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Fabrication Process of Spinel Powder for Plasma Spraying

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Abstract

Spinel powders for plasma spraying were fabricated for application as protective coatings against chemical attack from fused metal or glass. Due to the complex structure of spinels, the process of fabrication of the powder needed several steps to get rounded, well-crystallized grains. This consisted of spray-drying, sintering in an electrical furnace and then melting in an induction plasma. Several compositions were made and powders were then plasma sprayed on steels. Following the initial compostion, preferential volatilization was observed due to the successive thermal treatments, leading to coatings having compositions different from the powder. The microstructure and homogeneity of the coatings was also studied using scanning electron microscopy.

Résumé

Différentes poudres spinelles destinées à la projection plasma sont mises au point pour leurs propriétés de résistance aux attaques chimiques contre les métaux et les verres fondus. Le procédé de fabrication de telles poudres nécessitent plusieurs étapes avant d'obtenir des particules sphériques et bien cristallisées: après agglomération, les poudres sont frittées dans un four électrique puis fondues dans un plasma induction pour synthétiser la structure spinelle. Plusieurs compositions sont réalisées, puis les poudres sont projetées sur des aciers. En fonction des différentes compositions, des volatilisations préférentielles dues aux traitements thermiques successifs peuvent être observées. L'homogénéité et la structure des dépôts sont étudiées en microscopie électronique à balayage.

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1 Introduction

Plasma spraying applications have been growing rapidly and are now used in numerous industries such as aeronautic, nuclear or medical domains.[1,2,3] Many applications have been found especially with ceramics sprayed on to metallic substrates for properties such as wear resistance, corrosion resistance, thermal barriers, biocompatibility, etc. To fulfill industrial needs, a new plasma powder has been developed to protect metals against chemical attack from fused metal or glass. With a high melting temperature (2135°C) and a weak thermal conductivity ($15\,W\,mK^{-1}$),[4] spinels were chosen for their refractarity and because of the compact structure of the oxygen lattice. They are also very interesting materials for their stability in presence of borates and silicates.[5] The color of spinels depends on transition elements composing the material:[5] these elements adsorb visible wave lengths. The color depends not only on cations adsorbing visible light, but also on ionic environment because of the influence of the other elements on bonding force and electrons distribution. Several spinels have been made with different transition elements such as zinc, cobalt or iron to get, respectively, white, blue or green spinels. Because of its high melting temperature, and because of the complex structure of spinels, a specific fabrication process has been developed to obtain an homogeneous spraying powder. Several spinels with different compositions has been prepared to study the influence of spinel cations on metal/spinel adherence and chemical resistance. This article presents the fabrication process to produce homogeneous powder of these very complex materials.

2 Experimental procedure

2.1 Powder fabrication

The fabrication of powder took place in three steps: spray-drying, sintering, and plasma melting;

which were investigated with different characterisation methods: X-ray diffraction and microscopic observations.

2.1.1 Spray-drying
Figure 1 gives a schematic view of the spray-dryer apparatus. The spinel powders were prepared from fine powders (particle diameter $<3\,\mu m$) of elementary oxides MgO, Al_2O_3, ZnO, CoO and Fe_2O_3 to produce four powders of different compositions:

- $MgAl_2O_4$
- $(Co_{0,5},Mg_{0,5})Al_2O_4$
- $(Zn_{0,5},Mg_{0,5})Al_2O_4$
- $(Fe_{0,2},Mg_{0,8})Al_2O_4$

Powders were mixed with water, a dispersive agent and a polymeric binding to get a slurry with a viscosity between 400 and 600 cPo. The slurry was then sprayed in hot air to obtain spherical grains which were carried in a seperator by air flow. Finest particles are recovered in a filter.

