Synsint Research Group

Available online at www.synsint.com

Synthesis and Sintering

ISSN 2564-0186 (Print), ISSN 2564-0194 (Online)

*Research article*

# Influence of preheating temperature on splat morphology of spray deposited yttria-stabilized zirconia and lanthanum magnesium hexaaluminate in thermal barrier coatings

**Mohammad Mehdi Khorramirad [a,*], Mohammad Reza Rahimipour [b], Mohammad Mehdi Hadavi [c], Kourosh Shirvani [d]**

[a] *Faculty of Materials and Metallurgical Engineering, Semnan University, Semnan, Iran*
[b] *Ceramic Department, Materials and Energy Research Center (MERC), Karaj, Iran*
[c] *Department of Materials Engineering, Tarbiat Modares University, Tehran, Iran*
[d] *Department of Advanced Materials and New Energies, Iranian Research Organization for Science and Technology (IROST), Tehran, Iran*

ABSTRACT

The performance of thermal barrier coatings (TBCs) depends upon the morphology of individual splats and how a single particle flattens. A splat is a single unit cell of thermal barrier coatings. Its properties significantly influence the overall performance of the coating. The transition temperature of the substrate affects the splat morphology and influences the adhesion strength of the applied coating. This study investigates the effect of substrate preheating temperature on splat morphology and the critical transition temperature for yttria-stabilized zirconia (8YSZ) and lanthanum magnesium hexaaluminate ($LaMgAl_{11}O_{19}$, LaMA) powders deposited via atmospheric plasma spray (APS). Using scanning electron microscopy (SEM), a critical transition temperature of 400 °C was identified for both materials. Disc-shaped splats with improved adhesion formed at this temperature, while irregular shapes were observed below 400 °C, and disordered morphologies appeared above it. Notably, at 400 °C, 8YSZ splats exhibited surface cracks, whereas LaMA splats remained crack-free, highlighting differences in their thermo-mechanical properties. These findings emphasize the importance of optimizing preheating temperature to achieve desirable splat morphology and enhance TBC performance.


KEYWORDS

Thermal barrier coating
Splat
Transition temperature
Yttria-stabilized zirconia
Lanthanum magnesium hexaaluminate
Preheating

OPEN ACCESS

## 1. Introduction

Plasma spray coating is a common method used in deposition techniques for functional materials. It involves impingement and solidification of semi-molten or molten particles onto a substrate, creating individual splats, which are small, flattened droplets [1]. The deposition of splats coalesces to create the final coating [1]. The shape and structure of the splats are key factors in determining the general properties of the plasma spray coating [1–5], for example, its hardness, porosity, and mechanical strength [4]. To optimize coating properties, understanding the factors influencing splat morphology is crucial. Splat formation is a complex phenomenon governed by a combination of factors [3, 4]. Current models emphasize the effects of particle properties such as size, velocity, and thermophysical properties, as well as spray conditions, including temperature and velocity, substrate properties, including topography and preheating, and the surrounding

* Corresponding author. *E-mail address:* mm.khorramirad@semnan.ac.ir (M.M. Khorramirad)
Received 15 November 2024; Received in revised form 6 March 2025; Accepted 6 March 2025.

https://doi.org/10.53063/synsint.2025.51262

gas [3, 4]. These models usually consider the coupling between mass, momentum, and energy conservation during the phenomena of droplet impact and solidification [4]. The solidification process plays a key role in defining the morphology of splats [4]. Extended solidification, promoted by high substrate temperatures, promotes the formation of disk-like splats with low fragmentation [4]. In contrast, rapid solidification can result in splashing and fragmentation [4]. The ambient gas may also affect the development of splat by providing pathways for gas entrapment beneath the droplet, which can result in void formation in the coating [4]. The preheating temperature of the substrate is one of the most critical factors determining the splat morphology [1]. Exceeding a critical transition temperature (Ttr) promotes the formation of disk-like splats with a higher bonding strength [1, 2]. This transition has been attributed to factors including improved wettability, surface topographic changes, and the influence of adsorbates/condensates on the substrate [3].

The microstructure of TBCs, especially the morphology of individual splats formed during plasma spraying, considerably affects the overall performance of the coating. Understanding the parameters affecting the splat formation is necessary for the improvement of thermal barrier coating properties. Among the diverse TBC materials, yttria-stabilized zirconia (8YSZ) [6–11] and lanthanum magnesium hexaaluminate (LaMA) [10, 12–17] have been widely studied because of their excellent thermal properties. This study investigates the influence of substrate preheating temperature on splat morphology in 8YSZ and LaMA thermal barrier coatings (TBCs) deposited by atmospheric plasma spray (APS) deposition. The objective is to explain the correlation between substrate preheating temperature and the resulting splat morphology in these two TBC systems.

