Microstructure and Properties of an Enamel Containing Nano-sized Crystals of Titanium Dioxide

Liang Menglin[1], Xiao Hanning[2], Zhuang Liyuan[2] and Chen Anming[1]

1 Hunan Lifa Glaze Technologies Co. Ltd., Xiangtan 411104, China

2 College of Materials Science & Engineering, Hunan University, Changsha 410082, China

Abstract: An enamel containing nano-sized crystals of titanium dioxide was prepared from a special enamel frit under controlled sintering schedule. The enamel was sintered at 830°C for 3min, then crystallized at 500~600°C for 15~20min. The crystal phase was detected by X-ray diffractometer. The microstructure of the enamel was observed by scanning electronic microscopy. The properties including whiteness, hardness and wear resistance of the enamel were investigated. Results show that the enamel reheated at 500°C for 15min and 600°C for 20min has homogenously dispersed titanium dioxide crystals in nano size, which contributes good whiteness, better hardness and wear resistance.

Keyword： enamel; titanium dioxide; nano-sized crystal; sintering schedule; microstructure

1 Introduction

Enamel is a kind of special coating to protect metal from corrosion and abrasion. The microstructure of final enamel is mainly responsible for the corrosive and abrasive resistance of enamel, which depends on the chemical compositions and sintering schedule of the enamel. As well known, the structure of enamel is similar to glaze, consisting of glass and rare crystals. The size and amount of crystals have important effects on the properties of enamel. Enamel with micron crystals shows higher hardness and strength, good chemical stability [1-3]. ZrO_2 and TiO_2 were usually used as the nucleating agent in microcrystalline enamel [4]. The enamel with 5.3% ZrO_2 and 9% ZnO has good corrosion resistance to NaCl deposit and water vapor at 450 °C [5].

Titanium dioxide is an important opaque agent widely used in enamels and paints [6,7]. However, there is little research about the precipitation of titanium dioxide crystals in enamels up to now. This work is to investigate the precipitation of titanium dioxide crystals in enamels at different sintering schedule and analysis the effect of microstructure on the properties of the enamels with nano-sized titanium dioxide crystals.

2 Experimental

2.1 Raw materials

The chemical compositions of the enamel used in this work are listed in Table 1, in which the content of titanium dioxide was designed in 18-20 wt%. The raw materials included quartz sand, feldspar, borax, titanium dioxide, fluorite and phosphate. All the materials were in industrial grade and well mixed together, then melted at 1400°C in an electrical furnace to get the enamel frit.

Table 1 The chemical compositions of enamel

Chemical composition	SiO_2	Al_2O_3	B_2O_3	TiO_2	Na_2O	K_2O	MgO	F	P_2O_5
Content（wt%）	38~41	3~5	17~19	18~20	9~11	6~8	1~2	2~3	3~4

2.2 Experimental procedure

The enamel frit was first ground in a ball milling to get the enamel slip. The prepared steel plate was immerged into the enamel slip, then pulled out and dried in air. The samples were sintered at 830°C in a preheated electrical furnace for 3min. (signed as 0#), then crystallized at different heating schedules (1#~3#).

According to the DSC result of the enamel powder shown in Fig. 1, the glassy temperature (T_g) of the enamel is about 475°C, and the crystallization temperature (T_c) is near 590°C, so the nucleation and crystallization temperature were determined as 500°C and 600°C respectively.

In order to investigate the relationship between the microstructure and properties of the reheated enamels, the sintered enamel (0#) were put into the furnace and reheated from room temperature to elevated temperature and holding at the temperature for a certain time as shown in Table 2.

