International Journal of Applied Chemistry.
ISSN 0973-1792 Volume 12, Number 4 (2016) pp. 593-601

http://www.ripublication.com

Properties and Peculiarities of Ceramic Coatings on the Al_2O_3 and $ZrSiO_4$ Basis Formed by a New Multi-chamber Gas-dynamic Accelerator

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Abstract

$Al_2O_3/xZrSiO_4$ (where x = 0, 3, 25 wt.%) composite coatings were deposited onto corrosion-resistant steel substrates by a new multi-chamber gas-dynamic accelerator of mixed the cheap raw materials (alumina and zircon). X-Ray diffraction (XRD) was used to characterize the phase composition and scanning electron microscopy (SEM) examined the morphology of the polished cross-sections. The coatings were investigated using Vickers microhardness tester at a test load 200 g. The wear behaviour of coatings was carried out by the ball-on-disk tests. Microstructural investigation showed that the coatings were well-adhered onto corrosion-resistant steel substrate. The results show that the $Al_2O_3/xZrSiO_4$ coatings consist of both fully melted regions and partially melted regions, and the fully melted region has a lamellar-like structure. The effect of $ZrSiO_4$ addition on the properties of coatings was investigated in terms of microhardness and wear behavior. It was found that $ZrSiO_4$ improved the microhardness and reduced wear rate of the coatings.

Keywords: alumina, zircon, composite coatings, multi-chamber gas-dynamic accelerator, microstructure, hardness, wear behavior

INTRODUCTION

Aluminium oxide (Al_2O_3) and zirconium silicate ($ZrSiO_4$) are among the most used and cheapest spray-coating materials for refractory. Alumina (Al_2O_3) is an important ceramic which is widely used in various industrial applications, which require high wear and erosion resistance, corrosion protection and thermal insulation [1,2]. Zircon,

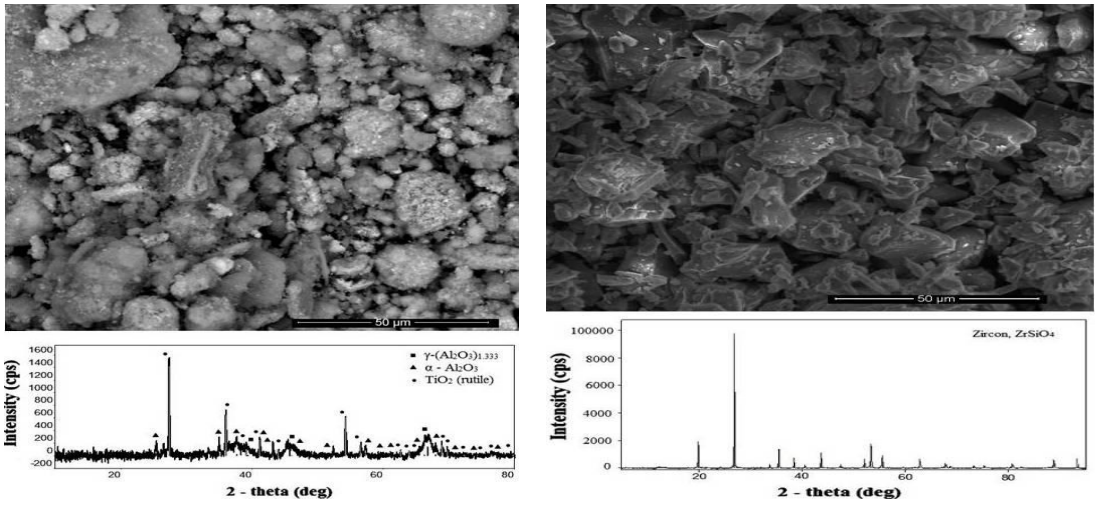
zirconium silicate $ZrSiO_4$ is a natural mineral used various applications as a refractory bulk material is due to its excellent thermophysical properties such as low thermal expansion, low thermal conductivity and good corrosion resistance. It is an excellent feedstock for the spraying of protective coatings [3].

