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Relation Between the YSZ Powder Properties and Vacuum Plasma Spray Deposited Layers

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Vacuum plasma spray deposition was used to produce yttrium stabilized zirconium (YSZ) (7 % mole) layers on ceramic and metal substrates using different conditions and way of preparation of powder. Powders were prepared in two ways, they were agglomerated and sintered or fused and crushed. It was found that YSZ layer chemical composition is the same as for used powders. Layers, produced by plasma spray deposition method with agglomerated and sintered powders, were more homogenous and dense.
Keywords: plasma spray, YSZ, SOFC.

1. INTRODUCTION

Solid oxide fuel cells (SOFC) are electrochemical energy converters, which directly transform the chemical energy of a fuel gas into electrical energy. Due to the high operating temperature (700 – 1000 °C) a wide variety of fuels can be processed. Typical configuration of SOFC and gases used are presented in Fig. 1.

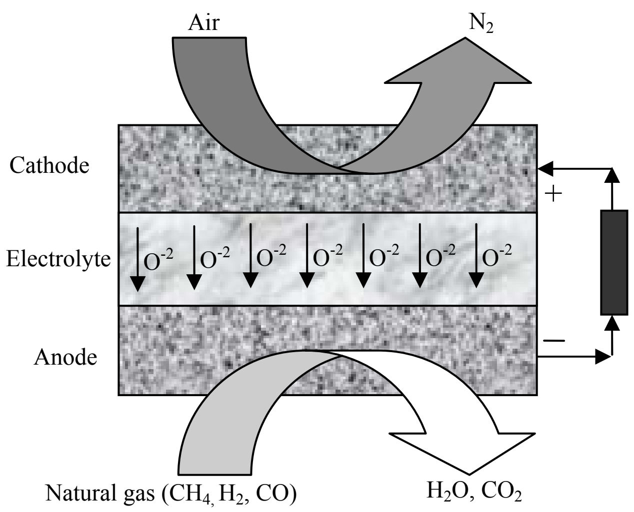

Fig. 1. Schematic illustration of Solid Oxide Fuel Cell (The arrows indicate fluxes of the gases involved and O^{-2} denotes flux of oxygen ions through the electrolyte)

There are different types of SOFC concepts, basically tubular and planar ones, which differ in the single cells design and arrangement, interconnector materials and gas flow. SOFC-stack materials have to fulfill different requirements. Electrolyte and interconnector have to be gas tight and purely ionic respective electronic conducting membranes whereas the electrodes have to enable the transport of electrons and of gaseous reactants and reaction products and therefore have to be porous. In case of a pure electronic conducting electrode material, the electrochemical reactions are restricted to the triple phase boundaries (tpb). The transport of oxide ions within the electrode material is advantageous concerning the number of possible reaction pathways. Therefore, electrodes should be a composite consisting of an electronic and an ionic conducting phase or a mixed conducting metal oxide to enlarge the active area into the electrode volume [1].

The electrode materials should exhibit a high catalytic activity for the desired chemical and electrochemical reactions [2].

Yttria-stabilized zirconia (YSZ) is the most commonly used electrolyte material for SOFC because of its unique combination of properties such as high chemical and thermal stability and pure ionic conductivity over a wide range of conditions [3]. As a result, YSZ today is still the standard electrolyte material in SOFC. Due to the high operational temperatures the material demands upon SOFC components are quite stringent. It would be desirable to lower the operational temperatures (to 700 – 800 °C) so that interconnect, heat exchangers, and structural components may be fabricated from relatively inexpensive metal components [4, 5]. One problem associated with lowering the temperature is the increase of the YSZ electrolyte resistivity. This can be overcome by lowering the electrolyte resistance either by decreasing the electrolyte thickness or with alternative materials of higher ionic conductivity at lower temperatures (e.g. Sc-doped zirconia, ceria solid solutions, doped bismuth oxide, etc.). In addition, for both strategies reduced electrode /electrolyte interfacial losses are beneficial [6].

