JOURNAL OF MATERIALS SCIENCE **39** (2004) 4887–4892

Fabrication and wear properties of Al_2O_3-SiC ceramic coatings using aluminum phosphate as binder

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Refractory and wear-resistant Al_2O_3-SiC ceramic coatings have been fabricated on A_3 steel using abrasive ceramics (Al_2O_3, SiC), aluminum phosphate binder (inorganic binder), and aluminate ($Al_2O_3 \cdot CaO$) as starting materials. The Powder X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques are used to investigate the chemical compositions of the in-house synthesized aluminum phosphate binder and the morphologies of the fabricated ceramic coatings after abrasion test. The XRD results indicate that monoaluminium phosphate ($Al(H_2PO_4)_3$) is the most effective binding phase in aluminum phosphate binder, and that aluminum phosphate binder at high temperatures is a mixture of several phases. It is also found that the addition amount of the stabilizer (oxalic acid) has remarkable effect on the storage life of aluminum phosphate binder. The wear test results show that the wear resistance of the A_3 steel covered with Al_2O_3-SiC ceramic coatings is about two times higher than that of the uncoated A_3 steel. The results also indicate that the wear properties of Al_2O_3-SiC ceramic coatings are dependent on fabrication conditions, such as the weight ratio of ceramics to the binder (RCB), the particle size distribution of ceramics, the density of the aluminum phosphate binder, and the Al/P atomic ratio in the aluminum phosphate binder. The optimal fabrication conditions for achieving good wear resistance of Al_2O_3-SiC ceramic coatings are suggested based on the above results.

1. Introduction

Ceramic coatings are widely used for the protection of base metal or cement components in chemical, power, and refractory industries against hot corrosion and oxidation and for the minimization of wear [1]. So far, some fabrication techniques are developed, including chemical vapor deposition (CVD) [2], ionization-assisted magnetron sputter physical vapor deposition (PVD) [3], ion beam assisted deposition (IBAD) [4], thermal spray [5], Sol-gel method [6], and plasma electrolytic oxidation (PEO) [7]. Besides these high-temperature fabrication processes, ceramic coatings can also been formed by spray, dip or brush ceramic paint on the surface of metal or cement components. This is undoubtedly an effective, economic, and workable way of protecting components against the severe environments.

Ceramic paint often consists of ceramic oxides (as abrasive materials) and binders, which not only adhere the ceramic particles together so that they do not fall out of the coating, but also adhere the coating to the substrate. Binders can be polymer or inorganic materials. Polymer binders, such as polyvinyl alcohol (PVA) are widely used at room temperature but cannot withstand temperatures above 200°C [8]. In contrast to polymer binders, oxysulphates, oxychlorides, sodium silicate, and hydraulic cement have high strength at room temperature, but exhibit low strength at high temperatures above 500°C [8–10]. Therefore, these binders are not suitable for use in corrosion and wear resistant coatings for high temperatures applications above 600°C.

Aluminum phosphate binder is a kind of inorganic binders used in refractory ceramic coating systems, which has been investigated and applied in the thermal spray coating systems [11–14]. It is reported that refractories bonded with aluminum phosphate have high strength, high temperature stability, and abrasion resistance [15, 16]. However, its use in ceramic paint system is quite limited in the literature.

In this work, Al_2O_3-SiC ceramic paints have been prepared using alumina (Al_2O_3) and silicon carbide (SiC) as the abrasive ceramics with aluminum phosphate as the binder and aluminate ($Al_2O_3 \cdot CaO$) as curing agent. Aluminum phosphate binder is in-house synthesized from phosphoric acid and aluminum hydroxide, and is stored with oxalic acid ($H_2C_2O_4 \cdot 2H_2O$)

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TABLE I Chemicals used for preparing ceramic coatings

