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Composite ceramic-metal coatings by means of combined electrophoretic deposition and galvanic methods

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A method based on the combination of electrophoretic and galvanic deposition techniques has been developed to fabricate metal-ceramic composite coatings on metallic substrates. A ZrO_2-Ni composite coating with interpenetrating microstructure was produced on stainless steel plates. For electrophoretic deposition of the ceramic component, a non-aqueous suspension consisting of zirconia nanoparticles, ethanol and addition of 4-hydroxybenzoic acid was optimised by electrokinetic sonic amplitude (ESA) measurements. The zirconia deposits were partially sintered to create an open porous structure (porosity = 40–50%), which was subsequently filled with Ni by galvanic deposition. The bonding strength between the composite coating and the stainless steel substrate was improved by a final heat-treatement at 950°C for 3 h which promoted the diffusion of Ni into the steel substrate and the formation of a diffusion interlayer. The high adhesion strength of the composite coating to the stainless steel substrate after the diffusion bonding heat-treatment was confirmed by 3-point flexural strength tests. The coating exhibited a homogeneous interpenetrating microstructure with hardness values >6 GPa. © *2004 Kluwer Academic Publishers*

1. Introduction

There is a continuous need for the development of anti-oxidation, anti-corrosion and wear resistant ceramic coatings for protection of metallic components, specially for high temperature applications in agressive and corrosive environments. These coatings should exhibit structural stability at high temperatures, high thermal shock resistance and they must be stronly bonded to the substrates. For several applications, they should also have a high resistance to fracture under impact loading, as well as adequate toughness and hardness. As an alternative to monolithic ceramic coatings, metal-ceramic composite coatings with improved properties are being developed, which can fulfill the above mentioned requirements [1–6]. In these coatings, the ductility of the metallic phase is combined with the high hardness and wear resistance of the ceramic leading to enhanced performance.

The most employed technique to produce composite coatings is the galvanic electrochemical co-deposition method, whereby small micrometric or nanometric ceramic particles, dispersed in an electrolyte, are co-deposited with the metal phase [5–10]. The use of nanosized ceramic particles in composite coatings has been shown to lead to improved hardness, wear resistance and to a higher temperature capability of composite coatings [11, 12]. However, the high surface area of the nanosized particles and their tendency to form large agglomerates present processing difficulties and only low concentrations of nanoparticles (<15 vol%) can be incorporated by the galvanic method; the properties of the composite coatings are therefore dominated by the metallic phase [12].

An alternative technique to produce metal-ceramic coatings is the co-deposition of metallic and ceramic particles by electrophoresis or the electrophoretic deposition of metal-coated ceramic particles [13, 14]. By a subsequent heat-treatment, the ceramic particles become embedded in the metallic matrix by a sintering process. The co-deposition of metallic and ceramic particles has also been developed to produce functional gradient materials [14].

In the present paper we report on a novel method, based on the combined use of both electrophoretic deposition (EPD) and galvanic deposition, developed to fabricate metal-ceramic composite coatings on metallic

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substrates. The innovative feature of the method developed here is that the electrophoretic and galvanic deposition processes are carried out one after the other, and that a heat-treatment is required after the electrophoretic deposition of the ceramic phase in order to accondicionate the ceramic deposit for the subsequent galvanic infiltration with the metal. The characterisation of the microstructure, hardness and adhesion strength of the composite coatings is also reported.

