Effect of Precursor Chemistry on the microstructure of $Ba(Mg_{1/3}Ta_{2/3})O_3$ during Hybrid Suspension/Solution Precursor Plasma Spraying

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Abstract: In this study, three distinct solutions and/or suspensions were chosen as precursors to deposit $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) as thermal barrier coatings (TBCs) by induction plasma spraying. Coatings prepared with a Ta_2O_5 powder dispersed in a Ba and Mg salts solution as precursor show a dense microstructure with a high deposition rate. However, the inhomogeneous mixture leads to component segregation within the coating, with Ba-rich regions having a vertical crystal structure. Coatings sprayed from a solution precursor, where the Ta source is $Ta(OC_2H_5)_5$ stabilized with acetic acid, result in a partially columnar structure at short spraying distances. In this case, the component segregation in as-sprayed coating is attributed to reactor pressure fluctuations. Finally, a hydrolysed and gelatinous $Ta(OC_2H_5)_5$-based precursor results in a homogeneous coating microstructure.
Keywords: suspension plasma spraying, solution precursor plasma spraying, precursor chemistry, microstructure, component segregation, thermal barrier coating.

1. Introduction

To increase the thermal efficiency of turbines, a key strategy and difficult one is to prepare reliable thermal barrier coatings (TBCs) on the high-pressure part of turbine engines, for example the mobile blade [1]. Since 1980s, the most popular method to deposit coatings on the blade is electron beam physical vapor deposition (EB-PVD) [2]. TBCs deposited by EB-PVD show a long lifespan because of the quasi-single crystal columnar structure having large intercolumnar gaps between them; however, the deposition rate is very low [3]. As such, exploring new materials and new technologies with high deposition rate to replace the EB-PVD deposited yttria stabilized zirconia (YSZ) has been a fertile research topic in the last 20 years. For example, the complex perovskite $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) was chosen as a new TBC material considering its high melting temperature [4] and low thermal conductivity ~2W/m-K (bulk properties) [5]. BMT coatings sprayed by traditional air plasma spraying (APS) show a dense laminar structure with a short thermal cycle life [6]. In this work, a hybrid suspension/solution precursor plasma spray process is designed to deposit BMT nanostructured coatings with high deposition rate and a columnar structure. The effects of precursor chemistry on the microstructure of as-sprayed coatings and deposition rate are discussed.

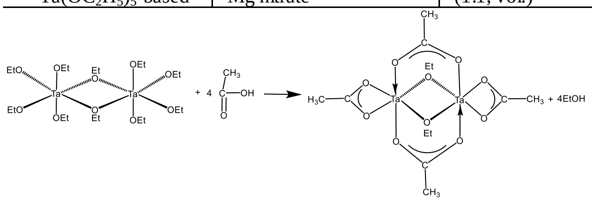
2. Methodology

Three kinds of suspensions and/or solutions were used in this work to synthesize and deposit BMT coatings, as seen in Table 1. Mg nitrate $Mg(NO_3)_2 \cdot 6H_2O$ (Alfa Aesar, America, 11564) and Ba nitrate $Ba(NO_3)_2$ (Sigma-Aldrich, Germany, 217571) were chosen as Mg and Ba precursor in all conditions, and twice the stoichiometric amount of Mg nitrate was added [7]. Nanocrystallized Ta_2O_5 [7] was used prepare the Ta_2O_5-based suspension in the salt solution. Because of the insolubility of Ta_2O_5 and $Ba(NO_3)_2$ in ethanol, they were dispersed by ultrasonic and magnetic stirring to form the precursor labelled S1.

For the precursors S2 and S3, $Ta(OC_2H_5)_5$ (Henan Tianfu Chemical Co. Ltd, China) is the tantalum precursor. Since the Mg nitrate salt is hydrated, the water molecules can lead to the hydrolysis of $Ta(OC_2H_5)_5$. Accordingly, acetic acid $C_2H_4O_2$ was added to stabilize $Ta(OC_2H_5)_5$ in precursor S2, as seen in formula 1. Insoluble $Ba(NO_3)_2$ is then dispersed in the transparent solution of $Mg(NO_3)_2$ and $Ta(OC_2H_5)_5$. As for precursor S3, water is added to the solvent to dissolve $Ba(NO_3)_2$. The large amount of water hydrolysed $Ta(OC_2H_5)_5$ and produced a gel. The complex chemical reaction is summarized in formula 2. The gelatinous precursor S3 has a homogeneous morphology and its particle size distribution is shown in Fig.1. The suspension/solution solid concentration is kept constant at 10 wt.% for the three precursors.

