

Hot Corrosion Resistance of $\text{La}_2\text{Zr}_2\text{O}_7$ Coat on Stainless Steel Alloy

S. M. Naga, M. Awaad, H. F. El-Maghraby, A. M. Hassan, Mohamed Elhoriny, Andreas Killinger, Rainer Gadow

Abstract— In the present study, $\text{La}_2\text{Zr}_2\text{O}_7$ was used as a coat for stainless steel alloy. Lanthanum zirconate coat was sprayed using plasma spray technique. The preparation and characterization of $\text{La}_2\text{Zr}_2\text{O}_7$ coat was studied. Hot corrosion of the coat surface was conducted in (1:1) V_2O_5 / Na_2SO_4 molten mixture at 900°C for 50 and 100 h. The results showed that molten mixture of V_2O_5 / Na_2SO_4 attacks $\text{La}_2\text{Zr}_2\text{O}_7$ coat heavily after 100 h. Depending on the nature of molten salt, $\text{La}_2\text{Zr}_2\text{O}_7$ can be considered either a strong basic oxide or strong acidic oxide.

Keywords— Plasma coating, Lanthanum zirconate, Hot corrosion resistance

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I. Introduction

For decades YSZ was the material of choice for thermal barrier coatings (TBCs), as it possesses low thermal conductivity and relatively high thermal coefficient that reduces the thermal expansion mismatch with the metallic substrate [1,2]. Due to the limited operation temperature for long-term applications of YSZ, researchers sought for new materials. Rare-earth zirconates ($\text{M}_2\text{Zr}_2\text{O}_7$) are investigated as alternatives for YSZ. They have two crystalline forms; ordered pyrochlore structure and disordered fluorite one [3]. The thermal stability and low thermal conductivity pointed pyrochlore zirconate as an interesting material for TBC applications. Pyrochlore $\text{La}_2\text{Zr}_2\text{O}_7$ (PLZ) is a significant candidate for TBC topcoat. Because of its low oxygen content; it has a better bond coat oxidation resistance in comparison to YSZ [4]. PLZ possesses cubic structure that consists of octahedra ZrO_6 at the corners; forming the backbone of the structure; and La^{3+} ions filling the holes formed by ZrO_6 octahedra [5].

$\text{La}_2\text{Zr}_2\text{O}_7$ is synthesized by various methods like, conventional solid-state reaction, co-precipitation, sol-gel, hydrothermal and molten salts methods [6-8]. Ramachandran et al [9] used transferred arc plasma (TAP) melting to produce lanthanum zirconate. They observed a variation in the LZ stoichiometry after TAP melting. They claimed that the variation is due to the evaporation of La_2O_3 from the mixture. Cao et al [10] suggested that doping of LZ with some elements, increasing the content of La_2O_3 in the LZ starting material and applying gradient coating with YSZ, could improve the thermal cycling life of LZ coating. Increasing the thermal expansion coefficient of LZ is an important issue, as its thermal expansion is relatively low ($\sim 9 \times 10^{-6}/\text{K}$). Low thermal expansion leads to thermal expansion mismatch and high thermal stresses [2].

II. Materials and Methods

A. Materials

For the preparation of lanthanum zirconate ($\text{La}_2\text{Zr}_2\text{O}_7$), chemically pure reagents of La_2O_3 , 99.99%-La (Strem Chemicals, Newburyport, MA, USA) and zirconium n-(IV) butoxide (Strem Chemicals, Newburyport, MA, USA) were used.