2. Experimental

Fig. 1 shows the flow chart of the method developed in this investigation for the fabrication of metal-ceramic coatings. The first step is the preparation of a stable, agglomerate-free colloidal suspension containing the ceramic particles to be used as ceramic phase in the composite coating. The ceramic particles are dispersed in a suitable solvent containing adequate concentrations of additives, which are used to enhance the electrophoretic deposition rate and to achieve deposits of high green density. In the present method, the EPD process is carried out under constant current density conditions for different deposition times. By a trial-and-error approach it is possible to find the optimal EPD parameters, such as current density and deposition time, as described below. The EPD cell should be designed such that two different electrode arrangements become possible: (i) parallel rectangular electrodes, and (ii) coaxial cylindrical electrodes, suitable for the coating of the internal wall of tubes. After EPD, the ceramic deposits are slowly dried, usually in air at room temperature. A heat-treatment at temperatures of 500–600°C is then carried out to burn-out the residual organics. Subsequently, the sample is sintered in order to improve the handling strength of the deposit, to enhance the adherence of the ceramic deposit to the metallic substrate and to produce a homogeneous open porous structure in the deposit. Ideally, after sintering, the porosity should be 40–50% and the pore size $<1\ \mu$m. The pores in the ceramic coating are subsequently filled with a metal by means of a conventional galvanic process. A heat-treatment in vacuum is finally carried out, which should improve the bonding strength of the composite coating to the substrate by activating diffusion processes at the interface, such as in a diffusion welding process.

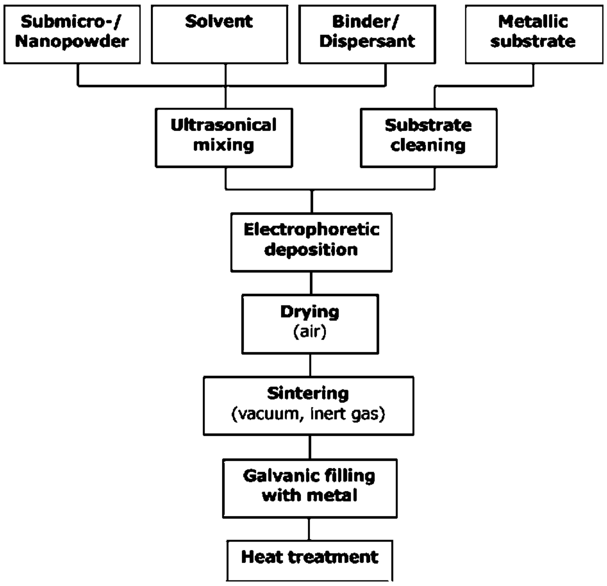

Figure 1 Flow chart describing the method developed to produce ceramic-metal composite coatings.

A ZrO_2 powder (TZ-8Y, Tosoh Corp., Japan) of mean particle size 40 nm was used. Stainless steel (X6Cr17) rectangular plates (30 × 30 mm) were used both as substrate (working electrode) and counter electrode in the EPD cell. The ZrO_2 powder was dispersed in ethanol with the addition of 4-hydroxybenzoic acid and a small amount of water. Ultrasound mixing was used to break down possible particle agglomerates.The 4-hydroxybenzoic acid was added both as a dispersing agent and as a binder. The relative amounts of ceramic powder, ethanol, dispersing agent and water were varied until a stable suspension suitable for EPD was obtained. The optimisation study to determine the correct relative amounts of ceramic particles, ethanol and 4-hydroxybenzoic acid was carried out by electrokinetic sonic amplitude (ESA) measurements. The optimal composition of the suspension, which was used for all successful EPD experiments, was: 100 g ZrO_2 particles + 100 g ethanol + 6 g water + 4 g 4-hydroxybenzoic acid.

The main process parameter, which was varied in different EPD experiments for optimisiation of the coating, was the electric current density. This was varied in the range 0.5–2 mA/cm^2. In each individual experiment series, the current density was kept constant while the deposition time was varied in the range 10 to 180 s.

After the EPD process, the coated electrode was removed from the cell and dried at room temperature in air. No microcracking development in the ceramic coating upon drying was observed. The dried samples were sintered at 1100°C in vacuum for 3 h (heating rate = 570 K/h; cooling rate = 150 K/h). The partially sintered deposits exhibited an open-pore structure. A standard Ni electrolyte bath was used for the electrochemical filling of the porosity in the zirconia layer with Ni. For this process, the coated substrate and a Ni counter electrode were immersed in the electrolytic bath. The parameters for the galvanic process were: pH = 4–4.2, current density = 2–4 A/dm^2, deposition time = 30–60 min, voltage = 3–4 V, working temperature = 55°C.