## 2. Materials and Methods

The LaMA powder was synthesized via a solid-state reaction route, as described in previous research works [16, 17]. $La_2O_3$ (MERCK 12220), MgO (ALDRICH 34279-3), and $\gamma$-$Al_2O_3$ (MERCK 101095) were used as the starting materials. To synthesize the LaMA powder, the raw materials were carefully weighed based on the stoichiometric ratios needed for the desired compound. Distilled water was added to the powder mixture to form a smooth, paste-like consistency. This mixture was then ball-milled in a planetary ball mill for 24 hours, using a ball-to-powder weight ratio of 10:1 and a rotation speed of 250 rpm. After milling, the mixture was dried in an oven. Finally, the dried powder was calcined in an electric furnace at 1400 °C for 6 hours in air to produce the hexaaluminate powder [16]. The 8YSZ powder (METCO-204NS-G) was supplied by Oerlikon Metco. To improve the flowability of the synthesized LaMA powders, a granulation treatment was performed. Polished stainless-steel plates were used as substrates. These substrates were ultrasonically cleaned in acetone and ethanol. Then the substrates were dried in an oven and heated to 100 °C for 60 minutes. Splats of LaMA and 8YSZ powders were prepared using an atmospheric plasma spraying (APS) system. To investigate the critical preheating temperature (also referred to as the transition temperature, Ttr) for LaMA and 8YSZ coatings, three samples were preconditioned and heated to temperatures of 200 °C, 400 °C, and 600 °C respectively. For this study, a custom-built, low-height furnace with a top-opening door was designed and constructed to preheat the samples. The furnace can operate at a maximum temperature of 1000 °C and is equipped with a PID temperature controller to ensure precise temperature regulation. The interior of the furnace is lined with high-purity alumina refractory bricks to maintain thermal stability and minimize contamination of the samples. The preheating temperature was measured and controlled using three thermocouples. The splat conditions were kept the same as the final coating conditions, as detailed in Table 1. A 3MB Metco plasma gun was employed for the process. The argon flow rate was set to 2.265 $m^3/h$, and the hydrogen gas flow rate was maintained at 0.425 $m^3/h$. The current and voltage were fixed at 500 A and 55 V, respectively. The powder feed rate was set to 11.34 kg/h, and the spray distance was maintained at 8 cm. These parameters were carefully selected to ensure optimal coating quality and consistency. The LaMA or 8YSZ powders were sprayed onto the preheated substrates using the APS system. The morphology of the splats was examined using VEGA-TESCAN SEM. A thin layer of gold was deposited onto the samples before SEM analysis. A Siemens D500 X-ray diffractometer was used for the Phase identification using Cu(Kα) radiation, scanning from 10 ° to 80 ° with a step size of 0.02 °.

**Table 1.** Plasma spray deposition parameters.

| **Gun type** | 3MB Metco |
|---|---|
| **Argon flow rate ($m^3/h$)** | 2.265 |
| **Hydrogen gas flow rate ($m^3/h$)** | 0.425 |
| **Current (A)** | 500 |
| **Voltage (V)** | 55 |
| **Powder feed rate (kg/h)** | 11.34 |
| **Spray distance (m)** | 0.08 |

## 3. Results and discussion

The crystal structure and morphology of the synthesized powders were characterized using SEM and XRD, as illustrated in Figs. 1 and 2, respectively. The SEM micrograph in Fig. 1 reveals that the synthesized LaMA powder exhibits a platelet-like morphology with a high aspect ratio and a thickness of approximately 446 nm [16, 17], which agrees with previous studies [13, 18]. The [0001] crystallographic direction of LaMA has the slowest growth rate, leading to the formation of these platelet-like particles [13, 18]. The SEM image of the granulated LaMA powder is shown in Fig. 3. The XRD pattern of the white LaMA powder (Fig. 2) matches well with the JCPDS cards for LaMA (ICDD 0873-026-00, ICDD 1845-078-00 Standard PDF Cards). This confirms the formation of the pure LaMA phase [16, 17].

The properties of thermal spray coatings are closely linked to the shape of individual splats and how each particle flattens. Since a splat is the smallest unit of the entire coating, its characteristics can be extended to the overall coating properties. The transition temperature affects the morphology of the splats and the adhesion strength. With an increase in the proportion of disk-shaped splats, the adhesion strength of the coating is enhanced [1].