Table 1. List of suspension/solution precursors combinations

No.	Solute	Solvent
S1: Ta_2O_5-based	Nanocrystallized Ta_2O_5 Ba nitrate, Mg nitrate	Ethanol
S2: Stabilized $Ta(OC_2H_5)_5$-based	Acetic acid stabilized $Ta(OC_2H_5)_5$, Ba nitrate, Mg nitrate	Ethanol
S3: Fully hydrolyzed $Ta(OC_2H_5)_5$-based	$Ta(OC_2H_5)_5$, Ba nitrate, Mg nitrate	Ethanol : Water (1:1, vol.)



(1)

$$Ta_2(OC_2H_5)_{10} + 5\ H_2O \rightarrow Ta_2O_5\ (gel) + 10\ C_2H_5OH \qquad (2)$$

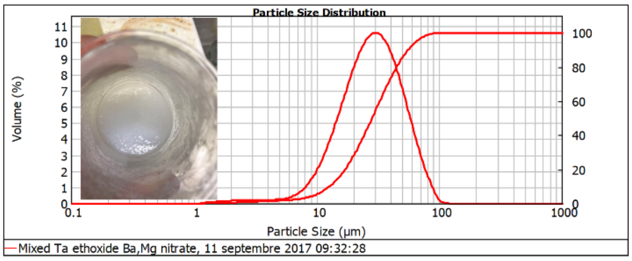


Fig. 1. Morphology of gelatinous precursor S3 and its particle size distribution.

The precursors S1, S2 and S3 were injected axially into an inductively coupled thermal plasma torch (PL-50, Tekna Plasma Systems Inc., Sherbrooke, Québec, Canada), as shown in Fig. 2. Coatings were formed on the surface of Ti-6Al-4V substrates. The plasma parameters used for coating deposition are shown in Table 2.

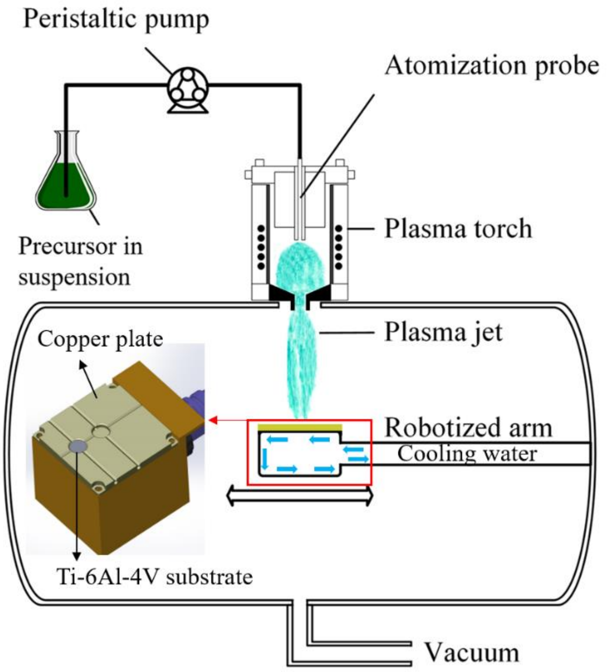


Fig. 2. Schematic reactor for BMT coating preparation

Table 2. Plasma parameters for BMT coating preparation.

Sheath gas (Ar)	6 slpm
Sheath gas (O_2)	63 slpm
Central gas (Ar)	23 slpm
Feeding rate	4 ml/min
Reactor pressure	15 kPa
Power	50 kW
Stand-off distance	34/60/80 mm/100mm
Translational	50 mm/s

3. Characterizations

The morphology of the coating surfaces and cross-sections were analysed by Scanning Electron Microscopy (SEM) (S-3000N, Hitachi, Japan) equipped with Energy-dispersive X-ray spectroscopy (EDS). The distribution of lamellae diameter was obtained by image analysis with Image J software (NIH, Bethesda, MD, USA).

