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Abstract: Vitreous enamel is an inorganic coating applied on metallic substrates as powder and fired at relatively high temperature in order to cover the surface forming the coating. This kind of layer shows, at the same time, very good functional and aesthetical properties. In several applications, good mechanical resistance together with corrosion protection is required and enamel is a good alternative to other coatings. Enamel presents optimum corrosion protection and high hardness values but the low fracture toughness reduces its resistance to abrasive wear related to brittle fracture. The microstructure of enamel, the chemical composition of the frit, and the deposition parameters are crucial for the final properties. Moreover, it is possible to introduce mill additives in the frit or hard particles inside the layers to improve final resistance.
In this paper, abrasion resistance of enamel is tested by Taber Abraser test. Mill additives (spodumene or quartz), hard (WC or SiC) or solid lubricant (graphite) particles have been added to the frit to study their influence on the abrasion resistance. The abrasion resistance of modified enamels was evaluated through mass loss after abrasion and wear track were observed by SEM in order to evaluate the abrasion damage. An improvement of the abrasion resistance was obtained modifying the frit with mill additives. The introduction of SiC and WC particles produced an important modification in wear mechanism of the glassy coating, reducing the crack nucleation due to the low pores quantity and good interface between vitreous matrix and particles. In these cases the wear mechanism is limited to scratches on the surface.

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Dear Editor,

the paper entitled "Abrasion resistance of vitreous enamel coatings in function of frit composition and particles presence" written by S. Rossi, N. Parziani, C. Zanella, was revised considering all comments of Reviewers.

We hope that the paper can now be considered for publication in the present form.

On behalf of all authors,
Best regards
Stefano Rossi

WEAR

Confirmation of Authorship

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Response to Reviewers

1. In revised abstract, please rewrite sentence "The microstructure of enamel, the chemical composition of the frit, and the deposition parameters are crucial for the final properties."
The requested modification was introduced.

2. In revised abstract, please add 1 or 2 sentences on main wear results of the study. There are presently no specific research outcomes of the work.
Two sentences were introduced in the abstract:
An improvement of the abrasion resistance was obtained modifying the frit with mill additives. The introduction of SiC and WC particles produced an important modification in wear mechanism of the glassy coating, reducing the crack nucleation due to the low pores quantity and good interface between vitreous matrix and particles. In these cases the wear mechanism is limited to scratches on the surface.

3. In revised experimental section, the authors' stage, "the WC particles present a spherical shape and hexagonal crystalline structures and the SiC ones a sharp geometry and the crystal structure is hexagonal." Hexagonal is not a crystal structure it is a crystal system. Thus revise sentence to read, "the WC particles exhibit a spherical shape with WC crystal structure (hexagonal lattice) and the SiC have a sharper/angular morphology with 4H-SiC crystal structure."
The sentence was revised as following:
the WC particles exhibit a spherical shape with 2P crystal structure (hexagonal lattice) and the SiC ones have a sharper/angular morphology with 4H-SiC crystal structure.

4. In revised results/discussion section, delete "fragile" from sentence to read, "the abrasion mechanism is the case of glassy enamel based fracture."
The requested modification was introduced.

Abrasion resistance of vitreous enamel coatings in function of frit composition and particles presence

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Vitreous enamel is an inorganic coating applied on metallic substrates as powder and fired at relatively high temperature in order to cover the surface forming the coating. This kind of layer shows, at the same time, very good functional and aesthetical properties. In several applications, good mechanical resistance together with corrosion protection is required and enamel is a good alternative to other coatings. Enamel presents optimum corrosion protection and high hardness values but the low fracture toughness reduces its resistance to abrasive wear related to brittle fracture. The microstructure of enamel, the chemical composition of the frit, and the deposition parameters are crucial for the final properties. Moreover, it is possible to introduce mill additives in the frit or hard particles inside the layers to improve final resistance.