Chemicals	Purity degree	Particle size	Sources
H_3PO_4	Chemical	\	Wuhan Chemical Reagents, Ltd.
$Al(OH)_3$	Analytical	\	Changsha Chemical Regents, Ltd.
H_2SO_4	Analytical	\	Beijing Chemical Regents, LT.
Na(OH)	Chemical	\	Shanghai Chemical Regents, Ltd.
Na_2CO_3	Chemical	\	Shanghai Chemical Regents, Ltd.
$Na_3PO_4 \cdot 12H_2O$	Chemical	\	Wuhan Chemical Reagents, Ltd.
CrO_3	Chemical	\	Tianjing Chemical Reagents, Ltd.
$Al_2O_3 \cdot CaO$	Industrial	\	Henan Boma Group
Al_2O_3	Industrial	40 μm, 1 μm	Yangzhou, Jiangshu, China
SiC	Industrial	14 μm, 3–5 μm	Zhenzhou, Henan, China
$H_2C_2O_4 \cdot 2H_2O$	Chemical	\	Changsha Chemical Regents, Ltd.

as the stabilizer. The prepared Al_2O_3-SiC ceramic paints have been spray-deposited on A_3 steel to form Al_2O_3-SiC ceramic coatings. The present work mainly focuses on the investigation of the aluminum phosphate binder and the wear properties of its related Al_2O_3-SiC ceramic coatings.

2. Experimental work

2.1. Aluminum phosphate binder

The aluminum phosphate binder was synthesized from aluminum hydroxide ($Al(OH)_3$) and orthophosphoric acid (H_3PO_4, 85%). One mole of aluminum hydroxide ($Al(OH)_3$) was dissolved in deionized water, and the solution was added with various moles of phosphoric acid. As a result, these solutions have the theoretical Al/P atomic ratio of 1:3, 1.1:3, 1.2:3, 1.3:3, 1.4:3 and 1.5:3, respectively. These mixed solutions were then permitted to react at 120–140°C. The reaction products were dried in air, and then analyzed with a Simens D500 diffractometer. The X-ray diffraction analysis was conducted using Cu K_α radiation at a voltage of 33 kV with a current of 55 mA and a scanning rate of 0.10°/sec.

In addition, CrO_3 and H_2O were added into the reaction products to adjust the pH value and density of the synthesized aluminum phosphate binder. The flow chart of synthesizing aluminum phosphate binder is illustrated in Fig. 1. The synthesized binders were then stored with the addition of oxalic acid as the stabilizer.

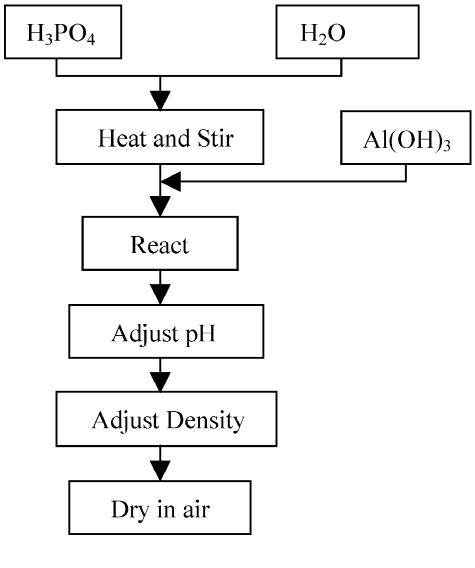

Figure 1 Flow chart of synthesizing aluminum phosphate binders.

2.2. Al_2O_3-SiC ceramic coatings

The raw materials used for preparing ceramic coatings are listed in Table I.

Rectangular plates (70 × 35 × 1 mm) of A_3 steel (containing only Fe and C elements) were used as substrate for the spray deposition of Al_2O_3-SiC ceramic coatings. A_3 steel substrates were pretreated prior to the coating process in order to get good adhesive strength between the ceramic coating and A_3 steel. The A_3 steel was first degreased with chemical solution shown in Table II, derusted by a solution containing H_2SO_4 (20–25 wt%) and Fe^{2+} (<130–150 g/l) at a temperature range of 40–60°C, and then rinsed with acetone and deionized water, and finally dried in air.

