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Influence of Mechanically Activated Ceramic particles on the Abrasion Resistance of Glass-Ceramic Coatings

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Abstract

Among several coating systems of ferrous materials for industrial and engineering applications, glass-ceramic coatings have numerous advantages of high-temperature stability, chemical inertness, superior mechanical properties, and aesthetic appearance. The effect of adding mechanically activated hard ceramic particles to diopside-based glass-ceramic coatings on wear behavior is studied in this work. Boron Carbide (B_4C), silicon carbide (SiC), and tungsten carbide (WC) particles were chosen for the mechanical activation process because of their high hardness, excellent wear resistance, and high impact resistance properties. The activation was done in a planetary ball mill for 30 min with the wt.% ratios of 1:1:1; 1:0.5:1.5; 1:1.5:0.5 for the B_4C, WC, and SiC respectively. The mechanically activated particles were incorporated into the glass-ceramic coating matrix during the milling step of the parent glass. A Taber Abraser was used to investigate the wear behavior of the produced coatings. Morphological, phase, and thermal properties of as-made samples were investigated with SEM, EDS, XRD, and heating microscopy. Mass loss, color change, gloss change, and morphological changes after the abrasion test is evaluated. The results showed that increasing the WC amount ratio increases the mass loss phenomena due to the high density (15.63 g/cm^3) of WC and the change in the surface properties of the studied coatings decreases with the increasing amount of WC and decreasing amount of SiC particles.

Cam-Seramik Kaplamaların Aşınma Direncine Mekanik Olarak Aktive Edilen Seramik Partiküllerin Etkisi

Özet

Endüstriyel ve mühendislik uygulamaları için demir esaslı malzemelerin çeşitli kaplama sistemleri arasında, cam-seramik kaplamalar, yüksek sıcaklık kararlılığı, kimyasal dayanım, üstün mekanik özellikler ve estetik görünüm gibi sayısız avantajlara sahiptir. Bu çalışmada, mekanik olarak aktive edilmiş sert seramik partikül ilavesinin diyopsit esaslı cam-seramik kaplamaların aşınma davranışı üzerindeki etkisi araştırılmıştır. Bor Karbür (B_4C), silisyum karbür (SiC) ve tungsten karbür (WC) partikülleri, yüksek sertlikleri, mükemmel aşınma direnci ve yüksek darbe direnci özellikleri nedeniyle mekanik aktivasyon işlemi için seçilmiştir. Aktivasyon, B_4C, WC ve SiC için sırasıyla ağırlıkça %'lik 1:1:1; 1:0.5:1.5; 1:1.5:0.5 oranlar ile bir planet tipi bilyalı değirmende 30 dakika süreyle yapılmıştır. Mekanik olarak aktive edilmiş parçacıklar, ana camın öğütme aşaması sırasında cam seramik kaplama matrisine dahil edilmiştir. Üretilen kaplamaların aşınma davranışını araştırmak için Taber aşındırıcı kullanılmıştır. Hazırlanmış örneklerin morfolojik, faz ve termal özellikleri SEM, EDS, XRD ve ısı mikroskobu ile incelenmiştir. Aşınma testi sonrası kütle kaybı, renk değişimi, parlaklık değişimi ve morfolojik değişimler değerlendirilmiştir. Sonuçlar, WC oranının arttırılmasının WC'nin yüksek yoğunluğu (15.63 g/cm^3) nedeniyle kütle kaybı olayını arttırdığını ve WC miktarının artması ve SiC miktarının azalması ile çalışılan kaplamaların yüzey özelliklerindeki değişimin azaldığını göstermiştir.

