

Effect of Cr₂O₃ on the Microstructure and Oxidation Resistance of Enamel Coating with TC4 Titanium Alloy

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By adding 0 % to 50 % Cr₂O₃ ceramic particles, the enamel composite coating is produced on the surface of TC4 titanium alloys. The detection analysis indicates that with the increase of the amount of Cr₂O₃ particles added, the density of enamel coating increases as well, and the amount of the pore holes decreases at the same time, but the enamel coating becomes porous with more than 30 % of the amount of Cr₂O₃ particles added. The main crystalline phases of enamel coating are NaAlSi₃O₈ and Ca₂SiO₄, whereas the Cr₂O₃ ceramic particles added are mainly presented as an independent phase, and part of the particles are in the form of Ca₅Cr₃O₁₂ phase after the reaction. The enamel coating with 30 % Cr₂O₃ ceramic particles added has the best high-temperature oxidation resistance, mainly because the main crystalline phase of NaAlSi₃O₈ is changed into Na₂Si₂O₅ during the high-temperature oxidation, which is beneficial to the self-healing of the coating.

Keywords: TC4 titanium alloy, enamel coating, Cr₂O₃ ceramic particles, high-temperature oxidation resistance.

1. INTRODUCTION

The application of titanium alloys as hot end components in the fields of aerospace and the modern gas turbine is gradually heading for high temperature [1–3]. The maximum operating temperature of TC4 titanium alloys (hereinafter referred to as TC4) is 450 °C. When the operating temperature exceeds 600 °C, the oxide film with poor oxidation resistance is formed on the surface of titanium alloys, resulting in severe performance degradation of alloys [4, 5]. Enamel coating is a composite coating of indifferent oxide with a compact structure, so the diffusion migration rate of oxygen is extremely low, and the coating can maintain high thermal stability under high temperature. Moreover, the enamel coating does not have degradation problems that other similar metal coatings have. Its mechanical properties and thermal expansion coefficients can be changed by controlling its chemical composition to meet the operating requirements for matrix metal [6, 7]. However, for quite a long time, enamel coating has been mainly applied in the surface protection of steel-based materials and generally recognized as low-end coating technology. Thus it is seldom applied in the surface protection of titanium alloys [8, 9].

In this study, by taking advantage of the merits of Cr₂O₃ such as high melting point (2,435 °C), high chemical stability and being the main component of high-temperature resistant materials [10, 11], composite enamel coating with reinforced Cr₂O₃ ceramic particles is produced on the enamel glaze of TC4 titanium alloy. The effect and mechanism of Cr₂O₃ ceramic particles on the

microstructure and high-temperature oxidation resistance of enamel coating are investigated, and the ways of enamel coating to significantly improving the high-temperature oxidation resistance performance of TC4 titanium alloy are discussed in order to expand the application temperature range of TC4 titanium alloy engineering.

2. EXPERIMENTAL PROCEDURE

2.1. Production of enamel coatings

The sample size of TC4 titanium alloys is Φ 20 × 5mm, preoxidized at 500 °C, ultrasonically cleaned with acetone for 20 minutes, and baked in the oven of 75 °C for 20 minutes. The formula of raw mineral materials is shown in Table 1. After being melted in the temperature of 1450 °C for 10 hours and then rapidly quenched into the cold water, bulk glasses are obtained under the conditions that the mixing speed of the ball mill is 180 r/min, the ball to powder weight ratio is 2:1, and the mixing time is 1 hour. Glass powders are then obtained by ball grinding of the bulk glasses. Weighing 100 grams of glass powders as a reference, Cr₂O₃ ceramic particles and other components are mixed up according to the formula in Table 2. After mixing, 6 groups of enamel glaze powders were obtained by grinding with mortar and then adding absolute alcohol to adjust the volume-weight ratio of the enamel glaze to 1.28–1.35 g/mL. Finally, the enamel glaze slurry for the experiment is obtained.

The TC4 titanium alloy samples are firstly sprayed evenly with enamel slurry on the surface, and then dried in the oven at 75 °C for 10 minutes. After 8 minute sintering at 900 °C, emerald composite enamel is produced.