Phase composition (XRD) of the coat showed that it composed totally of lanthanum zirconate, Fig.4. Its microstructure general view shows that the LZ coat thickness is ~ 50.68 μm, Fig. 5. The detailed microstructure of the coat layer is shown in Fig.6.a. It shows many cracks within the coat, nanoscale LZ grains and relatively large pores. The nanocrystalline structure of LZ was preserved by the short dwell time that LZ powder experienced during plasma spraying. The rapid cooling of the powders is also led to the presence of the nanoscale grains of LZ [11]. Berndt et al and Zhu et al also mentioned this observation in their studies [12,13]. The presence of Fe, Cr and Ni oxides in the EDS spectrum of the interface, Fig. 6.b, indicates the reaction between the substrate and the coat layer. Shane and Mecartne [14] claimed that the interfacial reactions strengthening the interface between the substrate and the ceramic coat. Higher magnification of the LZ coat layer is shown in Fig.7. It shows a lamellar, porous structure characteristic for plasma spray coating [15]. The interlamellar pores are resulting from the rapid solidification of the lamella, the cracks developed from the thermal stresses and tensile quenching relaxation stresses and the fine voids formed around the non-melted particles or by the incomplete intersplat contact [16]. We believe that the amount of melted particles to fill surface irregularities is not enough, which leads to the formation of pores between splats. Also, the presence of non-flattens non-molten/partially melted grains results in a very small area of intimate contact with other particles and the creation of large pores between the grains [17].

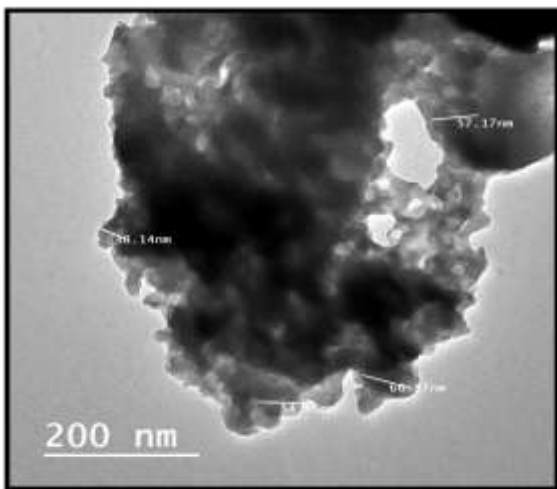


Figure. 2. TEM micrograph showing that lanthanum zirconate particle size.

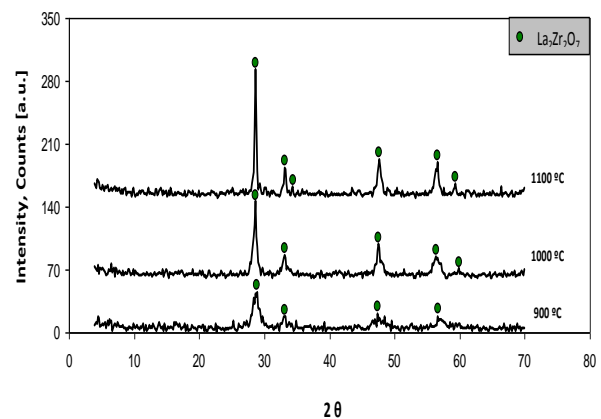
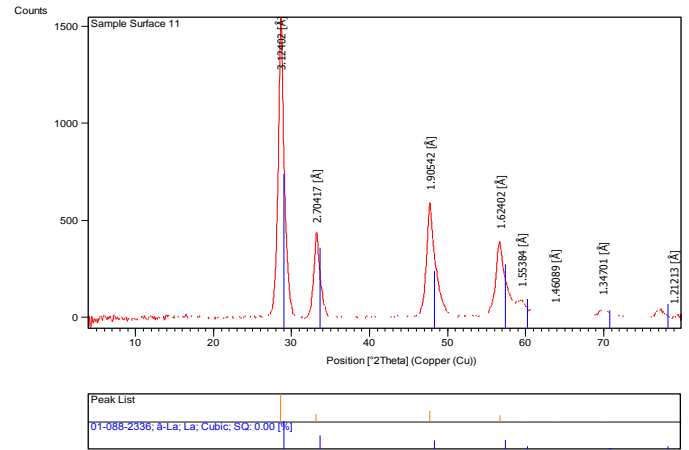


Figure. 3. XRD pattern of LZ powder calcined at different firing temperatures.