2.1.2 Sintering
Powder was then sintered in an electrical furnace at 1150°C for 10 h to consolidate particles and to burn out the organic binder. The temperature of 1150°C was the maximal temperature which could be reached with our equipment. Spinel was formed according to the reaction:

$$MgO + Al_2O_3 \rightarrow MgAl_2O_4$$

Sintering occurred in each particle and between particles. This second phenomenon led to necks between particles. These necks were broken during filtering. Table 1 indicates the change of powder color after sintering.

2.1.3 Induction plasma
The double inductor plasma torch used to do the treatment is described on Fig. 2. The plasma is initially created by an electrical arc due to the high tension. The plasma gas becomes locally conductive and inductive currents appear in the quartz tube because of the inductor producing an alternative magnetic field. The high frequency currents maintain a plasma state by inducing collisions between electrons and atoms.[6] The manufactured spinel powder was then melted in the induction plasma using axial powder injection and a low plasma speed ($10\,m\,s^{-1}$) in order to give an uniform powder trajectory and an homogeneous melting.

2.1.4 Sieving
Powders were finally sieved between 30 and 90 μm.

2.2 Plasma spraying
Powder was plasma sprayed with a PT A-3000S torch in a closed room with a robot (Fig. 3). Several samples can be made with the rotating tower. Air jets cooled samples during spraying and the apparatus provided good experimental reproducibility.

The substrate was an XC10 steel grit blasted with corundum. Spraying parameters were optimised for each powder (Table 2). However, some parameters were kept constant:

- Feeder gas: Ar
- Powder feed: $15\,g\,mn^{-1}$
- Injection diameter (mm): 1·5
- Spraying distance: 120
- Inclination: 85

3 Results and Discussion

3.1 Powder morphology
After spray-drying, powder was spherical but not very dense and particles could be broken easily (Fig. 4). Porosity of powders was not measured, but it was observed in scanning electron microscopy. After sintering at 1150°C, powder was more or less spherical with necks between particles (Fig. 5). The cohesion of particles was better than before sintering but powder was very porous. After fusion in the induction plasma, powder was spheroidized and densified (Fig. 6). The surface of the particles was smoother than after sintering, which improved the flowing of the powder. Some particles had an air bubble in their center resulting from the migration and coalescence of pores. Finally, particles size was between 30 and 90 μm.

3.2 Crystallographic structure
Diffractograms were obtained with Co-Kα radiation. Before sintering, powder was a mixture of the elementary oxides used to synthesize spinels. Figure 7 gives diffractograms after sintering and after induction plasma treatment for $MgAl_2O_4$ powder. After sintering, all oxides had not reacted to form spinel. Powder was a mixture of spinel, alumina, magnesia. After induction plasma treatment, powders had the spinel structure, but some magnesia had not reacted to form spinel. The presence of magnesia indicated that crystallization was incomplete, which could be due to a heterogeneous distribution of oxides in the slurry during spray-drying or an incomplete thermal treatment.

For all plasma sprayed coatings the main phase was spinel (Figs 8–11), but the repartition of

