Microstructural evolution of plasma sprayed submicron-/nano-zirconia-based thermal barrier coatings

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A R T I C L E   I N F O

Article history:
Received 14 October 2015
Received in revised form
25 November 2015
Accepted 2 December 2015
Available online 7 December 2015

Keywords:
Yttria partially stabilized zirconia
Thermal barrier coatings
Thermal shock resistance
Submicron-coating
Nano-coating

A B S T R A C T

Two types of agglomerates powder with grain sizes in the submicron-/nano-range were used as the feedstock to deposit yttria partially stabilized zirconia (YSZ) thermal barrier coatings (TBCs). The dual-modal submicron-coating and multi-modal nano-coating were fabricated. The results from thermal shock test indicated that, due to the weak bond and higher densification rate of unmelted nano-particles in the nano-coating, the interface between recrystallization zone and unmelted nano-particles linked up, which resulted in the decrease of content of unmelted nano-particles from 13% to 7%. The weak bond and higher shrinking rate of nano-particles led to the formation of coarse cracks that ran along the recrystallization zone/unmelted nano-particles interfaces. These cracks caused the premature failure of nano-coating. The submicron-coating can overcome the inherent deficiencies of nano-coating at high temperatures and show a higher thermal shock resistance, it is expected to become a candidate for high-performance TBCs.

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1. Introduction

Nanotechnology provides the potential for significant advances in the performance of new materials due to the improvement in physical and mechanical properties which resulted from the reduction of the grain size by factors from 100 to 1000 times when compared with conventional materials [1]. The study of nanostructured materials has been extended to coating process using thermal spray technique [2]. The possibility of fabricating the nanostructured thermal barrier coatings (TBCs) currently opens a wide range of opportunities for ceramic materials [3,4]. Thermal sprayed ceramic coatings are usually deposited from a powder feedstock. However, individual nanosized powders cannot be carried in a moving gas stream and deposited on a substrate due to their low mass and flowability. Thus, the nanostructured powders are generally agglomerated by sprayed-drying and then, partially sintered into microscopic particles [5].

Thermal spray process is intrinsically associated with the melting of feedstock powder. Some degree of melting is necessary to achieve a sufficient level adhesion and cohesion of coatings. However, if the nanostructured feedstock powder fully melts, its original nanostructure will be destroyed. Therefore, the current so-called nano-coating usually consists of some unmelted nanoparticles which embedded in the recrystallization zone formed by the solidification of melted feedstock powder [6–8].

The stability of the nano-coating at high temperature has a close relation with the sintering effect, which can increase the grain size and stress within the coating leading to its premature failure [9–12]. Some researchers found that the grain size increased from 57 to 88 nm within the annealing temperature range of 600–1150 °C and grains grew with preferential direction into a columnar structure [9]. This was attributed to the activation energy of nano-grains (6.5 kJ/mol), which was much lower than that of bulk YSZ (580 kJ/mol) [13]. The existence of micro-pores in the coating and the grain-rotation induced grain coalescence mechanism explained the lower activation energy of the unmelted nano-particles [14,15]. The work from Liang et al. also confirmed that the individual unmelted nano-particles (15–130 nm) reached a diameter of the order of 300 nm after 50 h at 1100 °C [16]. The higher surface area of the nano-grains resulted in a higher driving force for sintering, thus the unmelted nano-particles tended to densify at a faster rate than the recrystallization zone upon high temperature exposure. Although Lima et al. [5,17] found that the presence of a bimodal microstructure that consisted of two regions with different sintering rates in nano-coating, led to the formation of some coarse cracks which could counteract the sintering
effect to some extent, but these coarse cracks may result in the failure of TBCs. Therefore, the microstructural evolution of nano-coating, especially at the interface between recrystallization zone and unmelted nano-particles, is needed to be systematically studied in order to optimize the microstructure of nano-coating and to further improve its performance. Additionally, our previous work proved that the submicron-coating with a fine-lamellar structure showed a good thermal shock resistance [18]. However, the reason for the improved performance is not fully understood, although the submicron-coating is expected to overcome the inherent deficiency (such as the high sintering rate) of nano-coating at high temperatures.

Based on the above background, in this present study, two types of agglomerates with grain sizes in the submicron- and nano-range are used as the feedstock to deposit yttria partially stabilized zirconia (YPSZ) thermal barrier coatings (TBCs). The submicron-/nano-coatings are comparatively studied in order to clarify the microstructural evolution and failure mechanism of both coatings during the thermal shock test.