Figure. 4. XRD of surface layer coat.

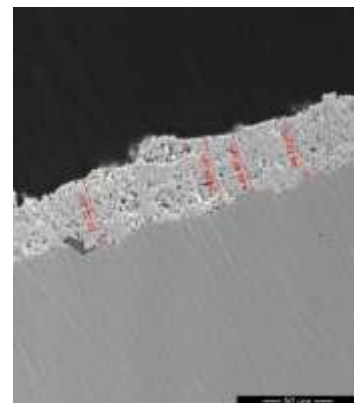
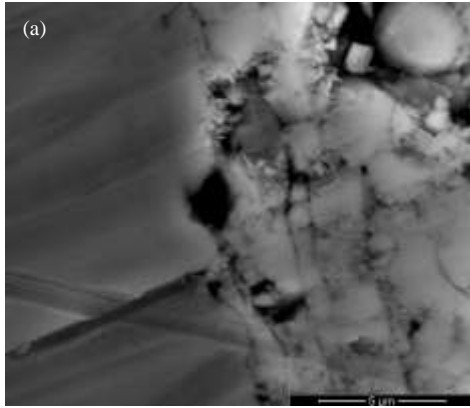
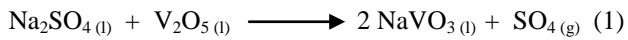


Figure. 5. General view and coat thickness of the sample.

It is to be noticed that when $\text{La}_2\text{Zr}_2\text{O}_7$ coat hot treated with $\text{Na}_2\text{SO}_4/\text{V}_2\text{O}_5$ mixture it shows heavily attacked surface. Figures 8.a and 9a show many corrosive pores, which are due to the deterioration of the coat by vanadium and sulfate salts. There are two different corrosion products are observed in the samples hot treated for 50 h; namely block –shaped and particle-shaped. EDS analysis identified the hot corroded products to be LaVO_4 for the block –shaped and $\text{La}_2\text{Zr}_2\text{O}_7$ for particle- shaped, Fig. 8.b and c.

Depending on the molten salts $\text{La}_2\text{Zr}_2\text{O}_7$ can consider either a strong basic oxide former or strong acidic oxide. From the phase diagram of $\text{Na}_2\text{SO}_4 - \text{V}_2\text{O}_5$ binary diagram system [18] and based on the reaction conditions used in the present study Na_2SO_4 and V_2O_5 will react according to the following equation:



(a)

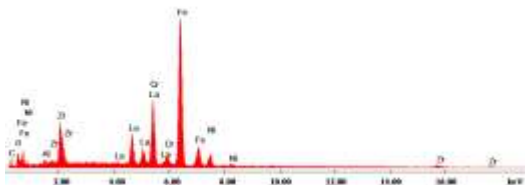


Figure 6. SEM micrograph of the sample layer: (a) nanoscale LZ grains and cracks within LZ coat (b) The interface between LZ and the metallic substrate.

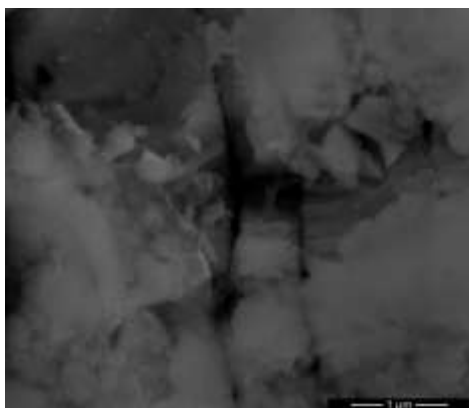
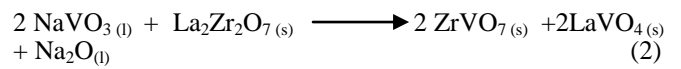


Figure 7. Lamellar, porous structure of LZ coat.