1. INTRODUCTION

Glass-ceramic coated cast iron system, which is defined as composite material containing both glass and ceramic materials, are obtained with the aid of controlled crystallization by heat treatment.[1] During the controlled crystallization process, the first step is nuclei formation next step of the crystallization process is the growth of the nucleus that increases the size of the nucleus, and the last step is size distribution through the glass-ceramic matrix. Taking account of the crystallization process, the GC(Glass-Ceramic) system consists of an amorphous structure provided from the base glass structure, and crystalline structure derived from nucleation of which contributes to ceramic structure. Result of efficiently controlled crystallization, randomly orientated grains, without voids, microcrack GC system is obtained. The combination of two different structure presents advantages in engineering properties, which are high-temperature stability, chemical inertness, superior mechanical properties, and aesthetic appearance. On the other hand, the engineering properties of GC systems offer high hardness value, but these properties affect fracture toughness negatively. Because of this reason, the wear resistance of GC is limited. So many aspects should take into consideration when inspecting of wear behavior of the GC system. Amount of porosity and dimension of porosity inside of GC matrix influence the aspect of abrasion behavior. Constitution of porosity and bubble is a prevalent feature of GC structure also the reason for the existence of this porosity and bubble is gas evolution during the heat treatment.[2] Decreasing the amount of porosity and bubble can reduce the probability of cracks or microcracks causing mechanical defects. After a mechanical defect occurred, the glass-ceramic coating can be detached from the substrate surface. Also, during abrasion sourced mechanical defect on coating surface, can lead to of marked loss of aesthetical properties in terms of gloss and color as well.[3]

In accordance with this purpose, studies to improve the wear resistance of glass-ceramic coatings have been carried out in literature. Considering how glass-ceramic coating can be improved, several possible ways can be chosen. They are modifications of chemical composition of GC, more innovatively addition of hard particle in glass matrix such a carbide; silicon carbide (SiC), boron carbide (B_4C), tungsten carbide (WC); or refractory oxides such as silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), zirconium dioxide (ZrO_2). However, one should also consider the compatibility of these particles with the enamel structure. Boron carbide can be preferred to improve the abrasion resistance of glass-ceramic matrix because it has high strength, high hardness (5000 $kg.mm^2$) [4], low density (2.52 g/cm^3) [5], etc. like that excellent engineering property. Also, oxidation products ($2B_2O_3$ and CO_2) are coherent with the glass-ceramic matrix. Silicon carbide has superior mechanical properties like hardness, wear.[6] Also, tungsten carbide has familiar excellent engineering properties except for density (15.63 g/cm^3). In addition, relatively high temperatures are achieved during the crystallization processes, so the oxidation behavior of these particles is very important because it can adversely affect the wear resistance of the enamel rather than increase it. Another possible way is the modification of mill additives and crystallization to provide limited improvement regarding abrasion resistance. One of the studies of the modification of mill additives was the examination of how potassium feldspar and zirconium silicate influence on abrasion mechanism of glass-ceramic coating.[7] Potassium feldspars possess a feature of high compatibility to the glass-ceramic structure and improves the abrasion resistance of the coating up to 10 wt.%. Another study of the modification of mill additives was the effect of the addition of quartz and spodumene on abrasion resistance. Quartz is a glass former so the addition of quartz as mill additive, shows good compatibility with glass-ceramic matrix. When considering the effect on abrasion resistance, quartz can develop the abrasion resistance of glass-ceramic coating up to 10 wt.%.[8,9] Studies about the investigation of the possible use of SiC and WC as mill additives were accomplished by Rossi S. et al.[8,10] Those hard ceramic particles provide a positively affect abrasion resistance only exploited at high concentrations, from 5 wt.% up to 10 wt.%. However, in the case of the addition of WC particles, slurry needs a homogenization process. Because of WC possess a very high density, WC particles sink to the bottom of the slurry. That situation chance abrasion behavior of coating surface because during mechanical damage WC particles do not interact between abraser surface so it may cause us to misinterpret effect of addition of WC particles in glass-ceramic structure. Another study relative to the influence of ceramic hard particles on the glass-ceramic matrix was a glass-ceramic coating reinforced with nano WC particles.[11] Nano WC particles was exhibiting a positive effect on the abrasion behavior of the coating, if particles distribution is homogeneous through the structure. Small particles size leads to agglomeration, so a high amount of additive presents a negative effect on abrasion resistance. Agglomerated particles cause local stress and porosity, which lead to crack initiation and propagation. If the complications of these hard particles, namely their compatibility with the matrix, oxidation behavior, agglomeration, etc., are exceeded, it can provide the opportunity to produce more resistant and durable enamel.