### 2. Experimental procedure

#### 2.1. Materials and plasma spray

The substrate, GH4169 nickel-base superalloy with dimension of \( \phi \) 25.4 mm × 6 mm, was ultrasonically cleaned and then grit-blasted with alumina powder in order to increase adherence capability between bond coat and substrate. A commercially available CoNiCrAlY powder (AMDRY 995M, Sulzer Metco Inc., USA) with nominal composition of Ni-32, Cr-21, Al-8, Y-0.4 Co-balance (wt.%) was used for spraying the bond coat of TBCs. Two spray-dried and sintered ZrO₂-8 wt.% Y₂O₃ powders were used as the original feedstock for depositing the top ceramic coat. The morphology and internal structure of the two powders are depicted in Figs. 1 and 2. The first feedstock exhibited a near-perfect spherical morphology with a particle size of 10–45 μm; the small particles inside the feedstock were well compacted, with a grain size of 150–580 nm (see Fig. 2a and b). The as-sprayed coating using this type of powder as the feedstock was named as “submicron-coating”. The second feedstock exhibited a sintered shell with a grain size of 20–60 nm inside the shell (see Fig. 2c and d). The particle size of the second feedstock varied from 30 to 70 μm. The coating produced from the second feedstock was named as “nano-coating”. The selected area electron diffraction (SAED) patterns (see the inset of Fig. 2c and d) suggested the grains belonged to the tetragonal phase. Two types of coatings were deposited by high efficiency supersonic atmospheric plasma spraying (SAPS) system. The spray parameters are listed in Table 1. The particles temperature and velocity were measured using Spray Watch 2i on-line monitoring system (Oseir, Finland) in Table 2.

### 2.2. Thermal shock test

Thermal shock test was conducted in a muffle furnace. When the temperature inside the furnace reached 1100 °C, the samples were pushed into the furnace. The holding time was 5 min, then the samples were directly quenched into water, the temperature of the water throughout the cycling was between 20 and 30 °C. More
than 10% of the spalled region of the surface of the top coating was adopted as criteria for the failure of the coating.

2.3. Specimen characterization

The phase compositions of the feedstock powder and as-sprayed coatings were characterized by X-ray diffraction (XRD, D/MAX-2400X, Rigaku, Japan) using Cu Kα radiation (λ = 0.15406 nm) produced at 40 kV and 40 mA. The range of scattering angle (2θ) was from 10° to 90° with a scan step of 0.008°. The feedstock powder and each type of coating were analyzed three times using XRD. During the following analysis with the X’Pert High Score Plus, the X-ray diffraction peaks produced by Cu Kα2 radiation were excluded in order to make the result accurate.

Microstructure of as-sprayed coating was observed by scanning electron microscopy (SEM, VEGAII XMU, Tescan, Czech Republic) and high resolution transmission electron microscopy (HRTEM, JEM-2100F, JEOL, Japan). After substrate was removed from the as-sprayed coating by wire-electrode cutting, plan-view and cross-section specimen for HRTEM analysis was prepared by mechanical grinding, polishing and dimpling, followed by Ar-ion milling using a Gatan 691 precision ion polishing system (Gatan Inc., USA). The HRTEM was equipped with an X-twin objective lens with a point resolution of 0.23 nm and operated at 200 kV accelerating voltage.

In order to further reveal grain boundaries, phases, and other microstructural details, ceramic specimens were etched [19]. The thermal etching process was conducted at 1250 °C for 3 h in a furnace, and then cooled down to room temperature. The grain size, crack, porosity and unmelted nano-particles content in the coatings were calculated by quantitative image analysis (IA) using Image-Pro Plus software (Media Cybernetics, Silver Springs, MD). The unmelted nano-particles and pores were selected from SEM images. It was worth noting that the pores that existed in unmelted nano-particles were considered as one part of unmelted nano-particles [20]. After converting the grayscale images to a binary images (see Fig. 3), the final statistical result was the average value from ten cross-sectional micrographs for an individual specimen.