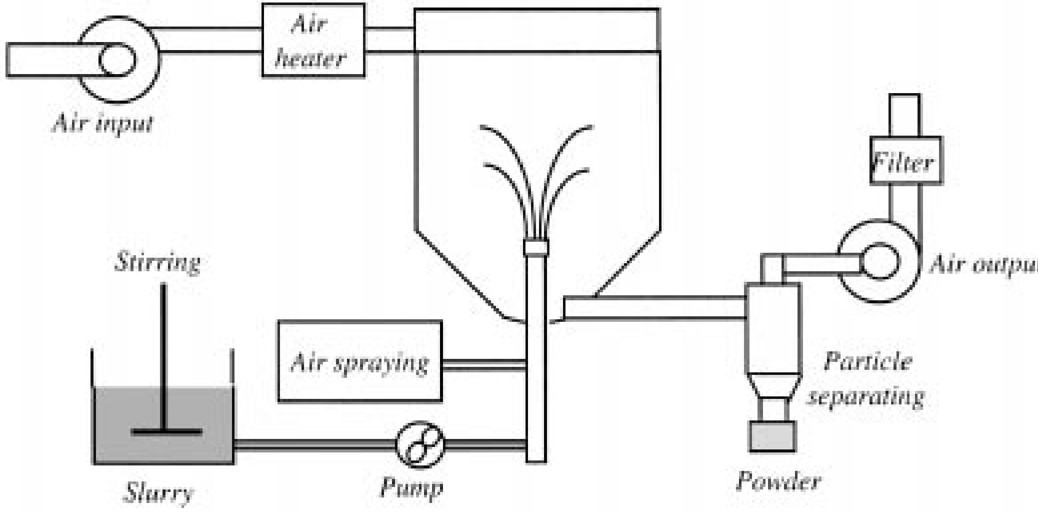

Fig. 1. Spray-dryer.

Table 1. Powder color before and after sintering

Powder composition	*Before sintering*	*After sintering*
$MgAl_2O_4$	White	White
$(Zn,Mg)Al_2O_4$	White	White
$(Co,Mg)Al_2O_4$	Black	Blue
$(Fe,Mg)Al_2O_4$	Red	Green

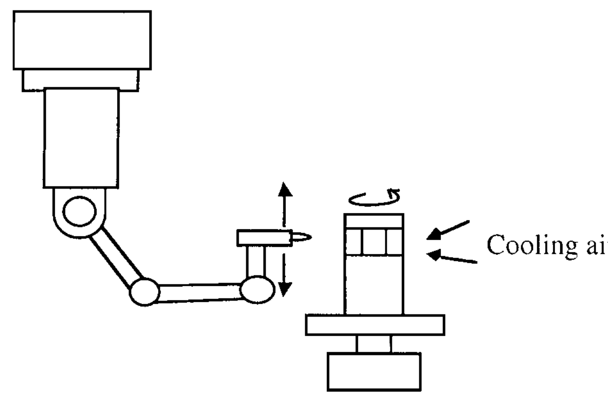

Fig. 3. Plasma spraying apparatus.

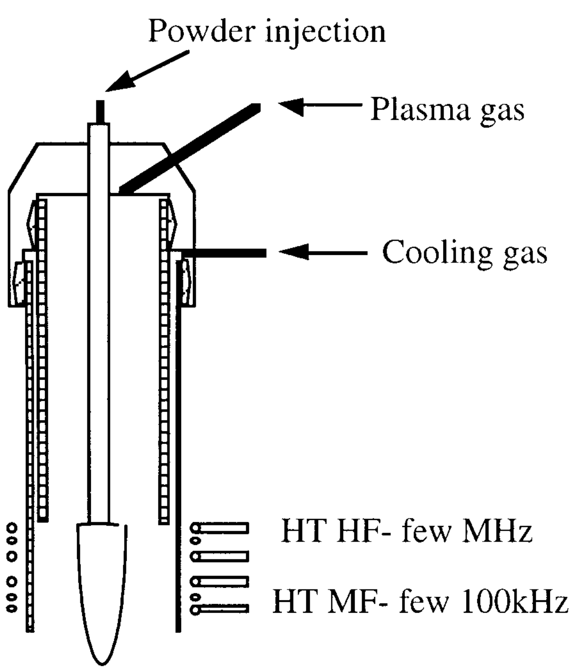

Fig. 2. Double inductor plasma torch.

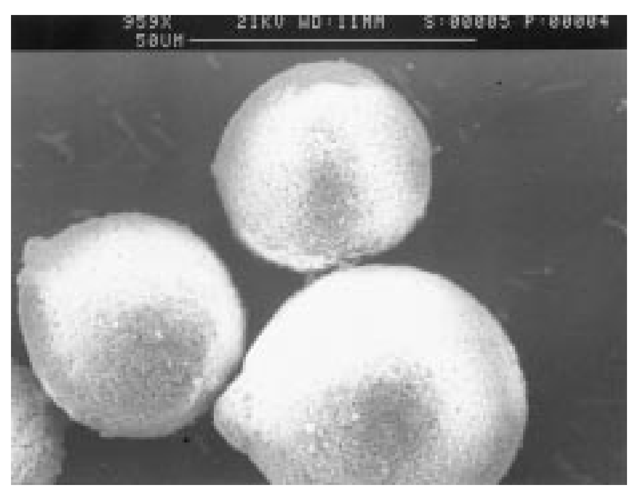

Fig. 4. SEM observation of powder after spray-drying.

