JOURNAL OF MATERIALS SCIENCE **32** (1997) 6661–6664

Fabrication of green films of single- and multi-component ceramic composites by electrophoretic deposition technique

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An electrophoretic technique for the formation of ceramic composites is demonstrated in the systems of biomedical hydroxyapatite–yttria-stabilized zirconia and ferroelectric barium titanate–strontium titanate. Ceramic powders show different behaviour depending on the nature of the solvent media chosen. For such purposes, a solvent mixture of acetylacetone and alcohols proved effective for adjusting the composition of deposited films.

1. Introduction

The electrophoretic technique has been applied to the coatings of ceramics with thicknesses of a few tens of micrometres to several millimetres. Its applicability ranges from magnetic [1, 2], electronic [3–5], electrolytic [6–9], and superconducting [10, 11] ceramic thick films to the coatings of bioceramics [12–15], structural [16–18] and high-temperature ceramics [19]. The technological factors have been well studied in the formation of Na^+-conducting β-alumina tubes [6, 8, 9]. These applications, however, have been confined to the coatings of single-component ceramics. The present work explored its application to the production of functional coatings or thick films. Recently, this method has been found effective in the composite coatings of hydroxyapatite–yttrium-stabilized zirconia [15], and zirconia–alumina [18]. It was the purpose of this work to develop not merely a universal method to form a ceramic coating, but to design a ceramic composite films.

As this method utilizes a d.c. electric current-driven deposition of suspended powders on an electrode in solution, the choice of a suspension medium is of great importance. Furthermore, the deposition of composite films depends on the behaviour of the individual constituent powders suspended in a solution medium. The behaviour of a suspended powder varies with different organic solvents; however, an appropriate medium for a given powder is conventionally established through experiments. The present authors have found a mixed solution of acetylacetone and alcohol to be effective as the medium for the electrophoretic deposition of barium titanate [4]. Application of a mixed solution was first proved to be effective in enhancing coatings of hydroxyapatite [14]. In the present work, the use of such a medium is also confirmed to be applicable to various kinds of ceramic powders. Furthermore, the use of a mixture of two kinds of solvents was found to have some additional advantages in the preparation of composites.

This paper first describes the applicability of a mixed solution to the preparation of various kinds of ceramics for refractories, ferro- and piezo-electrics, dielectrics, mechanical and biological materials. Based on these results, the electrophoretic deposition of the composites of the systems hydroxyapatite–yttria-stabilized zirconia and barium titanate–strontium titanate is demonstrated. Hydroxyapatite, an excellent biocompatible material, still needs to be strengthened for some practical implant applications. Additives, such as yttria-stabilized zirconia, are good candidates for such purpose. Strontium titanate acts as a shifter agent, which lowers the Curie temperature, for ferroelectric barium titanate. As detailed below, the term "composite" for barium and strontium titanates here means the solid solution $Ba_{1-x}Sr_xTiO_3$.

2. Experimental procedure

Ceramic powders of hydroxyapatite (HAp), yttria-stabilized zirconia (YSZ), barium titanate (BT), strontium titanate (ST), magnesia, alumina, and lead zirconium titanate (PZT) were employed as the starting materials for electrophoresis deposition. HAp powders were prepared by a wet-chemical method, and the other powders were the commercial products of Toso (YSZ), Kanto Chemicals (BT, ST, alumina), and Chichibuonoda (PZT). The sizes of these powders were in the range 1–10 μm. Reagent-quality ethanol (EtOH) or 1-propanol (PrOH), 2,4-pentanedione (acetylacetone) ($CH_3COCH_2COCH_3$, Acac), and their mixtures were mainly used as solution media without further purification. For the present study, two systems of mixed powders, HAp–YSZ and BT–ST, were chosen.

The mixed powders were ultrasonically dispersed in a mixed medium of Acac and PrOH or EtOH, and had a concentration of 2.5–10 $g\,l^{-1}$. This mixture was subjected to electrophoresis deposition with a d.c. field of 100 V. A distance of 3 mm between the anode and

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a substrate as the cathode was maintained during the experiment.