3. Results and discussion

3.1. Microstructure of as-sprayed coatings

Fig. 4 shows the microstructure of as-sprayed submicron-/nano-coatings. As shown in Fig. 4a, the submicron-coating had a denser microstructure and few irregular inter-splat pores and cracks. Meanwhile, as seen in Fig. 4b, the submicron-coating was composed of well-adhered lamellar structures (splat). The columnar grains within the splats were visible (see Fig. 4c) because rapid nucleation occurred at the cooler surface of the flattened droplet at large undercooling and the crystals grew rapidly opposite to the heat flow, forming a columnar grain structure. Fig. 4d–f shows the cross-sectional SEM images of the as-sprayed nano-coating. As seen from Fig. 4d–f, typical structures with columnar grains were also observed, since the molten droplets successively impinged and spread on the substrate or previously deposited layers to form continuous splats. However, the nano-coating was distinct from submicron-coating because some unmelted particles were loosely distributed in the recrystallization zone (splat). These unmelted particles retained the initial nanostructure of feedstock, as later
confirmed by TEM (see Fig. 7). During the plasma spraying, the momentum and energy transfer process between the plasma and injected particles were crucial in the melting state of the in-flight particles. For one injected particle, its temperature was higher at the surface and lower at the center. Therefore, the unmelted particles originated from the central part of the original feedstock powder and the crystal formed from the melted part [21]. The latter acted as a binder and retained the coating integrity (see Fig. 4e). The statistical results showed that the porosity and micro-crack content of submicron-coating were approximately 5.1 ± 0.5% and 3.7 ± 0.8%, whereas those of the nano-coating were approximately 5.8 ± 0.2% and 1.6 ± 0.2%, respectively. Compared with the columnar grains formed from the melt, the proportion of unmelted nano-particles was relatively smaller and its content was 13.3 ± 0.4% in the nano-coating. The higher porosity of nano-coating may be attributed to the loosely distributed feature of unmelted particles, which decreased the effective bonding surface between splats and led to the formation of inter-splat pores.

The SEM images of the submicron-coating surface after thermal etching are illustrated in Fig. 5. As can be seen from Fig. 5a, the submicron-coating consisted of grains with different sizes while some micropores were found at the intersection of multiple grains. It was clear from Fig. 5b that most of grain sizes were distributed in 100–400 nm and the 100–200 nm sized grains had the largest percentage (approximately 33%). The average grain size of submicron-coating was approximately 282 nm. Besides, some nano-grains were also found in the submicron-coating and its percentage was approximately 6%.
In order to further reveal the grain sizes and the grain boundaries, TEM images of the as-sprayed submicron-coating are shown in Fig. 6. The statistical results from Fig. 6a showed that the grain size was in the range of 150 to 450 nm with the average size of 250 nm, which was in agreement with the result (282 nm) from the thermal etching method. The stable polyhedron shape for the equiaxed grains was developed after the melting and recrystallization process of the original submicron-sized feedstock powder (grain size was 120–580 nm). Meanwhile, the selected area electron diffraction (SAED) patterns suggested that the grains in the submicron-coating belonged to the tetragonal phase with preferential growth along the [1 1 0] direction (as illustrated in Fig. 6a). The HRTEM image of a boundary among three grains is shown in Fig. 6b. It can be seen that the boundary appeared to sustain some form of lattice continuity, which did not contain any other phases. Fig. 6c shows the nanograins with size ranging from 20 to 90 nm in the submicron-coating. The polycrystalline structure was confirmed by the SAED pattern. In addition, the grain boundary appeared to sustain some form of lattice continuity (see Fig. 6d).

The appearance of the nanograins was associated with the recrystallization of molten particles. Our previous work confirmed that the in-flight particles melted and broke up through strong

Fig. 5. (a) SEM images and (b) statistical results on grain size of the as-sprayed submicron-coating after thermal etching at 1250°C for 3 h.

Fig. 6. (a) TEM image of submicron grains and electron diffraction pattern of grain A in the as-sprayed submicron-coating; (b) HRTEM image of intersection of multiple submicron grains marked by the white circle of (a); (c) TEM image of nanograins and selected area electron diffraction pattern of nanograins in the as-sprayed submicron-coating; (d) HRTEM image of boundary between two equiaxed nanograins marked by the white circle of (c).
coupling with the supersonic plasma jet in thermal and momentum transfer, which resulted in the deposited SAPS-particles being significantly smaller in size than either the original feedstock powders or the subsonic particles. After the fragmented particles in the supersonic plasma jet impinged onto the substrate, the rapid nucleation occurred at the cooler surface at large cooling rate. It was proved that the solidification time of fragmented SAPS-particles was about 0.3 μs \cite{22}. The higher cooling rate will lead to a larger under-cooling and nucleation rate \cite{23}, which resulted in the formation of nanograins in the submicron-coating.