If the electrolyte thickness is reduced from today's 100 – 200 μm to a 5 – 10 μm range a new design for the electrode/electrolyte structure is needed. As the thin electrolyte can no longer be the mechanically supporting component, one of the porous electrodes must take over this function. Then a thin electrolyte film may be deposited on the electrode layer followed by the deposition of the other porous electrode [4].

Compared with other coating methods, plasma spraying is unique in that the high temperatures (≈10000 K) and specific energy densities achieved in

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thermal gas plasmas enable the melting of any material which has a stable molten phase. Plasma spraying of materials such as ceramics and nonmetallics, which have high melting points, has therefore became well established as a commercial process [7].

The production of dense high – strength deposits using a modern system requires that a large fraction of the injected powder particles be heated to a molten state before they impinge on the substrate or the previously deposited particles, besides being in the molten the particles should also have sufficient velocity to be able to spread out and to flow in to the irregularities of the previously deposited layer and a strong interparticle or particle – substrate bond should be formed. This quality of sprayed deposit depends on the powder particle interaction with the plasma and environment. The interaction is related to the plasma (laminar or turbulent, the chemical composition, temperature, enthalpy and velocity), powder injection (the location of injection and velocity), the powder (the shape, size and density) and the duration of interaction (the torch – substrate spraying distance and repeatability of movement) [8].

Influence of the powder type and preparation way on the structure of plasma sprayed coatings was the main goal of the current research.

EXPERIMENTAL

In our experiments we have used a vacuum plasma spray deposition equipment (Fig. 2) that included: vacuum chamber and plasma spray gun SG-100, substrate holder.

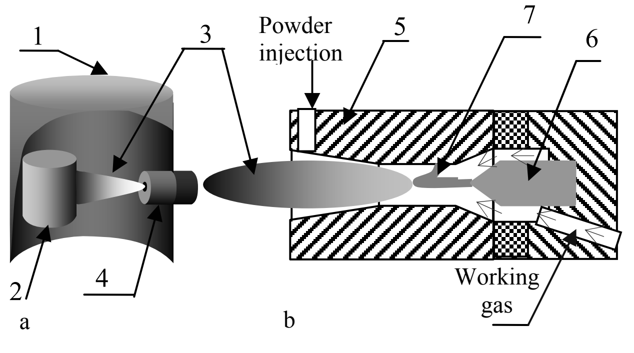

Fig. 2. Schematic diagram of the vacuum plasma spray equipment (a) and plasma spray gun (b): 1 – vacuum chamber, 2 – substrate holder, 3 – plasma torch, 4 – plasma spray gun, 5 – anode, 6 – cathode, 7 – electric arc

Table 1 summarises the main technological parameters of plasma spray technique used to deposit YSZ layers.

Table 1. Conditions of YSZ layers deposition by plasma spray

Discharge Current	600 A
Voltage	60 V
Working gas inflowing	35 l/min
Working gas composition	0.8 Ar + 0.2 H_2
Distance gun - substrate	8 cm
Pressure in a chamber	0.1 Pa

Different types of YSZ from H.C.Stark Company were examined in our work. Powder produced in two different ways – agglomerated and sintered (“Amperit 827.054”) or fused and crushed (“Amperit 825.0”, “Amperit 832.7”) (Fig. 3) was used. Concentration of Yttrium in all cases was 7 %mole.

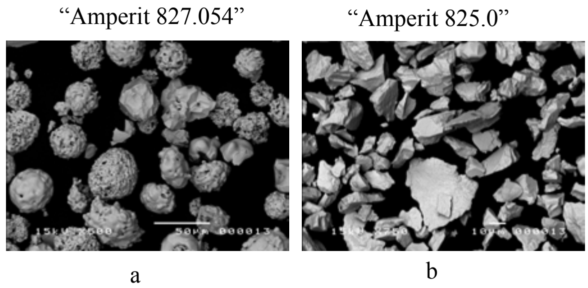

Fig. 3. SEM photographs of the raw YSZ powders: a – powders “Amperit 827.054” – agglomerated and sintered; b – powders “Amperit 825.0” – fused and crushed

YSZ layers were formed by vacuum plasma spray deposition technique on different types of substrates, using these two types of powders. Rolls-Roy’s spinel, LaScMgO, LaScCaO, Yttrium stabilized ZrO_2, with 8 % and 3 % mole of Yttrium, Gd doped CeO, stainless steel and Al_2O_3 were used as substrates. YSZ layers were analyzed with SEM (JEOL 840 scanning microscope equipped with X-ray spectrometer (EDX).