The mechanical properties and wear behavior of the ceramic coatings are usually strongly dependent on their microstructures such as phase composition, grain size, porosity, and second-phase particle distribution. Microhardness, toughness, and wear resistance of the Al_2O_3 coatings can be improved by the addition of other components to compensate deterioration of these properties of the coatings resulting from the transformation of Al_2O_3 to metastable state. For examples, addition of ZrO_2 and $ZrSiO_4$ is known to increase microhardness, fracture toughness, and wear behavior of the Al_2O_3 coatings [4,5].

In this paper, $Al_2O_3/xZrSiO_4$ (where x = 0, 3, 25 wt.%) composite coatings were deposited onto corrosion-resistant steel substrates by a new multi-chamber gas-dynamic accelerator. The effects of $ZrSiO_4$ addition on phase formation, microstructure, microhardness, and wear behavior of $Al_2O_3/ZrSiO_4$ coatings were investigated and discussed.

EXPERIMENTAL PROCEDURE

Mixtures of alumina and zircon powders (figure 1, table 1) have been used as the starting materials to deposit a dense layer on the steel substrate (table 1). The particle size of powders was measured by laser diffractometry Analysette 22 NanoTec. The composite powders were prepared by solid state mixing route. Both powder were mixed and milled for 3 h in ethanol using ball milling apparatus to form $Al_2O_3/xZrSiO_4$ (where x = 0, 3, 25 wt.%). Prior to spraying, a plate with dimensions of 30 x 30 x 5 (mm) of the corrosion-resistant steel (table 1) were degreased and grit blasted with 25A F360 alumina grits.



(a) (b)

Figure 1. SEM micrographs of alumina (a) (back-scattered electron mode) and zircon powders (b)

Table 1: The chemical composition of powders and coatings, and mechanical features of coatings

Chemical composition, all in wt pct	Powder		Coatings			Steel
			Al_2O_3	Al_2O_3/ $3ZrSiO_4$	Al_2O_3/ $25ZrSiO_4$	
	Alumina	Zircon	O-32.36 Al-57.95 Ti-7.29 Fe-2.40	O-32.69 Al-50.39 Si-1.05 Zr-3.51 Ca-0.59 Ti-8.33 Fe-3.43	O-30.68 Al-34.09 Si-2.10 Zr-24.22 Ca-0.44 Ti-6.29 Fe-2.18	Cr-17.5 Ni-9.4 C-0.06 Si-0.5 Mn-1.2 P-0.02 S-0.02 Ti-0.48
	O-37.13 Al-48.94 Ca-0.58 Ti-9.87 Fe-3.01 Zr-0.47	Zr-77.48 Fe-0.46 Si-8.23 O-13.77 Al-0.07				
Particle size distribution (μm)						
d(0.1)	5.4	2.56	-			
d(0.5)	34.22	18.29	-			
d(0.9)	58.80	46.68	-			
Porosity, ±0.05 (%)			0.28	0.28	0.18	-
Microhardness ($HV_{0.2}$)			476±50.05	652±79.28	567±81.80	187±11.64
Specific wear rate* ($x10^{-4}$) ($mm^3(m{\cdot}N)^{-1}$)			10.71	6.68	12.35	48.54
*counterbody (a 6 mm in diameter aluminum oxide (Al_2O_3) ball), 6 N normal load, 0.15 $m{\cdot}s^{-1}$ sliding speed, a total sliding distance of 1200 m. Surface roughness (polished surface) $R_a = 3.04 \pm 0.01$ (μm)						

In the present study, a multi chamber, vertically mounted gas-dynamic accelerator (MCDS) [6,7] was employed to deposit of the $Al_2O_3/xZrSiO_4$ coatings. The spray parameters employed for depositing of $Al_2O_3/xZrSiO_4$ coatings are listed in Table 2. After spraying, the coatings were cross-sectioned, finally polished with 1 μm alumina abrasive particles. The coatings with surface roughness of ≤1 μm were obtained. To determine the microstructure and elemental composition scanning electronic microscope (SEM) Quanta 200 3D was performed. Phase composition was determined using diffractometer Rigaku Ultima IV. Porosity was determined by the metallographic method with elements of the qualitative and quantitative analysis of the geometry of the

pores using an optical inverted Olympus GX51 microscope and "SIAMS Photolab" program. Micro-hardness test was performed by tester DM-8B on a cross section of coatings with a load of 200 g and dwell period of 15 sec.

