



## Study of (Ni, Cu, Co)-YSZ and Cu-Co-YSZ anode materials for SOFCs elaborated by atmospheric plasma spraying

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### Abstract

*Solid oxide fuel cells (SOFCs) are the most efficient type of fuel cells because of their high operating temperatures which confer them flexibility to various types of fuels such as methane. This is possible because the hydrogen is produced, in situ, from hydrocarbons like methane by internal reforming, an electrochemical reaction which can occur directly at the anodic compartment. So, this reaction requires the appropriate anode materials, catalysts and microstructure.*

*To improve methane internal reforming at SOFCs anode, catalytic anodes of (Ni, Cu, Co) and Cu-Co /YSZ cermets are elaborated by atmospheric plasma spraying (APS) under optimized conditions which were investigated by an orthogonal experiment to fabricate a gas-permeable cermet anode coating. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) are used to characterize the morphology and structure of coated film respectively. The porosity is deduced by the statistical image analysis method.*

### 1. Introduction

During this last decade, the excessive and prevalent use of the fossil resources of energy generated a considerable pollution by greenhouse effect, and led to a progressive exhaustion of fossil fuels which supports the fuel cells development as a new energetic technology. These last, are electrochemical devices that are able to directly convert

chemical energy to electrical energy, without any Carnot limitation that leads to very high energy efficiencies [1]. Among the various types of fuel cells, solid oxide fuel cells (SOFC) are operating at high temperatures, that is why they have many advantages such as simplicity of system design and multi-fuel capability so they can run on wide range of fuels, gaseous fuels such as hydrogen and natural gas or liquid fuels such as alcohols and gasoline [2]. This is possible because the hydrogen is produced, in situ, from hydrocarbons like methane by internal reforming, an electrochemical reaction which can occur directly at the anodic compartment. So, this reaction requires the appropriate anode materials, catalysts and microstructure.

At present, conventional SOFC are operated with pure hydrogen or partially to fully reformed natural gas implying an efficiency penalty. SOFC anodes are generally made of electrocatalytically active Ni-YSZ cermet ( $(Y_2O_3)_{0.08}-(ZrO_2)_{0.92}$  abbreviated as YSZ). For SOFCs running on direct  $CH_4$  feed, alternative anode materials to Ni-YSZ, or new anode formulations are necessary.

The most important requirements for the anode are physical and chemical stability under a reducing atmosphere at high temperature, a good electronic and ionic conductive phases as well as porosity, low polarisation resistance, a

matching thermal expansion coefficient to electrolyte one to prevent the electrode from flaking of the electrolyte and a high catalytic activity to promote reaction of the fuel with oxide ions [3]. To satisfy the above requirements and compete more effectively with other traditional power generating methods it is necessary to choose the appropriate nature of the starting powders, composition and the applied manufacturing technique. So, plasma spray process, especially, Atmospheric plasma spraying (APS) shows the best regards to be rapid and inexpensive process to fabricate components for SOFC [4,5], comparing with other deposition techniques such as electrochemical vapor deposition (EVD) [6] and vacuum plasma spray (VPS) [7], which need sophisticated equipment and controlled atmosphere that consequently increases the fabrication cost.

In addition, APS easily controls the constituent composition, the microstructure and material deposition rates through variation of spray parameters. So, it enlarges the coating area without sintering defects and improves its mechanical properties [8]. Ni, Cu, Co and Cu-Co based catalysts materials are studied here for their potential application as anodes in direct oxidation of  $\text{CH}_4$ . These compounds are good conductors and moreover, possess excellent catalytic activity for  $\text{CH}_4$  activation and combustion [9, 10].

## 2. Experimental

For  $D_n$  different coatings, the  $P_n$  spraying powders preparation is carried out by agglomeration - drying of the starting commercial powders to note yttria stabilized zirconia (8% mol YSZ, TZ-8Y Tosho-Zirconia) and copper (Cu, DIAMALLOY 1007) sieved at  $+20\text{-}50\ \mu\text{m}$  and nickel (Ni type 123). For monometallic cermets materials Ni-YSZ, Cu-

YSZ, Co-YSZ, percentages of Ni, Cu and Co are successively 40%, 50% and 60% in weight corresponding to weight ratio of (2:3), (1:1) and (3:2). For the bimetallic cermets materials Cu-Co-YSZ, the sum of Cu and Co percentages are successively 40%, 50% and 60% in weight and correspond to (0.5:1:2.5), (1:2:3) and (2:1:2) weight ratios. The obtained spraying powders listed in table 1 are sieved and dried during 72 hours at  $80^\circ\text{C}$  then subjected to a granulometric analysis on a Mastersizer 2000 particle measurement instrument.