In this paper, abrasion resistance of enamel is tested by Taber Abraser test. Mill additives (spodumene or quartz), hard (WC or SiC) or solid lubricant (graphite) particles have been added to the frit to study their influence on the abrasion resistance. The abrasion resistance of modified enamels was evaluated through mass loss after abrasion and wear track were observed by SEM in order to evaluate the abrasion damage. An improvement of the abrasion resistance was obtained modifying the frit with mill additives. The introduction of SiC and WC particles produced an

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Keywords: vitreous enamel; composite coatings; mill additive; Taber test

1. Introduction

Porcelain enamel was used since antiquity (1500 BC) for decorative purposes. Today it is well established as a coating both for technical and aesthetical purpose. It is characterized by good durability since it shows very good corrosion resistance, water resistance, chemical and high temperature resistance [1-3].

Enamel can be applied both on steel and aluminum alloys substrates. Steel components, such as water heaters, electrical appliances, chemical plants and road infrastructure parts are extensively protected using this type of coatings, in particular where high durability is required. In recent decades, the application on aluminum alloys substrates has been increased for several reasons: lightweight, resistance to heat and corrosion together with the possibility of a wide customization in terms of shape and color. Enameled aluminum is required in the field of the crockery, but also in building construction, facades, interior of tunnels, outdoor furniture and lighting systems.

However, in the case of aluminum alloys substrate, some critical aspects should be taken into account. Lower firing temperature is required in order not to modify aluminum substrate microstructure and the adhesion substrate/coating could be affected by this and be limited.

An aluminum alloy is defined enamelable when a good adhesion at the interface between metal and enamel can be obtained and the coating layer is free of defects. Unlike for steel, enamels developed

for aluminum and its alloys, should have a low melting temperature, since the substrate cannot exceed 600°C in the firing step. Since 30 years, vanadium-based enamels are used for aluminum alloys and among various vanadium compound divanadium pentoxide (V_2O_5) is the most common. However, this compound is dangerous to human health and environment [4] therefore vanadium-free enamels have been developed and are used in this study.

Independently on the substrate, enamel coatings show excellent durability, but from a mechanical point of view impact and abrasion resistance is not optimal despite the good hardness values of the coating because of its glassy nature and therefore its brittleness [5]. Abrasion is a very common mechanism of degradation of enamelled surfaces. Any mechanism where the hard asperities or particles of one surface cause damage to the surface in contact under respective motion can be defined as abrasion. The damage that they produce can be of two general types: material deformation or particles formation with material removal. As common for brittle material, the wear and abrasion resistance of enamels decreases by increasing the hardness value, since under loaded conditions fracture may occur and propagate [6, 7]. By abrasion enameled surface can lose their surface glassy layer, leading to open the intrinsic porosity and reducing so the chemical resistance and durability. Moreover if cracks propagate to the interface with the substrate corrosion protection is also negatively affected.

In the last years, the research has been focused to develop enamel coatings with improved mechanical properties. To improve hardness and mechanical resistance there are different options. First of all it is possible to modify the enamel frit and often the best results are obtained by using mill additions [3, 8]. Another alternative, more innovative, is to add particles into the enamel matrix [5]. In this work these two options were considered and their effect on the abrasion resistance was tested. The first part of the study regards enamel coatings deposited on steel where the enamel composition was changed by mill additions. More details about coating preparation, optimization and characterization have been published elsewhere [8].

The second part deals with the abrasion resistance of composite enamel layers. The particles must resist at the temperature of enamel firing (about 600°C) and at the same time have a good affinity with the vitreous matrix. Since it is a new field of research, very few information about compatibility between particles and vitreous matrix is available. In this study, the focus was on hard materials such as silicon carbide (SiC), tungsten carbide (WC) and on particles with self-lubricating properties (graphite). PTFE and MoS_2, used in composite metallic coatings as solid lubricant, can not be used because these materials degrade at the enamel curing temperatures. The particles should bind to the glassy matrix and be well incorporated, thus modifying the properties of the coating without introducing voids and weak points. In order to compare particles with very different density (2 g/cm^3 of graphite vs. 15 g/cm^3 of the WC) volume percentage has been consider.

While using different substrates, such as steel and aluminum alloys, which require different frit composition and firing temperature, the study focuses on the abrasion resistance and on the strategies to improve it. So even if not directly comparable the two sets of samples will be discuss and compared to a reference with standard composition.