Fig. 7 gives the TEM images of the as-sprayed nano-coating. It can be seen from Fig. 7a that the coating consisted of polycrystalline grains with different sizes. The smaller grains were surrounded by some larger equiaxed grains. It was clear from Fig. 7b and c that the sizes of smaller grains were ranging from 30 to 90 nm, however, the sizes of larger grains were in the range of 110–900 nm. The SAED pattern (inset in Fig. 7c) suggested that the equiaxed grains belonged to the tetragonal phase. Fig. 7d shows that the unmelted particles distributed in the nano-coating. The sizes of unmelted particles were in the range of 20 to 60 nm indicating these unmelted nano-particles retained the initial nanostructure of feedstock powder (see Fig. 2c and d). Fig. 7e shows the fusion zone between partially melted particles and recrystallization zone. The distinct feature was mainly attributed to the heat transfer and energy diffusion of the in-flight particles when they impinged onto the solidified surface of splat. Thus, the partially melted particles and recrystallization zone were coalesced together. In addition, as seen from Fig. 7f, some amorphous phases were discovered in the nano-coating. There were some faint rings in SAED patterns (inset in Fig. 7f), which showed the amorphous nature. Crystal nuclei were almost not formed at extremely rapid cooling rate, which resulted in a disorder solid state in the molten region. Based on the above analysis, the nano-coating exhibited a multi-modal microstructure, including the nanograins (30–90 nm in size), submicron grains (110–900 nm in size), unmelted nano-particles (20–60 nm in size) and amorphous phase.

3.2. Microstructural evolution during thermal cyclic test

3.2.1. Microcrack and porosity of the submicron-coating

Typically, the defects of plasma-sprayed coatings mainly consisted of microcracks and pores. Fig. 8 shows that some microcracks and pores were homogeneously distributed in coatings after different thermal cycles. Some short cracks propagated into several millimeters in length as shown in Fig. 8a–d. The statistical results showed that the microcrack content gradually increased from 3.7 ± 0.8% to 4.6 ± 0.7% after 261 thermal cycles (see Fig. 8e). Obviously, the microcrack content linearly increased. When thermal cycles reached to 237 numbers, some coarse vertical cracks were clearly observed. These vertical cracks could improve the thermal shock resistance of coating to some extent \cite{24}. The main reason for the formation of vertical cracks can be explained by the fact that the inter-lamellar gaps acted as the pre-cracks in the as-sprayed coating. These pre-cracks initiated and propagated when the coating was subjected to the mechanical or thermal tension stress \cite{25}. In addition, the porosity decreased from 5.1 ± 0.5% to 3.4 ± 0.5% due to the sintering effect after 261 thermal cycles (see Fig. 8f).

3.2.2. Microcrack, porosity and unmelted nano-particles of nano-coating

Fig. 9 shows the microstructural evolution of nano-coating during thermal shock test. It can be seen from Fig. 9a that some cracks were almost paralleled to the top/bond coat interface and propagated at the interfaces between unmelted nano-particles and recrystallization zone (splats). Moreover, the microcrack content increased from 1.6 ± 0.2% to 3.5 ± 0.2% after 170 thermal cycles (see Fig. 9b). However, the content of unmelted nano-particles decreased from 13.3 ± 0.4% to 7.3 ± 0.7% (see Fig. 9c) and porosity reduced from 5.8 ± 0.2% to 4.1 ± 0.5% (see Fig. 9d) after 170 thermal cycles.

The interface between the unmelted nano-particles and recrystallization zone in nano-coating is shown in Fig. 10. The unmelted
Fig. 8. Microstructural evolution of the submicron-coating after different thermal cycles: (a) as-sprayed coating; (b) 100 cycles; (c) 237 cycles; (d) 261 cycles; (e) microcrack; (f) porosity.