The plasma spraying was carried out using a Sulzer-Metco Pt F4 torch for atmospheric plasma spraying (APS), assembled on ABB robot arm (Fig.1.). Two means of cooling are used jointly: compressed air blasts (pressure of 6 bars) placed each side of the torch and two tubes Venturi (pressure of 6 bars) behind the substrate.

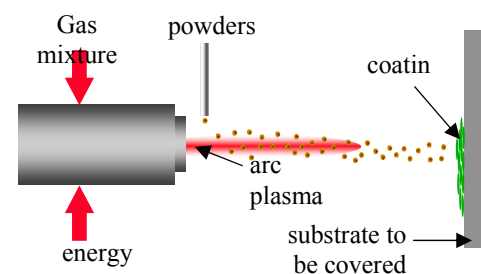


Fig. 1. APS principle.

For improving the SOFC's anode performance with regard to the electrocatalytic activity for  $\text{H}_2$  oxidation, and number of three-phase boundary (TPB) sites [11], it is necessary to spray a gas-permeable anode coating as porous as possible. Therefore, powder particles with low temperature and velocity are desired. So, it mainly depended on a dwell time of the plasma, while the higher velocity would decrease the dwell time. Therefore, the spray parameters must be optimized to give attention to both temperature and velocity.

Table 1  
Spraying powders  $P_n$  composition

Powder ( $P_n$ )	Coating ( $D_n$ )	Composition	Weight ratio
P <sub>1</sub>	D <sub>1</sub>	Ni-YSZ	2:3
P <sub>2</sub>	D <sub>2</sub>	Cu-YSZ	2:3
P <sub>3</sub>	D <sub>3</sub>	Co-YSZ	2:3
P <sub>6</sub>	D <sub>6</sub>	Ni-YSZ	1:1
P <sub>7</sub>	D <sub>7</sub>	Cu-YSZ	1:1
P <sub>8</sub>	D <sub>8</sub>	Co-YSZ	1:1
P <sub>21</sub>	D <sub>21</sub>	Ni-YSZ	3:2
P <sub>22</sub>	D <sub>22</sub>	Cu-YSZ	3:2
P <sub>23</sub>	D <sub>23</sub>	Co-YSZ	3:2
P <sub>4</sub>	D <sub>4</sub>	Cu-Co-YSZ	05:1:2.5
P <sub>13</sub>	D <sub>13</sub>	Cu-Co-YSZ	1:2:3
P <sub>30</sub>	D <sub>30</sub>	Cu-Co-YSZ	2:1:2

Table 2  
Thermal spraying parameters

Parameters	Value	
Powder conditions	Granulometry ( $\mu\text{m}$ )	90-125
	Carrying gas flow rate (l/min)	3.4
Spray conditions	Spraying distance (mm)	150
	Argon flow rate (l/min)	38
Plasma conditions	Hydrogen flow rate (l/min)	8
	Current (A)	500

The  $P_n$  ; starting powders were sprayed with the optimized parameters, listed in table 2. They are offering the best coating porosity. So, the minor argon flow rate, middle hydrogen and carrying gas flows rates and superior spray distance yielded a decrease in both particle velocity and temperature and led to a porous anode coating.

The X-ray diffraction (carried on Philips model Expert MPD with Cu  $K\alpha$  radiation  $\lambda=1.54 \text{ \AA}$ )

and scanning electron microscopy (JEOL JSM-5800LV, 25 keV) are used to characterise respectively the structure and morphology of coatings achieved with the optimized parameters. The porosity was deduced by the statistical image analysis method from SEM cross-sectional images.

### 3. Results and discussion

The optimized parameters listed in Table 2: minor argon flow rate, middle hydrogen and carrying gas flow rates and superior spray distance, lead to coatings with thicknesses of about 200  $\mu\text{m}$  and the best microstructure regard for SOFC's anodic application.