4. Results and discussion

As-sprayed coatings with S1 show a dense lamellar structure for all spraying distances, as seen in Fig. 3 (left). Since the density of liquid or molten droplets is maximum at the outlet of the torch and decreases with distance, the deposition rate is also maximum at short spray distances. The coating sprayed at 80 mm shows a smooth surface morphology (f), while at 34 mm (b) the surface is rougher.

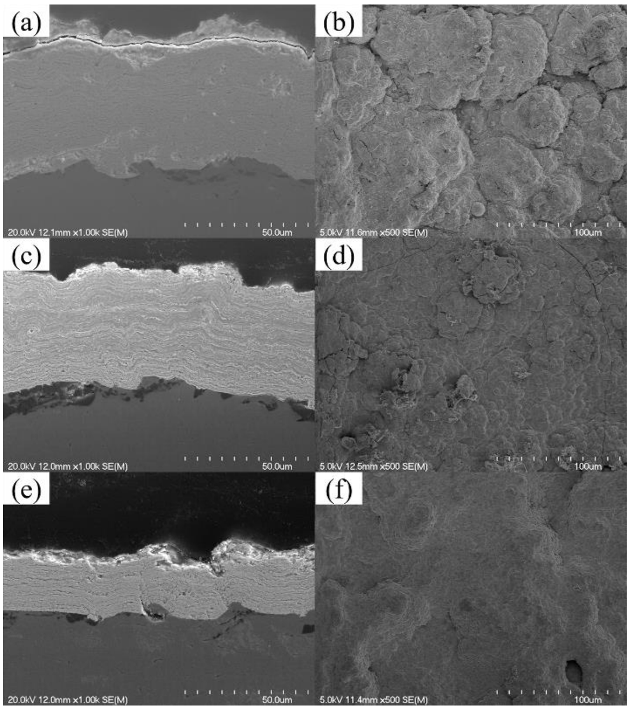


Fig. 3. SEM micrographs of cross-sections (left side) and surfaces (right side) of coatings sprayed with S1 for different spray distances (a)(b) 34 mm, (c)(d) 60 mm, (e)(f) 80 mm.

Without a chemical dispersant, ultrasonic and magnetic stirring are insufficient to stably disperse the solid powder (Ta_2O_5). Ta_2O_5 settled and the suspension S1 became inhomogeneous during spraying. As such, Ta oxide splats accumulated together and formed a continuous layer, as seen in Fig. 4a. As a result, component segregation occurred in as-sprayed coating. The magnified region clearly reveals three different phases (Fig. 4b): Ta-rich phases present a lamellar structure, Ba-rich phases are in the form of vertical crystals, and Mg-rich phases appear as black dots.

As-sprayed coatings with S2 show microstructures that varied with spray distance, from 34 mm to 80 mm, as seen in Fig. 5 (left). Compared to Ta_2O_5 used in S1, dissolved $Ta(OC_2H_5)_5$ in S2 makes a better (more homogeneous) solution that can form more tiny droplets during spraying. With a short spraying distance, the small molten droplets formed a pseudo-columnar structure initiated by surface roughness (raised and sharp hump or the heart-shaped black sand), as seen in the Fig. 5a-b. With a long spraying distance, molten droplets formed a dense lamellar structure, even near the raised hump, as seen in Fig. 5e-f.

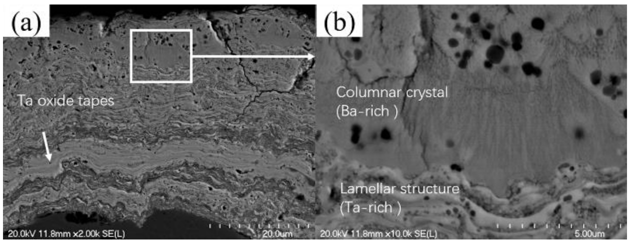


Fig.4. Component segregation of coatings sprayed at 80 mm using the inhomogeneous precursor S1.

