Manufacture of Electroless Nickel/YSZ Composite Coatings

N. Bahiyah Baba, W. Waugh, A.M. Davidson

Abstract**—**The paper discusses optimising work on a method of processing ceramic / metal composite coatings for various applications and is based on preliminary work on processing anodes for solid oxide fuel cells (SOFCs). The composite coating is manufactured by the electroless co-deposition of nickel and yttria stabilised zirconia (YSZ) simultaneously on to a ceramic substrate. The effect on coating characteristics of substrate surface treatments and electroless nickel bath parameters such as pH and agitation methods are also investigated. Characterisation of the resulting deposit by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDXA) is also discussed.

Keywords**—**Electroless deposition; nickel; YSZ; composite

I. Introduction

EXTENSIVE research has been carried out in recent years on electroless nickel deposition - especially on electroless cermet/ nano-composite plating including the co-deposition of diamond, silicon nitride, silicon carbide and alumina particles [1,2,3,4]. This work finds applications in many fields including thermal barrier coatings (TBCs) and composite coatings. Additionally, work has been performed on nickel / yttria stabilised zirconia (YSZ) as an anode material for solid oxide fuel cells (SOFCs) in various manufacturing techniques including conventional ceramic process [5,6], thermal spraying [7], vapour deposition [8] and laser deposition [9] technologies.

The traditional and most common techniques for producing anodes for SOFCs involve producing cermets through silk screening and subsequent sintering [10,11] followed by consolidation by sintering. Three recent techniques for producing anodes for SOFCs are (i) applying an electroless coating on the ceramic powders [12,13], (ii) chemical precipitation coating [14] and (iii) chemical co-precipitation [15] - all followed by solid state sintering. Problems arise in the sintering process where the reduction of nickel oxide produces larger nickel grains which reduces the cell's performance [16] and adds processing steps and costs.

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A more recent development carried out at Napier University by Davidson and Waugh [17] has resulted in the replacement of the sintering and reduction stages with a single plating operation. This is more cost-effective and greatly simplifies manufacture of almost any cell design. This technique can provide different ceramic to metal ratios and porosity levels and allows deposition on specific areas only, thus aiding cell design.

Electroless nickel plating is used extensively within industry and in fact is the most prevalent electroless coating used for engineering purposes. It has some unique physical properties, including excellent corrosion, wear and abrasion resistance, ductility, lubricity, electrical properties, high hardness, (especially when deposited as a nickel-phosphorous system and heat treated) and good solderability [18]. The deposits typically contain 2 – 14% by weight of phosphorous, depending on the plating solution type, and the plating is carried out by means of an autocatalytic reaction which does not require an external electrical current source.

Phosphorus content in the coating is very importance in determining the properties of the overall coating. As the phosphorus content increases from 2 to 14 %, the microstructure changes from crystalline to amorphous [19,20,21]. The process relies on a reaction proceeding at a specific temperature, typically around 90°C, when a suitably activated substrate is immersed in the solution. The deposition rate for this process is approximately 16 to 20μm per hour depending on the condition of the bath pH, concentration and salt loading. An advantage of this process is that both metallic and non-metallic substrates can be coated provided they have been suitably pre-treated. The process follows the chemical reactions as detailed in equations 1 to 4 as shown below [22],

$$(H_2PO_2)^- + H_2O \xrightarrow{Catalyst\&Heat} H^+ + (HPO_3)^{2-} + 2H_{abs} \quad \cdots \text{ Equation 1}$$

$$Ni^{2+} + 2H_{abs} \rightarrow Ni + 2H^+ \quad \cdots \text{ Equation 2}$$

$$(H_2PO_2)^- + H_{abs} \rightarrow H_2O + OH^- + P \quad \cdots \text{ Equation 3}$$

$$(H_2PO_2)^- + H_2O \rightarrow H^+ + (HPO_3)^{2-} + H_2 \quad \cdots \text{ Equation 4}$$

In equation 1, H_{abs} is hydrogen on the surface that initiates the nucleation process of autocatalytic growth of the electroless coating [23]. This can be controlled by adequate substrate pre-treatment and adjusting bath condition.

The deposited nickel coating has an even, uniform thickness - even down deep bores and recesses, and at corners and edges. The uniformity of the deposit reproduces the substrate surface finish.