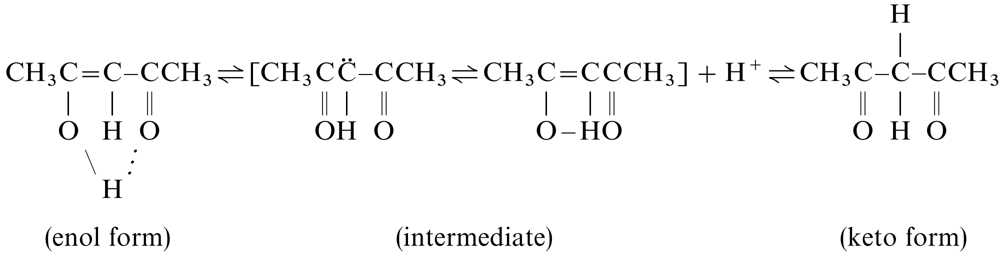
Deposition yields were determined by weighing the dried deposits on platinum foil. The yields are referred to as y_w(H–Y) and y_w(B–S) (mg cm^{-2}) for the systems HAp–YSZ and BT–ST, respectively. A mixed ratio of Acac to EtOH ([Acac]/[EtOH]) or PrOH ([Acac]/[PrOH]) (vol %) is expressed below as r_v(A/E) or r_v(A/P), respectively. The mixed ratios of YSZ to HAp and ST to BT are designated as r_w(Y/H) and r_w(S/B) (wt %), respectively.

The various weight ratios of the individual components in the prepared composite films were semi-quantitatively evaluated with an X-ray diffraction analytical (XRD) method. In this analysis, a standard relationship of mixed ratios and XRD peak intensity ratios was first required for both the systems. Scanning electron microscopic observation was also performed for the characterization of deposited and sintered composites films.

3. Results and discussion

3.1. Electrophoresis deposition of various ceramic powders in Acac–EtOH mixed solution

Despite its effective deposition in EtOH, HAp was rarely coated in Acac. ST also preferred EtOH to Acac as its solution medium; on the other hand, the deposition yield of both YSZ and MgO increased with an increase in the amount of Acac in the mixed solution. Fig. 1 summarizes those relationships between deposition yield and composition of organic solvents for various kinds of ceramic powders. These figures demonstrate the applicability of the present method to a variety of ceramics under an appropriate choice of a mixed ratio of alcohol to Acac. Those powders which favour EtOH or Acac for their deposition are classified as Group E or A, respectively. In contrast to Groups E and A, the powders of PZT, Al_2O_3 and BT [4] were effectively deposited in the mixed solutions of EtOH and Acac, neither of which was experimentally confirmed appropriate as a medium solution for these powders. These mixed solutions of ceramic powders are designated as Group E–A. Because all of these powders were driven to the cathode in a d.c. field, they are considered to be positively charged in the organic media, whether mixed or not. In case of Group E–A, the adsorbed species on the powders were assumed protons, which were the by-products of the intermediate species in the following keto-enol equilibrium reaction



$$\mathrm{CH_3\underset{O}{C}{=}\underset{H}{C}{-}\underset{O}{C}CH_3} \rightleftharpoons [\mathrm{CH_3\underset{OH}{C}\underset{O}{\ddot{C}}{-}CCH_3} \rightleftharpoons \mathrm{CH_3\underset{O}{C}{=}C\underset{HO}{C}CH_3}] + \mathrm{H^+} \rightleftharpoons \mathrm{CH_3\underset{O}{C}{-}\overset{H}{\underset{H}{C}}{-}\underset{O}{C}CH_3} \qquad (1)$$

It is therefore considered important in the design of composites films to know which groups of given powders are to be combined for a composite, because the composition of a composite can be determined not merely from the ratio of the mixed powders but also from that of organic solution. In this work, the combinations of Groups A with E, and Groups A with E–A were demonstrated in the systems of HAp–YSZ, and BT–ST, respectively.

3.2. Exemplary application to hydroxyapatite–yttria-stabilized zirconia and barium titanate–strontium titanate systems

Fig. 2 demonstrates the dependence of the deposition yield on both the composition of solution media and the mixed ratio of the powders. With increase in the ratio of Acac to EtOH, r_v(A/E), there is first a steep decrease in the yield, y_w(H–Y) to a minimum, then an increase to the maximum values, thereafter a decrease again to 0. With a smaller mixing ratio of YSZ to HAp (r_w(Y/H)), larger yield y_w(H–Y) was attained in low r_v(A/E), while higher r_w(Y/H) resulted in a larger yield y_w(H–Y) in a medium to high r_v(A/E). No significant deposition was observed in Acac ($r_v(A/E) = 100\%$). The relationships between $y_w(H–Y) - r_v(A/E) - r_w(Y/H)$ can be explained by evaluating the individual powders in a medium, based on the results shown in Fig. 1. The yield of HAp abruptly decreased with r_v(A/E) between $r_v(A/E) = 0\%$ and 20%, and remained almost constant up to $r_v(A/E) = 80\%$, and thereafter gradually decreased to 0 at $r_v(A/E) = 100\%$. The yield of YSZ first gradually increased for r_v(A/E) from 0%–80%, then slightly decreased. Here the yields y_w(H) and y_w(Y) are defined for HAp and YSZ (mg cm^{-2}), respectively. Assuming the dependences of y_w(H) and y_w(Y) on r_v(A/E), based on the results given in Fig. 1, as shown with the dotted lines in Fig. 3, the overall yield of a composite, y_w(H–Y), is given by Equation 2, in cases where powders of HAp and YSZ behave independently of each other