#### 3.1 Scanning electron microscopy

Scanning electron microscopy (SEM) results are given in Fig. 2 and Fig. 3. These figures show respectively Cross-sectional microstructure and fracture profile of D<sub>1</sub>, D<sub>2</sub>, D<sub>3</sub> and D<sub>30</sub> coatings which were sprayed with the optimized parameters. Fig. 2 (a), (b), (c) and (d) exhibit a porous lamellar microstructure. It appears in Fig. 3 that some lamellas deposited by spray scanning have a columnar structure within the splat, they are about 4-5  $\mu\text{m}$ , 2-3  $\mu\text{m}$ , 4-5  $\mu\text{m}$  and 2-3  $\mu\text{m}$  thick for D<sub>1</sub>, D<sub>2</sub>, D<sub>3</sub> and D<sub>30</sub> coatings respectively, with 1-2 splat layers in each lamella and the thickness of a splat layer was about 1  $\mu\text{m}$ .

The evolution of porosity, measured by statistical image analysis, for all coatings sprayed with optimized conditions, is illustrated in the Fig. 4. We can see that for both monometallic and bimetallic cermets the cross-section pores are closed and interconnected pores and the porosity is dependent of metal weight ratio. In fact, when the metal percentage increases, the porosity decreases. We can see for monometallic cermets: Ni-YSZ, Cu-YSZ and

Co-YSZ with weight ratio of (3:2) that they are less porous than those with (1:1) and (2:3) weight ratios respectively. For bimetallic cermet: Cu-Co-YSZ, D<sub>4</sub> coating with weight ratio of (0.5:1:2.5) is more porous than D<sub>13</sub> and D<sub>30</sub> coatings with (1:2:3) and (2:1:2) weight ratios respectively.

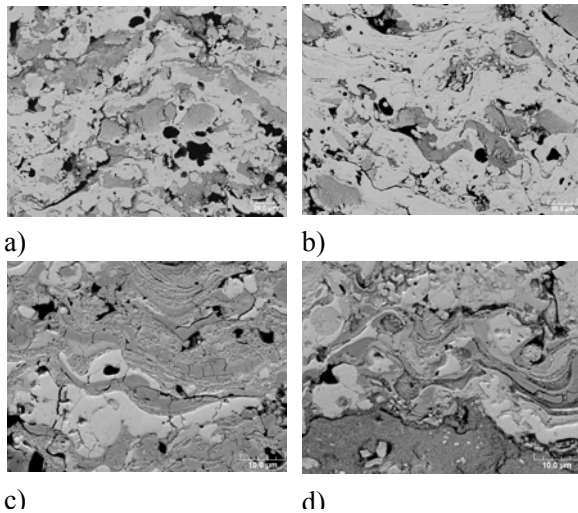


Fig. 2. SEM cross-sectional microstructure of (a) D<sub>1</sub>, (b) D<sub>2</sub>, (c) D<sub>3</sub>, (d) D<sub>30</sub> coatings.

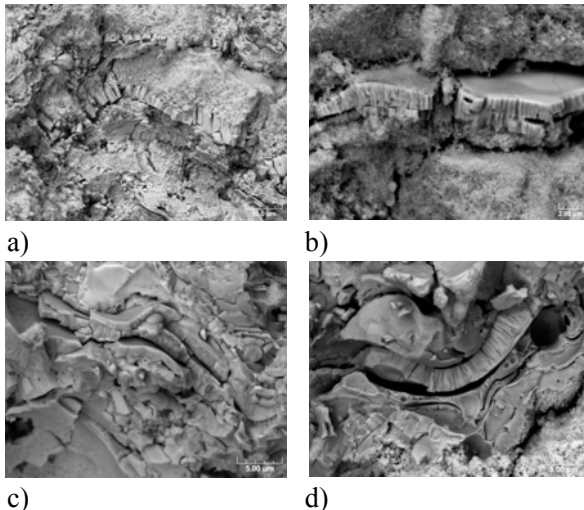


Fig. 3 fracture profile of (a) D<sub>1</sub>, (b) D<sub>2</sub>, (c) D<sub>3</sub>, (d) D<sub>30</sub> coatings.