Table 2. Plasma spraying parameters of spinel coatings

Materials	*U (V)*	*I (A)*	*Ar* ($1\,mn^{-1}$)	H_2 ($1\,mn^{-1}$)
$MgAl_2O_4$	70	600	38	13
$(Zn,Mg)Al_2O_4$	70	650	41	14
$(Co,Mg)Al_2O_4$	70	530	41	14
$(Fe,Mg)Al_2O_4$	70	650	38	13

cations in the tetraedral and octaedral sites was not known. Furthermore, it is difficult to be sure that all oxides have reacted or to know if several spinels have been formed because Fe_3O_4, Co_3O_4, $FeAl_2O_4$, $CoAl_2O_4$, $MgAl_2O_4$, $ZnAl_2O_4$ have the same spinel structure and their cell parameters are very close. Yet, the powder color change for $(Fe,Mg)Al_2O_4$ and $(Co,Mg)Al_2O_4$ after sintering indicates that Fe

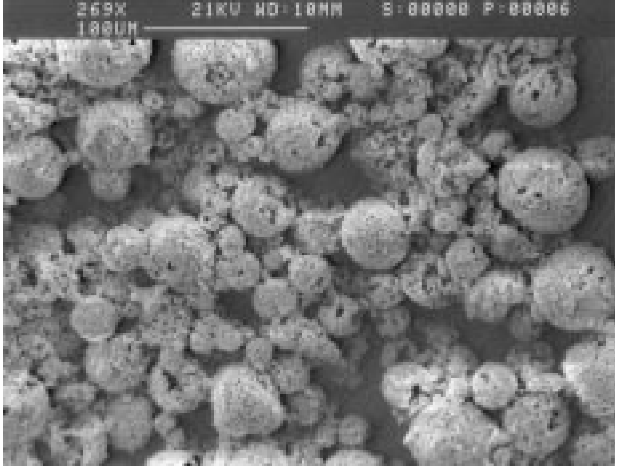

Fig. 5. SEM observation of powder after sintering.

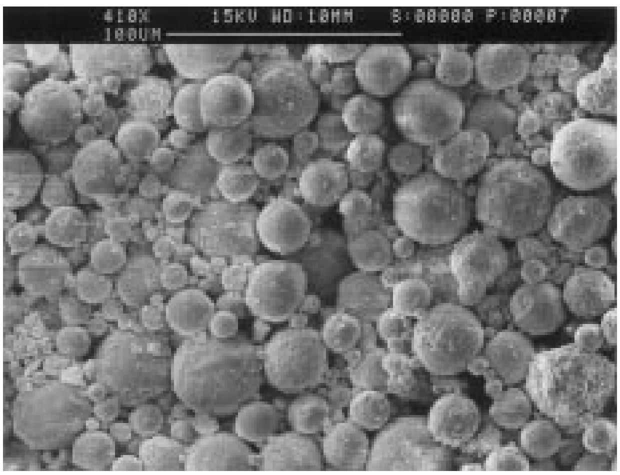

Fig. 6. SEM observation of powder after induction plasma treatment.