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Table 1. The formula of raw mineral materials (wt.%)

Composition	SiO ₂	Al ₂ O ₃	B ₂ O ₃	CoO	TiO ₂	ZrO ₂	MgO	CaF ₂	NiO	Na ₂ O + K ₂ O
Content	55–65	3–5	8–10	1.5–2.5	1.5–2.5	1.5–3.0	3.5–4.5	2.5–3.5	0.5–1.5	8–10

Table 2. The formula of enamel glaze powder

No.	Glass powder, g	Grinding compositions, wt.%					
		Cr ₂ O ₃	V ₂ O ₅	CeO ₂	Y ₂ O ₃	Clay	Bentonite
1	100	0	5	1.5	1.5	3	0.5
2	100	10	5	1.5	1.5	3	0.5
3	100	20	5	1.5	1.5	3	0.5
4	100	30	5	1.5	1.5	3	0.5
5	100	40	5	1.5	1.5	3	0.5
6	100	50	5	1.5	1.5	3	0.5

2.2. Testing method

The micromorphology of enamel composite coating is observed with S-4700 SEM (Scanning Electron Microscope), the elements of the micro coating area are analyzed with EDS (Energy Dispersive Spectrometer). During the observation, the acceleration voltage is 20 KV, and the emission current is 10 A. The phase composition of the coating is analyzed with D/Max-2200VPC XRD (X-ray Diffraction).

The high-temperature oxidation resistance of the coating is evaluated by the oxidation kinetic curves of coating, which is drawn by measuring the changes in the coating weight after oxidation at a constant temperature. The testing conditions are: the isothermal oxidation is carried out at 700 °C, and the total oxidation time is 100 hours. The surface area of the sample is S (cm²). The initial weight of the sample before oxidation is M_0 (mg), and the measured weight is M_1 (mg). The samples are taken out for weighting for every 10 hours. The weight change of the coating sample in the corresponding oxidation time is obtained according to the formula $\delta = (m_1 - m_0)/s$.

The oxidation resistance of metals or coated metals can be evaluated by the oxidation kinetics curve. The kinetic curves of oxidation generally have four types: straight line, parabola, logarithm and cube. The corresponding antioxidant capacity reduces following the order of logarithm, cube, parabola and straight line.

All the phase diagrams in this paper are obtained by using phase equilibria diagrams database software, so no references are given.

3. RESULTS AND ANALYSIS

3.1. Effect of Cr₂O₃ ceramic particles on the morphology of enamel coatings

Fig. 1 shows the surface morphology of enamel coating with different proportions of Cr₂O₃ ceramic particles added. Fig. 1 a is the coating structure without Cr₂O₃ ceramic particles. There are a great number of pores on the surface of the coating and the size of the pores is rather large. Because the clay in the glaze dehydrates and decomposes during the sintering process, producing a large amount of gas, which is not timely or sufficiently discharged out of the fused ceramic glaze. When the proportion of Cr₂O₃ ceramic particles is less than 30 % (as

shown in Fig. 1 b–d, the number of pores inside the coating decreases with the increase of the content of Cr₂O₃ ceramic particles added. The crystals separated out during the cooling of the fused ceramic glaze are dispersed in a dotted shape and cohered with the enamel amorphous phase, making the coating structure more compact and smoother. However, when the proportion of Cr₂O₃ ceramic particles is more than 30 % (as shown in Fig. 1 e and f), there are scarcely any pores on the coating surface. The crystals separated out are distributed in a dendritic shape, and the coating structure becomes rough and shaggy, because the Cr₂O₃ ceramic particles become the nucleating agents for crystallization during the sintering process of the enamel coatings, making crystals separate out and grow up in large quantities. But due to the high melting point of Cr₂O₃, excessive Cr₂O₃ ceramic particles cannot be well cohered with amorphous glass phase. It results in the incomplete coating sintering and underfiring, which makes the coating structure rough and shaggy.