The Al_2O_3-SiC ceramic paint was fabricated by mixing the synthesized aluminum phosphorous binder with abrasive ceramics (Al_2O_3 and SiC) and the curing agent ($Al_2O_3 \cdot CaO$). Small and big particles of Al_2O_3 and SiC are selected in order to get an appropriate particle size distribution of ceramics. It is worth to note that the total amount of ceramics is the weight sum of Al_2O_3 (large and small particles) and SiC (large and small particles). For decreasing the stress due to thermal mismatch between the ceramic coating and the A_3 steel, the weight ratio of Al_2O_3/SiC is designed to be 4:6 and remains constant for all the fabricated coatings. The obtained ceramic paints were jet-sprayed on the treated A_3 steel and cured at room temperature (25°C) for 2 h.

After the curing process, the refractory and wear-resistant Al_2O_3-SiC ceramic coatings were fully formed on A_3 steel with a thickness of 300–500 μm (measured with Talyor–Hobson profilometer). The wear properties of the resultant coatings on A_3 steel and the bare A_3 steel (for the purpose of comparison) were determined on a PMJ-1 wear machine (Shenyang

TABLE II Solution and conditions for degreasing A_3 steel

Na(OH)	60 g/l
Na_2CO_3	20 g/l
$Na_3PO_4 \cdot 12H_2O$	40 g/l
OP-10	1–2 g/l
Temperature	70–90°C
Time	10–20 min.

Instruments Institute, China). The A_3 steel covered with Al_2O_3-SiC ceramic coatings and the uncoated A_3 steel were abraded with emery cloth ($180^{\#}$) under a load of 0.5 kg with a sliding frequency of 60 Hz. The wear property of the tested material was evaluated by its weight loss after abrading for 35 min. Three tests were performed for each evaluated material, and the weight loss is the average value given by the three tests. The weight loss is accurate up to 0.1 mg. The morphologies of the ceramic coatings after abrasion test were studied by a KYKY-2800 scanning electron microscope (SEM) at 20 kV with appropriate magnifications.

3. Results and discussion

3.1. The synthesized aluminum phosphate binders

3.1.1. Aluminum phosphate binders synthesized at 120–140°C

Aluminum phosphate binder was synthesized from phosphoric acid and aluminum hydroxide. One mole of aluminum hydroxide ($Al(OH)_3$) was dissolved in deionized water, and various quantities of phosphoric acid were added. The reaction products, which have the theoretical Al/P ratio of 1:3, 1.1:3, 1.2:3, 1.3:3, 1.4:3 and 1.5:3, respectively, were then analyzed by XRD after being dried in air. Fig. 2 shows the XRD patterns of the dried reaction products with different Al/P ratios. It is clear that $AlH_3(PO_4)_2 \cdot 3H_2O$ is the dominant phase of all reaction products with different Al/P ratios. However, there are characteristic peaks of H_3PO_4 when the Al/P ratio is of 1:3, 1.1:3, 1.2:3, respectively. This suggests that the amount of H_3PO_4 in reaction solution be excess. Contrarily, characteristic peaks of $Al(OH)_3$ are observed when Al/P ratio is of 1.4:3 or above, which indicates the excess of $Al(OH)_3$. Therefore, the optimal Al/P ratio in aluminum phosphate binder should be in the range of 1.3:3–1.4:3.

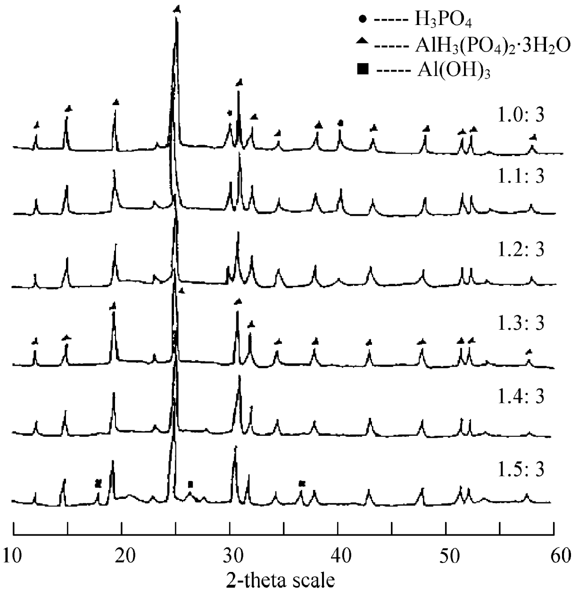

Figure 2 XRD patterns of the dried aluminum phosphate binders with different Al/P ratios.