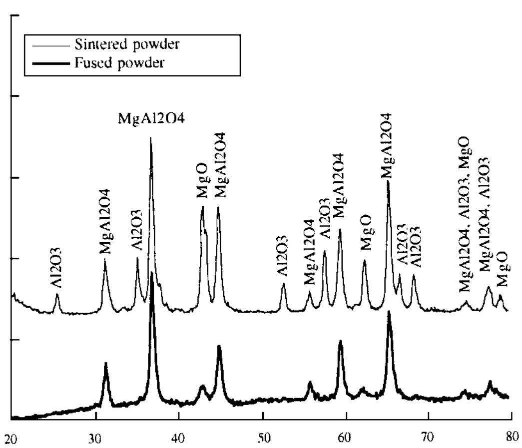

Fig. 7. XRD of $MgAl_2O_4$ powder after sintering and after fusion in induction plasma.

and Co ions are not in the same ionic environment as before sintering. Although spinel was the predominant phase, a secondary phase was detected in small quantity:

- for pure spinel or with adds of iron or zinc: periclase magnesia MgO;

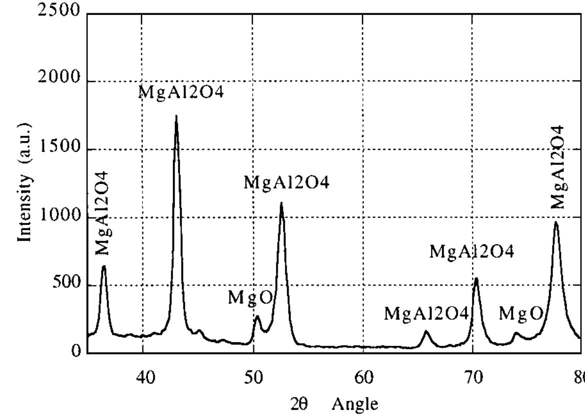

Fig. 8. XRD of $MgAl_2O_4$ coating.

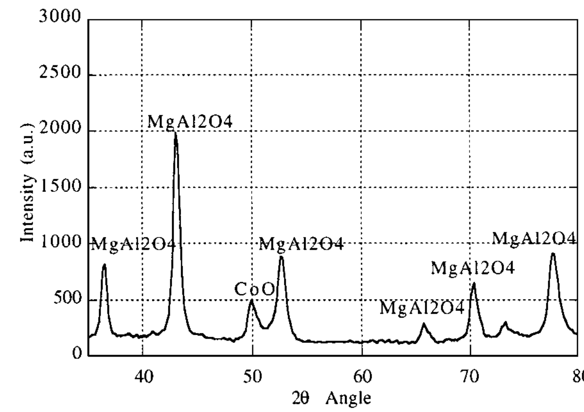

Fig. 9. XRD of $(Co,Mg)Al_2O_4$ coating.

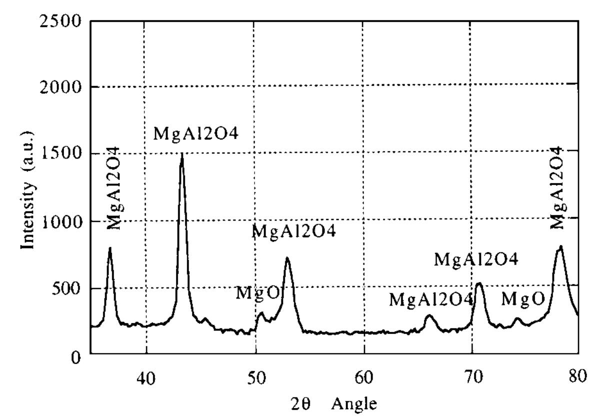

Fig. 10. XRD of $(Zn,Mg)Al_2O_4$ coating.

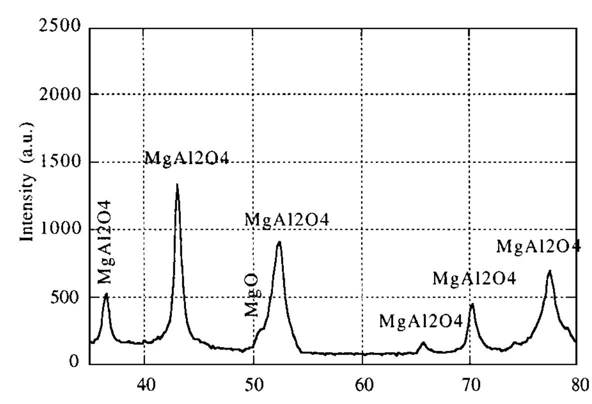

Fig. 11. XRD of $(Fe,Mg)Al_2O_4$ coating.