Among the most likely mechanisms for splat morphology modification are surface topography alteration, surface

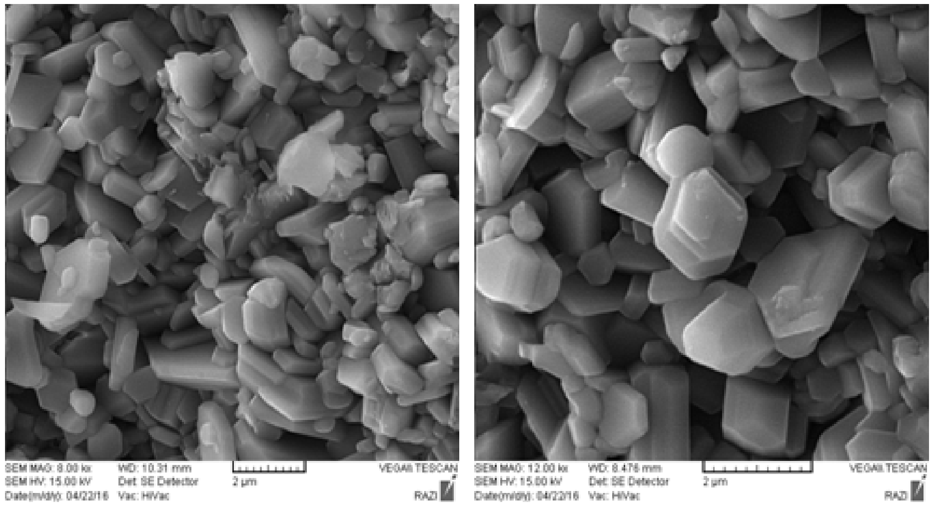

**Fig. 1.** Synthesized LaMA powders with different magnifications [16, 17].

chemistry modification by preheating the substrate, evaporation of surface-adsorbed species, and solidification, which were studied by Pakseresht et al. [2, 3] on barium titanate. Fig. 4 shows irregular splats of LaMA with radially outward fingers at a preheating temperature of 200 °C. Fukumoto et al. attribute the formation of splashed splats to the solidification of molten droplets as they spread over the substrate [19].

In addition, three models have been proposed for splat spattering: 1) the adsorbed gas model, 2) the substrate melting model, and 3) the K model. In the K model, the parameter K is a function of the Weber and Reynolds numbers and is not applicable under plasma spray conditions [1].

According to Sampath and Herman [20], the solidified particles exhibit a characteristic three-zone microstructure resulting from thermal gradients: (1) central equiaxed grains formed through rapid cooling at the particle-substrate interface, (2) radially elongated grains in peripheral regions developing under slower cooling rates due to indirect heat transfer, and (3) an outer rim with minimal thermal contact. This specific morphological configuration was exclusively observed in LaMA-processed splats at substrate temperatures below 200 °C, as further supported by the experimental data presented in Figs. 5 and 6 of this study.

Over 50% of the splats formed fully disc-shaped at a substrate preheat temperature of 400 °C. A sample of the disc-shaped splats is shown in Fig. 7. Increasing the substrate temperature resulted in the transformation of the splats from teardrop-shaped to disc-shaped, but the three structural regions were no longer