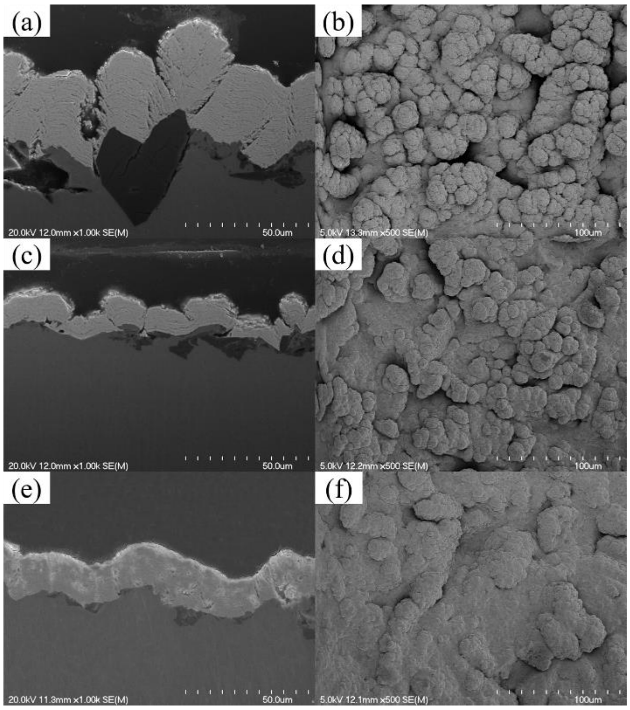


Fig. 5. SEM micrographs of cross-sections (left side) and surfaces (right side) of coatings sprayed with S2 at different spray distances (a)(b) 34 mm, (c)(d) 60 mm, (e)(f) 80 mm.

With precursor S2, Ba nitrate remains insoluble in ethanol, which may lead to the component segregation observed by EDS along the columnar structure, as seen in Fig. 6. The columnar structure is separated into two regions: a Ba-rich periphery and a Ta-rich central part.

In order to avoid the inhomogeneity of a suspension, water was added to dissolve Ba nitrate in precursor S3, but it also hydrolysed $Ta(OC_2H_5)_5$ to form a homogeneous gel. The reaction product shows gelatinous state S3. The coatings sprayed with S3 show a similar lamellar structure at long spraying distances (Fig. 7a, 7b), but present vertical cracks at short spraying distance instead of a columnar structure, as seen in Fig. 7c. Tilting the sample holder by 60° formed columnar structures, as seen in Fig. 7d. It is caused by the shadow effect.

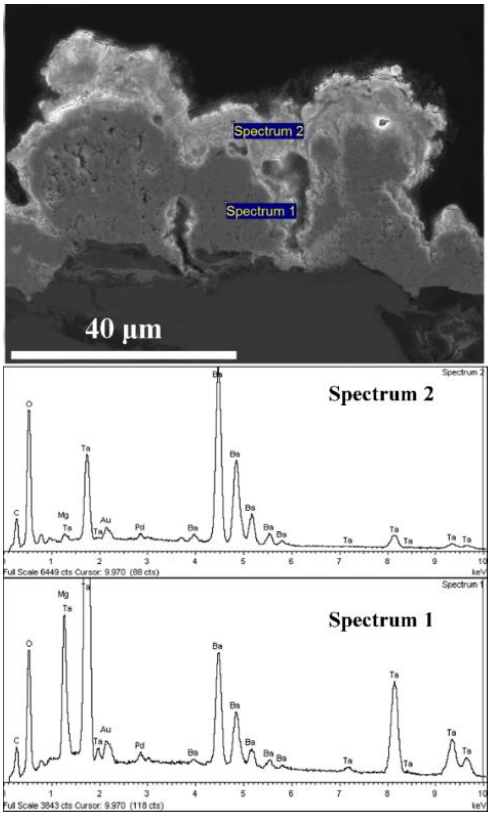


Fig.6. Component segregation of coatings sprayed at 34 mm using the inhomogeneous precursor S2.