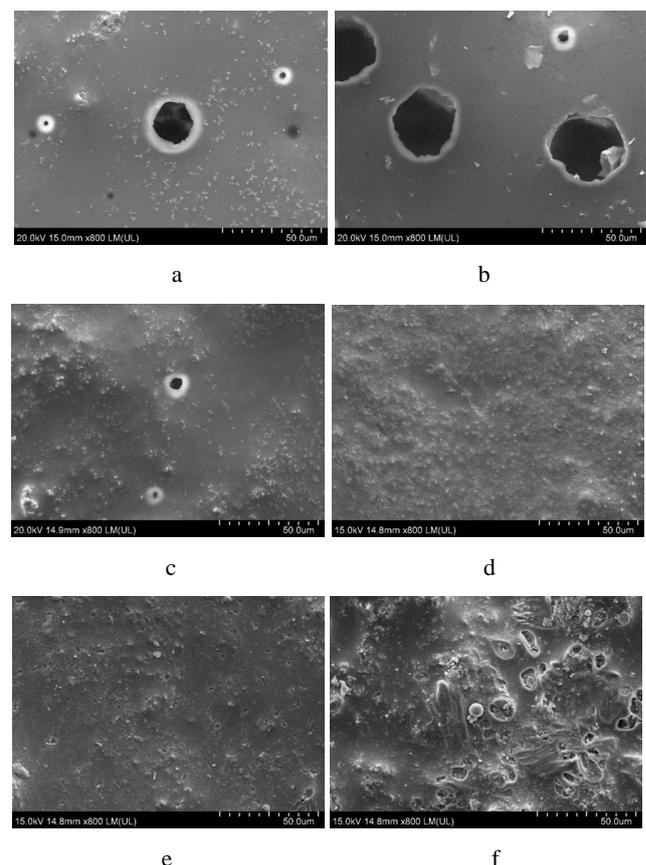
**Fig. 1.** Surface morphology of enamel containing different Cr₂O₃ ceramic particles

Fig. 2 shows the XRD patterns of enamel coatings with 0 % and 30 % Cr₂O₃ ceramic particles added. It can be seen from the figure that the main phase in the enamel coatings is NaAlSi₃O₈, and the phases of Ca₂SiO₄ and CaZrTi₂O₇ are also detected in the enamel coating, but it is an only single-peak spectral line. The reason is that the

enamel coating is non-crystal, there is only a small amount of crystal phases precipitating from the crystal nucleus with opacifier(CaO, TiO₂ and ZrO₂ in the mineral raw materials with less introduction amount) in the sintering process, so there is less precipitation of Ca₂SiO₄ and CaZrTi₂O₇ phase. Moreover, the independent phase of Cr₂O₃ is also detected in the enamel coating with 30% Cr₂O₃ ceramic particles. By inquiring the CaO-TiO₂-ZrO₂ ternary phase diagram (Fig. 3), it can be concluded that the coating sintered will form Ca₅Cr₃O₁₂ phase at 900 °C, which means that ceramic particles as the wild phase in the composite coating partly exist as independent phase and partly chemically react with glaze oxide of the coating to combine with each other.