2. Experimental details

The samples used in this research were produced in the industrial laboratory of Wendel Email Italia (Chignolo d'Isola, BG, Italy). Two series of samples were produced. In the first one the frit composition was modified by mill addition in order to improve the abrasion resistance. The second series regards the modification induced by the addition of particles that remain embedded in the enamel layers during firing and their effect on the microstructure and abrasion resistance.

For the first set of samples an enamel glass with typical alkali borosilicate composition vitreous was used with approximately 50 wt% SiO_2, 15 wt% B_2O_3, 10 wt% Na_2O, 8 wt% K_2O, 3 wt% LiO_2 and

other metal oxides such as BaO and CoO to guarantee good adhesion with the metal substrate [9,10].

The standard mill additives are 3% wt% quartz and 3% wt% feldspar and were used for producing the reference coating but were then substituted by 10 wt% of spodumene $LiAl(Si_2O_6)$ or 10 wt% quartz (SiO_2) for the modified samples.

These layers were deposited on low-carbon steel panels (10cm x 10cm) using electrostatic dry powder application. The enamel was fired at 845°C and remained in the heating chamber for 3 min and 30 sec. The total time inside the tunnel kiln was 16 minutes.

The initial roughness R_z of the samples is respectively 0.66 μm for the standard sample, 0.72 μm for one containing quartz and 1.2 μm for the one with spodumene [8].

For the second series, a low temperature frit without vanadium oxide was used (50 wt% SiO_2+TiO_2, 35 wt% Na_2O+K_2O+LiO_2, 10 wt% B_2O_3, Al_2O_3+ZnO+P_2O_5+SrO bal.). The particles were added in a slip obtained adding to the frit 38 wt% water and 2 wt% sodium silicate. In some cases, the particles tended to agglomerate. To avoid this agglomeration, ultrasound stirring was used (400 Watt – 24 kHz) when specified. Different particles were studied: graphite, tungsten carbide (WC) and silicon carbide (SiC). The particles dimensions are in the range of 1-10 μm. The graphite particles show a lamellar morphology; the WC particles exhibit a spherical shape with 2P crystal structure (hexagonal lattice) and the SiC ones have a sharper/angular morphology with 4H-SiC crystal structure. Different quantities of particles are added to the slip: to study the interaction between particles and glassy matrix 1 vol% of particles was added, then higher amount of particles was considered. Table 1 summarizes the parameter of studied samples.

The composite enamel was deposited on AA4006 aluminum alloy (0.80 wt% Si, 0.50 wt% Fe, Al bal) sheets (10cm x 10cm) by wet spraying method. After the spraying deposition a thermal treatment at 100°C for 30 minutes for the water evaporation was carried out followed by the curing treatment at 570°C for 15 minutes.

Topography and enamel structure were observe by optical and scanning electron microscope (SEM) on both surfaces and the cross sections. The gloss was measured using digital gloss meter and the adopted values are relative to the 60°. Data are obtained as the average of 4 measurements.

The surface roughness was measured by profilometer, on a stretch of length 5.6 mm, and the reported values are the average of 4 measurements.

The abrasion resistance was evaluated using Taber test according to ASTM D4060-10 standard, which simulates a two-body abrasion process. The surface is in contact with 2 abrasive loaded wheels and rotates at a steady speed of 60 rpm. The rotation of the sample platform moves the wheels in opposite directions forming an abraded pattern of crossed arcs in a circular band [11,12, 13]. During the test a vacuum system removes the produced debris.

Different conditions were adopted for the two sets of samples, since each part focused on different aspects: change of mill additives affects the vitreous matrix while the addition particles transform the enamel into a composite coating. Therefore, after some preliminary tests, the test parameters were chosen in order to highlight the differences of the samples among the same set.

For the set with different mill additives, H22 grinding wheels were used with a 250 g applied load. These wheels are composed of vitrified clay, silicon carbide and alumina particles embedded in an organic matrix [14]. The mass loss was recorded every 500 cycles for a total of 1500 cycles.

For the composite enamels, CS17 grinding wheel were used [14-16] and 1000 g of applied load. The wheels have a rubber matrix with tungsten carbides [11]. These wheels are less abrasive due to the rubber matrix, and therefore a higher load was applied. The test was stopped every1000 cycles and the mass loss, the gloss and roughness were recorded.