TABLE III Relationship between the addition amount of oxalic acid and the storage life of the synthesized aluminum phosphate binder at 25°C

Addition amount (wt%, oxalic acid)	Storage life (days)
0	35
1	47
2	58
3	65
4	71

3.1.2. Effect of the stabilizer on the storage life of the aluminum phosphate binder

Dehydration and crystallization tend to occur in aluminum phosphate binder when the Al/P ratio is above 1:3. Ersin *et al.* reported the following reaction occurred during storage [17]:

$$Al(H_2PO_4)_3 \leftrightarrow AlPO_4 \cdot XH_2O + 2H_3PO_4$$

The above reaction will degrade the performance of aluminum phosphate binder. Lyon *et al.* suggested several ways of avoiding this degradation reaction [18]. One effective way is to add stabilizers, such as oxalic acid, citric acid, gluconate, and tartaric acid, into the synthesized binder. In this work, oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) is selected as the stabilizer. Table III gives the relationship between the addition amount of oxalic acid and the storage life of the binder at 25°C. It is obvious that the storage life of the binder after adding 4 wt% $H_2C_2O_4 \cdot 2H_2O$ is about two times that of the binder without oxalic acid.

3.1.3. Aluminum phosphate binder upon heat-treatment

The synthesized aluminum phosphate binder is designed for ceramic paint system used at high-temperature environment. Therefore, the in-depth investigation on the aluminum phosphate at high temperatures is very important. In this work, the aluminum phosphate binder with Al/P ratio of 1.4:3 was heated in a range of 60–1000°C to investigate the chemical compositions of aluminum phosphate binder at high temperatures. Fig. 3 shows the XRD results of the binder at different temperatures, which indicate that the binder after heat-treatment is a mixture of several phases. Similar results are reported in the literature [16, 20]. It is clearly seen from Fig. 3 that the composition of the binder changes from $AlH_3(PO_4)_2 \cdot 3H_2O$ to $Al(H_2PO_4)_3$ accompanied by $AlH_3(PO_4)_2 \cdot H_2O$ when the temperature is slightly elevated to 105°C. When the temperature reaches 200°C, the peaks are characterized as monoaluminium phosphate ($Al(H_2PO_4)_3$), which is the most effective binding phase. Then $Al(H_2PO_4)_3$ converts into phases of $AlH_2P_3O_{10} \cdot 2H_2O$ and $AlPO_4$ (trigonal system) at 220°C. No more dehydration happens after 400°C. However, variations on the crystal system are identified at high temperatures ranging from 400 to 1000°C.