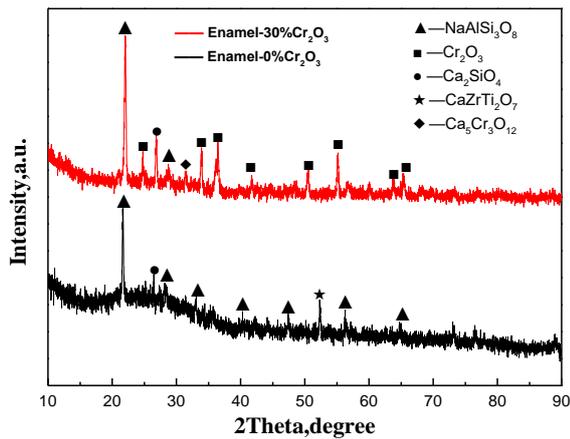


Fig. 2. XRD patterns of enamel coating 0 % and 30 %Cr₂O₃

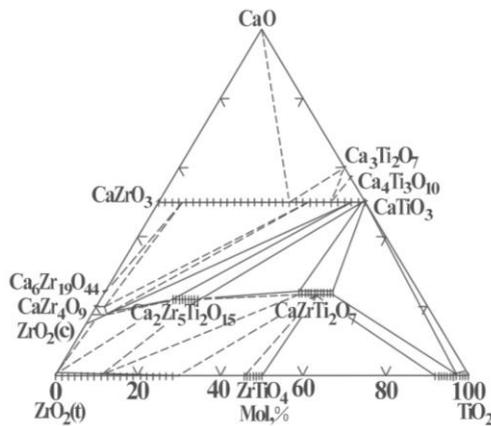


Fig. 3. CaO-TiO₂-ZrO₂ ternary phase diagram at 900 °C

3.2. Effect of Cr₂O₃ ceramic particles on high-temperature oxidation resistance of enamel coating

Fig. 4 provides oxidation kinetics curves of TC4 alloy and enamel layer containing different amount of Cr₂O₃. It can be seen from the figure that, after 100 hours of oxidation at 700 °C, the oxidation resistance of TC4 titanium alloy with coating protection is much stronger than the oxidation resistance of the alloy without coating protection. The oxidation weight gains of enamel coating with 10 %, 20 %, and 30 % of Cr₂O₃ ceramic particles added respectively are all less than those of enamel coating without Cr₂O₃ ceramic particles, among which the least weight gain happens at enamel coating with 30 % Cr₂O₃ ceramic particles, with a ratio of 0.571 mg/cm², which is 38.71 % less than enamel coating without Cr₂O₃ ceramic particles. However, enamel coating with 40 % Cr₂O₃ ceramic particles, although it has the same oxidation weight gain as enamel coatings with 10 %, 20 %, and 30 % Cr₂O₃ ceramic particles in the first 40 hours, has a significant oxidation weight gain and exceeds the coating without Cr₂O₃ ceramic particles when the oxidation time is longer than 40 hours. Enamel coating with 50 % Cr₂O₃ ceramic particles has fallen off distinctly after 40 hours of oxidation, so there is no more subsequent oxidation test conducted.

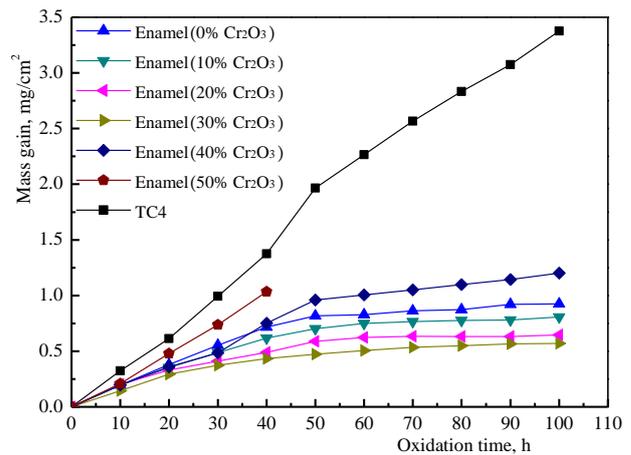


Fig. 4. Oxidation kinetics curves of enamel coatings with different Cr₂O₃ content at 700 °C

The oxidation weight gain and the oxidation time of enamel coatings with different Cr₂O₃ content is fitted and tested by F using ExpAssoc model of Origin 9.0 software, and the significance of fitting can be identified by F-test. Table 3 lists the fitting equations and the test results.

Table 3. Fitting equation of oxidation weight gain of enamel coatings with different Cr₂O₃ content

Cr ₂ O ₃	Fitting equations	F Value	Prob > F
0 %	$y = -0.03259 + 0.51461 \times \left[\left(1 - e^{-\frac{t}{34.08278}} \right) + \left(1 - e^{-\frac{t}{34.08073}} \right) \right]$	646.54	4.95E-8
10 %	$y = -0.02017 + 0.44164 \times \left[\left(1 - e^{-\frac{t}{33.01778}} \right) + \left(1 - e^{-\frac{t}{33.01934}} \right) \right]$	1016.29	1.27E-8
20 %	$y = -0.00233 + 0.34169 \times \left[\left(1 - e^{-\frac{t}{29.25635}} \right) + \left(1 - e^{-\frac{t}{29.2588}} \right) \right]$	960.69	1.51E-8
30 %	$y = -0.00552 + 0.6016 \times \left(1 - e^{-\frac{t}{30.63344}} \right)$	5233.39	9.41E-11
40 %	$y = -0.00233 + 0.76342 \times \left[\left(1 - e^{-\frac{t}{56.39777}} \right) + \left(1 - e^{-\frac{t}{56.39817}} \right) \right]$	311.094	4.40E-7