Table 2 Heat treatment schedule of the sintered enamel

Sample No.	Holding at 500°C (min)	Holding at 600°C (min)
0#	0	0
1#	15	15
2#	15	20
3#	20	20

2.3 Testing apparatus and conditions

The thermal analysis (DSC) of the enamel powder was conducted by Netzsch STA449C calorimeter at a heating rate of 10°C/min. The crystal phase was determined by Rigaku D/max 2200 X-ray diffractometer (XRD) using Cu Kα radiation at 40kV and 40mA. The microstructures of the samples were observed by scanning electron microscope (JEOL, JSM-6700F). The Whiteness of the samples was tested by Xinrui WSB-1 (R457 blue-ray whiteness), and the micro-hardness was conducted by MC010-HVST-1000ZA tester. Wear testing was completed in a polishing machine (UNIPOL-1202) using the sample size of 50mm×50mm.

3 Results and discussion

3.1 Nucleation and crystallization temperature of the enamel

Fig. 1 shows the DSC curve of the enamel powder. The glassy temperature (T_g) is usually to determine the nucleation temperature (T_n). The T_n should be 20~30 °C higher than the T_g, so 500°C was used as the nucleation temperature in this work. The crystallization temperature (T_c) of the enamel is about 590°C, so 600°C was used as the controlling temperature for the crystallization of the enamel.

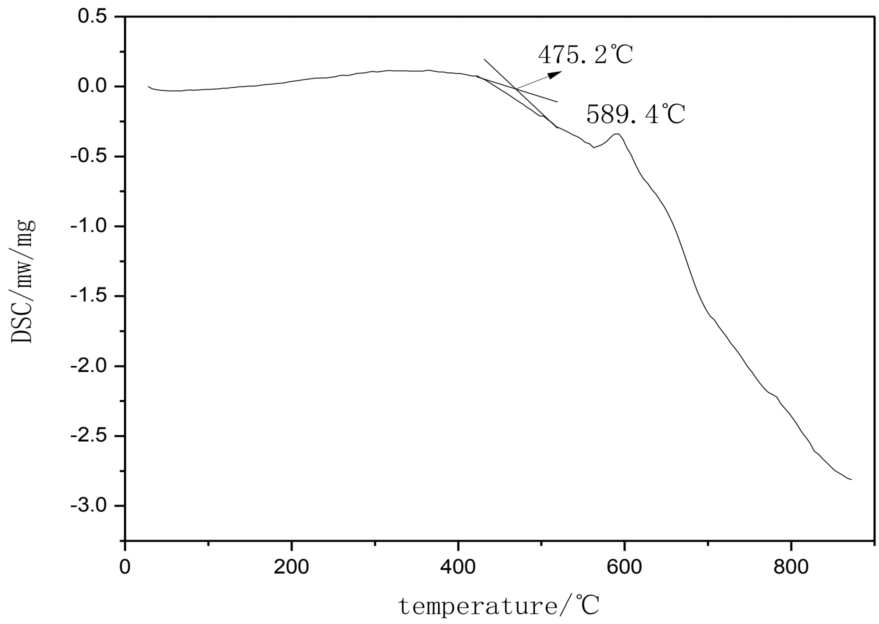
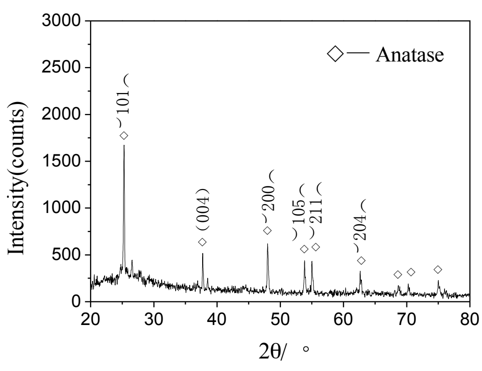


