INFLUENCE OF MILLING ADDITIONS ON THE WEAR RESISTANCE OF MICROCOMPOSITE ENAMELS WITH THERMAL BARRIER PROPERTIES

Mihăiţă IOAN[1], Ramona-Nicoleta TURCU[2 *], Mihai TÂRCOLEA[3]

The paper addresses the wear resistance variation of enamels depending on different Al_2O_3 and TiO_2 additions. The enamels were deposited on non-alloyed steel substrates, using 6 different recipes, by varying the percentages of oxides. The samples were tested by the Calowear method and investigated by XRF and UV-VIS spectrometry and optical microscopy. The addition of Al_2O_3 and TiO_2 oxides significantly increases the wear resistance, with better results for Al_2O_3 recipes. The main novelty of this paper is the use of Al_2O_3 and TiO_2 as mill additives. Also, the quantification of the wear resistance improving of the enamel layer through proper Al_2O3 and TiO_2 additions is another novelty. This way of increasing of the wear resistance of the enamel coatings used as thermal barrier is cost-effective and can be easily implemented in coating manufacture.

Keywords: Enamel, wear resistance, abrasion resistance, Calowear test, mill additive

1. Introduction

Thermal barrier coating (TBC) enamels are increasingly researched and used in applications involving high operating temperatures and sudden temperature variations (thermal shock). The wide variety of enamels developed in recent decades allows their properties to be tailored to specific operating conditions and the demands they must withstand, without deterioration of their characteristics over time [1, 2, 3]. The abrasion resistance of enamel is influenced by two similar properties, but with antagonistic effects: high hardness improves abrasion resistance, but the same high hardness also means low tear strength and low toughness, characteristics that decrease abrasion resistance [4]. Enamel coatings have excellent durability, but mechanically, the impact and abrasion resistance is not optimal, despite the good hardness values of the coating, due to its glassy nature and therefore it is brittleness [5]. In many specific applications,

[1] PhD Candidate, Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: mihaita.ioan@gmail.com
[2 *] PhD, Metallic Materials Science & Physical Metallurgy Department, University POLITEHNICA of Bucharest, Romania, e-mail: ramona.turcu@upb.ro;
[3] PhD, Metallic Materials Science & Physical Metallurgy Department, University POLITEHNICA of Bucharest, Romania, e-mail: mihai.tarcolea@upb.ro.

thermal stresses are compounded by significant mechanical stresses caused by solid particles accompanying the hot gas in motion. The result of these micro-impacts is abrasive wear of enameled surfaces, and the phenomenon is called erosion.

Erosion therefore involves the removal of fragments of material from the surface by the action of micro-impacts at the high velocity of the flow of solid and hard particles accompanying the moving gas [6]. There are two types of erosion: cavitation erosion and particle erosion [7]. Cavitation erosion occurs in components subjected to low transient pressures of the moving fluid and occurs at the local impact of low-pressure vapor bubbles on the surface of the components. Particle erosion occurs when a fluid flow contains hard particles that strike the surface of components. Particle erosion can occur intentionally, in the case of sandblasting, or it can occur inadvertently, in pipes carrying slam, oil or flue gas.

Abrasive wear occurs when fragments of material are detached from the surface of a material by cutting (chipping) or multiple penetration of the surface by hard end sharp-edged particles. These processes may occur in a controlled manner, as part of the manufacturing technology of a component, or they may occur incidentally, during basic technological operations. Wear can also occur when two surfaces rub against each other, contaminating each other with hard particles. Worn surfaces can have anything from fine scratches to deep scratches. If the components are made of ductile materials, the wear debris may have a spiral appearance, and if the materials are hard, the wear debris may be in the form of splinters [6]. Abrasion is a very common degradation mechanism for enamel surfaces. Any mechanism in which roughness or hard particles on a surface cause surface damage can be defined as abrasion. The damage they cause can be of two general types: deformation of the material, for ductile materials, and formation of particles with loose material, for brittle materials. Wear and abrasion resistance of enamels decreases by increasing the hardness value, because under loading conditions fracture can occur and propagate [8, 4]. In view of the above-mentioned phenomena, the last decades have seen an intensification of research to improve the abrasion resistance characteristics of TBC enamels [9-11]. There are many ways to improve these email features. The first and probably one of the easiest approaches is to modify the composition of the frit using mill additives in powder form. Other innovative methods used are controlled crystallization of the enamel [12] or adding hard or self-lubricating particles to the enamel matrix [13].

