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Inhibition of the formation of the B metastable phase in yttrium oxide plasma-spray coatings by the addition of zirconia

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Yttrium oxide plasma-spray deposits show a metastable B phase together with the cubic stable form. This B form is prejudicial for thermal applications of these coatings (i.e. weakens mechanical properties, etc.). Attempts have been made to avoid the formation of this metastable phase during the plasma-spraying operation by use of an inhibitor, such as ZrO_2. A large solid solution with cubic C phase was found to form between ZrO_2 and Y_2O_3 ($Y_{1-x}Zr_xO_{1.5+x/2}\square_{0.5-x/2}$). A method is described for preparing powders suitable for plasma spraying. Several compositions were tested. B phase is no longer formed for ZrO_2 additions as low as $x = 0.03$. The influence of ZrO_2 addition on Y_2O_3 coatings properties is discussed.

1. Introduction

Owing to their thermal and mechanical properties, ceramic deposits are now widely used in several fields. Such coatings are mainly obtained by plasma-spray deposition. In this method, the molten particle undergoes an ultra-fast quenching and a high impact pressure on the substrate. This technique has been used to prepare yttrium oxide coatings. This oxide was chosen mainly because of its high refractoriness ($T_m = 2450\,°C$) [1].

Because of its similar properties, yttrium is classified as a lanthanide. Rare-earth oxides can adopt three stable forms, A (hexagonal), B (monoclinic) and C (cubic), according to the atomic number of the element, Fig. 1 [2]. Considering the size of the ion, Y^{3+} is identical to Ho^{3+} (0.104 nm) [3]. So, under normal pressure and temperature, Y_2O_3 exists only in the cubic form. However, a B-Y_2O_3 phase can be obtained by the combined effect of a very high pressure (25 kbar) and a high temperature (1000 °C) [4, 5]. This modification is metastable.

In a recent work [6], we reported the existence of a small quantity of this phase, together with the C stable form, in Y_2O_3 plasma-spray deposits. The examination of the influence of some spraying parameters has shown that this metastable phase is due to the impact pressure, the ultra-fast quenching keeping the phase down to room temperature [7]. In fact, this B modification may be converted to the stable cubic form by thermal treatment. The transition, which occurs between 400 and 700 °C, involves a significant volume increase ($\Delta V/V = 8.4\%$) and leads to a weakening of the mechanical properties of the coatings. Therefore, the existence of the B-Y_2O_3 phase in the coatings is prejudicial for their use, and it is necessary to avoid its formation during plasma spraying. With this aim, we have tried to stabilize the cubic C form by the addition of ZrO_2 to the starting powder. The ZrO_2–Y_2O_3 phase diagram shows the existence of a large range of solid solution, particularly in the Y_2O_3-rich domain [8]. This solid solution can be written $(1-x)\,YO_{1.5}\square_{0.5} + x ZrO_2 \rightarrow Y_{1-x}Zr_xO_{1.5+x/2}\square_{0.5-x/2}$.

This paper reports the preparation of such powders and a study of the deposits obtained.

2. Experimental procedure

2.1. Starting materials

Two methods were used to prepare the starting powders: coprecipitation in the amorphous state from precursors, and spray drying of Y_2O_3–ZrO_2 slurry.

2.1.1 Y_2O_3 – ZrO_2 solid solution obtained by coprecipitation

An amorphous precursor was obtained by coprecipitation of (Y, Zr) hydroxides by ammonium hydroxide, from a solution of zirconium and yttrium chlorides. The chloride solution was prepared by mixing the solution of $ZrOCl_2 \cdot 8H_2O$ in water, and Y_2O_3 in hot