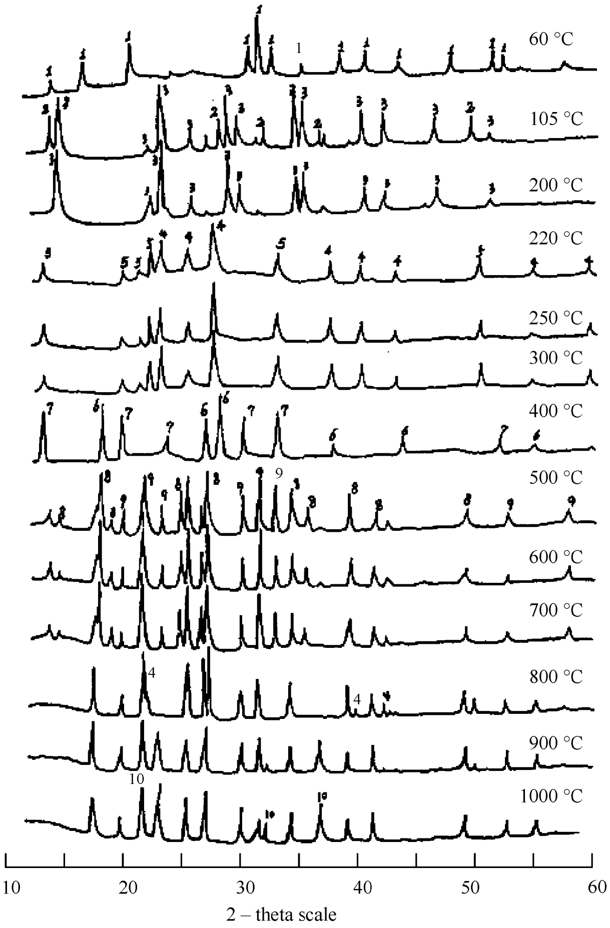

Figure 3 XRD patterns of the aluminum phosphate binder (Al/P = 1.4:3) heat-treated in a range of 60–1000°C, 1. $AlH_3(PO_4)_2 \cdot 3H_2O$; 2. $AlH_3(PO_4)_2 \cdot H_2O$; 3. $AlH_3(PO_4)_2$; 4. $AlPO_4$ (trigonal system); 5. $AlH_2P_3O_{10} \cdot 2H_2O$; 6. $Al(PO_3)_3$ (hexagonal system); 7. $AlH_2P_3O_{10} \cdot 2.5H_2O$; 8. $Al_2P_6O_{18}$; 9. $Al(PO_3)_3$ (cubic); 10. $AlPO_4$ (rhombic system).

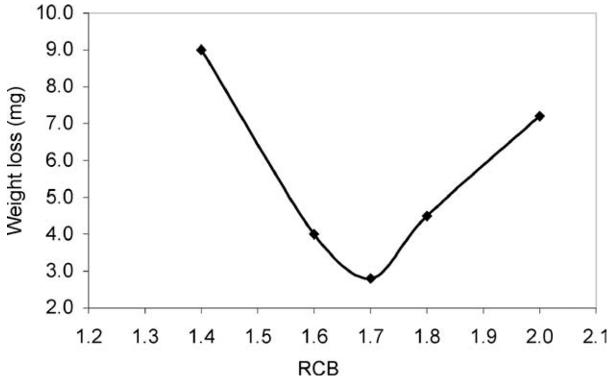

Figure 4 Effect of RCB on the wear property of Al_2O_3-SiC ceramic coatings (used binder:Al/P = 1.4: 3, $\rho = 1.65$ g/cm^3).

3.2. Wear properties of Al_2O_3-SiC ceramic coatings

3.2.1. Effect of the ratio of ceramic particles to the binder (RCB)

Al_2O_3-SiC ceramic coatings were prepared by mixing ceramic particles (Al_2O_3 and SiC) with aluminum phosphate binder (Al/P = 1.4: 3, $\rho = 1.65$ g/cm^3) and aluminate (curing agent). RCB presents the weight ratio of ceramic particles (Al_2O_3 + SiC) to the aluminum phosphate binder. A number of ceramic coatings were fabricated with different RCB values of 1.4, 1.6, 1.7, 1.8, and 2.0, respectively. Fig. 4 shows the effect of RCB on the wear properties of Al_2O_3-SiC ceramic coatings. It can be seen clearly that the weight loss of the ceramic coated A_3 steel is only 2.8 mg at an optimal point (RCB) of 1.7 as compared with 5.8 mg of the uncoated A_3 steel tested under the same abrasion conditions. This indicates that the wear durability of the A_3 steel covered with Al_2O_3-SiC ceramic coating is about two times that of the uncoated A_3 steel. The wear resistance of the fabricated Al_2O_3-SiC ceramic coating is comparable to the abrasive Al_2O_3 coating developed by A. Matthews research group using plasma electrolysis [7]. A. Matthews *et al.* reported that the weight loss of Al_2O_3 coating (150 μm) was 15 mg compared to 32.5 mg of the uncoated stainless steel at a revolution of the rubber wheel of 2000 under the same abrasion conditions [7]. It is also noted that prior to the optimal point (1.7), the weight loss of Al_2O_3-SiC ceramic coating decreases with the increase of RCB. After the optimal point (1.7), contrarily, the weight loss of Al_2O_3-SiC ceramic coating increases with the increase of RCB. The result can be explained by the morphologies of Al_2O_3-SiC ceramic coatings after abrasion. The morphologies of the ceramic coatings with RCB of 1.4, 1.7 and 2.0 after abrasion test are shown in Figs 5, 6