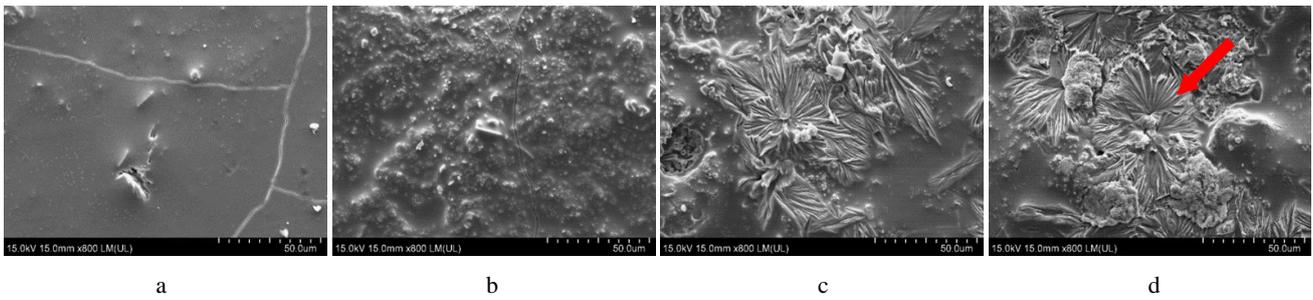


Fig. 5. The SEM images of enamel containing different Cr_2O_3 after oxidation 100 h at 700 °C

It can be summarized from the table that the probability of all the F values of the fitting equations is far less than 0.05, which shows that the regression equation is significant. The F value of the fitting equation of 30 % Cr_2O_3 enamel coating is at its maximum, and the corresponding probability value is at its minimum, which indicates that the fitting effect is the best.

Fig. 5 presents the SEM images illustrating morphology of enamel coatings containing different amount of Cr_2O_3 ceramic particles after 100 hours of oxidation at 700 °C. From this figure it can be observed that after high-temperature oxidation some microcracks appear on the enamel coatings without Cr_2O_3 ceramic particles. Microcracks also appear on the coatings with 10 % Cr_2O_3 ceramic particles in a smaller quantity. When the proportion of Cr_2O_3 ceramic particles in the enamel coating reaches 20 % and 30 %, there are no distinct cracks on the surface, but the radiation morphology like chrysanthemums appears.

Through the EDS test with the position of the arrow shown in Fig. 5 d, the result is displayed in Table 4 and Fig. 6.

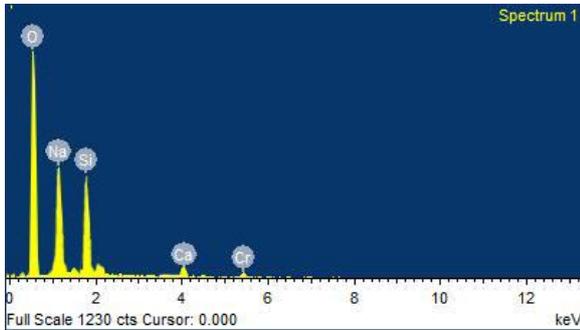


Fig. 6. EDS test results of 30 % Cr_2O_3 enamel coating after oxidation at 100 h at 700 °C

Table 4. EDS test results of 30 % Cr_2O_3 enamel coating after oxidation at 100 h at 700 °C

Element	O	Na	Si	Ca	Cr	Total
Weight %	45.15	25.53	28.32	0.66	0.34	100.00
Atomic %	56.88	22.36	20.30	0.33	0.13	100.00

There are two reasons why Cr_2O_3 ceramic particles can reduce the cracking tendency: one is that the Cr_2O_3 as high-temperature oxide has a high melting point and chemical stability, which improves the high-temperature resistance of enamel coatings. The other is that the coefficient of linear expansion of enamel coating is different from that of Cr_2O_3 ceramic particles, so stressed

zones are formed around Cr_2O_3 ceramic particles. The stressed zones will hinder cracks from extending in a straight line and deflect them, which prevents fast crack propagation and increase the rupture work of composite enamel coating [12–14]. Thus, the cracking tendency is reduced.

