength and toughness to metal, thereby leveraging on the advantageous characteristics of both zirconia and alumina[7,8].

At the same time, the electrophoretic deposition (EPD) method has become widely used for ceramic processing[9,10]. This method seems to make it possible to fabricate a dense, uniform framework — even if it entails complicated shape. Therefore, if the aforementioned ceria-stabilized zirconia/alumina nanocomposite can be deposited successfully using the EPD method, an excellent framework could be fabricated more easily and completed in a shorter time.

Against this background, an experiment was carried out in this study to determine whether ceria-stabilized zirconia/alumina material could be charged and dispersed in a solvent, and then properly deposited by EPD. At the same time, optimal conditions for EPD — in terms of slurry concentration and voltage — were also investigated.

MATERIALS AND METHODS

Ceria-stabilized zirconia/alumina (Ce-TZP/Al_2O_3) granulated powder

Ceria-stabilized zirconia (Ce-TZP) powder (particle size 50−100 nm) and alumina (α-Al_2O_3) powder (particle size 100−180 nm) (30 vol%) were mixed. Ethylene glycol was added as a binder, and the mixture was spray-dried to prepare Ce-TZP/Al_2O_3 granulated powder (Matsushita Electric Works, Osaka, Japan) (Fig. 1). This preparation was used as the starting material for the experiment. Non-aqueous ethanol was used as the solvent to prevent the deposit from becoming porous, owing to entrapped gases generated by the electrolysis of the medium.

Slurries with 10 and 20 wt% concentrations

Two types of slurry — with powder-to-solvent ratios of 10 wt% and 20 wt% respectively — were prepared as follows. A 500-ml aliquot of each type of slurry was dispersed and mixed for three minutes using an ultrasonic homogenizer (U200S, IKA Labortechnik, Stanfen, Germany) (Fig. 2), and then the zeta

potential was measured without adjusting the pH.

Another 500-ml aliquot of each type of slurry was divided into two portions of 250 ml each. Acidimetry and alkalimetry were performed by adding, respectively, nitric acid (60%, Nakalai Tesque, Kyoto, Japan) and ammonia solution (28%, Nacalai Tesque) in increments of 0.1 ml each to the slurry. One minute after preparing the slurries, the zeta potential of each slurry was measured using an acoustic and electroacoustic spectrometer (DT-1200, Dispersion Technology, Bedford Hills, NY, USA) at different pH levels.

Next, using a 500-ml aliquot of each type of slurry with different concentrations of 10 wt% and 20 wt% prepared in the same manner, EPD was performed to measure the weight of the deposited particles. Electrodes were carbon rods with a 5 mm diameter. They were wrapped with insulating tape, leaving only an area 10 mm from the tip exposed. Electrophoresis was carried out three times for five minutes each, at varying pH levels and at two voltages (50 V and 100 V). Weight values of the deposited particles obtained by three rounds of electrophoresis were averaged, and the mean value was used as the deposit weight for each pH level.

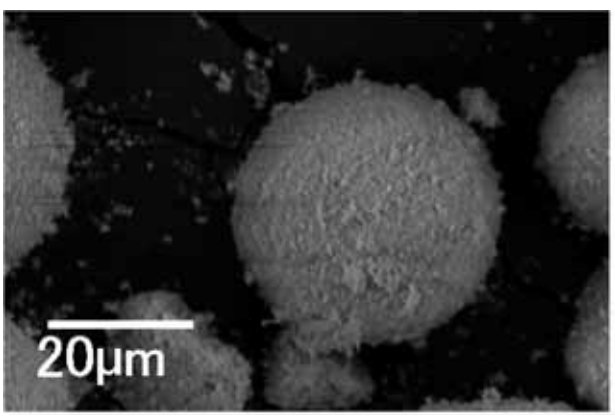

Fig. 1 SEM micrograph of Ce-TZP/Al_2O_3 granulated powder at the beginning of the process. A large mass granulated by spray drying can be observed.

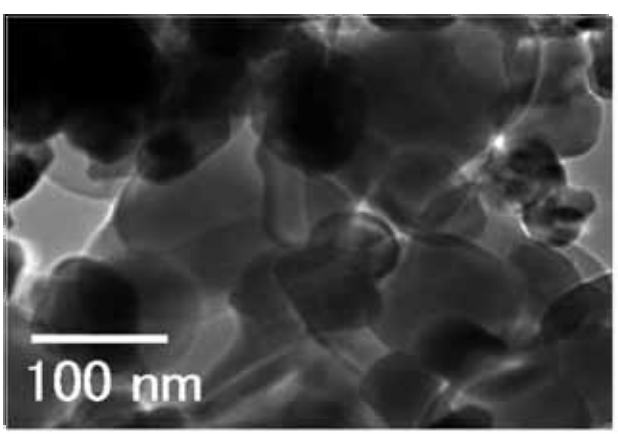

Fig. 2 TEM micrograph of Ce-TZP/Al_2O_3 powder after dispersion. White particles (alumina) and small, black particles (zirconia) can be seen.