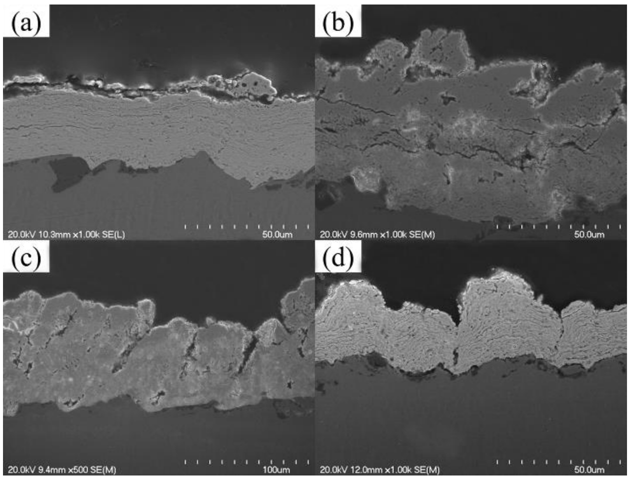


Fig.7. Cross-sectional images of coatings sprayed with precursor S3 at different spraying distances. (a) 80 mm, (b) 60 mm, (c) 34 mm and (d) 100 mm with a 60° spraying angle.

In order to appreciate the differences between the molten droplets of precursors S1, S2 and S3 during spraying, collected lamellae morphologies and diameters are analyzed in Fig. 8. Because of the high density of molten droplets at the outlet of the torch, it is hard to collect separate splats at 34 mm even with a single pass coating. The splat diameter distributions (analyzed by image J) of distinguishable lamellae are shown in Fig. 8d. Single pass coatings sprayed with S1 (Fig. 8a) and S2 (Fig. 8b) have much small splat diameters, whereas the gelated precursor S3 formed the largest splats, as seen in Fig.8c and 8d.

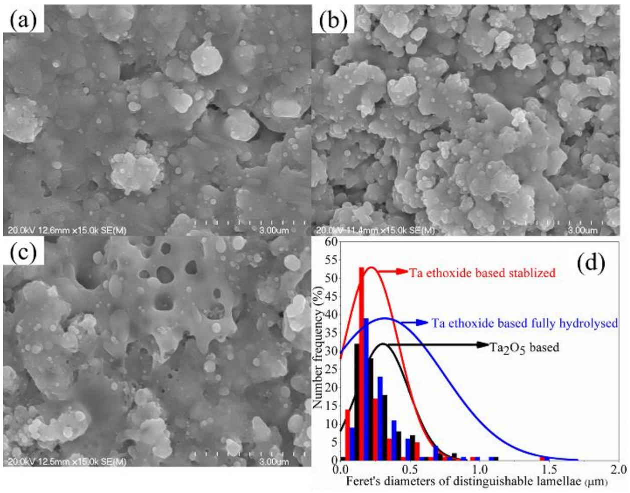


Fig.8. SEM micrographs of single pass coatings at 34 mm sprayed with precursors (a) S1, (b) S2 and (c) S3. (d) shows the distributions of distinguishable lamellae diameters.

5.Conclusion

Three kinds of suspension and/or solution precursors were used to spray BMT coatings: Ta_2O_5-based precursor S1, acetic acid stabilized $Ta(OC_2H_5)_5$-based precursor S2 and fully-hydrolysed $Ta(OC_2H_5)_5$-based precursor S3. Different spraying distances were also tested for each precursor. Coatings sprayed with precursor S1 had the highest deposition rate, but they always showed a dense lamellar structure. Coatings sprayed with S2 produced a pseudo-columnar structure at short spraying distance (34 mm). Component segregation happened in coatings sprayed with S1 and S2, likely because of their inhomogeneous suspension-based precursors. When injecting precursor S3, large molten droplets formed which led to large splats on the coating surface. Coatings sprayed with S3 resulted in a microstructure with vertical cracks at the short spraying distance (34 mm) instead of a columnar structure. When changing the spraying angle to 60°, a pseudo-columnar structure was obtained at a 100 mm spraying distance because of the shadow effect.

Acknowledgements

The financial support by the Fonds de recherche du Québec - Nature et technologies (FRQNT), the Natural Sciences and Engineering Research Council of Canada (NSERC), and the Université de Sherbrooke is gratefully acknowledged. The authors also appreciate the technical support from Marc G. Couture and Kossi Béré.

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