To confirm the experimental data the measurements are carried out using 3 samples for each composite enameled type.

At the end of the test (1500 in the case of the first series of samples and 5000 for the second one) the damaged surfaces were observed by scanning electron microscope.

3. Results and discussion

3.1 Effect of mill addition

In this paper only the main results related to the abrasion resistance and how it is affected by the mill additions will be presented. A more extensive discussion can be found on a paper already published [8]. Fig. 1 shows the cross sections of the samples with reference and new mill additions. The porosity inside the layer is a typical defect of enamel layer [2,8,17] due to the gas evolution during the firing treatment [18], nevertheless its shape, size and quantity depends on the frit composition.

The reference frit has low viscosity, which leads to the formation of big bubbles that remain in the layers, as clearly visible in Fig. 1a. In both cases the change of mill additions increases the viscosity of the glassy matrix that leads to the reduction of bubbles dimension. In the previous work [8] is shown that porosity is also related to the quantity of mill addition: increasing the mill additions the porosity decreases. Regarding the composition of the enamel, SEM micrographs in the backscattering mode (BSE) help to evaluate the uniformity of enamel structure and composition. Considering the layer with spodumene addition (Fig. 1b), big crystals of residual spodumene are visible (marked with the arrow) due to the only partial dissolution. On the contrary the quartz (Fig. 1c) showed a good solubility and it was dissolved in the matrix producing a more uniform structure.

Usually the mass loss is the parameter used to evaluate the abrasion resistance of a coating [11, 15], therefore Fig. 2 reports the mass loss during Taber test of the different samples as a function of the number of cycles.

A clear effect of the mill additive on the mass loss is visible. At every number of cycles the reference sample shows higher mass loss. This beneficial effect could be connected with the porosity [19]. The samples with additives show less and small porosity and then the probability of the formation of cracks and brittle removal of enamel is smaller.

Comparing the sample with mill additives, the sample with quartz shows the best behavior with a lower mass loss. Probably, the presence of big not soluble crystals, which could be more easily removed due to mechanical action, increases the abrasion rate.

These considerations are confirmed by the observation of the abraded surfaces after 1500 cycles of Taber test shown in Fig. 3. The standard sample presents several open pores (Fig. 3a). The abrasion mechanism probably starts from the pores where crack nucleates and then propagates from one pore to the other. Due to the brittle fracture of these glassy deposits, the high presence of big pores reduces the mechanical resistance of the layer and act as critical defect for the crack propagation.

On the contrary, the samples with mill additives do not show so many open pores but still the surfaces show brittle fracture mechanism. Probably in these layers, the abrasion results more uniform and not concentrated on the pores and the removal or brittle material by fracture interests smaller portion of material. Comparing the sample with spodumene (Fig. 3b) to the one with the quartz (Fig. 3c) the surface of the last sample appears less damaged confirming the values of mass loss previously discussed. This aspect is related to the effect of the SiO_2 which produce a more uniform structure due to its good solubility and compatibility with glassy matrix and the reduced porosity.

3.2 particles addition

Fig. 4a-d show the cross section of the enamel layers without and with 1 vol% of particles.

Due to the different atomic number between particles and glass matrix, in fig 4c it is possible to clearly observe the WC particles, which appear white. The other particles are visible in the micrographs considering the shapes and difference gray tone. The sample without particles and the composite coatings with graphite and SiC particles appear compact with very small amount of

pores. The added particles are well dispersed within the coating. Signs of lack of cohesion between particles and the glass matrix have not been observed.

For all the samples the adhesion between coating and substrate are excellent [20, 21].

Considering the sample with 1 vol% of WC particles the situation is very different. The deposit appears less homogeneous in comparison with the previous samples. The WC particles are agglomerated and appear not totally embedded by the glassy matrix. As a result, the enamel is locally not very compact and presents several big pores.

Fig. 5 shows the mass loss for the samples containing 1 vol% of particles during Taber test. All composite samples have similar or greater mass loss than the reference sample. The reason for this behavior is related to the amount of particles added that is insufficient to improve the abrasion resistance or their agglomeration that lead to a bigger porosity with a great increase of the abrasion rate. Particles agglomerates and pores are weak points that promote the nucleation and propagation of cracks, reducing the abrasive resistance of these coatings.