Mechanical activation provides a simple, practical method to constitute ultrafine composite powder. During the mechanical activation process, which decreases the particle size of the powder, the changing of powders' shape due to repeated extruding and crushing occurs.[12] During mechanical activation operation, powder particles are repetitively trapped between grinder balls. As a result of these repeated movements particles are plastically deformed, generating a wide number of dislocations as well as other lattice defects.[13] This process is associated with the reactants interface formation, increase of internal and surface energy as well as surface area.[14]

The purpose of this study, investigation of mechanical activated ceramic hard particles addition on glass-ceramic matrix and the effect on abrasion behavior of glass-ceramic coating. The change in mass loss, gloss, and color value were analyzed. Based on measured data, the abrasion resistance of glass-ceramic coating with the addition of mechanical activated particles were analyzed.

2. MATERIALS & METHODS

2.1 Materials

In the present study, B4C (99.99% purity, 325 mesh), WC (325 mesh), and SiC (325 mesh) were selected for investigation of the effect of added hard ceramic particles to the glass-ceramic matrix. GC matrix was obtained amorphous and diopside crystal phase with the help of suitable precursor glass through heat treatment. The Precursor glass contains SiO_2, CaO, B_2O_3, Na_2O, and MgO. Three of HCP (hard ceramic particle) mixtures were compose of B_4C, WC, and SiC with the mass ratio of 1:1:1; 1:0.5:1.5; 1:1.5:0.5. Those powders are activated with a planetary ball mill in a wet medium. Tungsten carbide balls were used during this study. Ethanol was selected for process control agent and 2 wt.% added to the powder mixture. The ball-powder mass ratio and rotation speed were 8:1 and 500 rpm for 30 min.

The main crystalline phase of the used glass precursor was diopside ($CaMgSi_2O_6$). The diopside phase has high mechanical properties such, are thermal shock, erosion, impact, and abrasion-resistance[1]. $CaMgSi_2O_6$ GC (glass-ceramic) system, and added mill additives (clay, sodium nitrite) were provided by Akcoat Advanced Chemical Coating Materials (Sakarya, Turkey).

2.2 Sample Preparation

Alumina-zirconia ball mills were used for the milling process. Precursor glass to be used was ground in the mill for 12 min. After the milling process of precursor glass, mill additives were added to the mill and the milling process was continued for another 3 min. Mechanically activated hard ceramic particle mixture was added like a mill additive.

After the milling process, a mixture of glass precursor, mill additive, and activated particles was screened with 60- mesh sieve. In order to obtain a slip, 40 % water was added to the sieved powder and mixed with the purpose of obtaining uniform slurry.

Cast iron substrate was chosen for glass-ceramic coating application and the dimension of the substrate was 100 mm × 100 mm × 5mm. Before applying of coating, sandblasting and degreasing processes were carried out. The application method was chosen as wet-spraying method. After the coating process, samples were dried at 300 ° C with the purpose of evaporating water in-side of the coating. Controlled crystallization was conducted in the furnace at 770 ° C for 12 min. The ratios and sample codes used in the mill and the addition of HCP are shown in Table 1 and Table 2.

Table 1. Sample codes and ratio of mill additives.

Sample Code	Frit Comp.	Ultrasil	Clay	Na_2O	HCP
BWS-Ref	100	0.8	4.5	0.3	-
BWS-BC	100	0.8	4.5	0.3	5
BWS-8	100	0.8	4.5	0.3	5
BWS-12	100	0.8	4.5	0.3	5
BWS-4	100	0.8	4.5	0.3	5

Table 2. Sample codes and the ratio of HCP addition.

Sample Code	HCP Addition
BWS-Ref	-
BWS-BC	5 wt.% B4C
BWS-8	5 wt.% HCP (B4C-WC-SiC, 1:1:1)
BWS-12	5 wt.% HCP (B4C-WC-SiC, 1:0.5:1.5)
BWS-4	5 wt.% HCP (B4C-WC-SiC, 1:1.5:0.5)

2.3 Characterization Studies

The chemical composition of the used precursor glass was analyzed with a Bruker AXS S8 Tiger model of the X-ray fluorescence (XRF).

Investigation of glass-ceramic coating surface of samples for surface morphologies and microstructure were analysed with Scanning electron microscopy (Jeol SEM JSM-6060LV) with an energy dispersive X-ray spectrometer (EDS) attachment. During analysis with SEM and EDS were executed in the backscattered electron mode (BSE), which was implemented with an acceleration voltage of 15 kV and an operating distance of 9.5 mm.