2. Theory

For monolayer materials or for materials where layer penetration does not occur, the volume of the wear crater is calculated with [14]:

$$V = \frac{\pi b^4}{64R} \tag{1}$$

where:
b is the crater diameter and R is the radius of the ball (b<<R).

The mathematical relationship assumes that the shape of the crater is identical to the spherical shape of the ball, an assumption that in reality has proven true in the vast majority of cases.

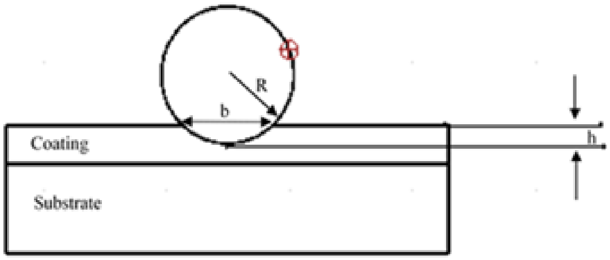

Fig.1 Principle scheme of the ball cratering testing installation

Archard's law (wear law) states that the wear volume is V = KSN where K is a constant (wear rate), S is the sliding distance and N is the applied load. It has often been found that this dependence is true, but in some cases a strong dependence of the wear rate on the number of revolutions and therefore on the sliding distance is observed. In this context, the wear rate can be described as:

$$K = \frac{\pi b^4}{64R} * \frac{1}{SN} \tag{2}$$

It can be appreciated that the wear rate is influenced by the sliding distance S and the applied force N [15] and the wear resistance can be determined with the relation [16]:

$$WR = \frac{1}{K} = \frac{SN}{V} \tag{3}$$

The article describes the behavior of TBC enamel recipes subjected to abrasive wear resistance estimation tests using the method described above and according to EN ISO 26423:2016. The abrasive wear resistance was determined according to "Measurement Good Practice Guide No. 57" [14].

3. Materials and methods

UV-VIS and XRF spectrometric analyses

The deposition substrate for the enamel layers was non-alloy steel. The chemical composition was estimated with the UV-VIS spectrometer

SPECTROMAXx LMM004. The results are shown in Table 1, together with the expanded uncertainty, for a 95% confidence level.

Table 1

Chemical analysis of the steel substrate

Elements	**C**	**Mn**	**P**	**S**	**Si**	**Cr**	**Ni**	**Al**	**Cu**	**Fe**
% mass	0.04	0.23	0.012	0.008	0.009	0.015	0.031	0.05	0.02	rest
U (95%)	0.004	0.07	0.006	0.002	0.002	0.003	0.003	0.005	0.003	-

Circular specimens, 40 mm in diameter, were cut from 0.5 mm thick steel plate. The discs were cleaned by sandblasting with 80-140 Mesh ASTM-E11 grit, then cleaned with compressed air and washed with ethyl alcohol. The frit used as a base recipe was ground and homogenized, then analyzed by x-ray fluorescence with an AMETEK SPECTRO XEPOS-03 spectrometer. The results of the determinations are shown in Table 2.

Table 2

Chemical analysis of frit basic recipe

Oxide	SiO_2	Na_2O	CuO	Fe_2O_3	Al_2O_3	CaO	CoO	TiO_2	K_2O	MnO	Cr_2O_3
% mass	47.11	11.16	7.53	5.10	1.56	6.03	3.49	1.07	4.91	2.67	2.14

Abrasive wear resistance tests were performed on two recipes derived from the basic recipe, with Al_2O_3 and TiO_2 as grinding additives, respectively in percentages of 3, 5, and 8% of the basic frit. Al_2O_3 powder is MERCK quality, granulation 70-230 mesh ASTM-E11 and TiO_2 powder is HERMAN quality, granulation 80-300 mesh ASTM-E11. The corresponding sample coding is shown in Table 3 and Table 4.