For monometallic cermets with same weight ratio, the porosities of Co-YSZ cermets

21.57%, 19.5% and 17.56% respectively are higher than those of Ni-YSZ cermets 20.79%, 18.28% and 16.42% respectively and Cu-YSZ cermets 18.36%, 17.61% and 15.23% respectively.

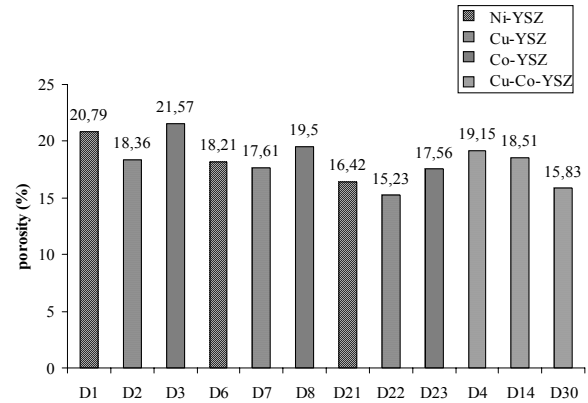


Fig. 4. Porosity level by image analysis of SEM cross-sectional microstructure of Ni-YSZ, Cu-YSZ, Co-YSZ and Cu-Co-YSZ coatings.

If we compare bimetallic and monometallic cermets, it appears that D<sub>4</sub>, D<sub>13</sub> and D<sub>30</sub> respective porosities are closed to those of D<sub>1</sub>, D<sub>6</sub> and D<sub>21</sub> Ni-YSZ cermets.

### 3.2 X-ray diffraction

The XRD results for D<sub>1</sub>, D<sub>2</sub> and D<sub>3</sub> monometallic coatings, sprayed with the optimized parameters, are shown in Fig. 5. The characteristic peaks of Ni ( $\Delta$ ), Cu ( $\circ$ ) and Co ( $\diamond$ ) respectively are revealed. We also see that the Ni-YSZ and Co-YSZ coatings contain Ni ( $\Delta$ ) and NiO ( $\blacktriangle$ ) and Co ( $\diamond$ ) and CoO ( $\blacklozenge$ ) respectively crystalline phases with few amount of oxide form whereas, the Cu-YSZ coating contains essentially Cu ( $\circ$ ) crystalline phase with very small residue of Cu<sub>2</sub>O ( $\bullet$ ) phase. So, formation of oxides crystalline phases is due to atmospheric spraying high temperature. These oxides are then precipitated on cubic lattice which is the most stable one at high temperatures. In fact, at above 800°C, copper

oxidation under ambient oxygen pressures has been extensively studied [12-14] and it appears that only  $\text{Cu}_2\text{O}$  is thermodynamically stable and  $\text{CuO}$  with monoclinic lattice couldn't be formed, if oxygen pressure isn't above the dissociation pressure of  $\text{CuO}$ .

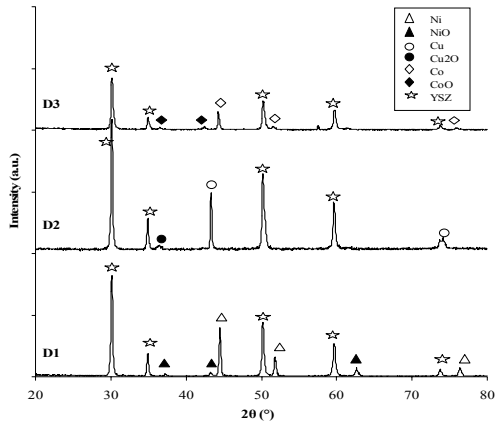


Fig. 5. X-ray diffraction of D<sub>1</sub> (Ni-YSZ), D<sub>2</sub> (Cu-YSZ) and D<sub>3</sub> (Co-YSZ) coatings.