X-ray diffraction spectroscopy (Bruker XRD/D8 Advance) analysis was used for the examination of the crystallinity of the GC matrix. Also, analyses of XRD aided to understand the effect of mechanically activated HCP on the glass-ceramic matrix and coherence to the matrix. X-ray diffraction spectroscopy analysis was performed using Cu K_α radiation under x-ray generator settings of 40 kV and 25 mA. Diffractograms were taken in θ - 2θ configuration from 10° to 90°.

The abrasion resistance of glass-ceramic coatings was analyzed with Taber 5135 Rotary Platform Abraser device with CS17 wheels and S33 strips under the 250 g weight. During abrasion test analysis, every 250 cycles, gloss change, color change, and mass loss values of samples were examined. The total cycles of the abrasion test were 1000 cycles.

The effect of abrasion on the color change of surface was evaluated by Konica Minolta CM-700d Spectrophotometer in terms of L*, a*, and b* represent colors. ΔE, which shows the difference between the start and the final of the color analyses test, is calculated with the following Eq. 1;

$$\Delta E= [(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2]^{1/2} \tag{1}$$

3. RESULTS AND DISCUSSION

3.1. Chemical Structure

Table 3 shows that obtained XRF analysis of used precursor glass composition. The frit composition consists of SiO_2, CaO, B_2O_3, Na_2O, and MgO. This precursor glass was chosen because the diopside phase ($MgCaSi_2O_6$) with good wear resistance and high engineering properties was obtained after heat treatment, so it is a suitable choice for investigating wear behavior. Figure 1 shows obtained XRD analysis of GC coating, as it can be seen diopside phase exists.

Table 3. The chemical composition of the studied frit composition.

Oxide Group	Composition wt.(%)
RO (CaO, MgO, ZnO, CoO)	18.7
R_2O (Na_2O, K_2O, Li_2O)	10.7
RO_2 (SiO_2)	50.5
R_2O_3 (Fe_2O_3, Al_2O_3, B_2O_3)	11.1
R (F)	1.2
TiO_2	7
Total	100

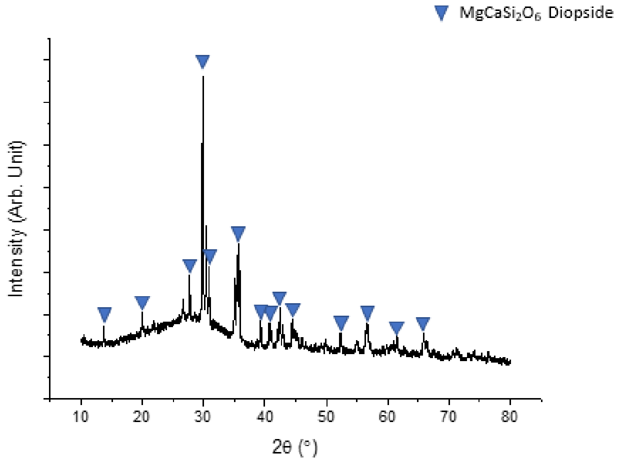

Figure 1. XRD analysis of studied glass-ceramic coating.

Figure 2 shows SEM analysis of mechanically activated hard ceramic particles. Three types of HCP are homogeneously distributed in each other during the milling process help with the planetary ball mill. In addition, SEM images prove no agglomeration observed during or after the milling process. SEM images demonstrate that after the milling process particle size of WC and SiC are smaller than B_4C particles. On the other hand, HCP particles were selected with almost the same dimensions before milling. The reason for this can be the discrepancy in the hardness value of HCPs. In terms of hardness value, B_4C has the most hardness value than other particles and WC and SiC particles have an almost the same hardness values.