In the evaluation of the mass loss it is important to keep in mind that the loss of particles, with high densities as the WC, can produce higher values of mass loss even with a limited damage. For this reason the mass loss, while being a significant index, requires confirmation with the feedback of other parameters.

Fig. 6 shows the percentage change of gloss with respect to the initial value, measured at an angle of 60°.

Considering the trend of gloss it is possible to observe that the abrasive effect causes for all the studied samples a decrease of enamel surface gloss. The abrasive action of the grinding wheels causes a removal of coating parts and the formation of surface damages. It causes a more diffused reflection of light with a reduction of specular reflection light. The sample with 1 vol% graphite particles has a quickly decrease of the gloss values. This behavior is probably due to the tendency of the lamellar graphite to produce flakes during the mechanical damage process. A tendency to spreading on the surface could be observed (see later the observation of damaged surface). Initially,

the graphite particles present close to the surface were covered by a layer of glass matrix able to ensure high gloss values; with the abrasive process and loss of enamel flakes these particles are exposed on the surface influencing the gloss data.

The other composite samples highlight a more gradual change in the gloss very similar to the reference sample for the first 2000-3000 cycles. Then, a decrease, greater than the reference, is observed probably because of the formation of a higher damage on these samples.

The trend of the roughness could provide useful indications on the damage process. Fig. 7 shows the roughness average value after every 1000 cycles of Taber test.

The samples containing graphite and WC particles exhibit a gradual increase of surface roughness, in a very similar way to the reference sample without particles. At end of the test, after 5000 cycles, the roughness values of these samples result very similar. The non-linear trend with the number of cycles is correlated to the non uniform damage given by abrasion of brittle materials. It is possible to have the formation of cracks, the opening of the pores, detachment of flakes and particles from the surface that results not uniformly damaged with local roughness variations. Differently from the others samples, the S1 coating have a value of Ra that remains almost unchanged during Taber test. This fact combined with the low value of the mass loss allows to conclude that the addition of SiC particles leads to an improvement of the mechanical resistance of the enamel layer.

Fig. 8 shows the damaged surface of the samples at the end of the Taber abrasion test.

The surface of S1 sample with SiC particles (Fig. 8f) shows a very limited damage due to abrasion. Only some scratches could be observed. These samples present low pores quantity and good interface between glassy matrix and particles. These aspects reduce the nucleation of cracks and the wear mechanism is limited to scratches on the vitreous surface. Considering these signs of abrasion, it is clear why the surface roughness does not change, as previously observed (Fig. 7).

Contrary to what observed considering the mass loss, the surface of the reference sample without the presence of particles after Taber test results damaged (Fig. 8a and 8b). The damage locates in correspondence with the porosity that remains open after the abrasion. This layer shows a classic

brittle fracture typical of ceramic and vitreous materials [7]. In several cases the vitreous flakes, produced by abrasion action, tend to occlude such porosity. This fact is an additional aspect that makes difficult the interpretation of the mass loss values and the comparison of the behavior of this sample with those containing particles.

The W1 sample surface results very damaged (Fig. 8d and 8e). The nucleation of cracks in correspondence with the WC particles clusters and pores is observed, with the consequent production of enamel flakes, typical of brittle fracture behaviour. In addition, the poorly incorporated particles tend to come off increasing the value of the mass loss, due to the very high density of WC (about 15 g/cm^3). Also the surface of the coating containing graphite particles (Fig. 8c) appears damaged with detachment enamel in correspondence of the graphite flakes.

In conclusion, the surface of the sample containing SiC particles is the least damaged with scratches that seem to affect only the outer surface of the layer. Probably in this layer with a lower porosity, the crack nucleation is less probable and the wear action is therefore diminished.

It is therefore proved that the addition of particles has a great influence on the abrasion behavior of the enamel surface. Generally they seem to not have a positive effect both due to the production of flakes in the case of graphite and to agglomeration of WC particles as well as increased porosity in the case of WC confirming that, the abrasion mechanism is the case of glassy enamel is based on fracture [7].Only the SiC particles show a beneficial effect with a very limited abrasion and because of its good dispersion.