A final heat treatment in vacuum at 950°C for 3 h was carried out in order to enhance the bonding of the composite coating to the metallic substrate by activation of a diffusion process. Moreover, the heat-treatment was used to induce the relaxation of possible internal stresses developed during the previous sintering process.

The microstructure of coatings was observed by scanning electron microscopy (SEM). The existence of a diffusion zone between the composite coating and the metallic substrate was qualitatively confirmed by energy dispersive X-ray (EDX) analysis. A preliminary assessment of coating quality was done by universal hardness tests (Fisher-Scope H100) using a Vickers' indentor. The adhesion strength of the coatings to the substrate was determined by 3-point bending test (span = 20 mm) using rectangular samples of 8 mm width.

3. Results and discussion

For a successful EPD process, it is imperative to achieve a high and uniform surface charge of the suspended particles. The following variables are affected by the particle charge: (i) the migration velocity of the particles during EPD, (ii) the electrochemical stability of the suspension, i.e. the coagulation and sedimentation behaviour of the particles, and (iii) the green density of the deposit.

The effect of the particle charge on the particle migration velocity (v) is given by the ζ-potential, as explained in the literature [15]. Moreover, the dependence of the stability of the suspension from particle charge is given by the DLVO-theory, as it is well-known [16]. The overall stability of a system depends on the interaction between individual particles in the suspension. Two mechanisms affect this interaction, which are due to electrostatic and van der Waals forces. The probabilty of coagulation of a dispersed system depends on the interaction energy which results from the interaction of the mentioned forces. A high electrostatic repulsion, i.e., due to high particle charge, is required to avoid particle agglomeration. The particle charge also affects the green density of the deposits. During formation of the deposit, the particles become closer to each other and with increasing attraction forces, the particles tend to coagulate. If the particle charge is low, the particles would coagulate even for relative large interparticle distance, leading to porous, sponge-like deposits. On the contrary, if the particles have a high surface charge, during deposition they will repulse to each other, occupying positions which will lead to a high particle packing density. It is therefore very important to control the solids (ceramic particles) loading and concentration of solvent and additives in the EPD suspension, in order to reach the highest possible green density of the deposit.

In the present study, an ethanol suspension with addition of 4-hydroxybenzoic acid was optimised. It was also found that addition of water led to better results in terms of green density of the deposits. Fig. 2 shows for example the measured values of ESA signal, which is related to the ζ-potential of the suspension, as function of 4-hydroxybenzoic acid concentration. These results were used to determine the ideal concentration of 4-hydroxybenzoic acid. After determination of the optimal suspension composition, other EPD parameters, i.e. current density and deposition time, were determined. Fig. 3 shows the relationship between deposit thickness and deposition time for different current densities. The thickness of the deposits was measured by microscopy observations after drying. It is observed that for constant current density, a linear correlation between deposition time and deposited thickness exists. Fig. 3 also shows that a deposit of 100 μm can be formed already after 30 s for a current density of 1.94 mA/cm^2. This confirms that EPD is a very efficient method of low energy consumption to prepare ceramic coatings, which is one of the main advantages of EPD over other coating techniques [17].

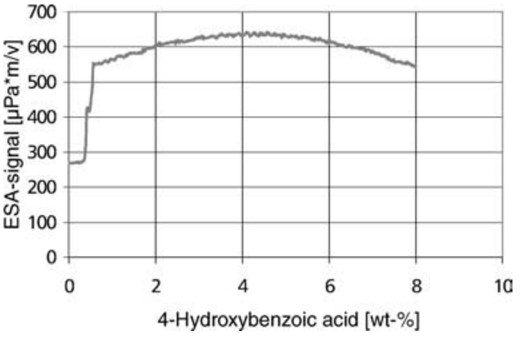

Figure 2 ESA signal as function of the 4-hydroxybenzoic acid concentration in ethanol suspensions of zirconia nanoparticles.