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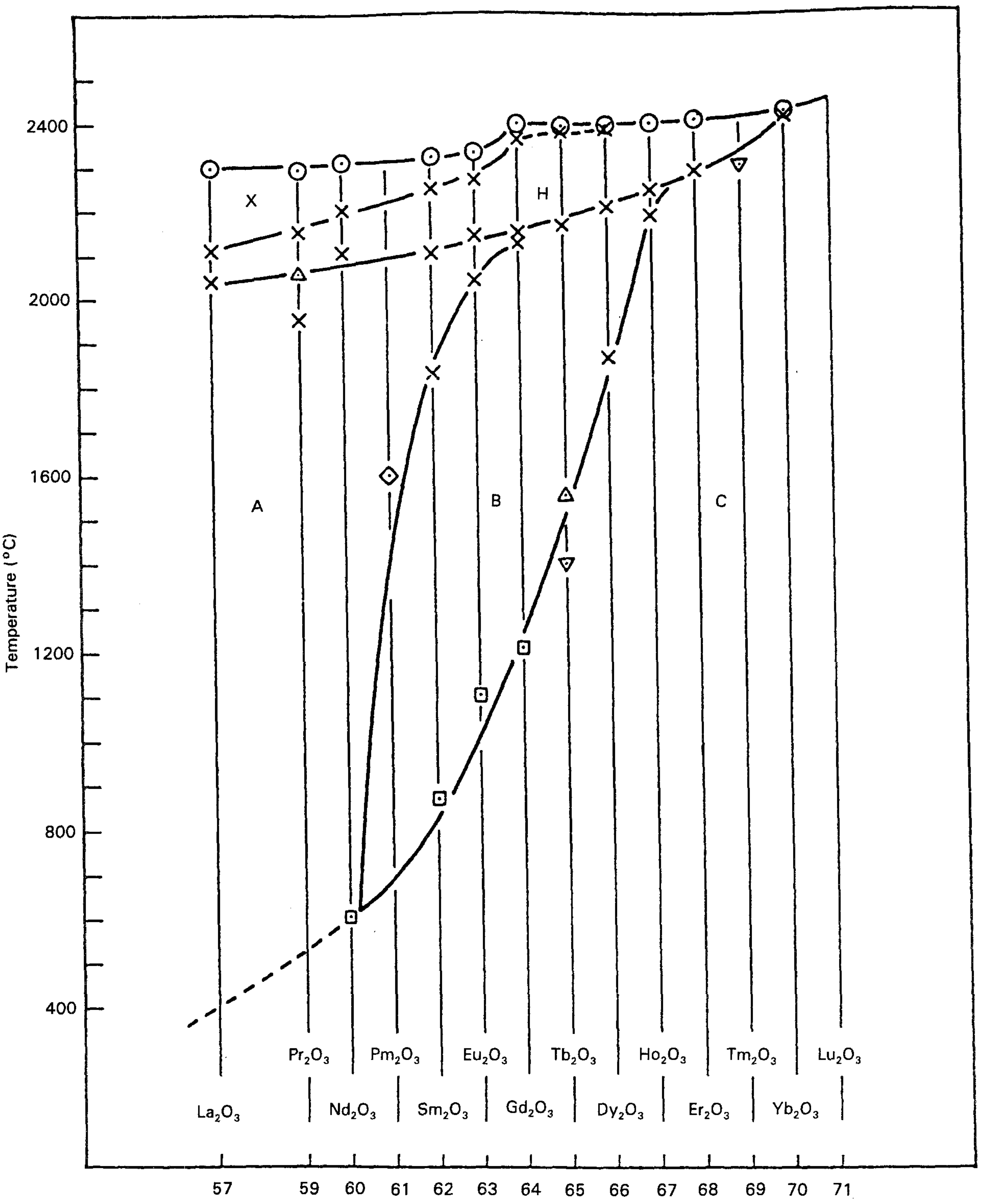

Figure 1 Stability relationships of rare-earth sesquioxides [2].

HCl. To remove water and NH_4Cl, the coprecipitate was heated at about 450 °C. However, yttrium oxychlorides can also be formed. Consequently, it is necessary to heat the product at temperature as high as 1000 °C to decompose these (YOCl, Y_3O_4Cl) and to form the crystallized solid solution $Y_{1-x}Zr_xO_{1.5+x/2}\square_{0.5-x/2}$ (only one composition was chosen, $x = 0.03$). For comparison, we have prepared, under the same conditions, a precipitate of pure Y_2O_3 without ZrO_2 ($x = 0$). In order to obtain a powder suitable for the plasma-spraying technique (specific granulometry), it is necessary to compact the product and to heat it at about 1500 °C. It is then crushed and sieved before the plasma operation.

However, the morphological powder obtained is not well adapted to the spraying, its flow to the plasma flame being poor. Therefore, another technique of powder preparation was developed.

2.1.2. Spray drying of $Y_2O_3 - ZrO_2$ mixtures

The spray drying process consists in transforming a fluid feed material (slurry) into a dry powder by spraying the feed into a hot drying medium. Here, the slurry is a water-based suspension of Y_2O_3 and ZrO_2 powders. A binder is added (polyvinyl alcohol) to provide strength in the compacted material. This slurry is pumped to an atomizer located in a drying