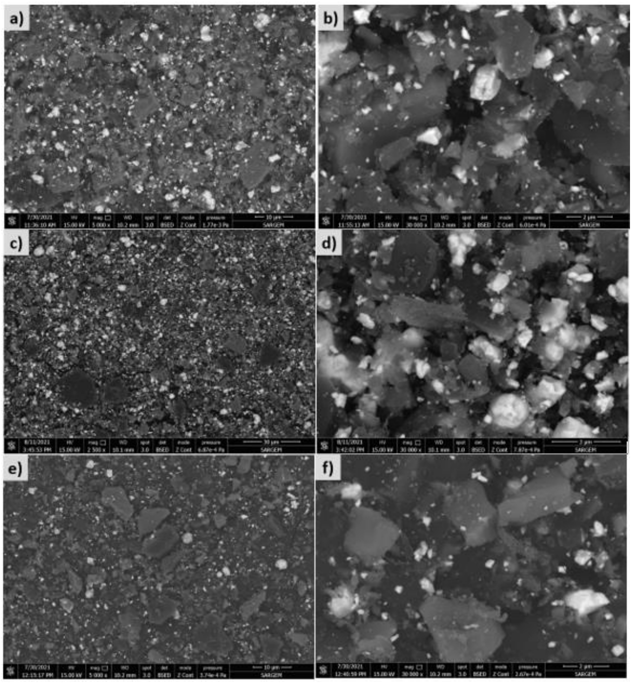

Figure 2. SEM images of mechanically activated hard ceramic particles a) and b) BWS-8, c) and d) BWS-12, e) and f) BWS-4.

Color values of the studied GCC samples were given in Table 4. Considering Table 2 the value of L of GCC samples decreases when the addition of HCP to GC composition. Sample of BWS-Ref does not have any addition of HCP in the composition. The L value of BWS-Ref samples has the highest L value of all of the other samples.

Table 1. Measured properties.

Sample Codes	**SCE D65**		
	L	**a**	**b**
BWS-Ref	48,90	-4,86	-3,15
BWS-BC	34,95	-0,12	-0,12
BWS-8	37,80	-0,25	0,05
BWS-12	39,15	-0,32	-0,16
BWS-4	38,97	-0,27	0,13

The gloss measurement is another important parameter for the understanding the aesthetic properties of GCC. The addition of HCP to GC composition caused a decrease in the gloss value of samples. Surface roughness is a parameter for the examination of gloss value. Rough surface causes scattering light rather than reflected light so scattered light leads to decreasing gloss value of the surface. The reason for the rough surface could be the oxidation HCP particles at around crystallization temperature which is 770°C. During oxidation, oxidation products, which are carbon dioxide gases, can drifted part and can be trapped inside of GCC. Trapped gas in structure leads to pore on the GCC surface and pores cause and increase in the roughness of the surface. The oxidation reactions of HCPs are explained as follows;

$$B_4C + 4O_2 = 2B_2O_3 + CO_2 \ (550°C) \tag{2}$$

$$WC + 5/2O_2 = WO_3 + CO_2 \ (500\text{-}600°C) \tag{3}$$

$$SiC + 2O_2 = SiO_2 + CO_2 \ (700\text{-}800°C) \tag{4}$$

The oxidation products of HCPs during recrystallization processes are B_2O_3, WO_3, SiO_2, and CO_2. CO_2 is either left from GC structure if the viscosity allows it to release from the matrix or remain in GC structure if the viscosity is low for an escape to the structure. The oxidation product of B_2O_3 has affected the viscosity of the GC structure because amorphous B_2O_3 structure and has a low viscosity so the oxidation product decreases GC matrix viscosity. On the other hand, this oxidation product constitutes a dense structure. Also, B_2O_3 is coherent to GC so that the coating consists smooth and crack-free. Taking into consideration that B_4C HCP is suitable for improve abrasion resistance both aspect of chemical and physical of the coating. WO_3 provides a dense structure of the GC matrix, which increases the abrasion resistance of the coating, but WC is a very dense material hence it causes agglomeration and sinking in the bottom of slip during the application step to the substrate. That can affect the abrasion behavior of GCC negatively during abrasion. So, if WC particles were chosen for mill additive to improve the abrasion resistance of GCC, agglomeration of particles should be prevented. Another oxidation product of HCP is SiO_2, which is glass-forming oxide, and very coherent to the GC matrix. SiO_2 provides higher wear resistance and higher viscosity. The result of higher viscosity is that CO_2 cannot leave from the GC matrix to comprise pores inside the structure.