RESULTS AND DISCUSSIONS

Deposition at constant discharge power and different substrates lead to the formation of YSZ layers with typical thickness ~20 μm and deposition rates ~1 μm/min.

It was found that use of powders, such as “Amperit 827.054”, brings to well adheared layers of the similar composition for all analysed substrates. Results of Energy dispersion X-ray analysis (EDX) presented in Table 2 show that chemical content of the used powders and formed layers is approximately the same.

Table 2. Results of YSZ composition by EDX analysis (powders and layers)

Sample	Min Y_2O_3 mole%	Max Y_2O_3 mole%	Comments
“Amperit 827.054”	6.90	7.52	Same range as given by powder provider
“Amperit 825.0”	6.73	7.87	
YSZ layers from both powders	6.11	7.41	Layer content is approx. the same as in powders

One can conclude that for the used plasma spray discharge conditions the content of the used powder is found in the YSZ layers and plasma spray process has no influence on the chemical content of YSZ layers.

Surface morphology of YSZ layers deposited by plasma spray deposition technique are presented in Fig. 4. The YSZ layers morphology was dependent on the type of used powders (agglomerated and sintered or fused and crushed).

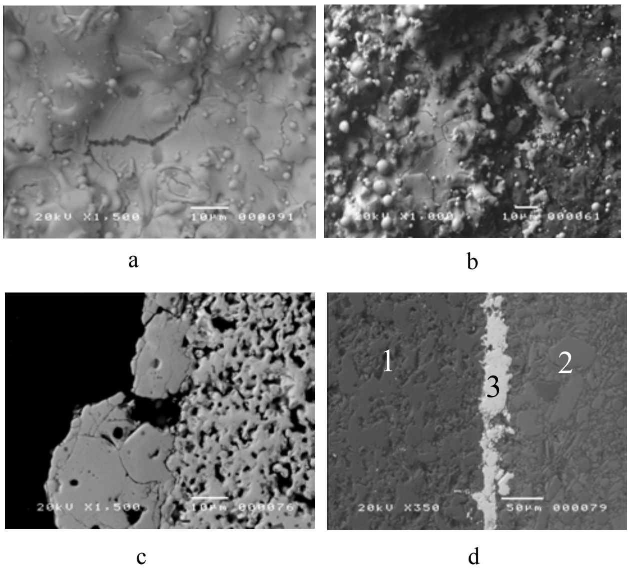

Fig. 4. SEM photographs of the plasma spray deposited YSZ layers on LaScMgO (a, c) and spinel (b, d): a – "Amperit 827.054", b – "Amperit 825.0", c and d – crossection view of same layers (1 – Spinel from Rolls-Royce comp. 2 – plastic used for the mechanical hardness, 3 – YSZ layer)

One can see that layers produced from powder prepared in agglomerated and sintered way, is more homogeneous and particles look like more melted (Fig. 4, a, c). Despite that these layers contain less macropores they still contain a lot of cracks. On the other hand agglomerated and sintered powder will be more preferable for thin and dense electrolyte production, and fused and crushed powder for the porous anode and cathode.

X-ray diffraction patterns in Fig. 5 present three different "Amperit" powders, where "Amperit 832.7" and "Amperit 825.0"were produced by fusing and crushing YSZ, and "Amperit 827.0547" by agglomerating and sintering.