According to Rapp [19] the presence of NaVO_3 will

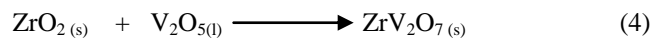
enhance the acidic solubility and $\text{La}_2\text{Zr}_2\text{O}_7$ will react with NaVO_3 according to the equation:



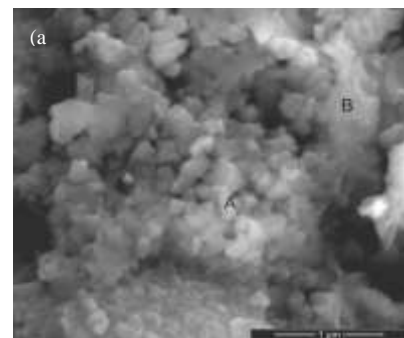
But ZrVO_7 melts incongruently at $\sim 747^\circ\text{C}$ to form $m\text{-ZrO}_2$ and a mixture of $m\text{-ZrO}_2$ and V_2O_5 [20,21]. Accordingly, the hot corrosion mechanism in this case could be:



Due to the low boiling point of Na_2O ; 882.9°C ; Na_2O will evaporate and Na-containing phases will be undetectable. With increasing the heat treatment time to 100 h, $\text{Na}_2\text{SO}_4 / \text{V}_2\text{O}_5$ mixture aggressively attack the ZrO_2 coat, according to the reaction:



The obtained products are well-crystallized rod-like shape LaVO_4 and corroded areas containing Cr and Fe oxides; Fig.9a. EDS analysis, Fig.9b, shows the chemical analysis of the examined area.



(a)



(b)

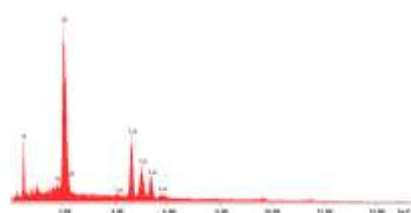


Figure 8. SEM micrograph of the sample: (a) block and particle shaped microstructure of 50h treated sample, (b) EDS spectra of LaVO₄ particles, (c) EDS spectra of La₂Zr₂O₇ particle.

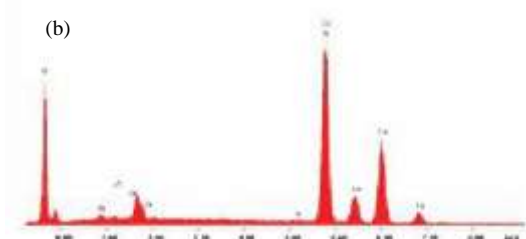
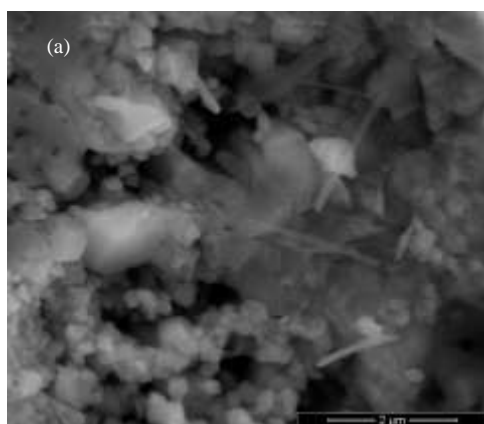


Figure 9. SEM micrograph of the sample heated for 100h at 900 °C, (a) well-crystallized rod-like shape LaVO₄ and corroded areas containing Cr and Fe oxides, (b) EDS spectra of the examined sample..

iv. Conclusions

1- Pure nano- size Lanthanum zirconate phase was prepared using the sol- gel technique with particle size of 38- 66 nm.

2- La₂Zr₂O₇ coat suffered from severe corrosion when exposed to a molten mixture of Na₂SO₄/V₂O₅ (1:1) for 100 h.

3- Two different corrosion products are observed in the hot treated samples treated with molten salt mixture for 100 h; block –shaped and rod like LaVO₄ grains and solid solution of Fe and Ni.

v. References

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