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Anticorrosion properties of enamels with high B_2O_3-P_2O_5-$AlPO_4$ content in molten aluminum①

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[Abstract] The new enamels with high H_3BO_3-$(NH_4)_2HPO_4$-$AlPO_4$ content were studied, and the melting temperature of the enamels was adjusted by adding carbonate of alkali metal and alkaline earth metal. The enamels could spread slightly in the molten Al alloy observed by SEM and experiment. The components of the enamels were not detected with electron probe (EDAX-S-520) on the interface of Al alloy, but elemental Si of aluminum alloy was found in the silica-free enamels. Moreover, the components of the boron-free enamels were detected on the interface of Al alloy. The results show that the enamels with high B_2O_3-P_2O_5-$AlPO_4$ content are resistant to the corrosion of molten Al.

[Key words] enamel; molten Al; corrosion; interface; electron probe

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1 INTRODUCTION

Molten aluminum is one of the most aggressive melt due to its high affinity to oxygen and its ability to dissolve a great number of materials. Some ceramic materials such as Al_2O_3, SiC, BN, the oxides of alkaline earth metals, Sialons (a new class of ceramics) and the composite material—a silicon nitride cordierite glass ceramic can resist corrosion of the molten aluminum[1~5].

The main inclusions in molten aluminum are Al_2O_3, and others are non-oxide inclusions such as Al_4C_3, TiB, $MgAl_2O_4$ and so on. The molten aluminum was filtered by glass fiber net, foam ceramic and deep-bed filter (DBF) in foundry industry. These ceramic filters can be resistant to the corrosion was of the molten aluminum under filtering temperature, but the non-metallic inclusions in molten aluminum are difficult to be captured by the rigid and smooth surface of the ceramic filters. In addition, the molten aluminum can not flow through the micro-pore ceramic filters by its own weight because of the non-wettability between the ceramic and the molten aluminum, while the processing difficulty of filtration may be increased when using external forces.

BACO (British Aluminum Corporation) filters molten aluminum with the packed bed of aluminum oxide spheres coated by flux with resistance to molten aluminum, but the flux is run off easily[6, 7]. The enlarged pore-size of the filters may be used if the viscous materials is coated on the surface of the ceramic filters, which may capture the relative smaller inclusions. Moreover, the wettability between the ceramic filters and the molten aluminum is improved in some degree because the enamel is a non-crystalline solids.

The purpose of this work is to synthesize a new enamel with resistance to corrosion of the molten aluminum that has a melting temperature of 740 ℃ or so, and can be coated on the surface of the ceramic filters to help capture the non-metallic inclusions in molten aluminum.

2 EXPERIMENTAL

Reagents of the enamels are mainly made of $(NH_4)_2HPO_4$, H_3BO_3, $Na_2B_4O_7\cdot 10H_2O$, $AlPO_4$, Al_2O_3, carbonate of alkali metals and alkaline earth metals, and the batch formula of enamels are tabulated in Table 1.

20 g of the reagents of the enamels were pulverized and mixed, and then put into a graphite crucible, where it was melt in the high temperature electric resistance furnace at 950, 800, 740 and 720 ℃ respectively. The melt samples were taken out from furnace and stirred with a ceramic rod, then put into the furnace again, kept at the molten condition for 30 min, poured out in the end, and taken as experimental material of resistance molten aluminum.

The enamels were immersed into molten Al-Si-Mg alloy (A319), Al-Si alloy (A356) and molten pure aluminum with two methods: 1) covering the surface of molten aluminum-alloy; 2) dipping into the molten aluminum-alloy. At 740 ℃, the enamels were kept in the molten aluminum alloy for 5, 5, 10 and 18 h respectively. The enamels were immersed into the molten aluminum according to Table 2, and the varied samples were prepared.