Pores inside of GCC are a very critical aspect for abrasion resistance. These areas lead to the increasing number of stress points and eventually cracking. The size and number of pores can help interpretation about the abrasion behavior of GCC. If pores' number and size increase, which leads to a stress point and crack, abrasion resistance affects negatively. So, one can say the amount and size of pores are inversely proportional to abrasion resistance.

Figure 3 shows the surface of samples before the abrasion test before abrasion test, and GC coating includes pores on the surface. BWS-Ref and BWS-BC possess a lower number of pores on the surface rather than others. Figure 4 shows after abrasion SEM images of BWS-Ref and BWS-BC samples. It can be said that the samples have a lower amount and size of pores than other samples because during the crystallization process evaporation of gasses and oxidation products leave from GC structure. On the other side, BWS-8, BWS-12, and BWS-4 include the high number of big pores that may be generated because of abrasion action due to the detachment of particles and the GC matrix.

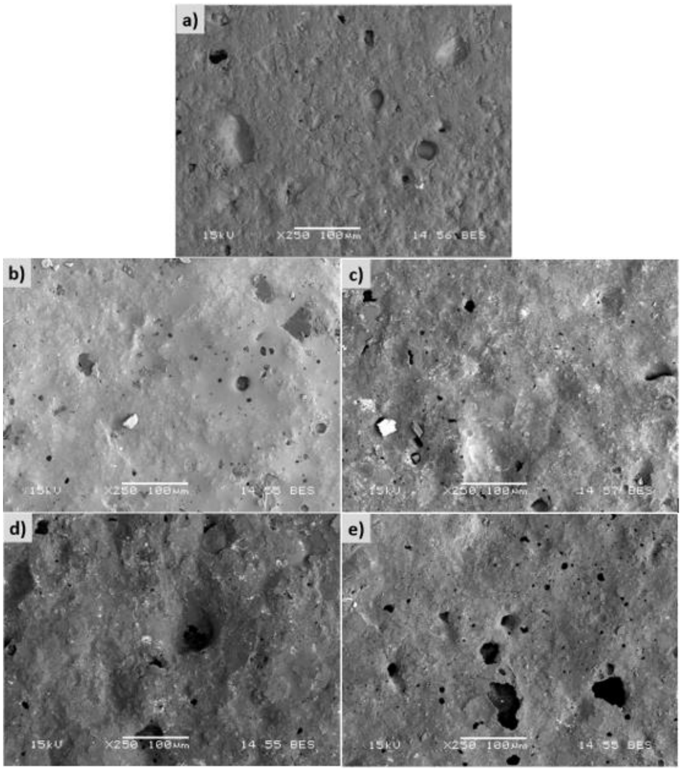

Figure 3. SEM analysis images of a) BWS-Ref b) BWS-BC c) BWS-8 d) BWS-12 e) BWS-4 before abrasion test.

The GC coating analyzed the behavior of abrasion resistance with three different methods: color change, mass loss, and gloss change.

Mass loss is the investigation of the abrasion resistance of coatings. Figure 5 shows the mass loss of the sample every 250 cycles. BWS-Ref has no abrasion barrier on GC coating because mass loss continues at a constant value during abrasion. When investigating the coating of BWS-BC, it can be interpretation an abrasion barrier exists. Because during abrasion, there is even a small decreasing mass loss that means that abrasion barrier exists. In term of the addition of mechanically activated HCPs, BWS-4 showed better abrasion resistance than BWS-8 and BWS-12 coating samples. SEM images, which are shown in Figure 4 support that presume because BWS-4 has a smaller size and lower pores than BWS-8 and BWS-12 GCC. BWS-8 shows an abrasion barrier until 500 abrasion cycles because from the first 250 abrasion cycles to the other 250 abrasion cycles it provides decreasing mass loss compared to the first 250 cycles. On the other hand, it was observed that after 500 wear cycles, BWS-8 exhibited a no-wear barrier due to the increase in mass loss value in subsequent abrasion cycles. BWS-12 has the highest mass loss value than other GCCs. Especially after the 750th abrasion cycle, dramatically increasing mass loss value was observed. That behavior can be the lack of GCC on the substrate and removed from the surface at the first 750 abrasion cycles.