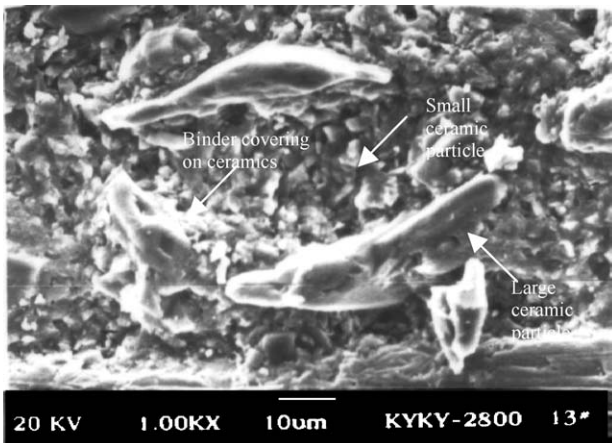

Figure 5 Morphology of the ceramic coating with RCB of 1.4 after abrasion test (used binder:Al/P = 1.4:3, $\rho = 1.65$ g/cm^3).

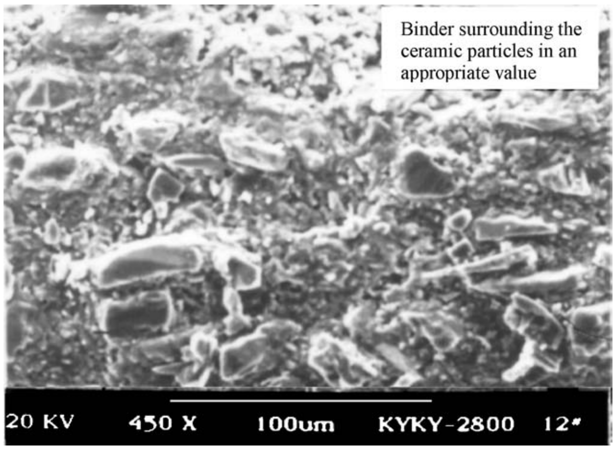

Figure 6 Morphology of the ceramic coating with RCB of 1.7 after abrasion test (used binder:Al/P = 1.4:3, $\rho = 1.65$ g/cm^3).

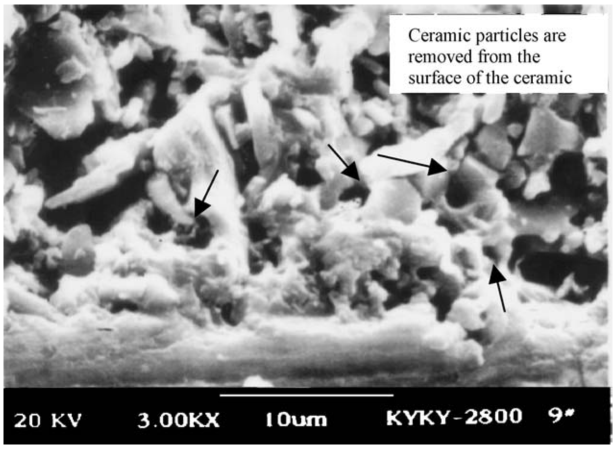

Figure 7 Morphology of the ceramic coating with RCB of 2.0 after abrasion test (used binder:Al/P = 1.4:3, $\rho = 1.65$ g/cm^3).

and 7, respectively. It is obvious that when RCB is less than 1.7, the abrasion occurs on the binder that is less abrasive than the ceramic particles. With the increase of RCB, ceramic particles are surrounded by an appropriate amount of the aluminum phosphate binder. Consequently, the binding strength between the ceramic particles and the binder is strong and the abrasion occurs on the ceramic particles that have good wear resistance. On the other hand, the amount of defects (such as pores) in the ceramic coatings decreases, which also improves the wear resistance of the ceramic coatings. This is demonstrated by hardness tests on HX-1000 micro-indenter. The test result indicates that the hardness (HV) of the ceramic coating with RCB of 1.7 is in a range of 500–550. However, when the RCB is above 1.7, the binding strength between the ceramic particles and the binder decreases, and ceramic particles are removed from the surface of the ceramic coating as shown in Fig. 7. Consequently the wear resistance of Al_2O_3-SiC ceramic coating decreases.