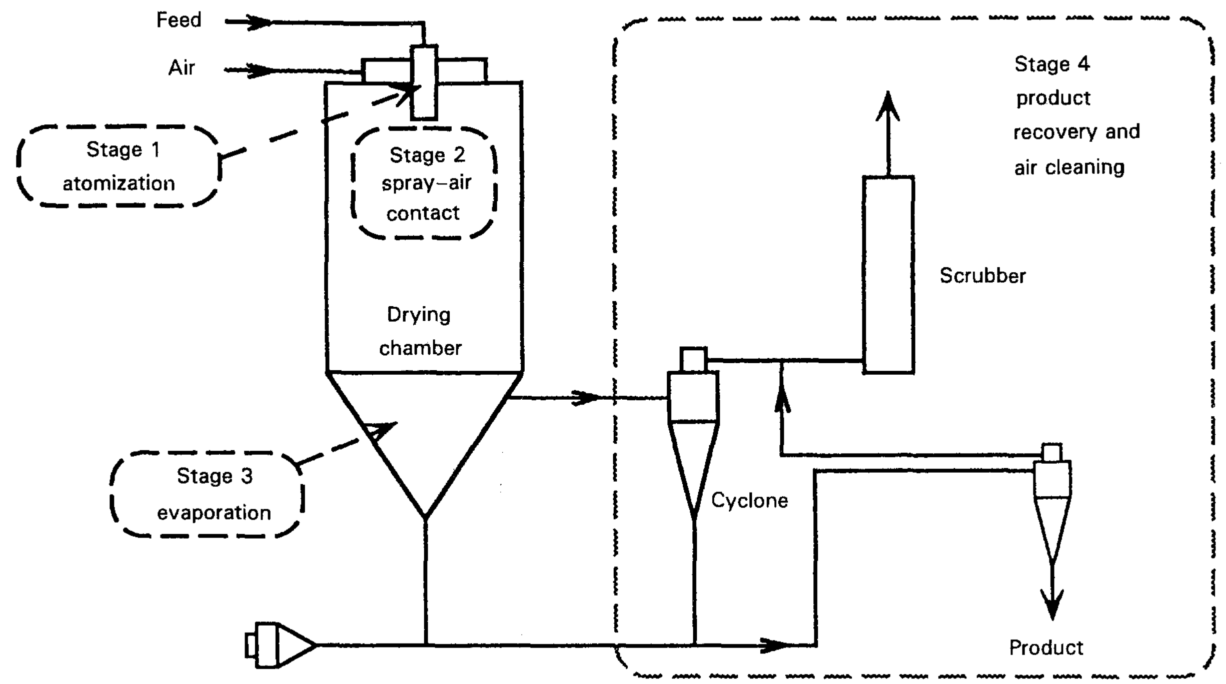

Figure 2 The spray-drying apparatus [9].

chamber (heated air) and broken into a large number of droplets which quickly achieve a spherical shape because of surface tension effects. There is a large surface/volume ratio of the droplets which allows a rapid evaporation of water. The obtained powder is separated from the hot air and stored. The apparatus is shown in Fig. 2. However, before use, it is necessary to remove the binder. Fig. 3 shows the morphology of a granule before thermal treatment at 1400 °C. Six compositions were prepared, corresponding to $x = 0, 0.015, 0.03, 0.05, 0.065, 0.08$ in the formula.

2.2. Plasma spraying

Deposits were obtained using a CEA (Commissariat à l'Energie Atomique)-patented technology and specific apparatus equipped with a "Plasma-Technick" treatment line [6]. The plasmagenic gas was a mixture of argon (40 $\mathrm{l\,min^{-1}}$) and hydrogen (10 $\mathrm{l\,min^{-1}}$). All experiments were performed in air. The substrate was graphite which was maintained at relatively low temperature (about 200 °C) using an air-cooling system (Vortex system). For mechanical tests, the substrate was separated from the coating by a dry cut-off with a diamond wheel.

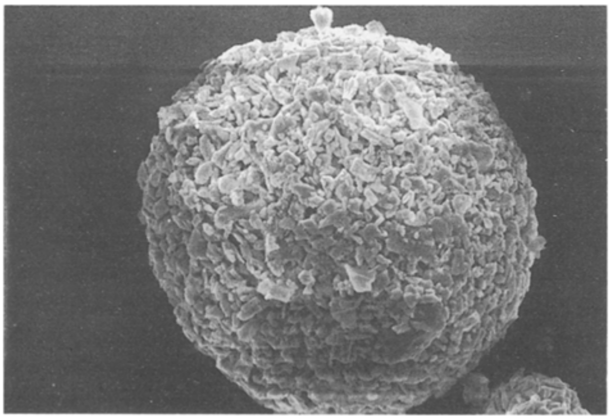

Figure 3 Scanning electron micrograph of a $Y_{0.97}Zr_{0.03}O_{1.515}\square_{0.485}$ granule before thermal treatment.