For this reason it was decided to produce new samples with a higher amounts of particles and, in case of the particles of WC enamel, sonication stirring of the enamel slip before application was considered to reduce agglomeration. This procedure results very effective in avoiding particles agglomeration, as shown in Fig. 9. The particles result well dispersed in the layer and very well embedded in the enamel. The porosity appears reduced in quantity and dimension and comparable to the other layers.

Fig.s 10-12 report the trend of the mass changes of the samples increasing the particles amount and using sonication stirring in case of the deposition of WC particles.

Considering the samples containing the graphite particles, (Fig. 10) increasing the percentage of graphite particles in the deposit results in a further decrease of the abrasion resistance. Such behavior is probably connected to the low hardness and to the tendency to flake of graphite particles.

Considering the samples containing WC particles (Fig. 11), the sonication leads to an improvement of the abrasion resistance by a decrease of the mass loss. The better particle distribution as well as the reduced porosity is both beneficial structural characteristic. In particular, the slip sonication can reduce the mass loss from more than 100 mg to less than 10 mg after 5000 abrasion cycles at the same particle addition. The values of mass loss are even further lowered by increasing the amount of particles (sample W5S). Increasing the particles content to more than 5 vol% the deposit was non-homogeneous and in some part the glassy matrix was not able to completely embed the particles. Considering this bad microstructure the abrasion resistance of these samples was not tested.

Fig. 12 shows the mass loss of the enamel coatings with different amounts of SiC particles.

Samples containing SiC show excellent behavior considering the mass loss.

Increasing the amount of particles from 1 vol% to 5 vol% an improvement of resistance to abrasion is obtained. A further increase of the particles content to 10 vol% does not bring any further improvement.

Conclusions

Considering the strategies adopted to improve abrasion resistance of enamel coating, the conclusions can be summarized:

- The mill additions of 10%wt of spodumene or quartz increase the abrasion resistance of vitreous enamel coatings. Therefore the modification of frit composition could improve the mechanical behavior.
- Graphite particles lead to a decrease of the abrasion resistance, due to the flakes production.
- Agglomerated particles induce higher and bigger porosity that lead to a tremendous decrease of the abrasion resistance.
- A sonication of the slip containing WC particles allows to obtain a more uniform dispersion and embedding into the layer with an effective improvement of the abrasion resistance.
- Composite enamels with low presence of pores and well dispersed particles are characterized by scratches limited to the outer surface of the coatings.

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References

1] A. Ubertazzi, N. Wojciechowski, Smalto porcellanato – vitreous enamel, Ulrico Hoepli Editore, Milano, 2002.

2] S. Pagliuca, W.D. Faust, Porcelain (vitreous) enamels and Industrial Enamelling Processes, The International Enamellers Institute, Mantova, 2011.

3] A.I. Andrews, Porcelain enamels: the preparation, application and properties of enamels, second ed., Garrard Press, Champaign (IL), 1961.

4] A. M. Compagnoni, Reduction or elimination of vanadium in enamel for aluminium. Proc. XXI International Enamellers Congress. IEC, Shanghai, 18-22 may 2008.

5] M. Fazel, M.R. Garsivaz Jazi, S. Bahramzadeh, S.R. Bakhshi, M. Ramazani, Effect of solid lubricant particles on room and elevated temperature tribological properties of Ni–SiC composite coating, Surf. Coat. Tech. 254 (2014) 252-259.

6] R.G. Bayer, Mechanical wear prediction and prevention, Marcel Dekker, New York, 1994.

7] I.M. Hutchings, Tribology: Friction and Wear of Engineering Materials, Hodder Headline PLC, London, 1992.

8] Rossi S, Zanella C, R. Sommerhuber, Influence of mill additives on vitreous enamel properties, Mater. Des. 55(2014) 880-887.

9] M.B. Lupescu, M. Zaharescu, A. Andrei, Electron spectroscopy studies of the steel/enamel interface, Mater Sci Eng A 232 (1997) 73–79.