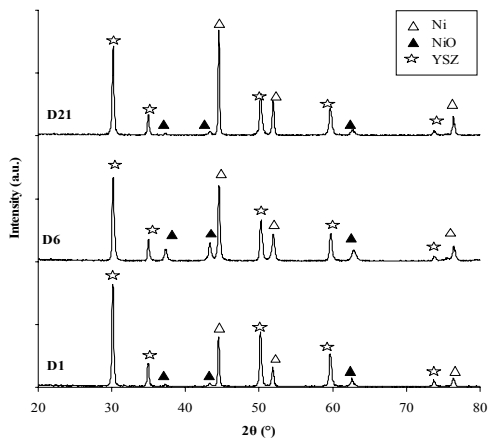


Fig. 6. X-ray diffraction of D<sub>1</sub>, D<sub>6</sub> and D<sub>21</sub> Ni-YSZ coatings.

The XRD profile for the same Ni-YSZ monometallic cermets at different weight ratios D<sub>1</sub>, D<sub>2</sub> and D<sub>3</sub> is shown on Fig. 6. We can see that percentages of metals in the cermets have a negligible influence on crystalline phase structures and it is only intensities of principal peaks that change.

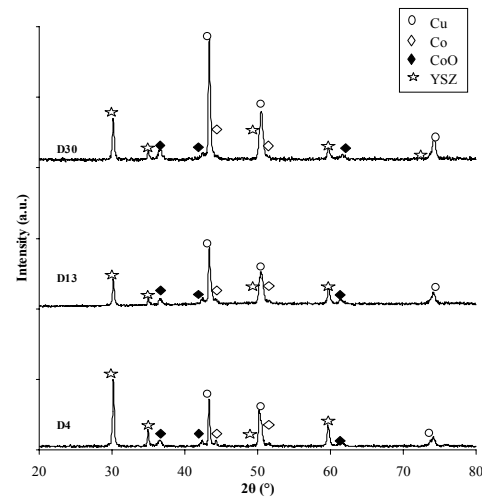


Fig. 7. X-ray diffraction of D<sub>4</sub>, D<sub>13</sub> and D<sub>30</sub> Cu-Co-YSZ coatings.

For Cu-Co-YSZ bimetallic cermets, XRD results for D<sub>4</sub>, D<sub>13</sub> and D<sub>30</sub> are given in Fig. 7. The characteristic peaks of Cu (○) and Co (◇) respectively are revealed. The Cu-Co-YSZ coatings contain Cu (○), Co and with few amount CoO (◆) crystalline phases. We can also see that according to weight ratios and with Cu metal percentage increasing, Co (◇) characteristic peaks at 44.21 and 51.52° respectively are less and less discernible of those of copper. This phenomenon could be explained by the process high temperature which leads to dissolution of f.c.c. cobalt in copper [15]. In fact, as copper and cobalt, at high temperatures, are having the same structures, the activation energies for diffusion should scale as the melting temperatures, 1357 and 1768 K, respectively. So, the diffusion of cobalt in copper at 550°C should be 2000 times faster than the self-diffusion of cobalt (in cobalt). This is due to the activation energy of lattice diffusion in copper which is approximately of 1.8 eV. That is enough to suppose that a distribution of very small precipitates of fcc cobalt forms within the copper matrix.

#### 4. Conclusions

Bimetallic Cu-Co-YSZ and Monometallic Ni-YSZ, Cu-YSZ and Co-YSZ cermets coatings, at different weight ratios, were elaborated with the optimized APS parameters which offer the best microstructure and porosity for SOFC's anodic application. The statistical image analysis revealed that the nature and the percentage of metal have a considerable influence on the cermets porosity. So, this last, decreased with metal percentage increasing and for each weight ratio of the same monometallic cermets, the Co-YSZ coatings porosities were the highest ones. For bimetallic cermets, porosity decreased with metal amount increasing and  $D_4$ ,  $D_{13}$  and  $D_{30}$  respective porosities appeared to be closed to those of  $D_1$ ,  $D_6$  and  $D_{21}$  Ni-YSZ cermets. Such anode's bimetallic materials are very interesting because carbon formation due to electrochemical anodic reaction, can often be avoided by replacing Ni with an electron conductor that does not catalyze carbon formation, such as Cu and Co as second metal that provides thermal stability [16,17].

The X-ray diffraction results showed that the metal content in the cermets have a negligible influence on the crystalline phase's structure and that for the bimetallic cermets Co diffused in Cu lattice offering thus, best: electronic conductivity, carbon tolerance and thermal stability.

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