$$y_w(\mathrm{H–Y}) = \theta_w y_w(\mathrm{Y}) + (1 - \theta_w) y_w(\mathrm{H}) \qquad (2)$$

where θ_w is the fraction of YSZ by weight. The simulated results according to Equation 2 are shown in Fig. 3. At $r_v(A/E) = 0$ (in EtOH), the decrease in the yield y_w(H–Y), with y_w(Y) increase as qualitatively described by Equation 2, and the results simulated appear to be consistent with those in Fig. 2 up to $\sim r_v(A/E) = 70\%$. At higher than 70% r_v(A/E), the deposition of mixed powders is limited, even in higher YSZ content, although YSZ is deposited well in Acac.

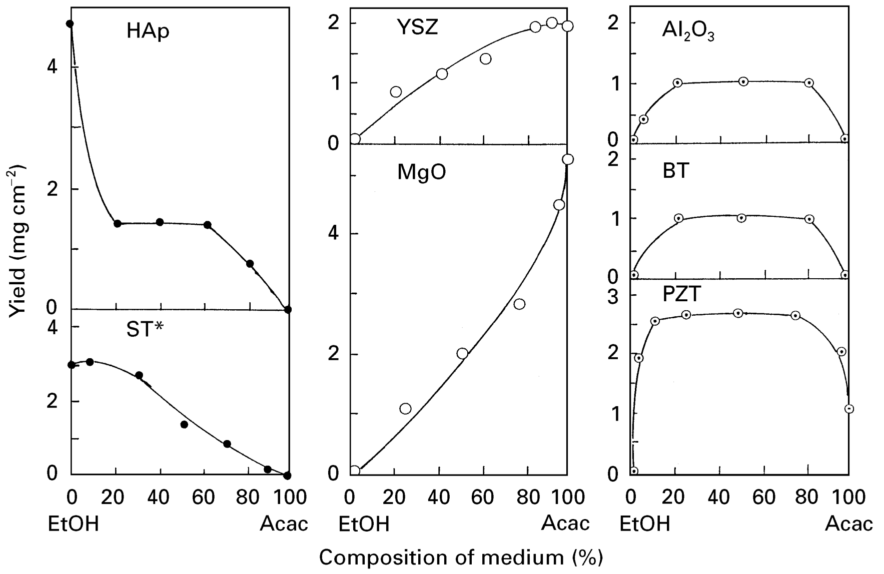


Figure 1 Characteristic electrophoretic deposition of various ceramic powders observed in mixed solution of acetylacetone (Acac) and ethanol (EtOH) under conditions of d.c. electric field of 300 V cm^{-1}, concentration of dispersed powders of 2.5 g l^{-1}, and deposition time of 2–3 min. For deposition of ST, propanol was used. The notation of ceramic powders is referred to in the text.