Fig. 9. Microstructural evolution of the nano-coating after different thermal cycles: (a) as-sprayed coating, 100 cycles, 145 cycles and 170 thermal cycled coatings; (b) microcrack; (c) unmelted nano-particles; (d) porosity.
nano-particles were surrounded by the recrystallization zone in which some micro-cracks and pores can be observed (see Figs. 9a and 10a). After 170 thermal cycles, many micro-cracks and pores healed up due to the sintering effect upon exposure to high temperature (see Fig. 10b). The unmelted nano-particles also sintered at high temperatures. In particular, the interface between the unmelted nano-particles and recrystallization zone of submicron-/nano-coatings resulted in the decrease of content of unmelted nano-particles from 13.3 ± 0.4% to 7.3 ± 0.7% after 170 thermal cycles. The above results can be explained by the fact that the densification rates of unmelted nano-particles were higher than recrystallization zone since the presence of nano-grains and pores within the unmelted particles that could produce a higher driving force for sintering and densification [17]. Therefore, the unmelted nano-particles tended to densify or shrink at a faster rate than the recrystallization zone, which resulted in the decrease of content of unmelted nano-particles and the appearance of cracks that ran along the interfaces between unmelted nano-particles and recrystallization zone. These cracks may cause the premature failure of nano-coating during thermal shock test.

The size of unmelted nano-particles in the as-sprayed nanocoating was 20–60 nm as illustrated in Fig. 7d. With the increase of thermal cycles, the particle size rapidly increased as shown in Fig. 11a–c and the average particle size increased from 120 to 280 nm as seen from Fig. 11d. This was due to the lower growth activation energy of the nano-particles, which came from the existence of micro-pores in unmelted nano-particles and the grain-rotation-induced grain coalescence mechanism [9,14].

3.2.3. Shrinkage of recrystallization zone of submicron-/nano-coatings

To further illustrate the shrinkage and densification of splats of submicron-/nano-coatings after different thermal cycles, the columnar crystals within splat and the splat–splat interface within the recrystallization zone are analyzed in Fig. 12. With increasing the thermal cycles, the microstructure of submicron-coating gradually changed, such as grooving and bridging of interfaces between splats. Fine-scale pores and intra-splat micro-cracks healed up, which may enhance the bonding between adjacent splats. After 100 thermal cycles, the columnar grains had a constricted deformation in both in-plane and through-thickness directions until the formation of some necks as shown in Fig. 12b. Some surface undulation developed on the surface of these columnar grains in the 180 thermal cycled coating (see Fig. 12c). The size of these undulations

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Fig. 10. Higher magnification of unmelted nano-particles and recrystallization zone/unmelted nano-particles interface in nano-coating: (a) as-sprayed coating; (b) 170 thermal cycled coating.

Fig. 11. Morphology of unmelted nano-particles: (a) as-sprayed coating; (b) after 145 thermal cycles; (c) after 170 thermal cycles; (d) particle size of 170 thermal cycled coating after thermal etched treatment.
increased with the increase of thermal cycles. After the distortion of columnar grains, the sintering stress accumulated which provided the driving force for the propagation of cracks [26,27]. After 261 thermal cycles, the intra-splat cracks and fine inter-lamellar pores exhibited significant healing up leading to the higher dimensional changes of columnar grains within splats and to form very densified structure (as shown in Fig. 12d). These results may be caused by the surface and grain boundaries diffusion, which dominated the sintering behavior [28].

The morphology of splats in nano-coating before and after thermal cycling is shown in Fig. 13. As seen from Fig. 13a–d that the sintering necks of columnar grains developed accompanied by the obvious healing-up of columnar grains and inter-lamellar cracks with increasing the thermal cycles. The volume shrinkage of splats of nano-coating was basically similar with submicron-coating. The higher dimensional change may cause the debonding at the top coat/bond coat interface leading to the spallation of top coat.