Table 3

Sample code of Al_2O_3-added samples

Sample code	Frit (% of mass)	Addition Al_2O_3
B	100	0
BAL3	97	3
BAL5	95	5
BAL8	92	8

Table 4

Sample code of TiO_2-added samples

Sample code	Frit (% of mass)	Addition TiO_2
B	100	0
BTI3	97	3
BTI5	95	5
BTI8	92	8

The 7 enamels obtained were deposited on the steel discs by the wet spray method, with a spray gun with a 1.8mm nozzle, at a pressure of 5-6 atm. After deposition, the samples were dried at room temperature for 30 min, then in an oven at 80-100^{0}C for 60 min. The dried samples were burned in an electric oven at 860^{0}C for 3 min.

4. Experimental conditions

CALOWEAR abrasive wear tests

Abrasive wear tests were carried out using the rotating abrasive ball or Calowear method**.** [14] The test consists of frictionally rolling a ball on the surface of the deposited layer and in the presence of an abrasive slurry, as shown in Fig. 2.

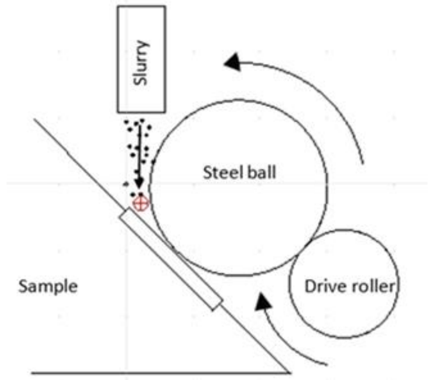

Fig 2. Testing device scheme

As abrasive material, SiC F1200 powder was used, with an average grain size of maximum 4 µm, in a mixture of 6.4 g abrasive to 8 ml distilled water, thus obtaining an abrasive slurry. The rotational speed of the ball was 80 rpm. The increment of the ball rolling distance was 45 m. The dimensions of the wear crater were measured at intervals corresponding to the increments of the rolling distance, after removal of the ball and using an optical microscope equipped with a micrometric reticle system. The normal force N was determined from the physical configuration of the system used, which allows variation of this force in the range 0.1-0.5 N. The force value was 0.31 N. The estimation of the normal force of the ball pressing on the sample shows high values of the measurement uncertainty [17] so that they only allow qualitative and/or comparative assessment of wear resistance.

5. Results and discussions

Measurement of the wear crater diameter was carried out in two perpendicular directions, depending on the direction of ball rolling, and the average of the two values was used in the calculations (Fig. 3).

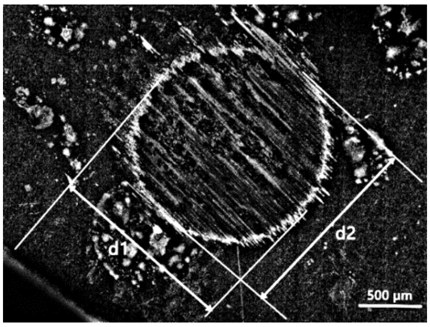

Fig. 3. Optical microscopy image of sample BTI8, showing the wear crater diameter measurement procedure.

For each sample 5 values were obtained and their average was used in the calculations. The results of the measurements are shown in Table 5.

Table 5

Measurement results of wear crater diameter (mm)

Crater diameter (mm)	Sliding distance (m)				
	45	90	135	180	225
B	1.245	1.575	1.795	1.995	2.050
BAL3	0.665	0.710	0.740	0.760	0.770
BAL5	0.700	0.830	0.920	1.000	1.070
BAL8	0.630	0.705	0.750	0.840	0.840
BTI3	1.205	1.350	1.365	1.425	1.640
BTI5	0.845	0.895	1.155	1.255	1.355
BTI8	0.720	0.950	1.215	1.495	1.810

Fig. 4 shows the variation of the wear crater diameter as a function of the number of sliding distance for BAL samples and Fig. 5 for BTI samples.