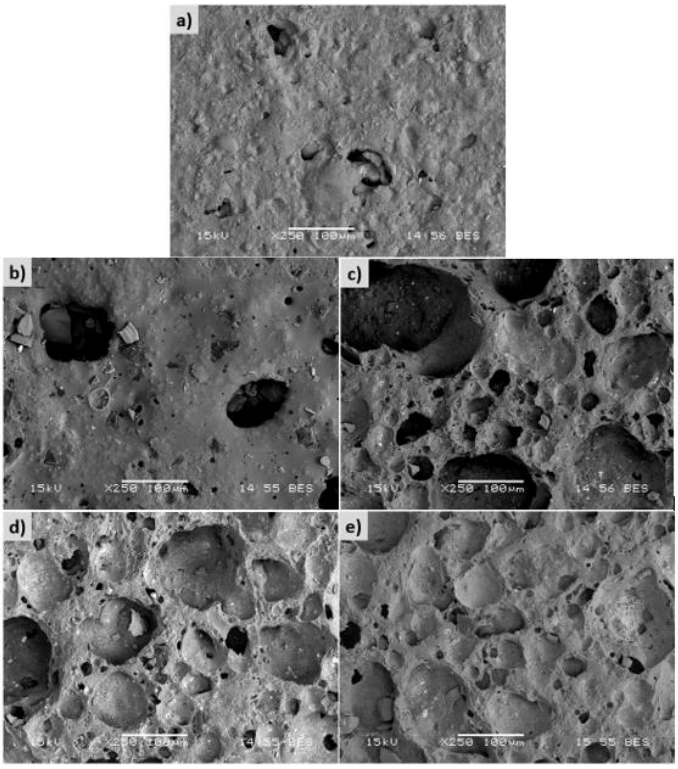

Figure 4. SEM analysis images of a) BWS-Ref b) BWS-BC c) BWS-8 d) BWS-12 e) BWS-4 after abrasion test.

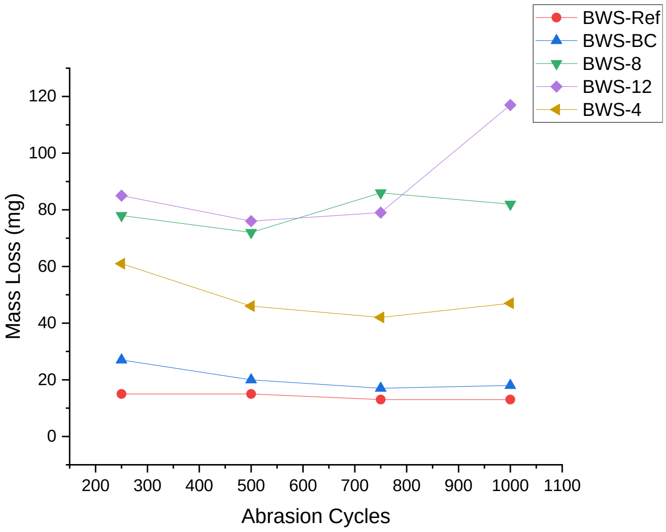

Figure 5. Mass loss values of the samples at every 250 cycles.

Figure 6 shows the color change value of GCC at every 250 cycles. ΔE Eq. (1) indicates a color change of samples. BWS-Ref sample exhibits higher color change rather than next cycles at first 250 cycles. At the beginning of abrasion, the bright coating surface is removed by abrasion so the value of L increases because of the produced glass flakes. After the first 250 cycles, the BWS-Ref sample demonstrates less color change in the next cycles. BWS-BC sample has lowest L value at initial situation because of oxidation product creates a decrease in L value. Before abrasion, the coating area appears black, but when the oxidation area appears after abrasion, that area appears gray because of the oxidation product. With increasing, abrasion cycles the color change value does not change so much during the abrasion test but at the last 250 cycles highest color change occurs for the BWS-BC sample. Samples of addition of mechanically activated HCP to GCC show color changing at first 250 cycles dramatically. When increasing abrasion cycles, the value of color change decreases next cycles except the BWS-12 sample. The sample of BWS-12 at last cycles indicates higher color change than BWS-8 and BWS-4 samples.