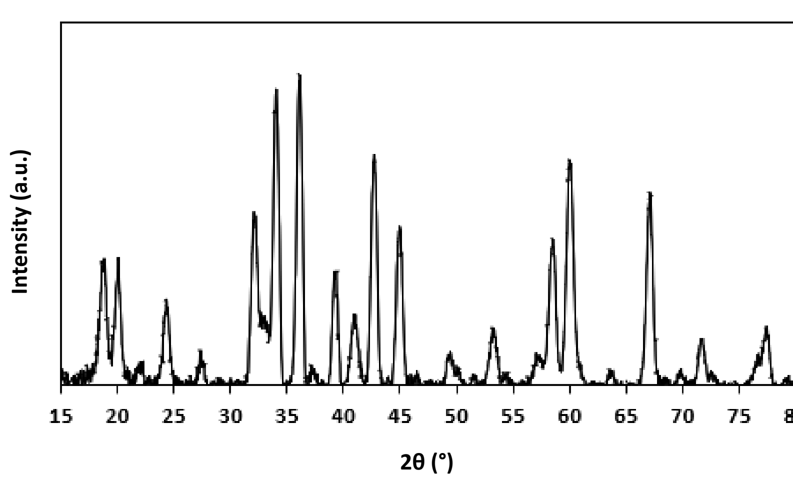


**Fig. 2.** XRD pattern of synthesized LaMA powders.

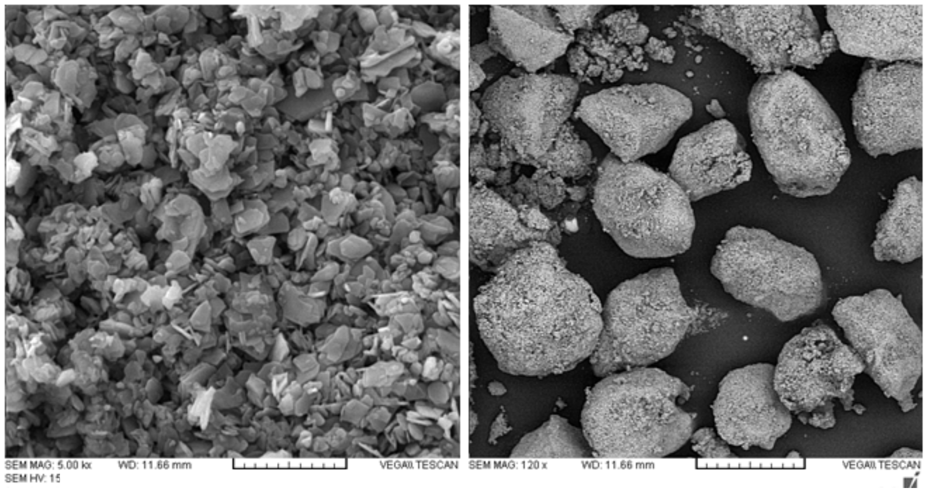


**Fig. 3.** Granular LaMA powders with different magnifications.

observed in the splats. It is thought that the size of the molten particles and the volume of the melt play a role. In other words, as the size and volume of the molten particles decrease, the three characteristic regions of the splats are no longer observed. At temperatures above the transition temperature, a disordered morphology is observed in the LaMA splats, as shown in Fig. 8.

Figs. 9, 10, and 11 display the 8YSZ splats morphology at different preheat temperatures of 200, 400, and 600 °C, respectively. As can be seen, the splats change morphology from teardrop-shaped to disc-shaped at 400 °C (Fig. 10), and then to a disordered morphology at 600 °C (Fig. 11). The splats at 400 °C (Fig. 10) are disc-shaped, but unlike the LaMA splats, they have cracks on the surface. This difference is attributed to the varying thermal and mechanical properties of the LaMA and 8YSZ. The change in morphology of the splats is thought to be due to the combined effects of surface tension, viscosity, and thermal stress. The cracks on the surface of the 8YSZ splats are thought to be caused by the differing thermal expansion coefficients of the splat and the substrate. The different thermal-mechanical properties of 8YSZ and LaMA are thought to be due to the different crystal structures of the two materials.

The morphology of splats at high temperatures is disrupted for both 8YSZ and LaMA powders. This is attributed to the development of a surface oxide layer and an enhancement of surface roughness. Pasandideh-Fard et al. revealed that the oxide layer was present on the surface even at low temperatures, and its thickness increased with increasing temperature. The formation of the oxide layer on the surface led to the higher thermal resistance at the interface [19]. As surface roughness increases, the spacing between peaks and valleys also increases. This causes molten droplets to first impact the peaks and then flow down the slopes, disrupting the splat morphology.

In this study, considering the similarity of the final coating conditions and the splat study conditions, a transition temperature of 400 °C is approximately assumed for both LaMA and 8YSZ compositions.