Table 2: Parameters employed for depositing $Al_2O_3/xZrSiO_4$ coatings

Parameter	Value		
	Al_2O_3	$Al_2O_3/3ZrSiO_4$	$Al_2O_3/25ZrSiO_4$
Spray distance (mm)	65		
Powder feed rate (g/h)	800		
Frequency (Hz)	10	20	
Barrel length (mm)	500		
Barrel diameter (mm)	16		
Flow gas rate (m^3/h)			
Oxygen	0.99*/1.26**	2.95*/3.07**	
Propane (30 %) + butane (70 %)	0.22*/0.28**	0.65*/0.63**	
Air	0.48*/0.6**	1.56*/0.92**	
*Cylindrical form combustion chamber. **Combustion chamber in the form of a disk			

The tribological evaluation of the coated substrates under dry conditions was performed using a ball on disc tribometer that was manufactured by CSM Instruments (Switzerland) according to ASTM wear testing standard G-99. The ASTM G-99 standard determines the amount of wear by measuring the appropriate linear dimensions of both specimens (ball and disk) before and after the test [8].

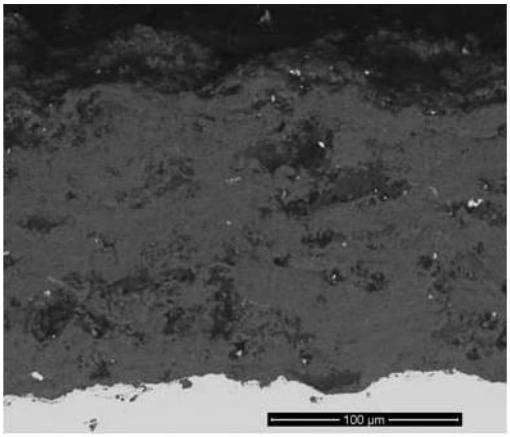
RESULTS AND DISCUSSION

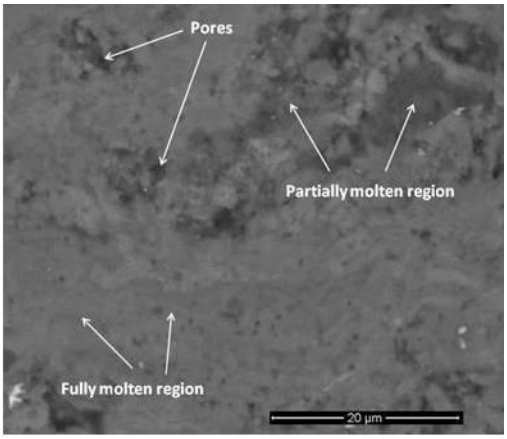
Figure 1 and 2 show XRD patterns of powders and sprayed coatings, respectively. The alumina powder contained γ-Al_2O_3 with a cubic lattice; α-Al_2O_3 with a trigonal lattice and TiO_2 (rutile) with a tetragonal lattice phases. Also the phase analysis shows that the main phase in the zircon powder is $ZrSiO_4$ with a tetragonal lattice.