The samples by method 2 were cut into small packet (15 mm × 10 mm × 5 mm), polished and

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Table 1 Compositions of enamels (%)

Sample	$(NH_4)_2PO_4$	$Na_2B_4O_7 \cdot 10H_2O$	$Na_3(AlF_6)$	$CaCO_3$	Li_2CO_3	K_2CO_3	$AlPO_4$	Al_2O_3	ZnO	$Mg_2(OH)_2CO_3$	H_3BO_3
S_1	20	4.35	3.2	2.3	4.84	5.29	19	4.0	5.06	2.00	30
S_2	20	4.35	3.2	2.0	5.84	4.00	19	3.0	5.06	1.59	34
S_3	21	5.50	4.0	1.0	5.84	4.00	20	1.5	3.06	1.10	34
S_4	28	0	10.0	2.6	6.8	6.20	30	0	5.80	0	0

Table 2 Process of sample preparation

Sample	Melt temperature (enamel) / ℃	Melt time (enamel) / h	Constant time (enamel) / min	Molten aluminum temperature/ ℃	Dipping molten aluminum / h
S_1	950	3.5	30	740	18
S_2	800	3.5	30	740	8
S_3	740	3.5	30	740	5
S_{3-1}	740	3.5	30	740	5
S_4	720	3.5	30	740	5

cleared to make it distinct on the interface between enamel and aluminum-alloy. The interface between enamel and aluminum alloy was observed with EDAX-S-52, and the components of the interface and bulk material were detected with electron probe.

3 RESULTS AND DISCUSSION

Relation between the enamel melting temperature and the components of the enamels may refer to the composition phase diagram. Fig. 1 shows the composition diagram of B_2O_3, P_2O_5 and SiO_2 [8]. Fig. 2 represents B_2O_3, P_2O_5 and Al_2O_3 ternary phase diagram of the glass-forming region and the glass compositions of the samples (mole fraction, %) [9].

Fig. 3 shows the SEM image of S_1 sample. Point 3 represents aluminum alloy bulk material, and points 1 and 2 are located at the interface approaching the side of aluminum alloy. The components of the three points are tabulated in Table 3. It is not obvious that the component contents occur to change between the bulk and the interface, and the components of enamels are not detected by electron probe at the interface of aluminum alloy. Thus, the molten aluminum don't dissolve the enamels.