3.2.2. Effect of the Al/P ratio in aluminum phosphate binder

Fig. 8 indicates the effect of Al/P atomic ratio of aluminum phosphate binder on the wear resistant properties of Al_2O_3-SiC ceramic coatings. The ceramic coatings exhibit good wear resistance when the Al/P ratio is within a range of 1.3:3–1.4:3. When Al/P ratio is lower than that of 1.2:3, extra phosphoric acid remains in the binder besides the dominant phase of $AlH_3(PO_4)_2 \cdot 3H_2O$ as discussed in the Section 3.1.1. The remaining phosphoric acid may react with the Fe element in A_3 steel and results in H_2. The resulting gases lead to the increase in porosity of the ceramic coatings, which may affect the wear resistance of the ceramic coatings. When Al/P ratio is a value above 1.4:3, $Al(OH)_3$ is observed besides the effective binding phase monoaluminium phosphate. The more $Al(OH)_3$ remains, the less the percentage of the monoaluminium phosphate in the ceramic paint will be. This results in the decrease of the binding strength between the ceramic particles and aluminum phosphate binder. Therefore, it is suggested that the Al/P ratio be controlled in a range of 1.3:3–1.4:3 to get ceramic coatings with good wear resistance.

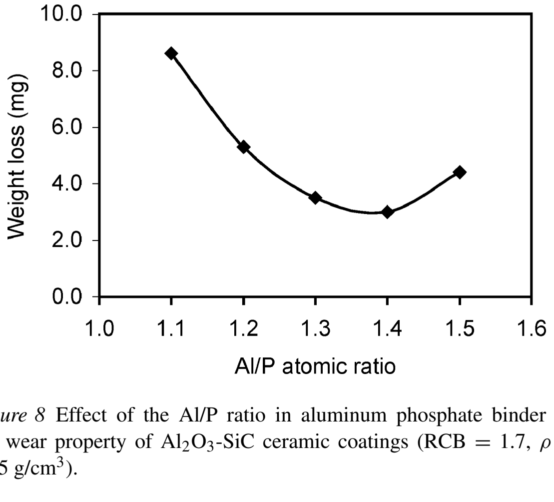

Figure 8 Effect of the Al/P ratio in aluminum phosphate binder on the wear property of Al_2O_3-SiC ceramic coatings (RCB = 1.7, ρ = 1.65 g/cm^3).

3.2.3. Effect of the content of the large Al_2O_3 particles

The particle size distribution of ceramics plays an important role on the wear resistance of ceramic coatings. The particle size distribution of ceramics can be regulated by changing the weight percentage of the large Al_2O_3 particles in the total amount of ceramics (Al_2O_3 + SiC). Fig. 9 gives a curve of the weight loss of ceramic coatings as a function of the content (wt%) of the large Al_2O_3 particles in the total amount of ceramics (Al/P = 1.4:3, RCB = 1.7, ρ = 1.65 g/cm^3). The best wear resistance is obtained at 40 wt%.

3.2.4. Effect of the density of the binder

It is generally accepted that the viscosity of a binder affects its binding performance and the properties of its bonded coating. Since the viscosity of a kind of binder is relevant to its density, thus the effects of the density of the binder on the wear properties of the fabricated ceramic coatings have been investigated in this work by adjusting the density of the aluminum phosphate binder to different values (1.59, 1.61, 1.63, 1.65, and