Acid etch solutions are used to remove any residual oxide films from the surface and to give the surface a rougher finish to improve the mechanical adhesion [24]. The bath parameters and bath content also influence the performance and properties of the coating [25].

II. Experimental Work

A. Materials

The 8% yttria stabilised zirconia powder used in this study was manufactured and supplied by Unitec Ceramics Ltd, and had a nominal particle size of 2µm. Aerospace Machining Technology Ltd provided the plating chemistries and the facilities for carrying out the plating operations. All non-proprietary solutions were prepared using AR grade chemicals and high purity deionised water. The electroless nickel chemicals were manufactured by Schloetter Company Ltd under the Tradename of Slotonip 2010 and produced a bright mid-phosphorous (6 – 9%) nickel deposit. The sensitising and activator solutions were manufactured by AlfaChimici under the tradename of Uniphase PHP.

A ceramic tile of 25 x 25 x 1 mm dimension was used as a substrate. The insulating materials substrate requires sensitising to activate the substrate surface [26]. This is followed by electroless co-deposition of Nickel /YSZ after the pre-treatment process sequence simplified in Fig. 1.

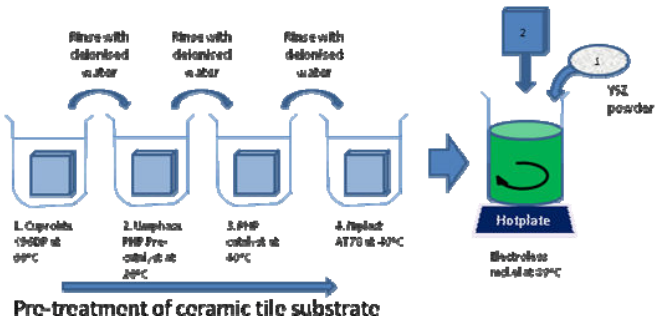


Fig. 1: Schematic diagram of novel electroless nickel co-deposition

50g/l of the YSZ powder was added to the electroless nickel solution and kept in suspension through mechanical stirring. The solution was heated and the temperature maintained at 89ºC using a Jenway hotplate /stirrer. All plating operations were carried out within 3 hours of the pre-treatment chemistries being prepared to minimize any possible effects of degradation of the chemicals.

B. Characterisation

Surface characteristics of the samples were determined using a Cambridge Stereoscan 90 Scanning Electron Microscope (SEM) and compositional analysis was carried out using energy dispersive X-ray analysis (EDXA).

C. Substrate Surface Treatment

The surface of the ceramic substrate was altered by two means, i.e. mechanical and chemical treatment. Mechanical treatment was carried out by blasting a strong air blast containing alumina particulates for 1-2 minutes while the chemical treatment involved etching the alumina in a strong hydrofluoric acid (HF) for 5 minutes. Both these treatments promote surface roughness and they will be compared with each other and with the as-received sample. The profile of these three surfaces was measured using a Talysurf profilometer at Aerospace Machining Technology (AMT).

D. Varying Bath Parameter

The pH of the plating solution bath was altered from 4.9 to the upper limit of the electroless nickel pH window – 5.4 [22]. The pH was altered by adding concentrated ammonium hydroxide.

The method of bath agitation was also investigated with magnetic stirring and air bubbling both being tried.

III. Results & Discussion

A. Initial Microscopy and Analysis

The nickel/YSZ composite was examined to ensure that both materials had been co-deposited. This was confirmed using EDXA as shown in Fig. 2. All major elements with primary Kα and Lα peaks were present for nickel, zirconium and yittrium. Quantitative analysis indicated a 70 to 30 weight percent ratio of nickel-YSZ.

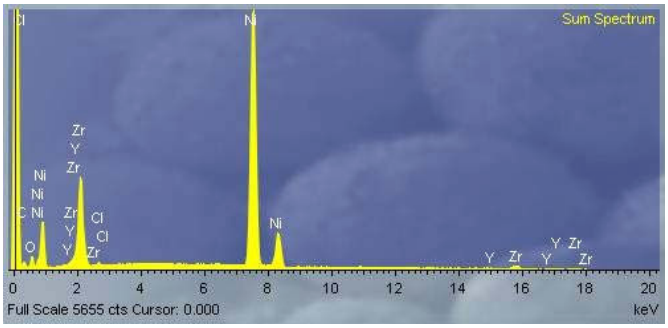


Fig. 2: EDXA spectrum of nickel-coated YSZ powder

Fig. 3 is the SEM micrograph of the deposited surface where the grey area represents nickel and the white areas are YSZ particles. An optical micrograph of the cross-section of the deposited layer of approximately 13 µm in thickness is shown in Figure 4. The coating thickness is consistently uniform with the dark parts being the ceramic particles embedded in the nickel matrix phase. The surface SEM micrograph of the co-deposited materials exhibits micro-pores which is one of the requirements of a SOFC anode. The