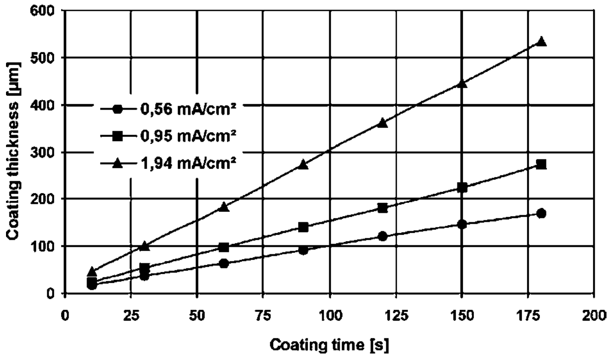

Figure 3 The relationship between deposit thickness and deposition time during EPD for different current densities.

Zirconia deposits prepared by the optimised EPD parameters were sintered in vacuum at 1100°C in order to form a uniform open porous structure in the deposit. Fig. 4a and b are images of a fracture surface of the sintered zirconia deposit, showing the homogeneity of the porous structure (Fig. 4a) and the level of sintering achieved (Fig. 4b). The porosity, estimated from SEM micrographs, was in the range 40–50%. The deposit has been partially sintered, so that it exhibits a certain structural integrity but retains an open porous structure to be filled by the metallic phase using galvanic deposition. Ni was chosen as the metallic phase since it has favourable chemical and physical properties and low brittleness.

The complete filling of the pores in the zirconia deposit with Ni was readily carried out by the galvanic method. Fig. 5 shows a Ni-infiltrated sample in which the galvanic process was interrupted before the Ni had reached the surface of the ceramic deposit. It is possible to observe that the Ni phase has grown from the surface of the metal into the pores of the zirconia deposit. The process can be continued until the Ni phase reaches the outer surface of the porous ceramic deposit. X-ray diffraction (XRD) analysis (not shown here) confirmed Ni as the only metallic phase in the coating.

The improvement of the bonding between the composite coating and the metallic substrate was obtained by a final heat-treatment at 950°C in vacuum. The good solubility of Ni in iron is used to create a diffusion layer at the interface, which was confirmed by SEM

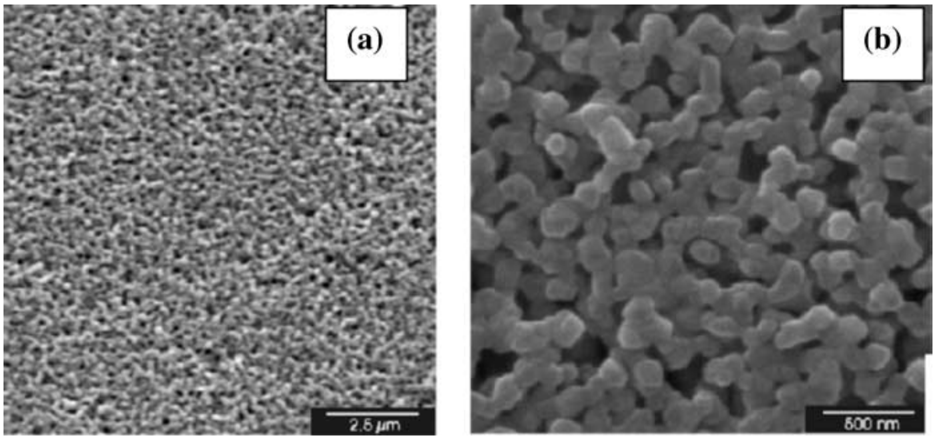

Figure 4 SEM images of a fracture surface of the sintered zirconia deposit, showing the homogeneity of the porous structure (a) and the level of sintering achieved (b).