Fig. 12. SEM observation of a fracture facies of $MgAl_2O_4$ coating.

- for spinel with cobalt: cobalt oxide CoO.

Coatings were well crystallized and no glassy phase was observed, but the presence of MgO and CoO indicates that the composition of coatings was not very homogeneous.

The fracture faces of the $MgAl_2O_4$ coating are shown in Fig. 12. Coatings were made of lamellae resulting from the deformation of liquid particles during plasma spraying. These lamellae have a columnar structure, each grain being orientated perpendicularly to the spreading droplet surface.

3.3 Evolution of the composition

Chemical analyses (mineralization and plasma dosage) were performed on coatings which were detached from their substrate by a traction test and then finely crushed. X-ray microanalysis in the scanning electron microscopy (SEM) was also performed. The composition of the powders after spray-drying and of the coatings are given on Table 3. Except for spinel with zinc, the composition of the coatings was very close to the composition of the initial powder. The $(Zn,Mg)Al_2O_4$ plasma sprayed coating had a low zinc content of 3·6 at % compared with the initial composition of 16·5 at %. The successive thermal treatments had a large affect on the composition of the coating. During the preparation of the powder (during sintering and during the fusion in the induction plasma) and during plasma-spraying of the coatings, the oxide ZnO was preferentially eliminated compared to the other oxides because of the great volatility of ZnO (completely volatilized at 1400°C).[7]

Table 3. Composition of the powder after spray-drying and composition of the spinel coatings

Materials	*Powder composition after spray-drying (at %)*			*Spinel coating composition (at %)*		
	M	Mg	Al	M	Mg	Al
$MgAl_2O_4$		33	66		29·5	70·5
$(Fe,Mg)Al_2O_4$	7	26	66	4·6	30·3	65·1
$(Co,Mg)Al_2O_4$	16·5	16·5	66	16·8	17·4	65·8
$(Zn,Mg)Al_2O_4$	16·5	16·5	66	3·6	24·4	75

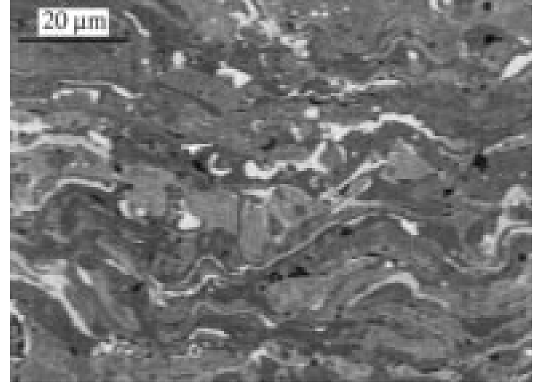

Fig. 13. SEM observation of the $(Co,Mg)Al_2O_4$ coating.

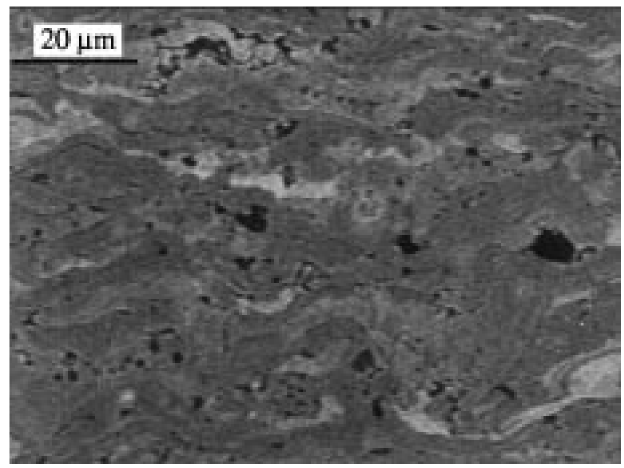

Fig. 14. SEM observation of the $(Zn,Mg)Al_2O_4$ coating.