3. Results and discussion

The amount of B phase was determined by X-ray analysis using Gd_2O_3 as a reference, which can adopt both B and C forms. Standards were prepared with known proportions of B and C phases. These were calibrated by plotting the ratio of the B-line ($4\,0\,\bar{2}$; $3\,1\,0$, $1\,1\,\bar{2}$) and C-line ($4\,2\,0$) intensities against the percentage of B introduced in the standard mixture.

3.1. Deposits obtained from the Y_2O_3/ZrO_2 coprecipitate

To show the influence of ZrO_2 addition, a deposit containing ZrO_2 ($x = 0.03$ in the formula $Y_{1-x}Zr_xO_{1.5+x/2}\square_{0.5-x/2}$) was compared with a coating without ZrO_2 ($x = 0$). X-ray analysis of these samples is given in Table I. From this table, we note the role of ZrO_2. A small amount of this oxide is sufficient to avoid the formation of the B-Y_2O_3 phase. This result shows that the addition of ZrO_2 can inhibit B-Y_2O_3

TABLE I X-ray analysis of $Y_{1-x}Zr_xO_{1.5+x/2}\square_{0.5-x/2}$ deposits (from coprecipitate)

x (ZrO_2)	Amount of B form (%)	Unit cell parameter of the C form (nm)
0	4.5	1.0602
0.03	0	1.0582

occurrence during coating production. Otherwise, a variation in the unit cell parameter confirms that ZrO_2 forms a solid solution with Y_2O_3.

However, the coprecipitation method does not provide large amounts of starting material powders. Therefore, this method cannot be applied in industrial techniques.

3.2. Coatings obtained from a Y_2O_3/ZrO_2 mixture

Deposits with different ZrO_2 amounts ($x = 0$, 0.015, 0.03, 0.05, 0.065, 0.08) were prepared under the same conditions as in Section 3.1.

3.2.1. Structural investigations

The results of X-ray analysis are given in Table II. The main result of this study is that the presence of ZrO_2 inhibits the formation of $B\text{-}Y_2O_3$ phase.

Although the Y_2O_3/ZrO_2 solid solution is not formed in the starting powders, it is probably already present when the molten particles strike the substrate, and ZrO_2 plays the role of stabilizer. The unit cell parameter, a, of the C modification decreases when the ZrO_2 content increases, Fig. 4. The variation of a with x is linear.

We have determined the minimal quantity of ZrO_2 necessary to prevent the formation of $B\text{-}Y_2O_3$: it is in the range $x = 0.015 - 0.03$.

TABLE II X-ray analysis of $Y_{1-x}Zr_xO_{1.5+x/2}\square_{0.5-x/2}$ deposits (from Y_2O_3-ZrO_2 mixtures)

x (ZrO_2)	Amount of B form (%)	Unit cell parameter of the C form (nm)
0	7.8	1.0602
0.015	1.0	1.0591
0.030	0	1.0583
0.050	0	1.0571
0.065	0	1.0558
0.080	0	1.0547

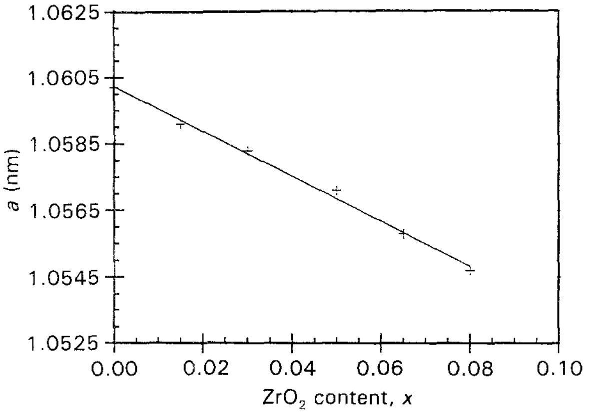

Figure 4 Variation of the C phase unit cell parameter a, with ZrO_2 content (x in the formula $Y_{1-x}Zr_xO_{1.5+x/2}\square_{0.5-x/2}$).