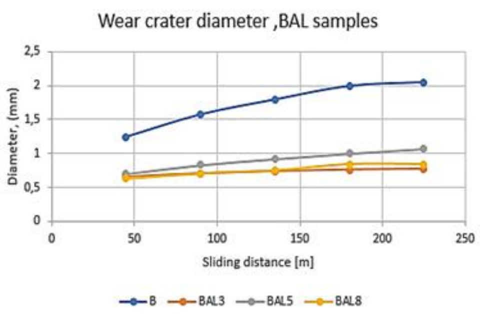

Fig. 4. Variation of wear crater diameter as a function of the sliding distance, BAL samples

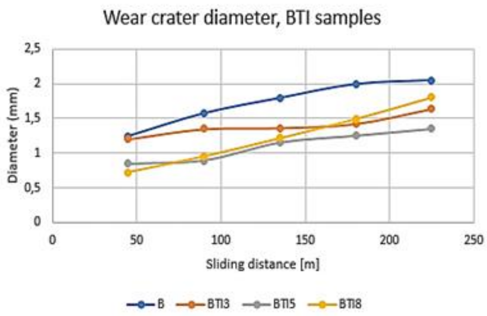

Fig. 5. Variation of wear crater diameter as a function of the sliding distance, BTI samples

Measurements to determine the diameter of wear craters show that the values obtained for BAL samples are lower than for BTI samples, which would lead to the conclusion that Al_2O_3-added micro-composites are more resistant to abrasive action compared to TiO_2-added enamels. It is also noted that in the case of the BTI samples, the deviation to the values of the control sample, B, is much smaller than in the BAL samples. The wear crater volume values for the 7 enamels deposited are shown in table 6.

Table 6

Results of the wear crater volume measurements

Crater volume (mm^3)	Sliding distance (m)				
	45	90	135	180	225
B	0.074	0.190	0.321	0.491	0.547
BAL3	0.037	0.087	0.122	0.233	0.281
BAL5	0.020	0.038	0.079	0.150	0.211
BAL8	0.010	0.038	0.070	0.085	0.105
BTI3	0.065	0.103	0.107	0.128	0.224
BTI5	0.016	0.020	0.055	0.077	0.104
BTI8	0.008	0.025	0.067	0.155	0.332

The variation of the volume of the wear crater as a function of the sliding distance is shown in Fig. 6 for BAL samples and in Fig. 7 for BTI samples.

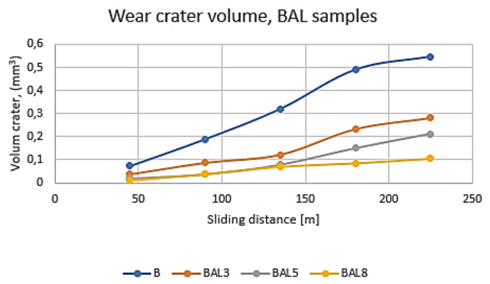

Fig.6. Variation of the volume of the wear crater as a function of the sliding distance for BAL samples

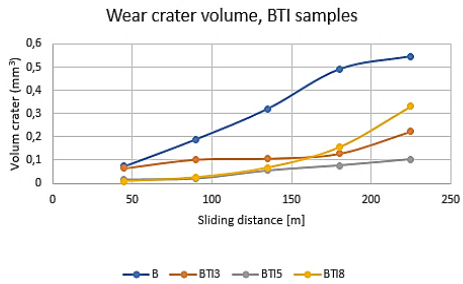

Fig.7. Variation of the volume of the wear crater as a function of the sliding distance for BTI samples

The presented graphs show that the addition of Al_2O_3 and TiO_2 mill additions significantly increase the wear resistance of the enamels compared to the reference sample, B. From Figs. 6 and 7 it is known that the volume of the abrasion wear crater increases with increasing abrasion sliding distance, both for samples BAL and BTI and for the reference sample, B. Compared to the reference sample B, it is observed that with increasing sliding distance, the differences from the volume values for the samples with mill additions also increase. Deviations from the volume variation trend may be caused by the appearance in the friction zone of hard particles torn from the enamel surface and added to the abrasion process. Calculation of the wear resistance of the 7 deposited enamels was performed with relation (3), and the results are shown in Table 7.