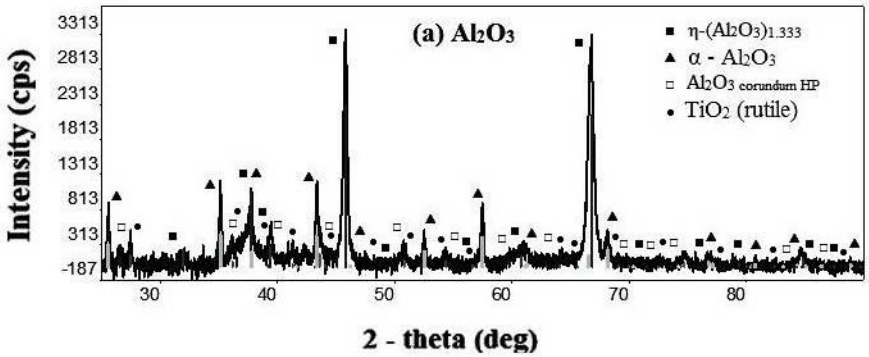
It has been established that zircon, when sprayed, dissociates in the high temperature flame (>5000ºC) into zirconia and silica, and recombination does not occur if cooled quickly enough (>10 K/s) [9]. The sprayed zircon deposits were observed with all three modifications of zirconia - monoclinic, tetragonal and cubic. Ault [10] reported ZrO_2 in cubic form while Krauth and Meyer [11] reported a mixture of monoclinic and tetragonal phases. In paper [12] was concluded that although SiO_2 has the lowest

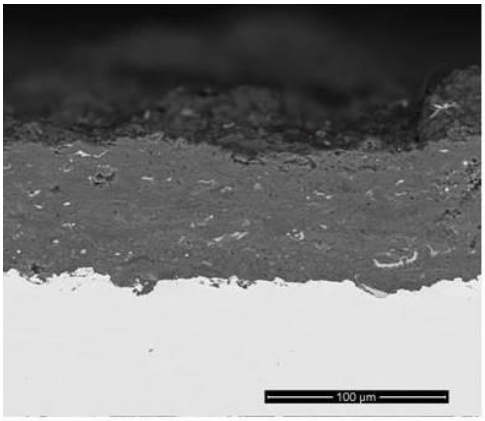
critical undercooling parameter, the large difference in melting points between silica and zirconia results in metastable zirconia first appearing from the melt instead of silica. The cooling rate determines if tetragonal-ZrO_2, monoclinic-ZrO_2 or cubic-ZrO_2 will form in the sprayed material. In this study, the cubic-ZrO_2 was found to prevail as a consequence of a faster local cooling rate. The XRD patterns of the Al_2O_3/x$ZrSiO_4$ coatings indentified the presence of γ-Al_2O_3, α-Al_2O_3, cubic-ZrO_2, monoclinic-ZrO_2, and tetragonal-$ZrSiO_4$ phases. The presence of the ZrO_2 phase is the indication of the dissociation of $ZrSiO_4$ that took place during spraying. Metastable γ-Al_2O_3 as the major phase was observed in all coatings, and was attributed to the rapid cooling rate (10^6-10^7 K/s) after spraying process. XRD analysis of the Al_2O_3/25$ZrSiO_4$ coatings (figure 2) revealed evidence of dissociated zircon in addition to monoclinic-ZrO_2. The zircon peak represents the unmelted fraction of zircon present in the coating. This is not unexpected, since all the powder may not undergo melting within the limited time off light. Similarly α alumina peaks stand for either unmelted or partially melted alumina powder [13].

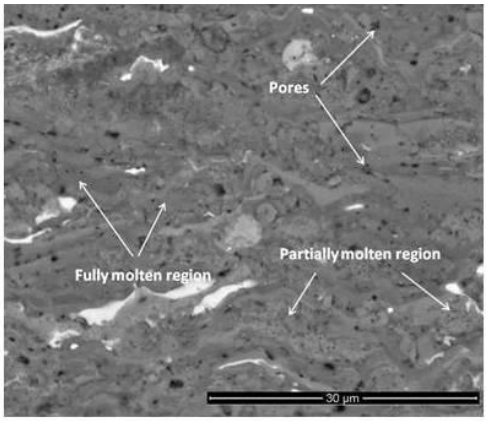
Microstructures of the polished cross-sections of the Al_2O_3/x$ZrSiO_4$ coatings were observed using SEM (figure 2). The thickness of observed coatings was varied in the range of 80 to 200 microns. The coatings showed a layered structure which was the result of full, partial, and un-melting of the ceramic feedstock powder and its solidification as ‘‘splats’’ on the substrate. It was found that the shape of the fully-melted region has lamellar-like structure typical for thermally sprayed coatings. Only a few pores are included in the coating. The porosity of ~ 0.3% was observed in the Al_2O_3/x$ZrSiO_4$ coatings. These pores were originated by the splashing of particles on impact onto previous deposited splats or it may be due to voids resulting from poor deformation of partially melted particles [5]. It can be noticed that the porosity content was not significantly different in each coating. This would be due to the similar original size of the feedstock powders (figure 1, table 1), which was close to the size of alumina matrix. Therefore, the ability of heat transfer between plasma flame and the powders, and their meltability were not too different.