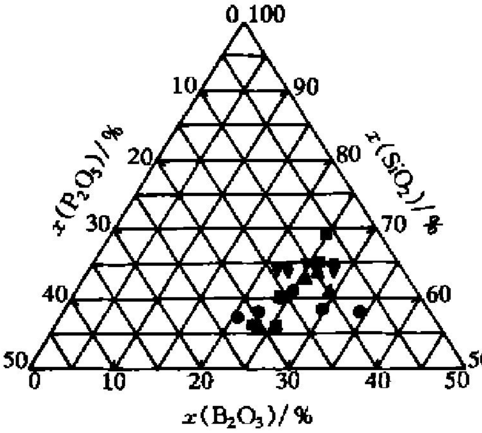

Fig. 1 B_2O_3, P_2O_5 and SiO_2 ternary composition diagram

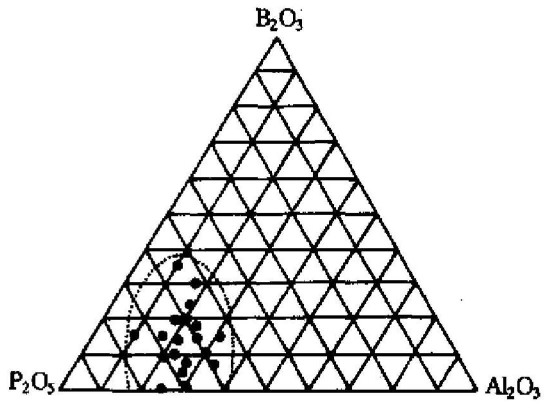

Fig. 2 B_2O_3, P_2O_5 and SiO_2 ternary phase diagram

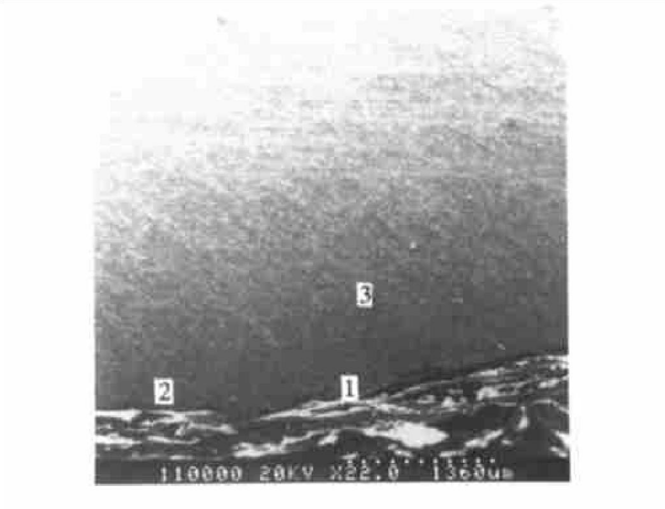

Fig. 3 SEM image of interface between enmels and aluminum alloy for sample S_1

SEM image of S_2 sample is shown in Fig. 4, where the dark part represents enamels. The components of three sampling points are tabulated in Table 3. Electron probe shows that Si content is high at point 2 located in the bulk Al-Si alloy due to

Table 3 Components of samples S_1 and S_2 (%)

Solid sample	Sample point	Element Na	Mg	Al	Si	P	K	Ca
S_1	1	0	1.41	94.89	3.71	0	0	0
	2	0	2.09	96.68	1.22	0	0	0
	3	0	1.75	96.31	1.93	0	0	0
S_2	1	0	0	81.70	18.30	0	0	0
	2	0	0	32.35	67.65	0	0	0
	3			9.23	90.77			
Interface		1.60	0	47.87	19.76	27.79	19.11	3.87

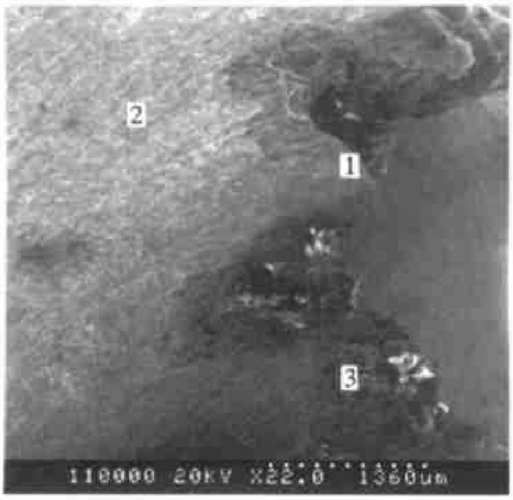

Fig. 4 SEM image of interface between enamels and aluminum alloy for sample S_2

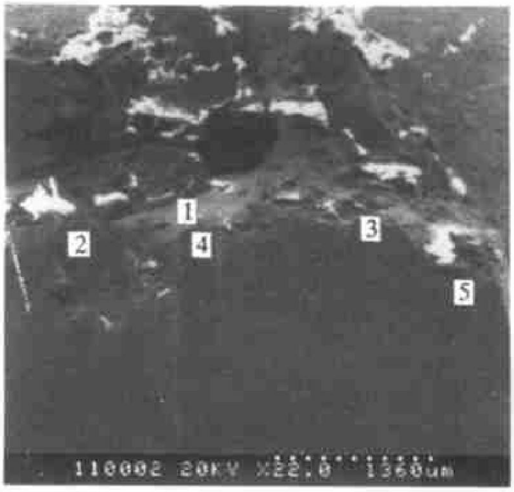

Fig. 5 SEM image of interface between enamels and aluminum alloy for sample S_3

Fig. 6 SEM image of interface between enamels and aluminum alloy for sample S_{3-1}

inhomogeneity of the component distribution of Si element.