Table 7

Results of wear resistance calculations

Wear resistance (J/mm^3)	Sliding distance				
	45	90	135	180	225
B	0.189	0.147	0.131	0.114	0.128
BTI3	2.879	3.668	4.294	3.637	4.542
BTI5	1.882	1.909	2.194	3.810	5.726
BTI8	2.307	3.553	4.531	5.422	6.438
BTI3	0.214	0.272	0.391	0.438	0.313
BTI5	0.680	0.490	0.610	0.720	0.671
BTI8	0.590	0.610	0.623	0.560	0.650

The variation of wear resistance as a function of the number of rotations of the ball, i.e. as a function of the sliding abrasion distance, is shown in Fig. 8 for BAL samples and in Fig. 9 for BTI samples.

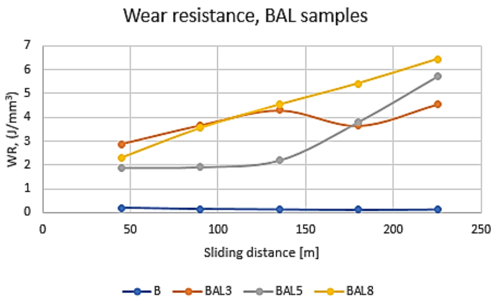

Fig. 8. Variation of wear resistance as a function of the sliding distance, for the BAL samples

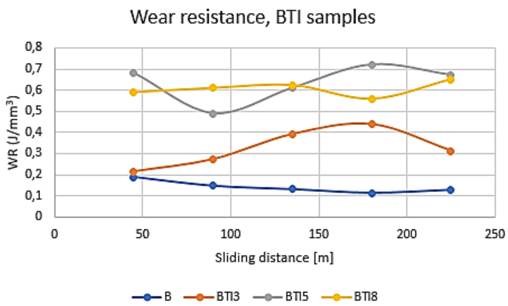

Fig. 9. Variation of wear resistance as a function of the sliding distance, for BTI samples

Analysis of the variation of wear resistance as a function of the proportion of mill additions shows that the presence of oxide particles in the base enamel leads to an increase in wear resistance. In the case of the BAL samples, with additions of Al_2O_3, a general increasing trend of the wear resistance is observed, with relatively close values of the three modified recipes. In the case of the BTI enamels, a separation of the behavior of the BTI3 and BTI5 samples, in relation to the reference sample B and BTI8, is observed, without the former showing a monotonic behavior. Such behavior may be due to the phenomenon mentioned above, i.e. the contribution to the abrasion process of the hard particles pulled out of the enamel layer during the test. It is to be investigated in the future what is the contribution of the particles pulled out of the enamel to the abrasion intensification in the friction zone.

6. Conclusions

The paper presents the effects of Al_2O_3 and TiO_2 additives to the enamel barbotine in the milling stage. Three different recipes have been investigated through XRFS and Calowear tests. The wear measurements show that the presence of Al_2O_3 and TiO_2 leads to a significant increase in the wear resistance of enamels. The effect of Al_2O_3 oxide additions produces a monotonic increase in the wear resistance, in cases where the additions were in the proportions of 3, 5 and 8% reported to frit mass.

An increase in wear resistance was also observed for TiO_2 additions, but without showing a monotonic variation regarding to the TiO_2 content.

Our data show that the Calowear test can be successfully used for the selection of mill additives in order to improve the abrasion and erosion resistance of enamels.

The main novelty of this paper is the use of Al_2O_3 and TiO_2 as mill additives. Also, the quantification of the wear resistance increasing of the enamel layer through proper Al_2O_3 and TiO_2 additions is another novelty. This way of increasing the wear resistance of the enamel coatings used as a thermal barrier is cost-effective and can be easily implemented in coating manufacture.

Future research is required to investigate the influence of the contaminants consisting in insoluble and hard particles on the abrasive wear resistance. In this regard, the chemical composition, morphology and phase contents of these particles should be assayed**.**

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