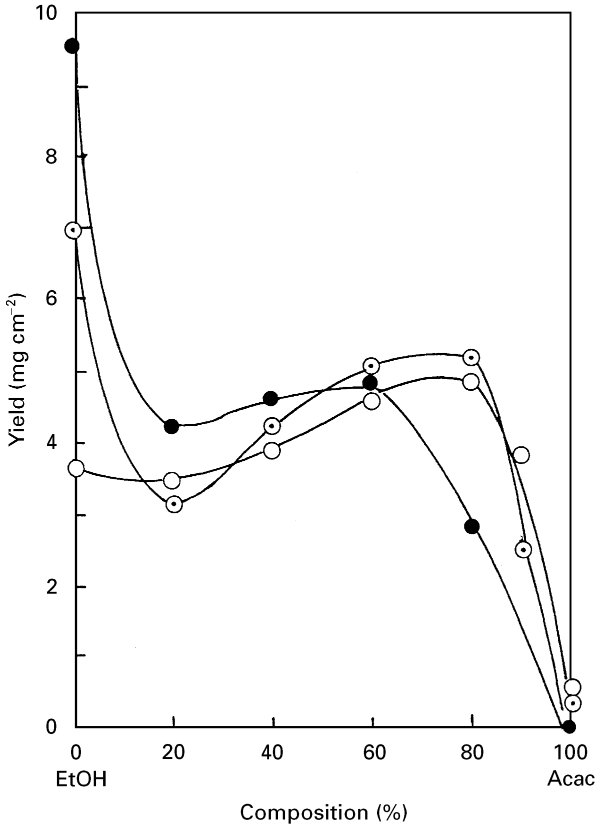


Figure 2 The dependence of deposition yield on the composition ratio of acetylacetone (Acac) to ethanol (EtOH) in the system hydroxyapatite (HAp) and yttria–stabilized zirconia (YSZ). Mixed ratios of YSZ to HAp were (●) 25, (⊙) 50 and (○) 75 wt %. Electrophoresis conditions: d.c. electric field = 300 V cm^{-1}, concentration of dispersed powders = 5 g l^{-1}, deposition time = 2 min.

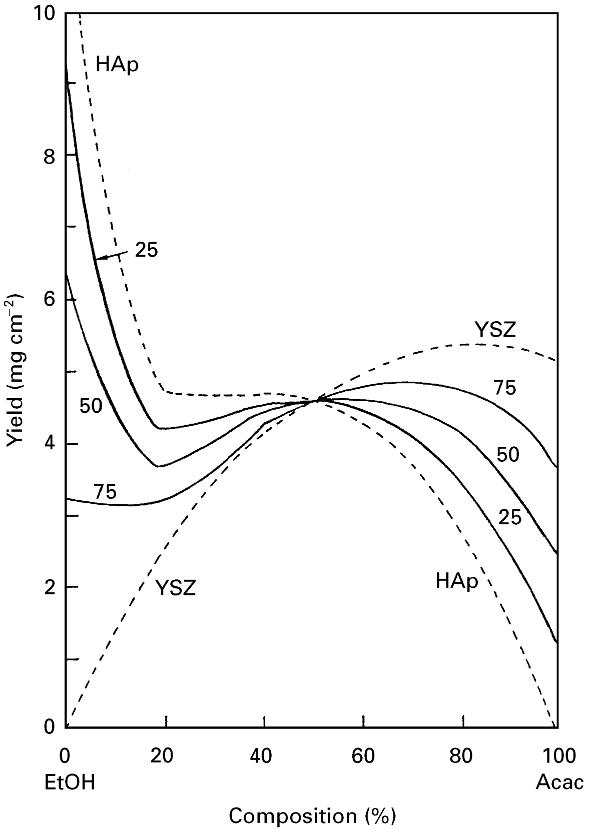


Figure 3 Simulated dependence of deposition yield on composition ratio of acetylacetone (Acac) to ethanol (EtOH) in the system hydroxyapatite (HAp) and yttria-stabilized zirconia (YSZ). (– – –) Assumed lines for the deposition of HAp and YSZ.

This large difference between simulated and observed results may suggest the interference of HAp with the behaviour of YSZ powders or the absorption of Acac on YSZ. It was also observed that the yield is changed with deposition time. The time-dependence of the ratio of YSZ to HAp in the deposited films indicates the tendency of the fraction of deposited YSZ to decrease with time.

Fig. 4 shows the dependence of the yield (y_w(B–S)) for the system BT(80%)–ST(20%) on the composition of mixed solution of Acac and PrOH, r_v(A/P). The deposition behaviour of this system is also evaluated

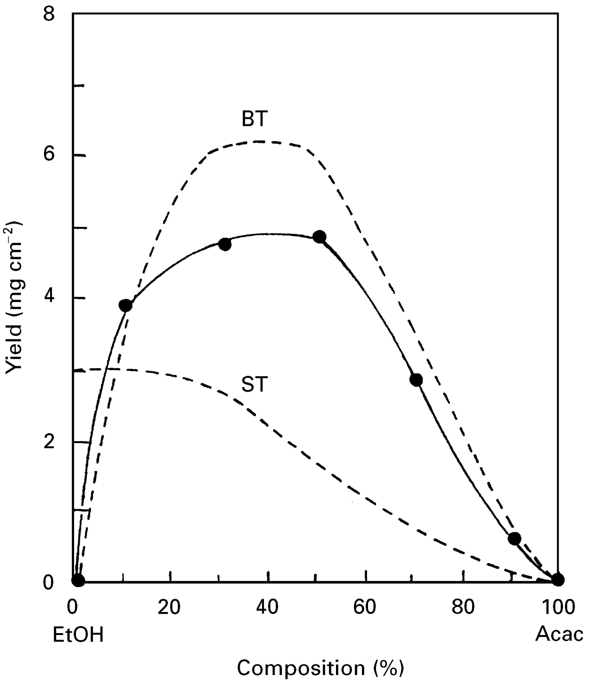


Figure 4 The dependence of deposition yield on composition ratio of acetylacetone (Acac) to ethanol (EtOH) in the system barium titanate (80 wt %)–strontium titanate (20 wt %). Electrophoresis conditions: d.c. electric field = 400 V cm^{-1}, concentration of dispersed powders = 10 g l^{-1}, and deposition time = 3 min. (– – –) The characteristic depositions for BT and ST measured under the same conditions.