Points 1 and 3 locate at the interface of aluminum alloy, and the enamel components are not found. Moreover, the elemental Si in aluminum alloy is detected by electron probe in the silica-free enamels, and Si content is lower at the interface than that of both bulk materials and enamels. It can be explained by the reason why the elemental Si diffuse into silica-free enamels, and the components of enamels don't infiltrate into molten aluminum alloy according to electron probe detection at the interface of aluminum alloy.

Fig. 5 shows SEM image of S_3 sample, and the black-white interphase represents enamel layer. The components at the interface are tabulated in Table 4. Sampling points 1 to 4 represent the area where the enamels are sloughed in the processing test samples according to the component analysis in Table 4, and element Si can not be found in sample point 5 in Al-Si alloy due to the inhomogeneity of the component distribution.

Light gray and grayish-white interphase represents aluminum alloy and the enamels respectively according to SEM image of S_{3-1} sample, as shown in Fig. 6. Besides, S_3 and S_{3-1} represent the different interface of the same sample. The components of six points from Al alloy bulk materials to enamels are tabulated in Table 4. Si content is decreased gradually from sampling points 1 to 3, and it is higher in sampling points 4 to 6 than that of at the interface of aluminum alloy. Moreover, the components of the enamels do not be detected at the interface of aluminum alloy with electron probe.

Light white and gray represent the enamels and aluminum respectively in Fig. 7. The components of

Table 4 Components of samples S_3 and S_{3-1}

Solid sample	Sample point	Element						
		Na	Mg	Al	Si	P	K	Ca
S_3	1	9.68	3.30	23.04	13.63	33.74	11.51	5.10
	2	0.17	36.35	17.63	11.94	33.32	0.31	0.37
	3	0	9.58	57.14	32.67	0.33	0.05	0.23
	4	0	0.69	78.70	16.18	1.56	1.87	0.99
	5	0	0	100	0	0	0	0
S_{3-1}	1	0	0	83.67	16.33	0	0	0
	2	0	0	91.78	8.22	0	0	0
	3	0	0	100	0	0	0	0
	4	2.98	10.94	9.57	10.03	34.78	19.63	12.07
	5	1.99	0.88	32.37	11.57	41.34	9.34	2.49
	6	7.25	0.69	19.97	9.60	36.44	20.02	5.76

Table 5 Components of sample S_4

Solid point	Element					
	Na	Al	P	K	Ca	Zn
1	3.58	52.51	11.93	9.86	7.38	14.74
2	5.53	69.63	10.89	7.70	3.22	3.02
3	0.94	98.33	0.28	0	0.39	0.07
4	0.07	98.75	0.38	0	0.03	0.14
5	4.38	77.66	12.72	4.13	1.10	0
6	1.24	97.11	0.36	0.11	1.04	0.15
7	0.46	99.19	0.15	0	0.19	0

Fig. 7 SEM image of interface between enalmels and aluminum alloy for sample S_4

seven points on the SEM image of S_4 sample are tabulated in Table 5, and point 1 represents the enamels on the surface of aluminum. Moreover, the points 2 ~ 7 on the interface are located in the side of aluminum, and element P is detected with electron probe in the seven points. It can be concluded from the above analysis that the components of the boron-free enamels infiltrate into molten aluminum.

The enamels exhibit the slight spread ability on the surface of the aluminum alloy due to the reason why enamel is a kind of non-crystalline solids[10]. Moreover, the enamels display slightly spread ability in molten aluminum by SEM image and experimental observation. Accordingly, the surface of ceramic filters is coated by the enamels with resistance to corrosion of the molten aluminum, and the wettability between the ceramic filters and the molten aluminum is improved in some degree.