RESULTS

Initially, prior to pH adjustment, 10 wt% slurry had a pH of 7.5 and a zeta potential of +32.2 mV, while 20 wt% slurry had a pH of 8.8 and a zeta potential of +9.6 mV. The isoelectric point of Ce-TZP/Al_2O_3 mixed powder used for this experiment was at approximately pH 8.5. The zeta potential tended to be negative when the pH became high enough to exceed the isoelectric point but became positive when the pH was low, with the absolute value showing a tendency to increase in either case (Fig. 3).

When EPD was performed at a voltage of 50 V, deposition of ceramic particles was observed in the range of pH 3 to pH 7, with a concomitant increase in the zeta potential (Figs. 4 and 5). However, no deposition of ceramic particles occurred at pH 7.8 or higher. Greatest deposition was found at pH 6.8 (81.0 mg/cm^2) for 10 wt% slurry and pH 7.3 (126.2 mg/cm^2) for 20 wt% slurry. In other words, greatest deposition occurred at around pH 7 in both cases (Fig. 6). Then, deposition tended to decrease as the pH level became lower than 7.

The same tendency was also observed at voltage of 100 V. When EPD was performed using a voltage of 100 V, the deposition of ceramic particles was greatest at pH 6.6 (90.4 mg/cm^2) for 10 wt% slurry and pH 6.8 (160.7 mg/cm^2) for 20 wt% slurry (Fig. 6). Therefore, deposition was apparently greater at 100 V than at 50 V. In addition, more ceramic particles were deposited from the 20 wt% slurry than from the 10 wt% slurry, regardless of the EPD voltage used.

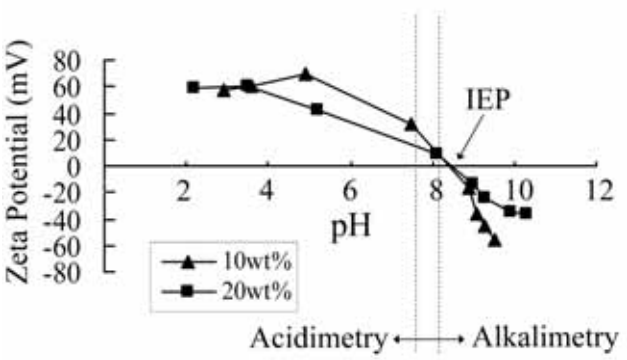

Fig. 3 Zeta potentials of Ce-TZP/Al_2O_3 powder at different pH levels. Isoelectric point (IEP) was at approximately pH 8.5.

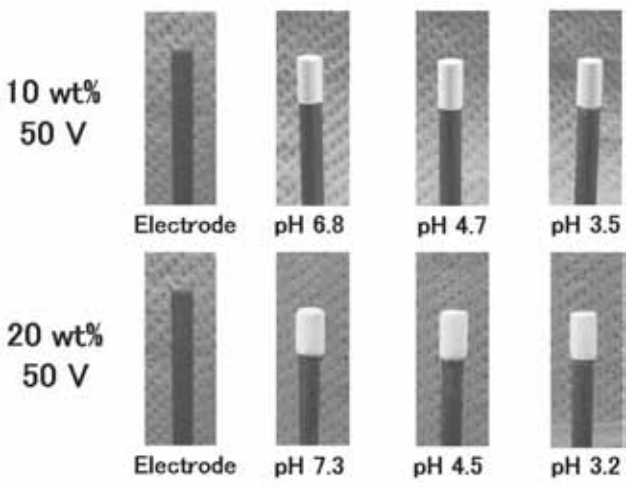

Fig. 4 Deposition of ceramic particles at a voltage of 50 V. More ceramic particles were deposited from the 20 wt% slurry than from the 10 wt% slurry.

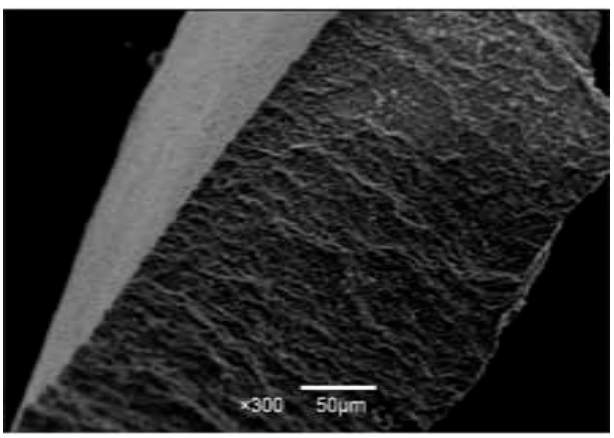

Fig. 5 SEM picture of a section of the deposit showing uniform deposition of ceramic particles.