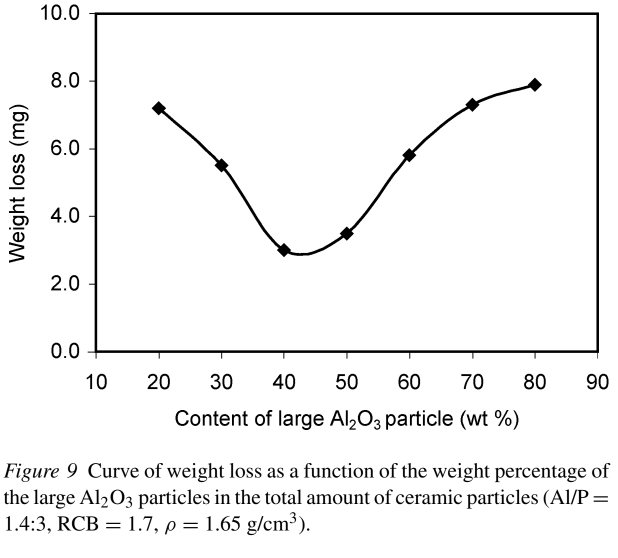

Figure 9 Curve of weight loss as a function of the weight percentage of the large Al_2O_3 particles in the total amount of ceramic particles (Al/P = 1.4:3, RCB = 1.7, ρ = 1.65 g/cm^3).

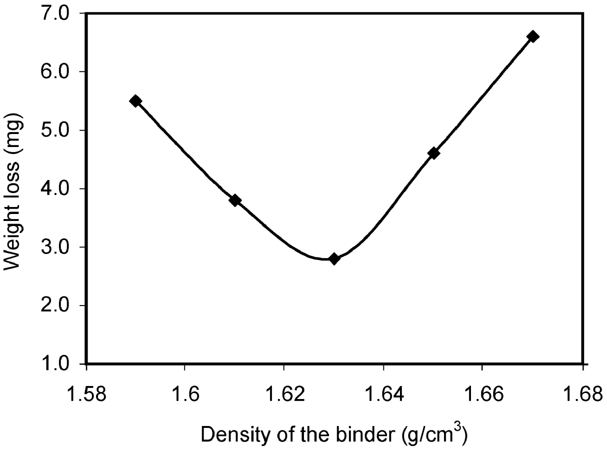

Figure 10 Relationship between the density of the binder and the wear property of ceramic coatings (Al/P = 1.4:3, RCB = 1.7).

1.67, respectively). The relationship between the wear property of the ceramic coatings and the density of the binder is presented in Fig. 10, which shows that the binder with a density around 1.63 g/cm^3 exhibits good wear resistance.

4. Conclusions

In this work, Al_2O_3-SiC ceramic coatings have been successfully fabricated on A_3 steel using alumina (Al_2O_3) and silicon carbide (SiC) as the abrasive ceramics, aluminum phosphate as the binder, and aluminate ($Al_2O_3 \cdot CaO$) as the curing agent. These ceramic coatings are designed to protect the metal or cement components in power and refractory industries against chemical corrosion, abrasive wear, and high-temperature environments. The XRD results indicate that monoaluminium phosphate ($Al(H_2PO_4)_3$) is the most effective binding phase in aluminum phosphate binder, and that aluminum phosphate binder at high temperatures is a mixture of several phases. The addition amount of the stabilizer (oxalic acid) has significant effect on the storage life of aluminum phosphate binder. The storage life of the binder after adding 4 wt% $H_2C_2O_4 \cdot 2H_2O$ is about two times that of the binder without oxalic acid. The abrasive tests show that the wear durability of the A_3 steel covered with Al_2O_3-SiC ceramic coatings is about two times higher than that of the uncoated A_3 steel. The results also indicate that the fabrication conditions, such as the ratio of ceramics (Al_2O_3 and SiC) to the binder, the particle size distribution of ceramics, the density of the aluminum phosphate binder, and the Al/P ratio in the aluminum phosphate binder, play important roles on the wear resistance of the fabricated ceramic coatings. For achieving good wear property of Al_2O_3-SiC ceramic coatings, the optimal fabrication conditions are suggested as follows:

(i) The Al/P ratio in aluminum phosphate binders should be in the range of 1.3:3–1.4:3.

(ii) The density of aluminum phosphate binder should be around 1.63 g/cm^3.

(iii) The optimal ratio between the ceramics and the binder (RCB) is 1.7.

(iv) The weight percentage of large Al_2O_3 particles in the total amount of ceramics should be around 40 wt%.

Acknowledgement

The authors would like to thank Dr. W. Chao and Dr. Z. Chen for their kind help in experimental work and helpful discussion.

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Received 5 February 2002
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