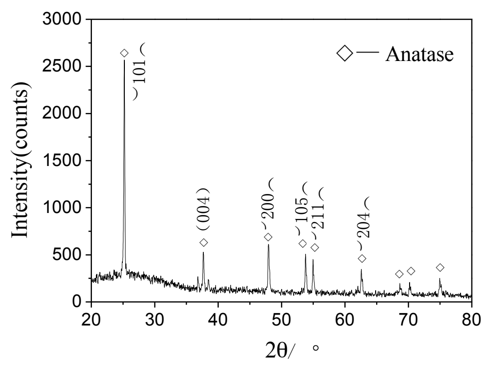
Fig 1 DSC curve of the enamel powder

3.2 The crystal phase and microstructures of enamels

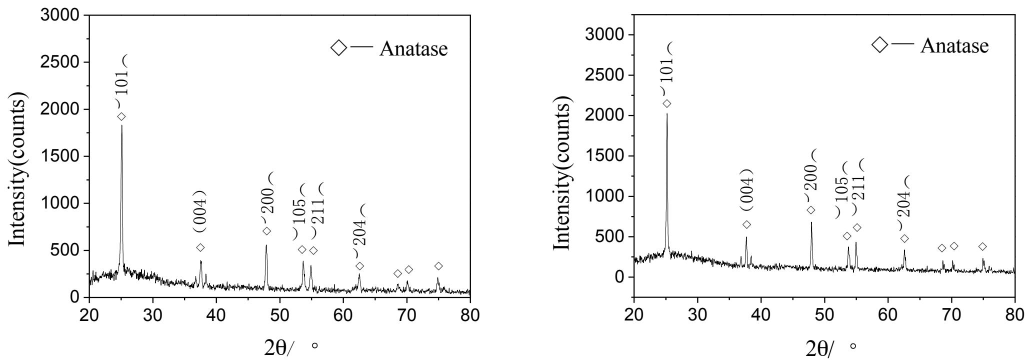
Fig 2 shows the XRD patterns of the enamels prepared at different conditions. Only anatase (a kind of TiO_2) phase was detected in all of the enamels. 0# is the enamel prepared at 830°C by normal processing. There is little difference in XRD patterns among the samples prepared at different conditions. However, the microstructure of the samples is much difference as shown in Fig. 3. 0# has relative rare crystals, while 1# has the most crystals and homogenously distributed. With the increase of crystallization time, the amount of precipitated crystals becomes fewer and larger.



(a) 0#



(b) 1#



(c) 2# (d) 3#

Fig 2 XRD patterns of the enamels heat treated at different conditions.