On the other hand, the ingredient of high B_2O_3-P_2O_5-$AlPO_4$ content enamels don't infiltrate into molten aluminum alloy by experimental results, but element Si in aluminum alloy diffuses into the silica-free enamels. The element Si is found in silica-free enamels with electron probe, and Si content at the interface is lower than that of the bulk aluminum alloy. It is transferred from interface to the enamels through diffusion, which is oxidized SiO_4 network former. In addition, SiO_2 and Al_2O_3 convert into SiO_4 and AlO_4 tetrahedron in enamels respectively, and the viscosity of enamels can be increased because SiO_4 and AlO_4 take part in the formation of the network[11, 12]. Further, both B_2O_3 and P_2O_5 formed a local network structure similar to BPO_4[13], and the conversion of trigonal boron to tetrahedral boron can increase the local density of the enamels. In addition, Al_2O_3 can be converted into tetrahedral coordination AlO_4 in the enamels, and the enamel can dissolve the inclusion (Al_2O_3) in molten aluminum. BO_3 or BO_4, PO_4 and AlO_4 are connected by tetrahedral apex angle oxygen (bridge oxygen) in three dimensions. Alkali metals and alkaline earth metals which are filled in the interstitial site of network bond with non-bridge oxygen through electrostatic interaction.

The network of P and B is connected by bridge oxygen for enamels with high B_2O_3 and P_2O_5. No P element was detected with electron probe at the interface near the side of aluminum alloy, which indicated that B-O-P chemical bond isn't broken by molten aluminum alloy, and element B doesn't infiltrate into aluminum alloy. Moreover, no K, Na and Ca elements are found at the interface of aluminum alloy, and no element Mg is measured in the aluminum-silicon alloy yet. Thus, enamels mainly composed of B_2O_3, P_2O_5 and APO_4 content have resisted the aggression of molten aluminum alloy according to the experimental results. The low solubility of the dense layer made of element B, P and Al is formed by bridge oxygen on the enamel surface in contact with molten Al alloy[14], and it can be resistant to the aggression of molten Al alloy. Meanwhile, alkali metals and alkaline earth metals which bond with non-bridge are filled in the interstice of P-B-Al network and don't infiltrate into molten aluminum alloy[15].

But the boron-free enamel isn't resistant to molten aluminum by the component analysis of the interface of solid sample S_4 because the boron-free enamels which have only element P doesn't composite the dense layer. The molten aluminum can dissolve completely the boron-free enamels with the time of corrosion prolonging, contaminating the molten aluminum, and the ceramic filters are without reactive filtering effect. In addition, the components of the enamels with high B_2O_3-P_2O_5-$AlPO_4$ don't infiltrate into the molten aluminum, that is the molten aluminum without dissolving the enamels, accordingly, the ceramic filters that are coated by the enamels don't contaminate the molten aluminum.

The enamels with high B_2O_3-P_2O_5-$AlPO_4$ are infiltrated into the molten Al-Si-Mg (A319), the molten Al-Si(A356) and the pure molten aluminum, and the components of the enamels don't permeate into the molten aluminum. The surface of the ceramic filters that are coated by the enamels may filter reactively the inclusion in the varied molten aluminum, which don't contaminate the molten aluminum. Moreover, the coated ceramic filters may remove impurity element Si in industrial pure molten aluminum.

S_1, S_2, S_3 and S_4 samples are melted at 950, 800, 740 and 720 ℃ respectively, but S_3 sample which has the same melting temperature as aluminum alloy has viscosity enough to capture non-metal inclusion (Al_2O_3) in molten aluminum alloy (physical dissolution). In addition, element Si in aluminum alloy can transfer into the porous ceramic that is coated with S_3 sample while filtering molten aluminum alloy. The melt temperature of S_1 and S_2 are higher than that of aluminum alloy, and it is not easy to capture inclusions in molten aluminum alloy due to the dependence of the viscosity on the temperature. Moreover, S_4 sample isn't resistant to molten aluminum.

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