3.4 Chemical homogeneity in coatings

Figures 13 and 14 show metallographic cross sections of $(Zn,Mg)Al_2O_4$ and $(Co,Mg)Al_2O_4$ coatings. Coatings were again made of a superposition of lamellae with pores between the lamellae. Color contrast is due to composition contrast, the brightest areas being the richest areas in heavy elements, i.e. cobalt or zinc. This contrast indicated that coatings were not very homogeneous in composition, particularly for coatings with cobalt. Figure 15(a) and (b) show the evolution of the composition in the $(Co,Mg)Al_2O_4$ coating. The distribution of cations is very different from one lamellar to another. This heterogeneity is related to the process of fabrication of the spraying powder, where elementary oxides are mixed together before spinel crystallization. Coatings are then made of stacked lamellae, each lamellar having the spinel structure but with its own composition.

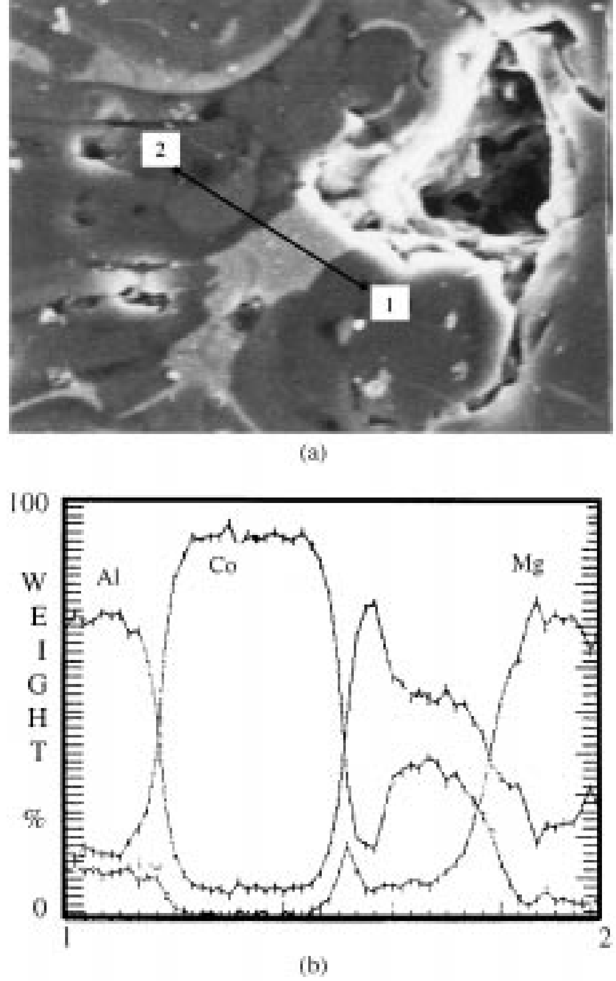

Fig. 15. (a) and (b) Composition evolution of the cations in the $(Co,Mg)Al_2O_4$ coating between points 1 and 2.

4 Conclusion

Spinel powders of various compositions have been manufactured for plasma spraying. They were obtained from elementary oxides such as MgO, Al_2O_3, Fe_2O_3, CoO and ZnO which were put into a slurry and spray-dried. Spinel structure was synthetized after two succesive heat treatments: sintering at 1150°C for 10 h in an electric furnace and then, fusion processing in an inductive plasma. After plasma spraying, the major phase of coatings was spinel. Because of the powder fabrication process, chemical heterogeneity was observed inside each coating. Further work will provide information on the microstructure of these coatings by transmisson electronic microscopy and on the adhesion of such coatings on metal substrates.

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