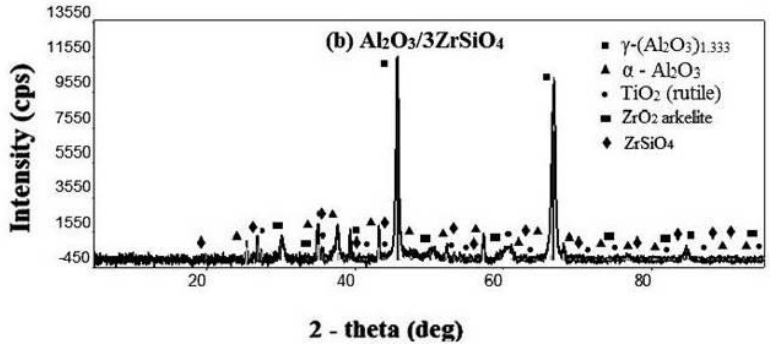

100 µm


Pores
Partially molten region
Fully molten region
20 µm


(a) Al2O3
η-(Al2O3)1.333
α - Al2O3
Al2O3 corundum HP
TiO2 (rutile)
Intensity (cps)
3313
2813
2313
1813
1313
813
313
-187
30
40
50
60
70
80
2 - theta (deg)


100 µm


Pores
Fully molten region
Partially molten region
30 µm


(b) Al2O3/3ZrSiO4
γ-(Al2O3)1.333
α - Al2O3
TiO2 (rutile)
ZrO2 arkelite
ZrSiO4
Intensity (cps)
13550
11550
9550
7550
5550
3550
1550
-450
20
40
60
80
2 - theta (deg)