required porosity in an SOFC anode is between 30-40 volume percent. This porosity allows fuel and reactant gas to flow in and out of the anode [27].

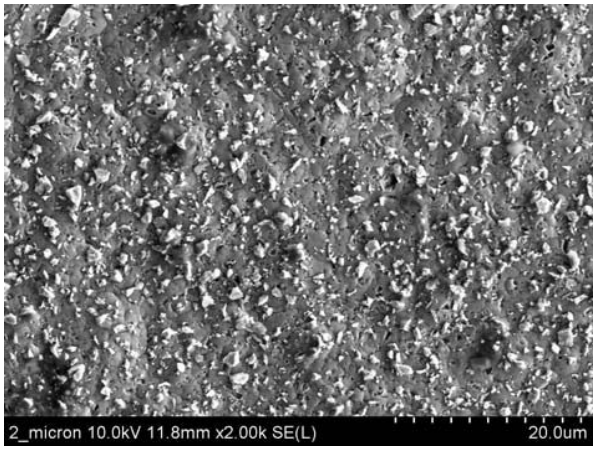


Fig. 3: EDXA spectrum of an electroless nickel / YSZ composite.

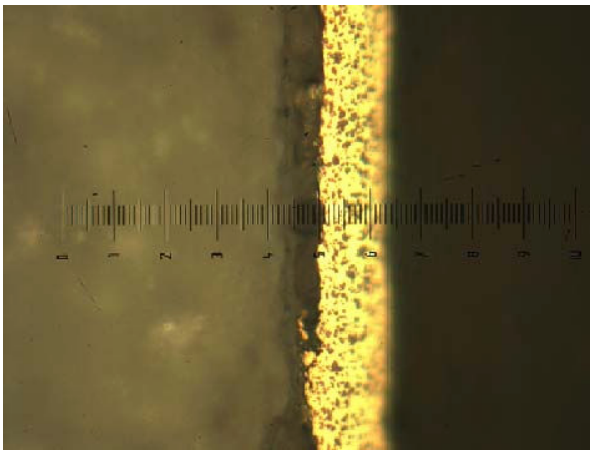


Fig. 4: Brightfield optical micrograph under 1000 magnification, 2.0 oblique function – each graticule represent 1 µm.

An SEM elemental mapping was carried out on the surface of the deposited coating and the distribution of both nickel and zirconium phases are shown in Fig. 5a and 5b respectively. It can be seen that the distribution of the embedded particles and matrix phases in the coating was uniform. This is very promising for the application of solid oxide fuel cell anodes as the nickel ensures good electrical conductivity and the ceramic phase ensuring good compatibility of coefficient of thermal expansion (CTE) between anode and electrolyte of SOFC [28].

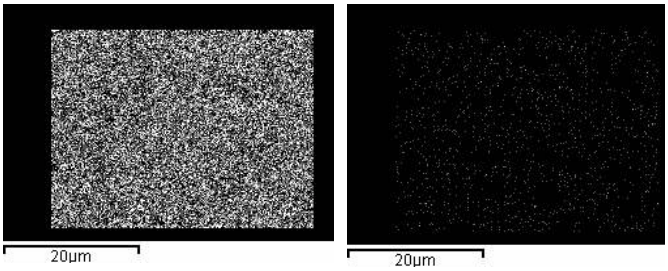


Fig. 5: Elemental mapping of (a) nickel distribution (b) zirconium distribution

B. *Effect of Substrate Surface Treatment*

Optical examination revealed that the untreated surface (Fig. 6a) exhibited alumina grains that were less well-defined compared to those subjected to chemical etching (Fig. 6c). Abrasive blasting showed a rougher surface (Fig. 6b) with the surface showing valleys of the blasting effect.