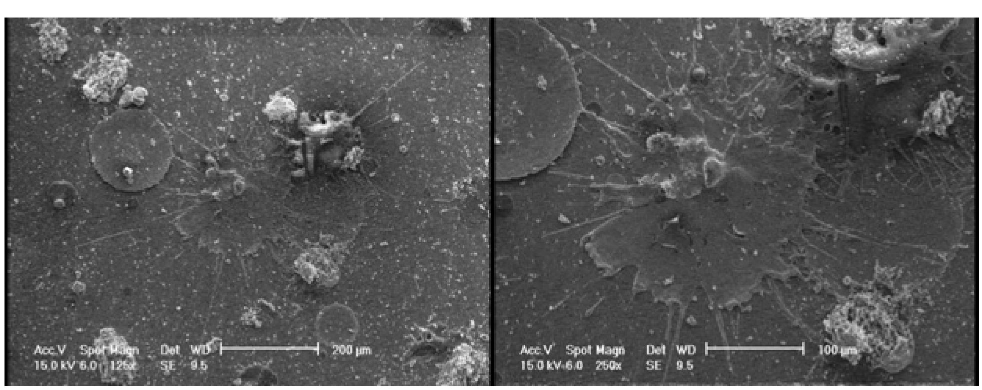


**Fig. 4.** LaMA splat morphology (preheating temperature: 200 °C).

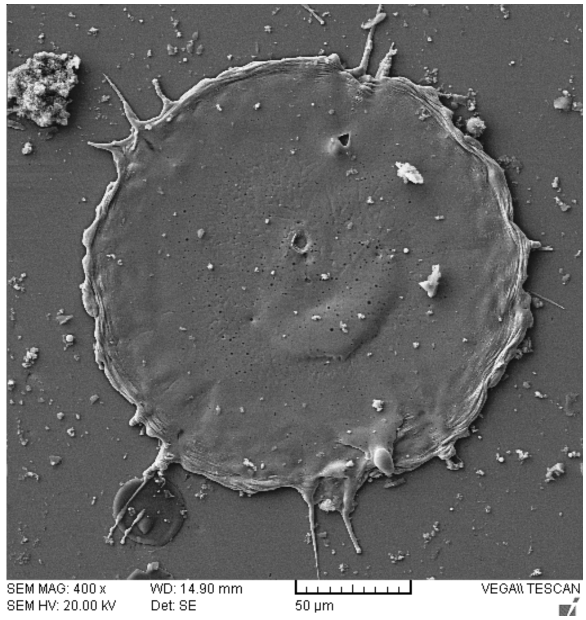


**Fig. 5.** LaMA splat morphology (preheatking temperature: 200 °C).

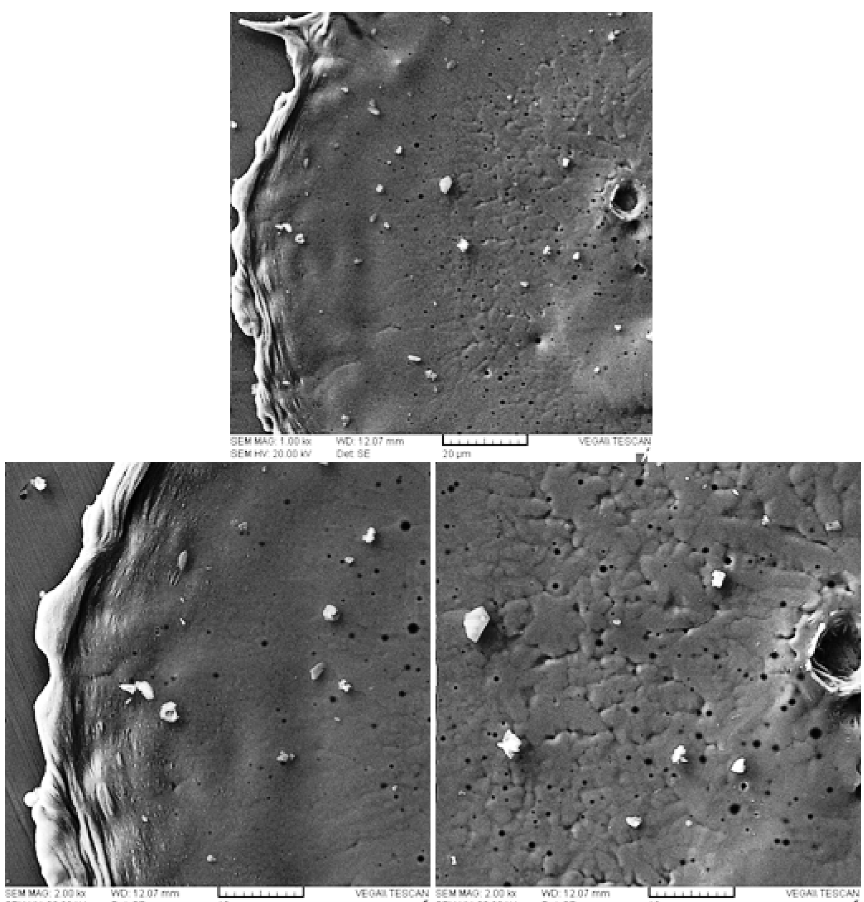

**Fig. 6.** Micrograph at higher magnification of different regions of a LaMA splat (preheating temperature: 200 °C).

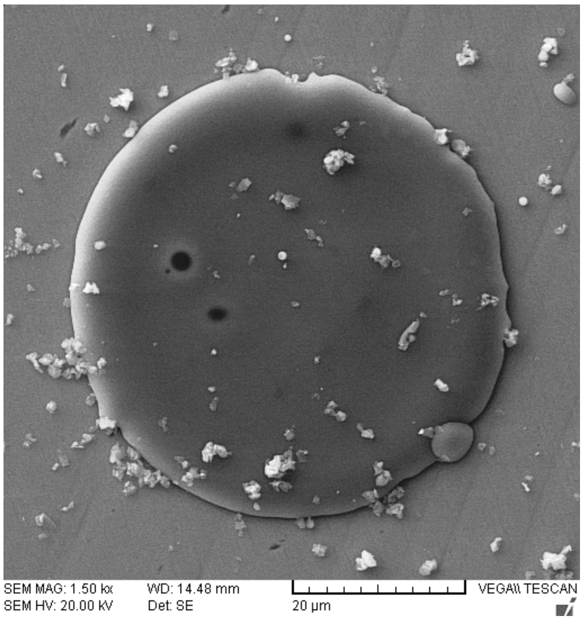


**Fig. 7.** LaMA splat morphology (preheating temperature: 400 °C).

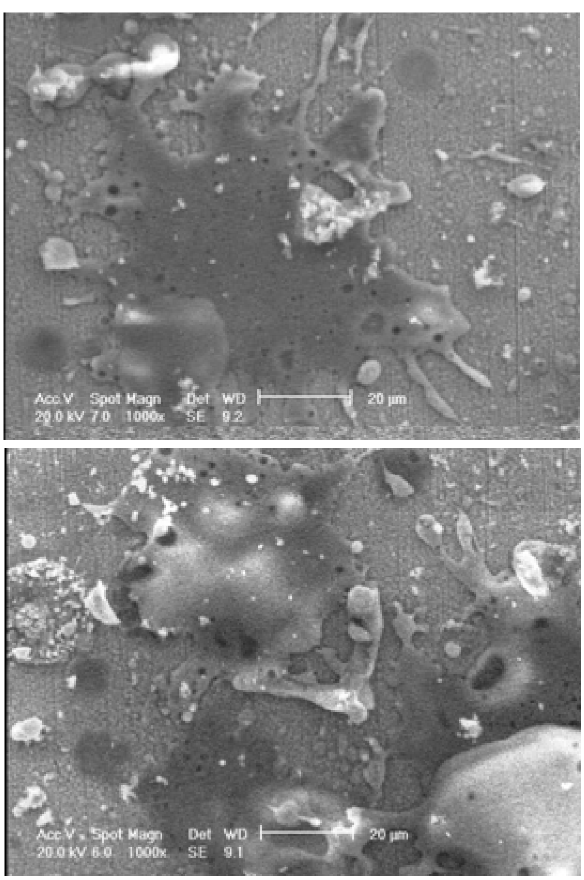


**Fig. 8.** LaMA splats morphology (preheating temperature: 600 °C).

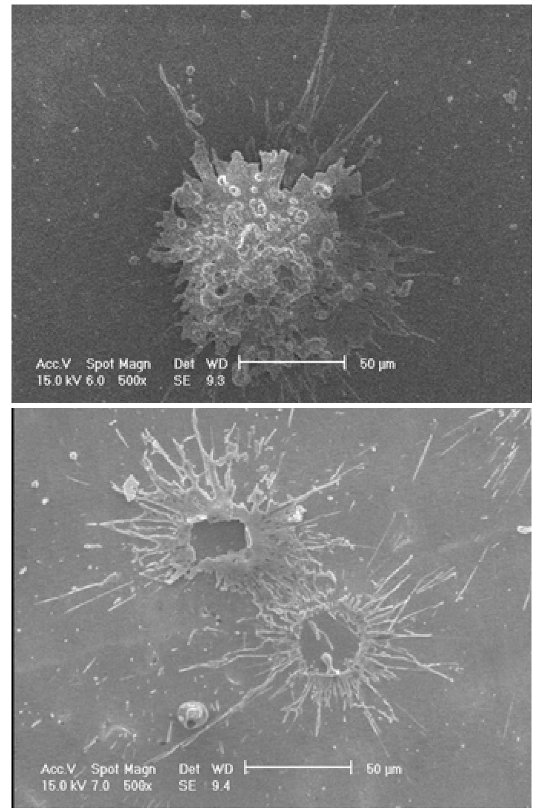


**Fig. 9.** 8YSZ splats morphology (preheating temperature: 200 °C).

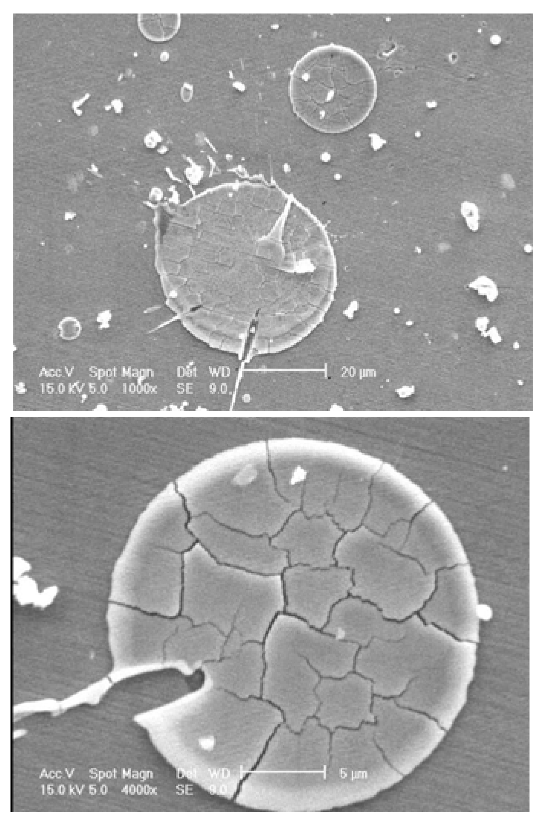


**Fig. 10.** 8YSZ splats morphology (preheating temperature: 400 °C).

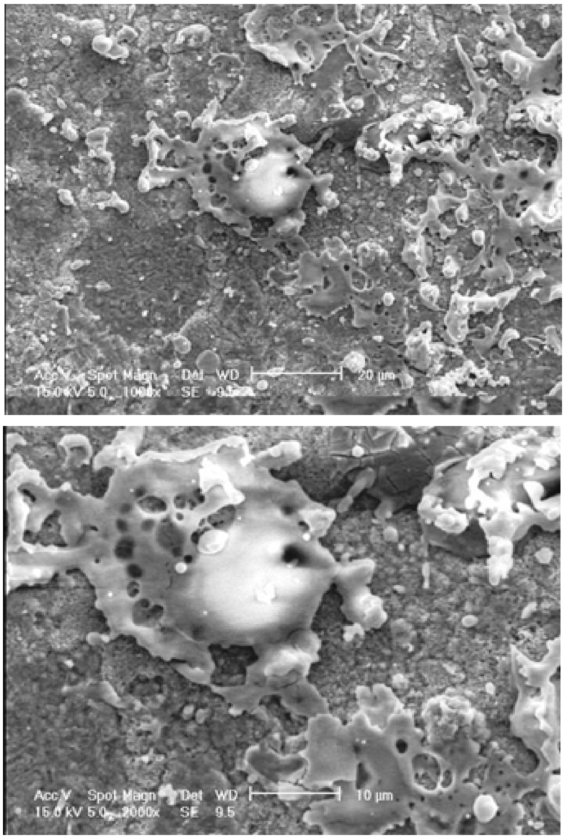


**Fig. 11.** 8YSZ splats morphology (preheating temperature: 600 °C).

## 4. Conclusions

The substrate preheating temperature significantly affects the splat morphology in LaMA and 8YSZ thermal spray coatings deposited via atmospheric plasma spray (APS). A critical transition temperature of around 400 °C is observed for both materials. Below this temperature, splats