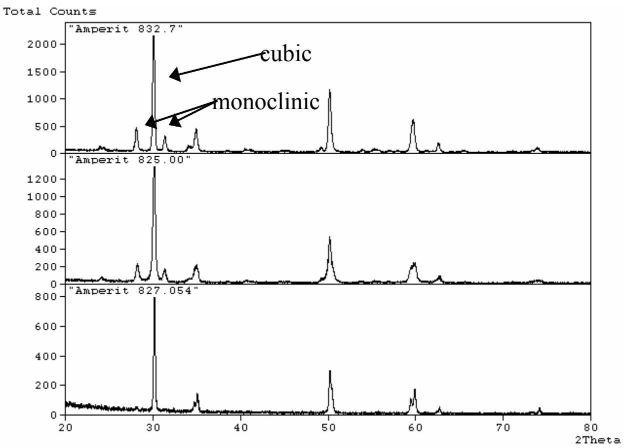

Fig. 5. XRD patterns of the three different Amperit powders: a – "Amperit 832.7", b – "Amperit 825.0", c – "Amperit 827.054"

According to the X-ray diffraction analysis powders prepared by fusing and crushing ("Amperit 825.0" and "Amperit 832.7") contain monoclinic ZrO_2. As a result this monoclinic ZrO_2 was found in the YSZ layers as well (Fig. 6 and Table 3).

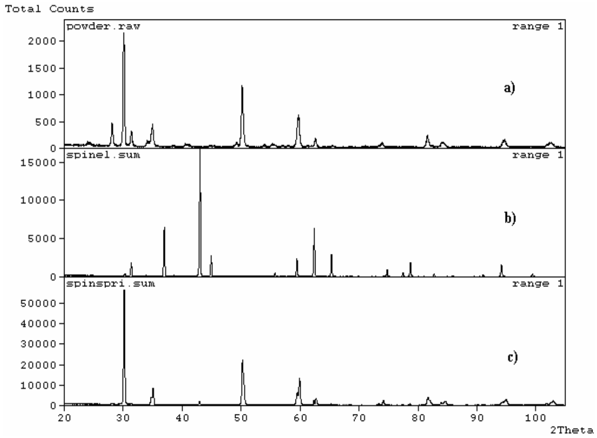

Fig. 6. X-ray diffraction patterns of YSZ layers deposited on substrate as compared with the substrate and raw powder: a – raw zirconia powder; b – Spinel substrate; c – Layer of plasma sprayed YSZ on spinel

Table 3. XRD analysis results of the substrate and YSZ layers

Sample	a_{cubic}/Å	Reference	Remarks
Spinel, $MgAl_2O_4$ type	8.0758 ±0.0009	8.0831 JCPDS 21-1152	–
Sprayed layer YSZ	cubic content: a ~ 5.14;	5.139 for $Zr_{0.85}Y_{0.15}O_{1.93}$ JCPDS 30-1468	traces of monoclinic ZrO_2, strongest peak from substrate spinel is also visible

Table 4 summarizes main structural analysis results for different types of powders. It should be noted, that from the practical view monoclinic ZrO_2 in the YSZ layers is unwishable for SOFC applications [8].

Table 4. XRD analysis of YSZ layers

Powder used	Lattice parameter a_{cubic}/Å	Remarks
"Amperit 825.0"	cubic content: a ~ 5.14	traces of monoclinic ZrO_2
"Amperit 832.7"	cubic content: a ~ 5.14	traces of monoclinic ZrO_2
"Amperit 827.0547"	cubic content: a ~ 5.14	no traces of monoclinic ZrO_2

The results show that independently on the way of production of powder for the investigated energy densities in the plasma spray deposition technique content and structure of the layers was the same as used powder. The same results were obtained for all used substrates that means that the substrate has no influence on the layer lattice parameter.

CONCLUSIONS

1. Agglomerated and sintered powders (such as "Amperit 827.0547") are more common to produce dense YSZ layers. Fused and crushed powders (such as "Amperit 825.0" and "Amperit 832.7") are more common to produced porous layers.

2. The YSZ layer lattice parameter is not influenced by the used substrate and remains the same (a ~5.14 Å) for all the used powders.
3. Chemical content of YSZ layers is the same as for powders, for the used plasma spray energy densities.

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