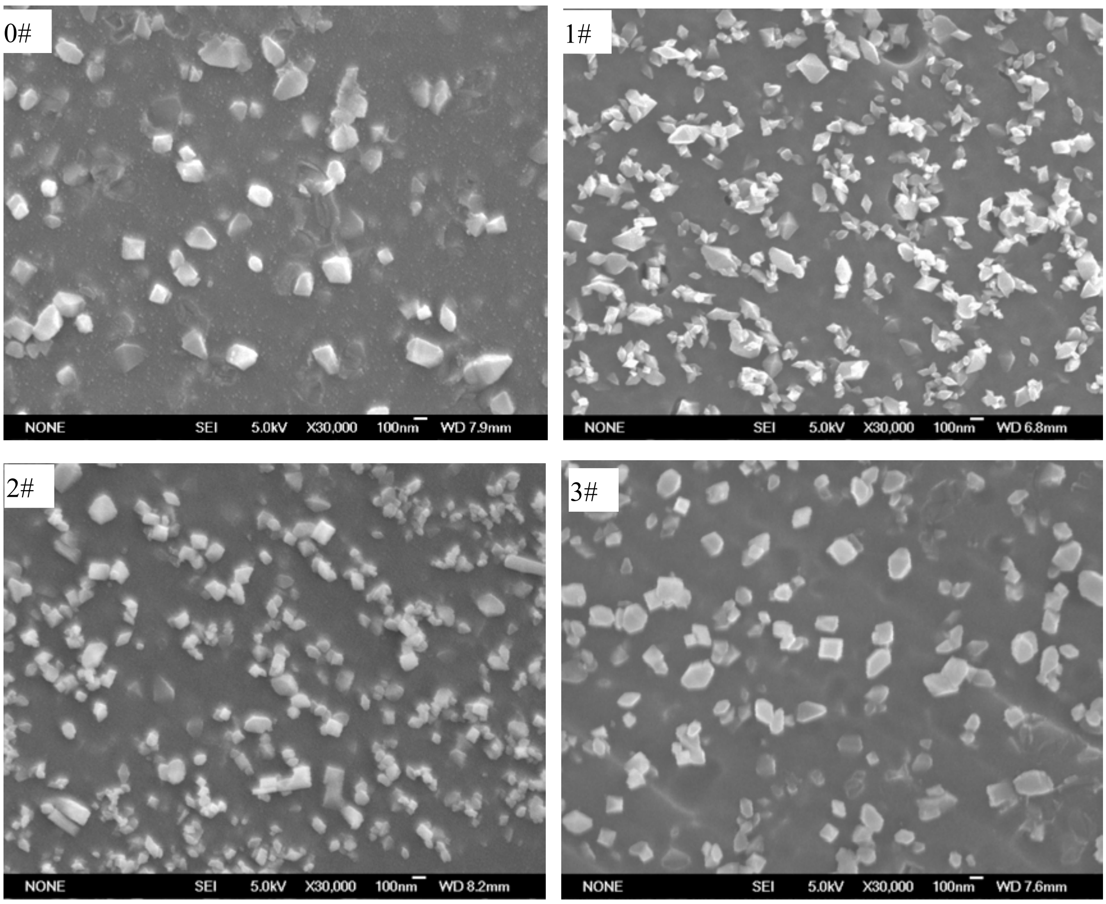


Fig 3 SEM photographs of the enamels prepared at different conditions

3.3 Influence of heat treatment on enamel properties

Table 3 shows the whiteness, Vickers hardness (Hv) and wear loss of the samples. The samples of 0#, 1# and 2# have the best whiteness, while the whiteness of 3# is decreased. When the crystals are small and homogenous in distribution, the whiteness of the sample is better. The hardness of 0# sample is the lowest and the wear loss is highest owing to its little crystals. Sample 2# has the highest hardness and lowest wear loss which are contributed by the more crystals and good distribution.

Table 3 Some properties of the prepared enamels

Sample No.	0#	1#	2#	3#
Whiteness (%)	91	91	91	89
Vickers hardness (Hv)	6.08	6.23	6.75	6.45
Wear loss (mm)	0.028	0.023	0.011	0.019

4 Conclusions

(1) The enamel containing titanium dioxide has favorable performance for crystallization. Anatase (TiO_2) is the only crystals phase in the enamel either in normal or in reheated processing.

(2) The properties of the enamel containing a large amount of anatase crystals can obviously improve the whiteness, hardness and wear loss.

(3) The best conditions for crystallization of the enamel are: reheating from room temperature to 500°C and keeping at this temperature for 15min, then increasing to 600°C and holding for 20min..

Reference

[1] USA patent No. 4358541, 1982

[2] UK patent No. 1467459, 1998

[3] Xiao Hanning, Li Xule and Huang Hongwu. Preparation of infrared radiative enamel and its application in iron pan. *J. Hunan Univ.* 24(5): 18~22, 1997

[4] Liang Zhongyou, Yuan Qingxi, Zhang Mingliang, et al. Study on Microcrystalline Enamel of Li_2O- CaO- Al_2O_3- SiO_2 System. Glass and Enamel, 26(3):11-15, 1998

[5] Deyou Zheng, Shenglong Zhu, Fuhui Wang. The influence of TiAlN and enamel coatings on the corrosion behavior of Ti6Al4V alloy in the presence of solid NaCl deposit and water vapor at 450 °C. Surface & Coatings Technology. 201: 5859~5864, 2007

[6] Lui Tiantian, Li Yan, Tian Yinliang, et al. Effects of melting process on the whiteness and crystallizing behavior of titanium contained enamel. 2009 Annual Conference on Glass Science and Technology. 2009

[7] L. L. Bragina and G. K. Voronov. Effect of complex of allovaent cations on process in an enamel melt-low-carbon steel system.. Glass and Ceramics. 65(1-2): 59~62. 2008