exhibit irregular shapes. At 400 °C, disc-shaped splats with improved adhesion form. Above 400 °C, the morphology becomes disordered. Surface tension, viscosity, thermal stress, and surface oxide layers influence splat morphology. Optimizing preheating temperature is crucial for achieving desirable splat morphology and enhancing coating performance. In comparison, at 400 °C, 8YSZ splats exhibit a disc-like morphology with cracks on the surface, whereas LaMA splats maintain a disc-like shape without cracks. This difference suggests a variation in the thermo-mechanical properties of these two materials.

## CRediT authorship contribution statement

**Mohammad Mehdi Khorramirad:** Conceptualization, Methodology, Investigation, Formal Analysis, Writing – original draft, Writing – review & editing, Visualization, Project Administration.

**Mohammad Reza Rahimipour:** Supervision, Validation, Resources, Writing – Review & editing.

**Mohammad Mehdi Hadavi:** Supervision, Validation, Writing – review & editing.

**Kourosh Shirvani:** Supervision.

## Data availability

The data underlying this article will be shared on reasonable request to the corresponding author.

## Declaration of competing interest

The authors declare no competing interests.

## Funding and acknowledgment

The Materials and Energy Research Center (MERC), Karaj, Iran, financially supported this research. The authors thank the Laboratories of the Materials and Energy Research Center (MERC) and the Advanced Materials Laboratory at the Faculty of Materials and Metallurgical Engineering, Semnan University, Semnan, Iran, for providing the necessary facilities and technical support to conduct this research.

## References

[1] K. Yang, M. Liu, K. Zhou, C. Deng, Recent Developments in the Research of Splat Formation Process in Thermal Spraying, J. Mater. 2013 (2013) 1–14. https://doi.org/10.1155/2013/260758.

[2] A.H. Pakseresht, Microstructural Investigation of BaTiO3 Plasma Sprayed Coating Deposited by Splash and Disk-Like Splats, J. Environ. Friendly Mater. 2 (2018) 1–6.

[3] A.H. Pakseresht, M.R. Rahimipour, M.R. Vaezi, M. Salehi, Effect of splat morphology on the microstructure and dielectric properties of plasma sprayed barium titanate films, Appl. Surf. Sci. 324 (2015) 797–806. https://doi.org/10.1016/j.apsusc.2014.11.041.

[4] J. Mostaghimi, S. Chandra, Splat formation in plasma-spray coating process, Pure Appl. Chem. 74 (2002) 441–445. https://doi.org/10.1351/pac200274030441.