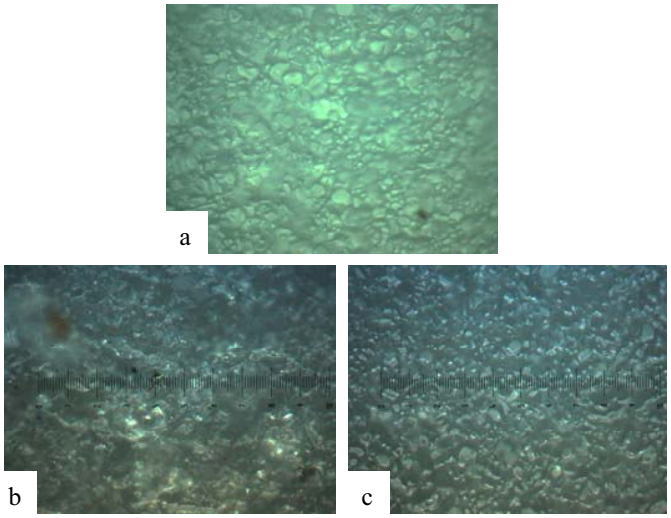


Fig. 6: Alumina surface under optical microscope. 1000x Brightfield Oblique function 3.0 (a) as received (untreated) (b) abrasive blasting (c) HF etching

The surface roughness values, R_a, after mechanical blasting and chemical etching were 40.95 and 25.03 µin respectively compared to the as-received ceramic substrate value of 21.33 µin. Comparing the SEM micrographs of these surfaces, more micro-pores appear to be present on the mechanically treated surface coating compared to the etched one (Fig. 7) with the etched surface coating appearing to be smoother and denser. These observations were confirmed with more high power SEM examination – as shown in Fig. 8.

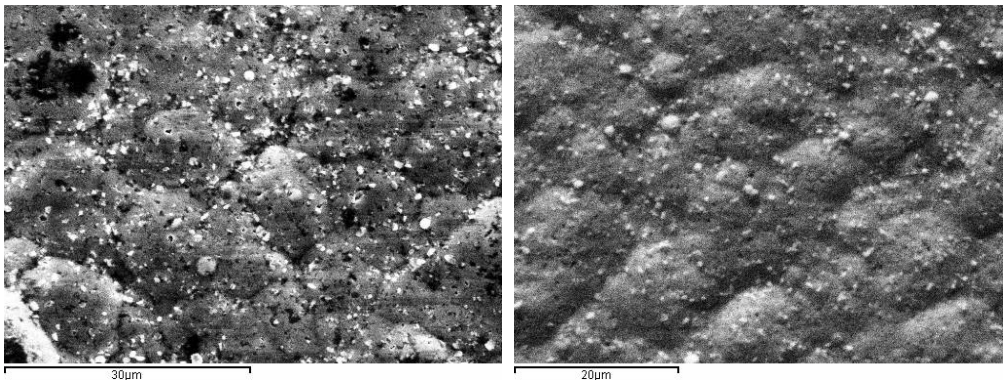


Fig. 7: SEM micrograph of mechanical treated coating (top) and chemical treated coating (bottom) at 2000x magnification