Fig. 7 presents the XRD patterns of enamel coatings with 0 %, 20 % and 30 % Cr_2O_3 ceramic particles added after high-temperature oxidation. It can be learned from the figure that the main phases of the enamel coating without Cr_2O_3 ceramic particles after high-temperature oxidation are still $\text{NaAlSi}_3\text{O}_8$ and Ca_2SiO_4 . The sodium silicate ($\text{Na}_2\text{Si}_2\text{O}_5$) peak is detected in the enamel coatings with 20 % and 30 % Cr_2O_3 , and the intensity of the peak was the highest. Combined with the EDS results of the position shown in Fig. 4 d, it can be concluded that when the content of Cr_2O_3 is more than 20 %, the main crystal phase changed from albite ($\text{NaAlSi}_3\text{O}_8$) to sodium silicate ($\text{Na}_2\text{Si}_2\text{O}_5$).

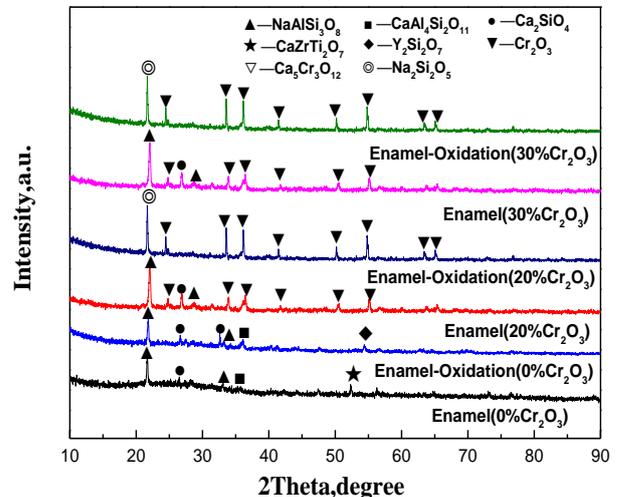


Fig. 7. XRD patterns of enamel coating 0 %, 20 % and 30 % Cr_2O_3

Fig. 8 shows the Na_2O - SiO_2 binary phase diagram. It can be learned from Fig. 6 that the melting point of sodium silicate is relatively low, so during the long-term oxidation at 700 °C, sodium silicate ($\text{Na}_2\text{Si}_2\text{O}_5$) can soften and bond cracks inside the enamel coating, so as to improve the protective performance of the coating, which can be called the “self-healing” phenomenon of enamel coatings. It is mainly because Cr_2O_3 ceramic particles possess the structure of $\alpha\text{-Al}_2\text{O}_3$. During the long-term high-temperature oxidation, Cr_2O_3 ceramic particles act as the

crystal nucleus to induce crystallization, changing albite into sodium silicate. Thus the high-temperature oxidation resistance of coatings is improved.

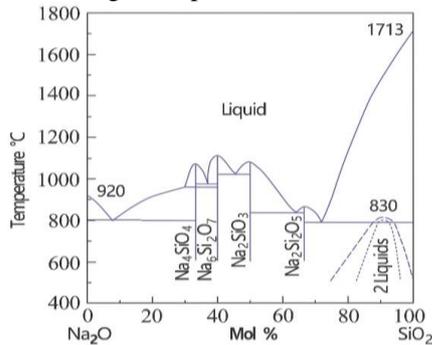


Fig. 8. Na₂O-SiO₂ binary phase diagram

4. CONCLUSIONS

The density of TC4 titanium alloy enamel coating increases and the number of pores inside the coating decreases with the increase of the amount of Cr₂O₃ ceramic particles. However, when the amount of Cr₂O₃ ceramic particles exceeds 30 %, the coating becomes loose. Therefore, the density of the coating is the best when the proportion of Cr₂O₃ ceramic particles is between 20 % and 30 %.

The main crystalline phases of enamel coating are NaAlSi₃O₈ and Ca₂SiO₄. The added Cr₂O₃ ceramic particles mainly exist as independent phase and partly take the shape of Ca₅Cr₃O₁₂ phase.

The high-temperature oxidation resistance of the coating is the best when the proportion of Cr₂O₃ ceramic particles added into the enamel coating is between 20 %–30 %. After 100 hours of oxidation at 700 °C, the oxidation weight gain of enamel coating is 0.572 mg/cm², 38.71 % less than enamel coating without Cr₂O₃ ceramic particles. The main crystalline phase of enamel coating with 30 % Cr₂O₃ ceramic particles changes from NaAlSi₃O₈ into Na₂Si₂O₅, which is beneficial to the self-healing of the coating. Thus, the high-temperature oxidation resistance of coatings is improved.

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