[5] S. Chandra, P. Fauchais, Formation of solid splats during thermal spray deposition, J. Therm. Spray Technol. 18 (2009) 148–180. https://doi.org/10.1007/s11666-009-9294-5.

[6] X.Q. Cao, R. Vassen, D. Stoever, Ceramic materials for thermal barrier coatings, J. Eur. Ceram. Soc. 24 (2004) 1–10. https://doi.org/10.1016/S0955-2219(03)00129-8.

[7] Z. Hong-song, C. Xiao-ge, L. Gang, W. Xin-Li, D. Xu-dan, Influence of Gd2O3addition on thermophysical properties of La2Ce2O7ceramics for thermal barrier coatings, J. Eur. Ceram. Soc. 32 (2012) 3693–3700. https://doi.org/10.1016/j.jeurceramsoc.2012.06.003.

[8] C. Friedrich, R. Gadow, T. Schirmer, Lanthanum Hexaaluminate — a New Material for Atmospheric Plasma Spraying of Advanced Thermal Barrier Coatings, J. Therm. Spray Technol. 10 (2001) 592–598. https://doi.org/10.1361/105996301770349105.

[9] R. Vassen, A. Stuke, D. Stöver, Recent developments in the field of thermal barrier coatings, J. Therm. Spray Technol. 18 (2009) 181–186. https://doi.org/10.1007/s11666-009-9312-7.

[10] X. Chen, Y. Zhao, W. Huang, H. Ma, B. Zou, et al., Thermal aging behavior of plasma sprayed LaMgAl11O19thermal barrier coating, J. Eur. Ceram. Soc. 31 (2011) 2285–2294. https://doi.org/10.1016/j.jeurceramsoc.2011.05.036.

[11] R. Gadow, G. Schaefer, Thermal insulating material and method of producing same, US 6,998,064 B2. (2006). https://www.google.com/patents/US6998064.

[12] X. Chen, Y. Sun, J. Hu, J. Li, C. Deng, et al., Thermal cycling failure of the multilayer thermal barrier coatings based on LaMgAl11O19/YSZ, J. Eur. Ceram. Soc. 40 (2019) 0–1. https://doi.org/10.1016/j.jeurceramsoc.2019.12.039.

[13] X. Chen, Y. Zhao, X. Fan, Y. Liu, B. Zou, et al., Thermal cycling failure of new LaMgAl11O19/YSZ double ceramic top coat thermal barrier coating systems, Surf. Coat. Technol. 205 (2011) 3293–3300. https://doi.org/10.1016/j.surfcoat.2010.11.059.

[14] M.M. Khorramirad, M.R. Rahimipour, S.M.M. Hadavi, K. Shirvani, High temperature oxidation behavior of Inc-738/NiCrAlY/LaMA thermal barrier coating system, Surf. Coat. Technol. 364 (2019) 70–80. https://doi.org/10.1016/j.surfcoat.2019.02.017.

[15] M.M. Khorramirad, M.R. Rahimipour, S.M.M. Hadavi, K. Shirvani, Preoxidation of bond coat in IN-738LC/NiCrAlY/LaMgAl11O19 thermal barrier coating system, Ceram. Int. 44 (2018) 22080–22091. https://doi.org/10.1016/j.ceramint.2018.08.318.

[16] M.M. Khorramirad, M.R. Rahimipour, S.M.M. Hadavi, K.S. Jozdani, The effect of magnesium compounds (MgO and MgAl2O4) on the synthesis of Lanthanum magnesium hexaaluminate (LaMgAl11O19) by solid-state reaction method, Ceram. Int. 44 (2018) 4734–4739. https://doi.org/10.1016/j.ceramint.2017.12.056.

[17] M.M. Khorramirad, M.R. Rahimipour, S.M.M. Hadavi, K. Shirvani Jozdani, Synthesis of the lanthanum magnesium hexaaluminate (LaMgAl11O19) powder in order to plasma spray coating on the nickel super alloy as a thermal barrier coating, New Process Mater. Eng. 12 (2018) 173–183.

[18] X. Chen, Y. Zhang, X. Zhong, Z. Xu, J. Zhang, et al., Thermal cycling behaviors of the plasma sprayed thermal barrier coatings of hexaluminates with magnetoplumbite structure, J. Eur. Ceram. Soc. 30 (2010) 1649–1657. https://doi.org/10.1016/j.jeurceramsoc.2010.01.013.

[19] M. Pasandideh-Fard, V. Pershin, S. Chandra, J. Mostaghimi, Splat shapes in a thermal spray coating process: Simulations and experiments, J. Therm. Spray Technol. 11 (2002) 206–217. https://doi.org/10.1361/105996302770348862.

[20] W. Zhang, Integration of Process Diagnostics and Three Dimensional Simulations in Thermal Spraying, Doctor of Philosophy, Stony Brook University. (2008).