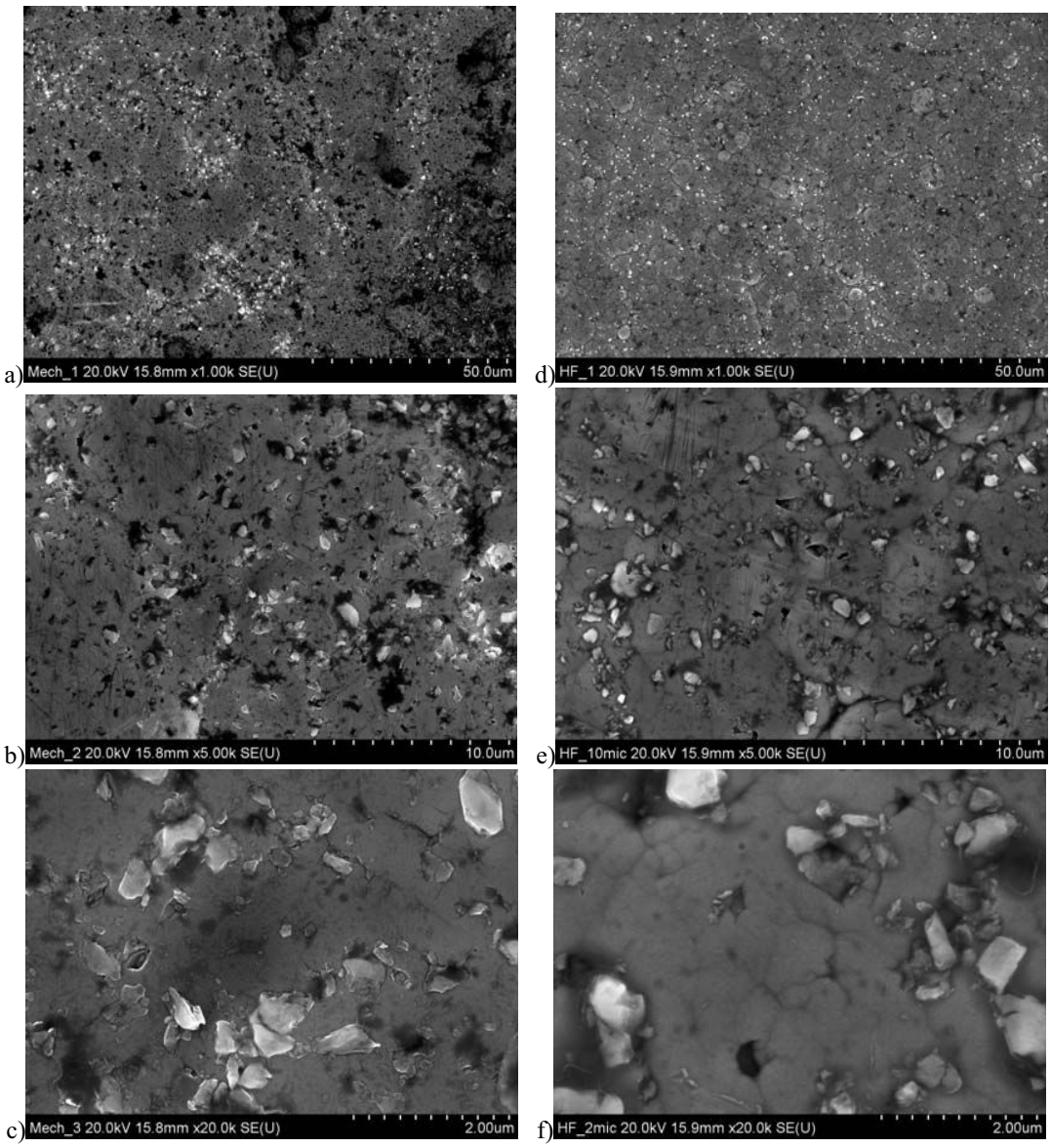
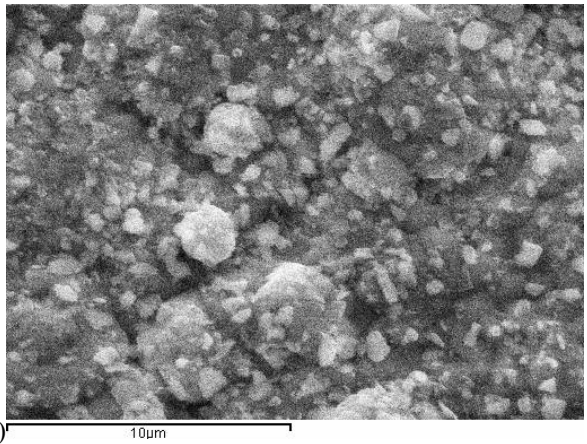


Fig. 8: SEM micrographs at 1000, 5000 and 20000 magnification. Mechanical treated surface coating (left: a, b, c) and chemical treated surface coating (right: d, e, f).

A. Bath pH

Increasing the bath pH is known to increase the deposition rate of electroless nickel coatings - caused by spontaneous decomposition of the nickel solution – resulting in a rougher deposit and reduced phosphorus content [29]. Therefore the pH of the bath was increased to 5.4 to provide this condition. Increasing the rate of deposition is also expected to increase porosity due to the randomized deposition of nickel at higher deposition rates. Fig. 9 compares the SEM micrograph of co-deposited coating at two different pH values. The SEM micrographs did not reveal significant differences in terms of porosity but the surface for pH 5.4 was rougher compared to the standard pH. Porosity is to be further investigated using a nitrogen BET surface area analysis to determine pore volume. The pores have to be continuous throughout the deposited coating thickness to allow passage of the gaseous species.