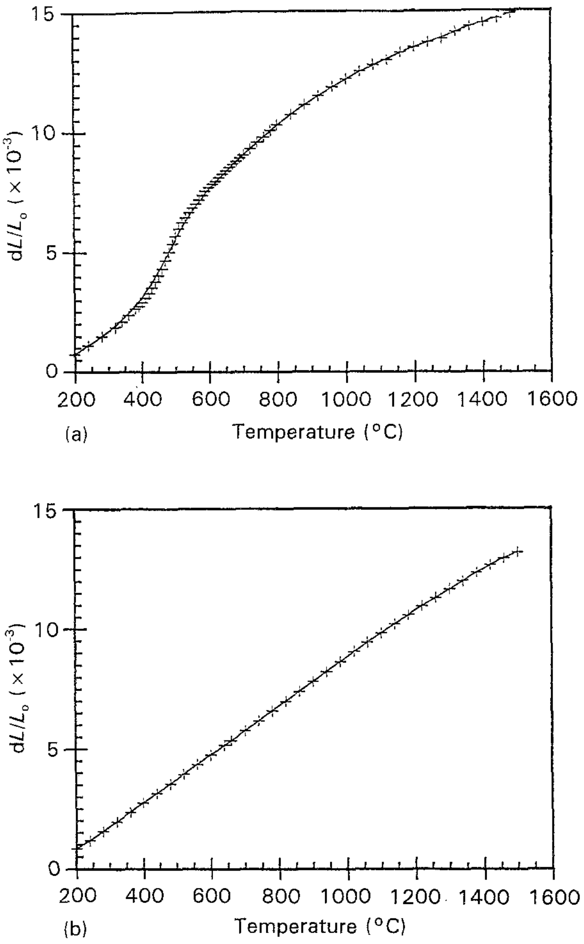

Figure 5 Dilatometric analysis of pure (a) Y_2O_3 and (b) Y_2O_3/ZrO_2 deposits.

Using dilatometric analysis we have compared the thermal behaviour of a pure Y_2O_3 deposit (B + C phases, Fig. 5a) with a coating containing ZrO_2 ($x = 0.05$, C form, Fig. 5b). The first heating curve of pure Y_2O_3 shows a significant dilatometric anomaly between 400 and 700 °C; this disappears in the cooling curve. A second heating does not show any anomaly. This behaviour is due to the metastable B form which converts irreversibily into the stable C form with a large increase in volume.

In the case of the Y_2O_3/ZrO_2 deposit, no anomaly was detected on the first heating curve. This result confirms the non-existence of the B variety in this deposit. ZrO_2 has stabilized the C form.

3.2.2. Mechanical properties

In order to determine the influence of C-form stabilization by ZrO_2 on the mechanical properties of the coatings, a thick deposit (2.7 mm) was prepared from a starting material Y_2O_3/ZrO_2 ($x = 0.05$). Small bars with 2.7 mm × 3 mm × 30 mm were cut. These samples were tested using the three-point bending method. The bars were of two types: as-sprayed or annealed. Porosity and density were also determined for each type. These results are summarized in Table III.

For comparison, previous results [6] on pure Y_2O_3 deposits, from commercial starting powder, are also reported. As-sprayed deposits contain $B\text{-}Y_2O_3$ phase which is prejudicial for mechanical properties after annealing at 700 °C, owing to the B → C transition.

TABLE III Mechanical behaviour (fracture strength, σ_f) of pure Y_2O_3 [6] and $Y_{0.95}Zr_{0.05}O_{1.525}\square_{0.475}$ coatings

Samples	Fracture strength, σ_f (MPa)		Density (g cm^{-3})		Porosity (%)	
	Y_2O_3/ZrO_2	Y_2O_3	Y_2O_3/ZrO_2	Y_2O_3	Y_2O_3/ZrO_2	Y_2O_3
As-sprayed deposit	53.5	61.2	4.72	4.73	7.4	6
Deposit annealed 5 h at 700 °C in air	52.2	47.5	4.75	4.62	6.8	8
Deposit annealed 8 h at 1650 °C in air	119.8	102.4	4.86	4.78	4.6	5

In the deposit stabilized by ZrO_2, the fracture strength, σ_f, is approximately constant when the temperature increases up to the point at which the sintering mechanism occurs. On the other hand, for pure Y_2O_3 coatings, the B → C transition induces a lowering of σ_f. This improvement only occurs when the sintering mechanism takes place.

4. Conclusion

In Y_2O_3 deposits obtained by the plasma-spraying technique, the presence of B metastable phase, together with the stable C form, is prejudicial to the mechanical properties of these coatings, because the B → C transition is accompanied by an important increase in volume.

To solve this problem, the addition of ZrO_2 to the initial powder can act as an inhibitor of the B form during plasma spraying.

An apparatus has been developed to prepare large quantities of Y_2O_3/ZrO_2 mixtures, suitable for the plasma-spraying technique. Amounts as low as $x = 0.03$ of ZrO_2 are sufficient to avoid the formation of the B variety in the coating. The mechanical properties of such deposits are good, because of the nonexistence of the B phase (no B → C transformation).

The stabilization of the C modification by the addition of ZrO_2 appears to be a good method for obtaining Y_2O_3 plasma-spray deposits which have good mechanical and refractory properties.

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