using Equation 3, analogous with Equation 2

$$y_w(B\text{–}S) = \theta_w y_w(S) + (1 - \theta_w) y_w(B) \qquad (3)$$

where θ_w is the fraction of ST by weight. The deviation of the observed from the simulated results is estimated to be a few per cent in the range of $r_v(A/P) = 30\%–50\%$, where BT powders are well deposited without ST. The same difference is also observed in PrOH ($r_v(A/P) = 0\%$), where powders were scarcely deposited, although ST layers are well formed in the absence of BT. It is, however, considered that the mixed powders are, roughly speaking, deposited according to Equation 3.

The above results therefore imply that a coating film with a given composition can be formed by adjusting both mixed ratios of powders ($r_w(Y/H)$, $r_w(S/B)$) and solvents ($r_v(A/E), r_v(A/P)$).

4. Conclusion

Ceramic composite coatings, by means of an electrophoresis deposition technique, were achieved from a suspension of mixed ceramic powders. Use of a mixed solution of acetylacetone with alcohol was experimentally proved to be effective for control of the composition of deposited layers, as was demonstrated in the systems hydroxyapatite–yttrium-stabilized zirconia and barium–strontium titanates.

Acknowledgements

This work was partially supported from the grants of The Murata Science Foundation and Nippon Sheet Glass Foundation for Materials and Science.

References

1. S. KUROSAWA, T. KISHI and T. NAGAI, *J. Electrochem. Soc. Jpn* **42**(1) (1974) 32 (in Japanese).
2. Y. TOKUOKA, T. KISHI and T. NAGAI, *ibid.* **42**(2) (1974) 80 (in Japanese).
3. J. MIZUGUCHI, K. SUMI and T. MUCHI, *J. Electrochem. Soc.* **130** (1983) 1819.
4. M. NAGAI, K. YAMASHITA, T. UMEGAKI and Y. TAKUMA, *J. Amer. Ceram. Soc.* **76** (1993) 253.
5. S. OKAMURA, T. TSUKAMOTO and N. KOURA, *Jpn J. Appl. Phys.* **32**(9B) (1993) 4182.
6. R. W. POWERS, *J. Electrochem. Soc.* **122** (1975) 490.
7. A. A. FOSSY and G. ROBERT, *Amer. Ceram. Soc. Bull.* **61** (1982) 251.
8. R. W. POWERS, *ibid.* **65** (1986) 1270.
9. *Idem*, *ibid.* **65** (1986) 1277.
10. C. T. CHU and B. DUNN, *Appl. Phys. Lett.* **55** (1989) 492.
11. M. HEIN, G. MULLER, H. PIEL, L. PONTO, M. BECKS, U. KLEIN and M. PEINIGER, *J. Appl. Phys.* **66** (1989) 5940.
12. VAN W. RAEMDONCK, P. DUCHEYNE and DE P. MEESTER, *J. Amer. Ceram. Soc.* **67** (1984) 381.
13. P. DUCHEYNE, VAN W. RAEMDONCK, J. C. HEUGHEBAERT and M. HEUGHEBAERT, *Biomaterials* **7** (1986) 97.
14. T. UMEGAKI, Y. HISANO, K. YAMASHITA and T. KANAZAWA, *Gypsum Lime* **218** (1989) 24 (in Japanese).
15. M. NAGAI, K. YAMASHITA and T. UMEGAKI, *Phos. Res. Bull.* **1** (1991) 167.
16. Y. HIRATA, A. NISHIMOTO and Y. ISHIHARA, *J. Ceram. Soc. Jpn* **99**(2) (1991) 108.
17. P. SARKAR, X. HAUNG and P. S. NICHOLSON, *J. Amer. Ceram. Soc.* **75** (1992) 2907.
18. *Idem.*, *Ibid.* **76** (1993) 1055.
19. D. U. K. RAO and E. C. SUBBARAO, *Amer. Ceram. Soc. Bull.* **58** (1979) 467.

Received 22 February 1995
and accepted 2 July 1996