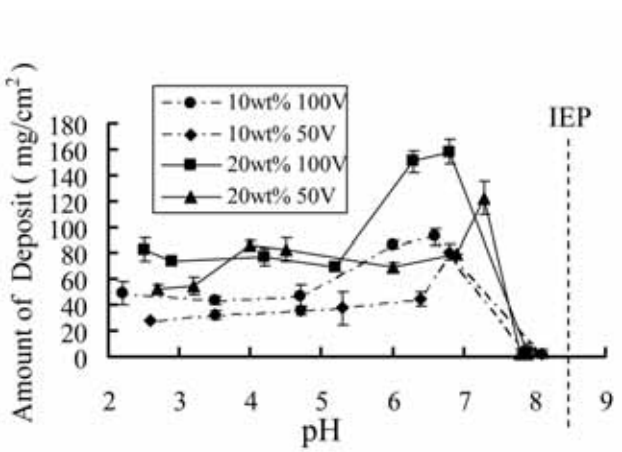

Fig. 6 Deposition amounts at different pH levels. Deposition tended to decrease as the pH level became lower than 7.

It should also be mentioned that the thickness of the deposits ranged from 0.2 to 0.8 mm, whereby this thickness value tended to be greater as the voltage and slurry concentration increased.

DISCUSSION

The aforementioned ceria-stabilized zirconia/alumina nanocomposite is strong and resistant to fractures[7,8]. As such, it is a suitable material for the framework of all-ceramic crowns and fixed partial dentures. When used for frameworks, this material is usually sintered into a block and the completely sintered block is milled mechanically using a CAD/CAM system. However, this method presents some problems, such as the setup and operating costs of the CAD/CAM system and premature wear of the cutting tool[11]. Furthermore, it has been reported that when subjected to milling, even high-strength zirconia-based materials are often reduced in strength[12] or that the process may generate microcracks[13].

Unlike the CAD/CAM system, EPD is a simple system in which ceramic is processed without milling. By virtue of this advantageous feature, EPD has been used for the fabrication of frameworks for all-ceramic crowns or fixed partial dentures and for ceramic coating[16] of implant surfaces.

Ceria-stabilized zirconia/alumina granulated powder had an isoelectric point at about pH 8.5, and its zeta potential varied when the pH value was changed. This finding agreed with a report[17] that alumina- and yttria-stabilized zirconia materials had isoelectric points ranging from 7.5 to 9.1 and 6.5 to 9.3, respectively. In this study, the zeta potential increased as the pH level decreased. Thus, it was hypothesized that electrophoresis increased the deposition of particles when the pH level was low. Indeed, when EPD was performed, the deposit weight increased when the pH level was lowered slightly from the starting point, but would decrease if the pH level were lowered further than this threshold value. Judging from the results of this experiment, the lower the pH level, the greater was the zeta potential, thereby leading to an increased migration speed of particles.

However, it was also suggested that an elevated zeta potential did not necessarily lead to an increase in the deposit weight of particles. This was probably because when the zeta potential was high, the migration speed of the particles increased. At the same time, therefore, the particles were also unwittingly repelling one another, thereby interfering with deposition.

Therefore, it is necessary to consider other factors which might increase the deposit weight of particles in EPD, such as the concentration and pH

of slurry, the particle size of powder, and the voltage used.

In the present study, deposit weight increased when both the slurry concentration and voltage were high. It has been reported that the deposit weight increased when the voltage used in EPD was high[18]. For the framework of dental crowns and fixed partial dentures, the thickness must be at least 0.3 to 0.5 mm to provide sufficient strength. Against this background, when EPD is used for the fabrication of frameworks, the slurry concentration and voltage may need to be set to relatively high values.

In addition, EPD was performed within the shortest possible time after the slurry was prepared. This was because if the slurry were left unused for a long period of time, the pH level of the slurry might change, thereby causing the charge state of the particles in the slurry to change. Otherwise, the ceramic particles might precipitate, thereby changing the dispersion state of the particles.

In this study, carbon rods were used as the electrodes. If an abutment model which has been surface-treated to be electrically conductive were used as an electrode, the material can be processed without milling. The method of using a working model as an electrode is called electroforming. This technique has long been applied in the fabrication of gold copings for the inner surface of porcelain-fused-to-metal (PFM) crowns by electrolytic deposition[19]. If the material used for this experiment is to be deposited by electrophoresis, it will be necessary to commercialize a system where the abutment model is used as an electrode.

A mixed powder consisting primarily of ceria-stabilized zirconia and alumina was used in the study, and neither was completely compounded. Therefore, for the ceria-stabilized zirconia/alumina nanocomposite to deliver excellent physical properties, the material needs to be a sintered composite powder or it must be sintered after electrophoretic deposition. In future investigations, we would therefore examine which kind of powder to use and which procedure to adopt to sinter particles after electrophoretic deposition, as well as how to process this material without impairing its excellent physical properties.

The greatest advantage of EPD lies in its ability to fabricate frameworks with complicated shapes with relative ease. In actual clinical settings, it is also preferable to deposit ceramic particles directly on the working model. To accomplish this, it is necessary to surface-treat the working model so that it can be used as an electrode. When the deposit is sintered at a high temperature, it can shrink greatly, causing cracks. On this account, it is difficult to get a good fit to the working model. To prevent this problem, it is necessary to devise a method of sintering the deposit at a low temperature and impregnating the sintered deposit with glass to enhance its strength.

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