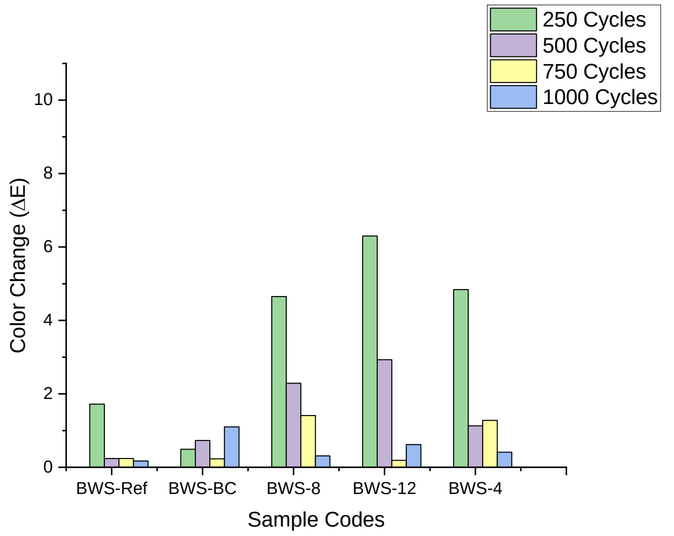

Figure 6. Change of the studied sample's properties at every 250 cycles of abrasion in terms of color change (ΔE).

Figure 7 shows to gloss change of studied GC coating samples in percent change. The gloss value of the sample of BWS-Ref increases after 750 cycles but starts to decrease at the last 250 cycles lightly.

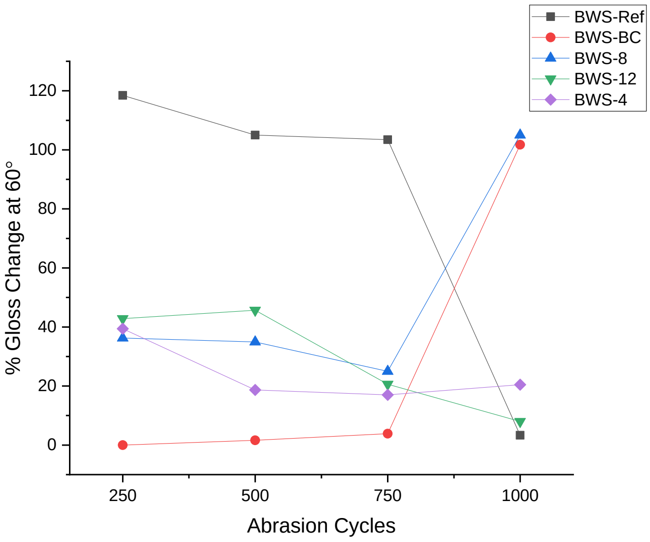

Figure 7. Change of the studied sample's properties at every 250 cycles of abrasion in terms of % gloss change.

It can be said that the BWS-BC sample possesses almost the same gloss value at each cycle because the amount of decreasing gloss change is limited. When examining the gloss value of samples of BWS-8, BWS-12, and BWS-4, samples possess a high amount of gloss change. The reason for the high amount of gloss change is related to the oxidation region, a high number of pores inside of the GC structure increasing roughness of the surface. So, roughness cause increasing the reflective angle of light, which effects the gloss value directly.

4. CONCLUSIONS

In this study, the effects of mechanical activated hard ceramic particles addition on abrasion behavior of the glass-ceramic coating was investigated. Samples of BWS-REF and BWS-BC possess a lower mass loss value rather than the BWS-8, BWS-12, BWS-4 samples. During the examination of the wear behavior of the sample, it should be considered that the mass loss value is affected by the parameters that can change. Those parameters are the number and size of pores inside GCC. Color change and gloss change provide information about the abrasion resistance of coating of GCC. Oxidation temperature of hard ceramic particles can change the abrasion behavior because the oxidation product effects experiment results directly. The addition of mechanically activated HCPs in the matrix did not improve the abrasion resistance of GCC. The diopside phase is suitable for the abrasing medium. Based on this study, alternative implementations can be carried out to improve the wear resistance of glass-ceramic coatings by changing the test parameters.

- The addition of mechanically activated HCPs in the matrix did not improve the abrasion resistance of GCC.
- The diopside phase is suitable for the abraser medium.

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