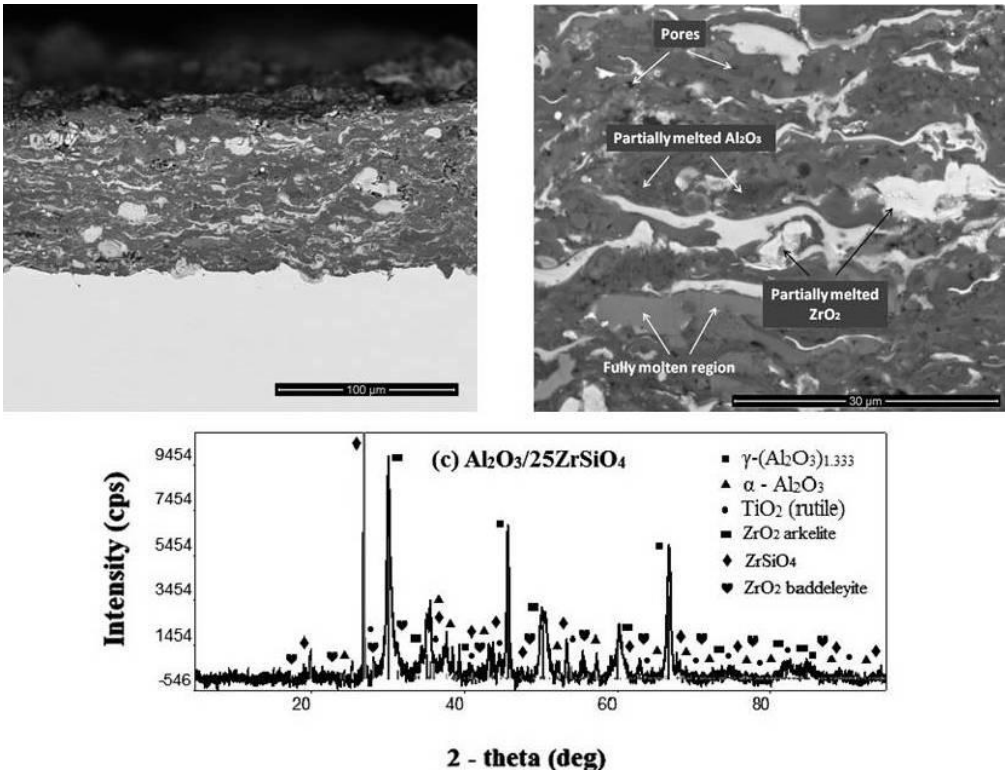


Figure 2. SEM micrographs (back-scattered electron mode) of cross-sections of the Al_2O_3/x$ZrSiO_4$ coating layers and XRD pattern

The hardness of Al_2O_3 coatings and Al_2O_3/x$ZrSiO_4$ composite coatings was different. Hardness varied due to variation of microstructural differences, porosity and phase distribution [4]. In comparison to the substrate, the microhardness of the coatings produced using a new multi-chamber gas-dynamic accelerator was 3.5-4 times harder. The alumina coatings exhibited a hardness of about 476 ± 50.05 $HV_{0.2}$. The variation in the microhardness was significant; the variation may be associated with the phase composition of the coatings (the presence of a higher level of harder α-alumina phase in this coating). The presence/formation of different alumina phases, i.e. α-alumina and γ-alumina, during the deposition of alumina coatings has been observed and described in the literature [14]. An addition of $ZrSiO_4$ effectively toughened the matrix of Al_2O_3-based coatings (table 1). For the composite coatings, the hardness values were found to slightly decrease with increasing $ZrSiO_4$ content due to an increase of monoclinic-ZrO_2 phase [5]. The Al_2O_3/3$ZrSiO_4$ and Al_2O_3/25$ZrSiO_4$ coatings exhibited a hardness of about 652 ± 79.28 and 567 ± 81.80 $HV_{0.2}$, respectively. They are in agreement with the work by Li et al. [2] (374–661 $HV_{0.2}$).

The Al_2O_3/25$ZrSiO_4$ composite coatings presented the high performance in reducing wear rate. The wear rate of Al_2O_3 in this study was found to be higher than those of Al_2O_3/3$ZrSiO_4$ composite coatings. For the composite coatings, the wear rate values

were found to slightly increase with increasing $ZrSiO_4$ content. An increase in the hardness of the composites by small amount could not simply explain a significant improvement of the wear resistance. The other possible explanation may involve additional phase transformation induced by the stress during sliding wear test.

CONCLUSIONS

The $Al_2O_3/xZrSiO_4$ (where x = 0, 3, 25 wt.%) composite coatings on the flat specimens of steel were produced by a new multi-chamber gas-dynamic accelerator. Dense layers at lamellas and deformed particles with porosity of less than 0.3 % were formed on the sample surface. It was found that an addition of $ZrSiO_4$ effectively toughened the matrix of Al_2O_3-based coatings. For the composite coatings, the hardness values were found to slightly decrease with increasing $ZrSiO_4$ content. An improvement of wear properties of $Al_2O_3/xZrSiO_4$ (where x = 3, 25 wt.%) coatings over those of monolithic Al_2O_3 coating was obtained. It seemed that $ZrSiO_4$ addition played an important role on mechanical and wear behaviours of Al_2O_3 coating. Both zircon and alumina are inexpensive and easily available, and this technique used in this study is highly attractive to large-scale industrial production.

The study was financial supported by the Russian Science Foundation, under grant No 15-19-00189. All of studies were carried out on the equipment of the Joint Research Center of Belgorod National Research University «Diagnostics of structure and properties of nanomaterials».

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