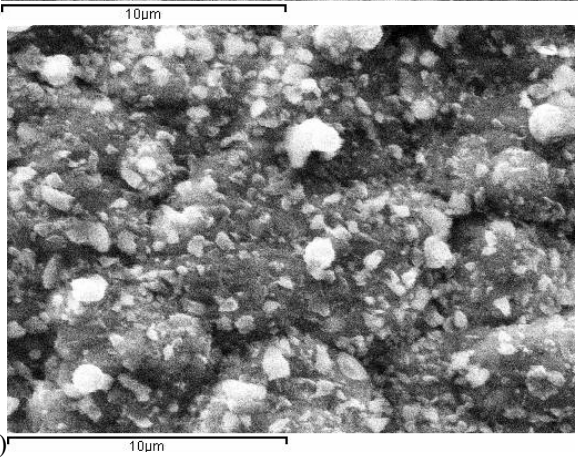


Fig. 9: Field Emission SEM micrograph of electroless co-deposition of Ni-8YSZ (2 µm) in electroless bath (a) pH4.9 (b) pH 5.4

The deposition rate was found to be decrease with increasing bath pH (Fig. 10). This is opposite to the literature [22] and might be due to several reasons. The plating condition - that is the area of the substrate to the bath volume is depleted from its optimum level after certain period of time due to evaporation of solution. On top of that, the addition of ceramic powder to the bath might have disturbed the system and caused this observation. Using larger bath volumes could minimize the effects of temperature variation and evaporation of the solution.

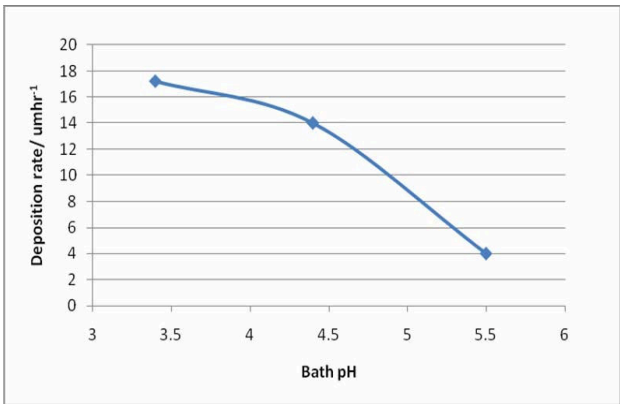


Fig. 10: Deposition rate varies with bath pH

B. Agitation Methods

The work involving altering the bath agitation is to try to increase the amount of embedded ceramic powders in the coating [30]. Summarised data of YSZ embedded in composite coating is given in Fig. 11. Substrates placed vertically in the bath show better deposition for both agitation methods than those placed horizontally while air agitation showed an increased amount of YSZ embedded in the coating. The aim is to increase the amount of YSZ phase to more than 60 vol.% (48 wt%) so as to be suitable for SOFC anodes [31] and thermal barrier coating [32].

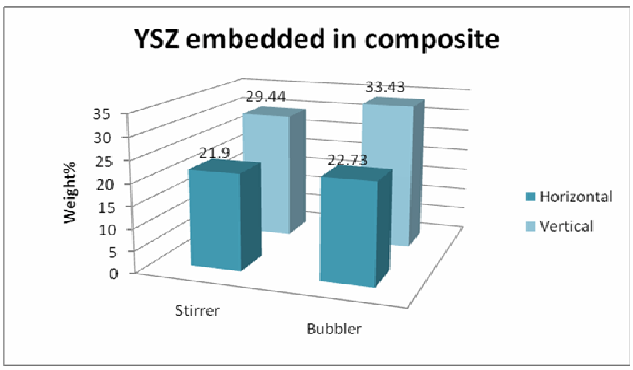


Fig. 11: Amount of YSZ particles embedded in the composite coating using different agitation methods.

IV. Conclusions

This paper highlights the importance of a new technique for manufacturing solid oxide fuel cell anodes. It also has potential for manufacturing thermal barrier coatings. The paper investigates how the ratio of ceramic to metal content can be altered to suit different applications and also addresses the issue of varying the porosity level.

Acknowledgment

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