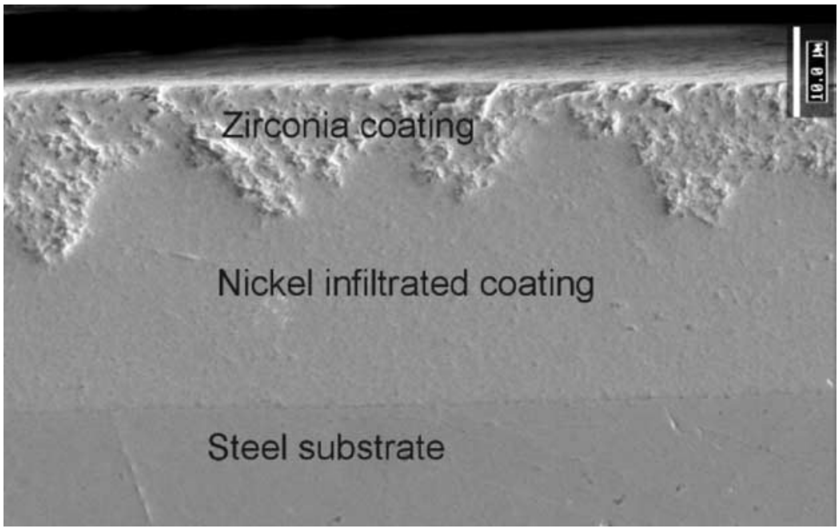

Figure 5 SEM image of a Ni-infiltrated sample in which the galvanic process was interrupted before the Ni had reached the surface of the porous zirconia deposit.

observations and EDX analyses, as shown in Fig. 6. Fig. 6a is a SEM micrograph of the interfacial zone (in a polished sample), indicating the areas where EDX analysis was carried out. It was found that Cr and Fe are present in the Ni-infiltrated zirconia coating (Fig. 6b) and Ni is present in the stainless steel substrate (Fig. 6c), forming a diffusion zone. Outside this zone, no Ni was detected by EDX analysis (Fig. 6d).

The 3-point bending test was used to assess, qualitatively, the adhesion strength of the coatings and to investigate the effect of the diffusion bonding heat-treatment. The results are documented in Fig. 7, which shows SEM micrographs of different coatings after having been flexured in the 3-point bending test. It was found that the porous sintered zirconia coating (before Ni filling) exhibited considerable microcracking at a bending strain of only 0.5 mm, which led to macroscopic fracture and complete detachment of the coating at a higher strain of 1 mm (Fig. 7a). The zirconia-Ni composite coating before diffusion heat-treatment was fractured also after a low bending strain, exhibiting microcracks and partial coating detachment at a bending strain of 1 mm (Fig. 7b). On the contrary, the sample that was heat-treated at 950°C did not show macroscopic fracture at bending strains of 1 mm (Fig. 7c) or even for larger bending strains of 2 mm. Detachment of the composite coating was not observed. However some microcracks were observed for large bending strains, perpendicularly oriented to the coating surfaces. The strong adhesion of the composite coating to the stainless steel substrate is thus thought to be the consequence of the diffusion bonding process activated by the heat treatment at 950°C. The actual effect of the microcracks observed after high bending strains on the corrosion and oxidation protection ability of the composite coatings remains to be investigated. It is possible that the plastic deformation of the metallic component in the coating counteract the microcracking development and propagation, impeding that the crack reaches the metallic substrate; in this case, the composite coating would retain its protective function. The results of the bending tests suggest also that the ceramic-metal composite coatings may have enhanced damage resistance against other mechanical loadings, in particular impact loading, in comparison to monolithic ceramic coatings, due to toughening imparted by the metallic phase.