3.2.4. Thermal shock resistance of coatings

The final thermal cycles of submicron-/nano-coatings were 261 and 170 numbers, respectively. More than 10% of the spalled region of the surface for the both top coatings was adopted as criteria for the failure of the coating. Compared with the nano-coating, the submicron-coating showed a higher thermal shock...
resistance. The possible reasons are as follows: due to the higher densification rate of the unmelted nano-particles, the interfaces between recrystallization zone and unmelted nano-particles linked up, which resulted in the decrease of content of unmelted nano-particles from 13.3 ± 0.4% to 7.3 ± 0.7% in the nano-coating. In addition, the weak bond and higher shrinking rate of nano-particles led to the formation of parallel cracks that ran along the recrystallization zone/unmelted nano-particles interfaces. These cracks caused the premature failure of nano-coating during thermal cycles test. Besides, the multi-modal structure of nano-coating was thermodynamically unstable at high temperatures. The nano-grains, unmelted nano-particles and amorphous phase were metastable in thermodynamics. The nanograins with lower activation energy grew to submicron grains (120–280 nm) under high temperature treatment. The transformation from the amorphous phase to crystal led to the decrease of volume due to the arrangement of atoms.
Then the volume contraction was generated and converted to the formation of cracks [29–32]. Hence, the high-temperature instability of the nano-coating increased the grain size and contraction stress within the coating, which resulted in its premature failure.

However, the dual-model structure of submicron-coating with a very dense microstructure overcame the inherent deficiencies of nano-coating at high temperatures. The submicron-/nano-grains in submicron-coating only came from the recrystallization zone. The abundant grain boundaries greatly prolonged the crack propagation path and enhanced the thermal shock resistance of submicron-coating. HRTEM results from our previous study indicated that the average height and width of columnar grains of SAPS-coating were 0.71 ± 0.08 and 0.31 ± 0.04 μm [33]. The fine lamellar structure enhanced the inter-splat cohesion and improved the formation of vertical cracks, which was helpful to improve the thermal shock resistance of submicron-coating.

3.3. Phase composition

Phase composition of submicron-/nano-coatings after different thermal cycles was characterized by X-ray diffraction. The XRD patterns are shown in Fig. 14. As seen from Fig. 14a and d, both of the coatings were composed of a mixture of non-transformable tetragonal t’ and tetragonal t zirconia phases. As seen from Fig. 14b and e, in the 27–32° low-angle region, the monoclinic phase was not observed, and the XRD peak position shifted to a small angle, because the volume inflation increased the crystalline inter-planar space and induced the excursion of the peak position. In addition, metastable tetragonal t’ and tetragonal phases (t) can be clearly separated through the position of (0 0 4) and (4 0 0) Bragg reflections [34]. Fig. 14c and f shows the high angular resolution X-ray diffractograms in the range of 72–75° of the as-sprayed and different thermal cycled coatings. The t/t’ mixture phases were proved in submicron-/nano-coatings. Some differences of peak position were closely related to crystalline cell lattice parameters [35]. However, the lattice strain that caused by the excursion of these peaks position was very small [36]. Therefore, the phase composition was not the main reason for the spallation of the submicron-/nano-coatings.

4. Conclusions

In this work, the microstructural evolution and failure mechanism of submicron-/nano-coatings during thermal shock test were comparatively studied. The main conclusions are as follows:

1) The submicron-coating mainly consisted of the submicron-grains (150–450 nm in size) with some nano-grains (20–90 nm in size) distributed in it, however, the nano-coating exhibited a multi-modal structure and consisted of recrystallization zone (including 30–90 nm sized nano-grains and 110–500 nm sized submicron-grains), 20–60 nm sized unmelted nano-particles and amorphous phase.

2) With the increase of the thermal cycles, the micro-crack density increased, and the content of the porosity decreased for both coatings. Especially, the content of unmelted nano-particles in the nano-coating decreased from 13% to 7% due to the link-up of interfaces between recrystallization zone and unmelted nano-particles.

3) The high-temperature instability led to the increase of the grain size and contraction stress within the nano-coating. The weak bond and higher shrinking rate of unmelted nano-particles resulted in the formation of parallel coarse cracks that ran along the recrystallization zone/unmelted nano-particles interfaces. These cracks caused the premature failure of nano-coating during thermal cycle test.

4) The submicron-coating showed a better thermal shock resistance compared with the nano-coating at high temperatures. The t/t’ mixture phases coexisted in as-sprayed and thermal cycled submicron-/nano-coatings. The monoclinic phase was not observed in both coatings.

Acknowledgements

This work was supported by National Natural Science Foundation of China (Grant No. 51202187), National Basic Research Program (Grant No. 2013CB035701), Fundamental Research Funds for the Central Universities (Grant No. xj2014125), Natural Science Foundation of Shaanxi Province, China (Grant No. 2015JQQ1538) and National Natural Science Foundation of China (Grant No. 51476131) and the State Scholarship Fund of China Scholarship Council (Grant No. 201406285038).

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