The final microstructure of the ZrO_2/Ni composite coatings corresponds to an interpenetrating composite

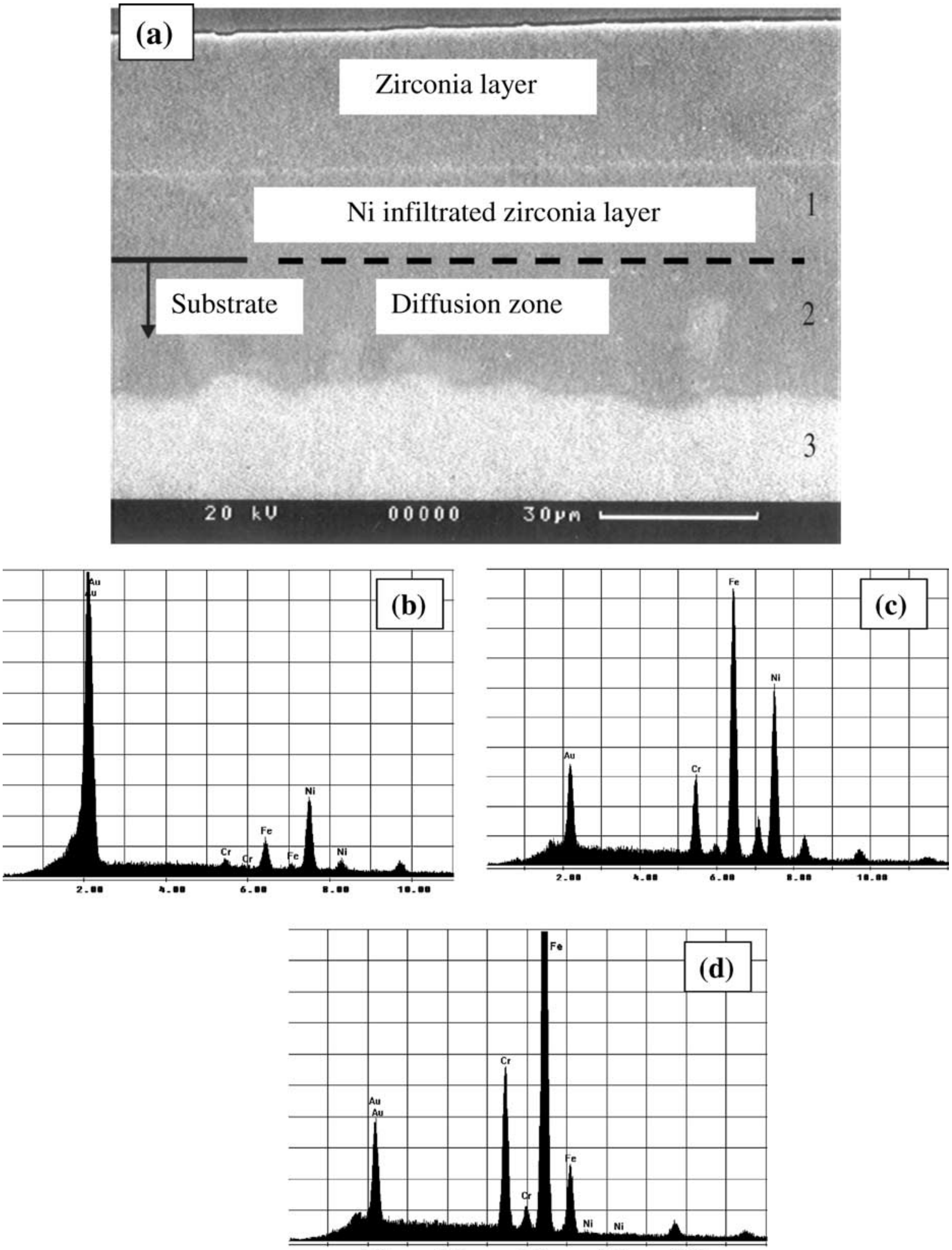

Figure 6 SEM micrograph of the interface between the stainless steel substrate and the composite coating showing the diffusion zone (a), results of the EDX analyses in the Ni-infiltrated zirconia deposit showing the presence of Cr and Fe (b), in the stainless steel substrate showing diffusion of Ni (c) and in the stainless steel substrate outside the diffusion zone (d). The Au peaks are due to the gold coating applied on the sample for SEM observations.

with submicrometric features. The effective properties of such interpenetrating microstructures are more complex than those calculated by a simple rule of mixtures [18]. In this study the hardness of the composite coatings was determined and the results compared with hardness data for the Ni and zirconia coatings. Fig. 8 shows the measured universal hardness values for the porous ceramic deposit, the Ni phase and the composite coating. This plot shows that the composite coating exhibit relatively high hardness values (>6 GPa) despite

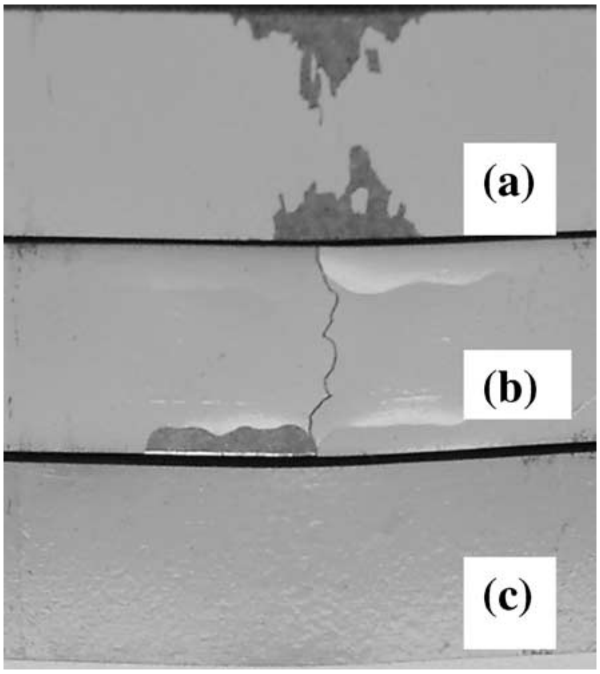

Figure 7 SEM micrographs showing different coatings after 3-point bending test up to 1 mm bending strain: (a) sintered porous zirconia deposit, (b) zirconia-Ni composite coating before diffusion bonding heat-treatment, and (c) zirconia-Ni composite coating after diffusion bonding heat-treatment. The different levels of damage in the different coatings is evident.

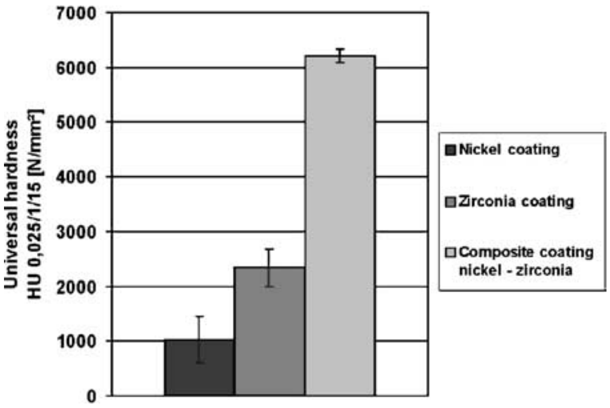

Figure 8 Universal hardness values of the nickel, zirconia and composite coatings.

the presence of the metallic phase, this suggests that the material may have a high wear resistance by combining high hardness and toughness. A detailed study of the wear resistance of the zirconia/Ni coatings is the focus of current research.

4. Conclusions

Electrophoretic and galvanic deposition techniques were combined to fabricate ZrO_2-Ni composite coatings of interpenetrating microstructure on stainless steel substrates. For electrophoretic deposition of the ceramic component, a non-aqueous suspension consisting of zirconia nanoparticles, ethanol and addition of 4-hydroxybenzoic acid was optimised. Partially sintered zirconia deposits exhibiting a homogeneous open porous structure were filled with Ni by galvanic deposition. The bonding strength between the composite coating and the stainless steel substrate was improved by a diffusion bonding heat-treatement at 950°C. The adequate hardness values (>6 GPa) and the expected toughness imparted by the metallic phase make the developed composite coatings interesting candidates for high performance applications, e.g., for wear resistant surfaces or under impact or thermal loads.

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