10] X. Yang, A. Jha, R. Brydson, R.C. Cochrane, An analysis of the microstructure and interfacial chemistry of steel–enamel interface, Thin Solid Films 443 (2003) 33–45.

11] S. Rossi, F. Deflorian, L. Fontanari, A. Cambruzzi, P.L. Bonora, Electrochemical measurements to evaluate the damage due to abrasion on organic protective system, Prog. Org. Coat. 52 (2005) 288–297.

12] S. Suzuki, E. Ando, Abrasion of thin films deposited onto glass by the Taber test, Thin Solid Films 340 (1999) 194-200

13] V. Vitry, A. Sens, A.-F. Kanta, F. Delaunois, Wear and corrosion resistance of heat treated and as-plated Duplex NiP/NiB coatings on 2024 aluminum alloys, Surf. Coat. Tech. 206 (2012) 3421–3427

14] S. Rossi, E. Scrinzi, Evaluation of abrasion resistance of enamel coatings, Chem. Eng. Proc. 68 (2013) 74–80.

15] Taber® Abrading Wheels. Wear and Abrasion Tests. Available from: ⟨http://www.taberindustries.com/documents/Taber%20-%20Abrading%20Wheels%20v4.pdf⟩ (accessed 13.01.15)

16] S. Rossi, F. Deflorian, E. Scrinzi, Reduction of aesthetical properties of organic coatings caused by mechanical damage, Mater. Des. 30 (2009) 1511–1517.

17] E. Scrinzi, S. Rossi, The aesthetic and functional properties of enamel coatings on steel, Mater. Des. 31 (2010) 4138-4146.

18] Materials Science and Technology: A Comprehensive Treatment, Vol. 17A, Processing of Ceramics, R. J. Brook (Editor), Wiley-VCH, Weinheim, 1996.

19] A. Petzold, H. Poeschmann, Email und Emailliertechnik, second ed., Leipzig: Deutscher Verlag fuer Grundstoffindustrie, Leipzig, 1992.

20] A. Zucchelli, M. Dignatici, M. Montorsi, R. Carlotti, C. Siligardi, Characterization of vitreous enamel-steel interface by using hot stare ESEM and nano-indentation techniques, J. Eur. Cer. Soc. 32 (2012) 2243-2251.

21] X. Yang, A. Jha, R. Brydson, R.C. Cochrane, An analysis of the microstructure and interfacial chemistry of steel-enamel interface, Thin Solid Film 443 (2003) 33-45.

Table Caption

Table 1: studied samples of second set.

Figures Captions

Fig. 1. Cross section of the samples: (a) standard, (b) with 10 wt% spodumene and (c) with 10 wt% quartz samples.

Fig. 2. Mass loss in function of cycles of Taber test for different samples with mill additions.

Fig. 3. SEM image of abraded surface after 1500 cycles of Taber test: (a) standard; (b) spodumene additive and (c) quartz additive.

Fig. 4. ESEM images of coatings cross section: (a) reference without particles, (b) with 1 vol% of graphite, (c) with 1 vol% WC and (d) with 1 vol% SiC. The arrows indicate some particles embedded in the deposits.

Fig. 5. Mass loss in function of cycles of Taber test for different composite samples with 1 vol% particles.

Fig. 6. Residual gloss measured every 1000 cycles of Taber test for different samples.

Fig. 7. Roughness values Ra of different samples detected every 1000 cycles of Taber test.

Fig. 8. ESEM images of abraded surfaces after 5000 cycles of Taber test: (a, b) sample without particles, (c) G1 with graphite particles, (d, e) W1 with WC particles, (f) S1 with SiC particles. Arrows indicate the scratches, on fig. a, d and f, and the cracks nucleation on fig. c.

Fig. 9. ESEM cross section of sample with 1 vol % of WC particles obtained after sonic stirring of the slip.

Fig. 10. Mass loss during Taber tests for samples with different quantity of graphite particles.

Fig. 11. Mass loss during Taber tests for samples with different quantity of WC particles and with sonication stirring of the slip (for W1 sample consider the y-axes on the right).

Fig. 12. Mass loss during Taber tests for samples with different quantity of SiC particles.

Figure1a

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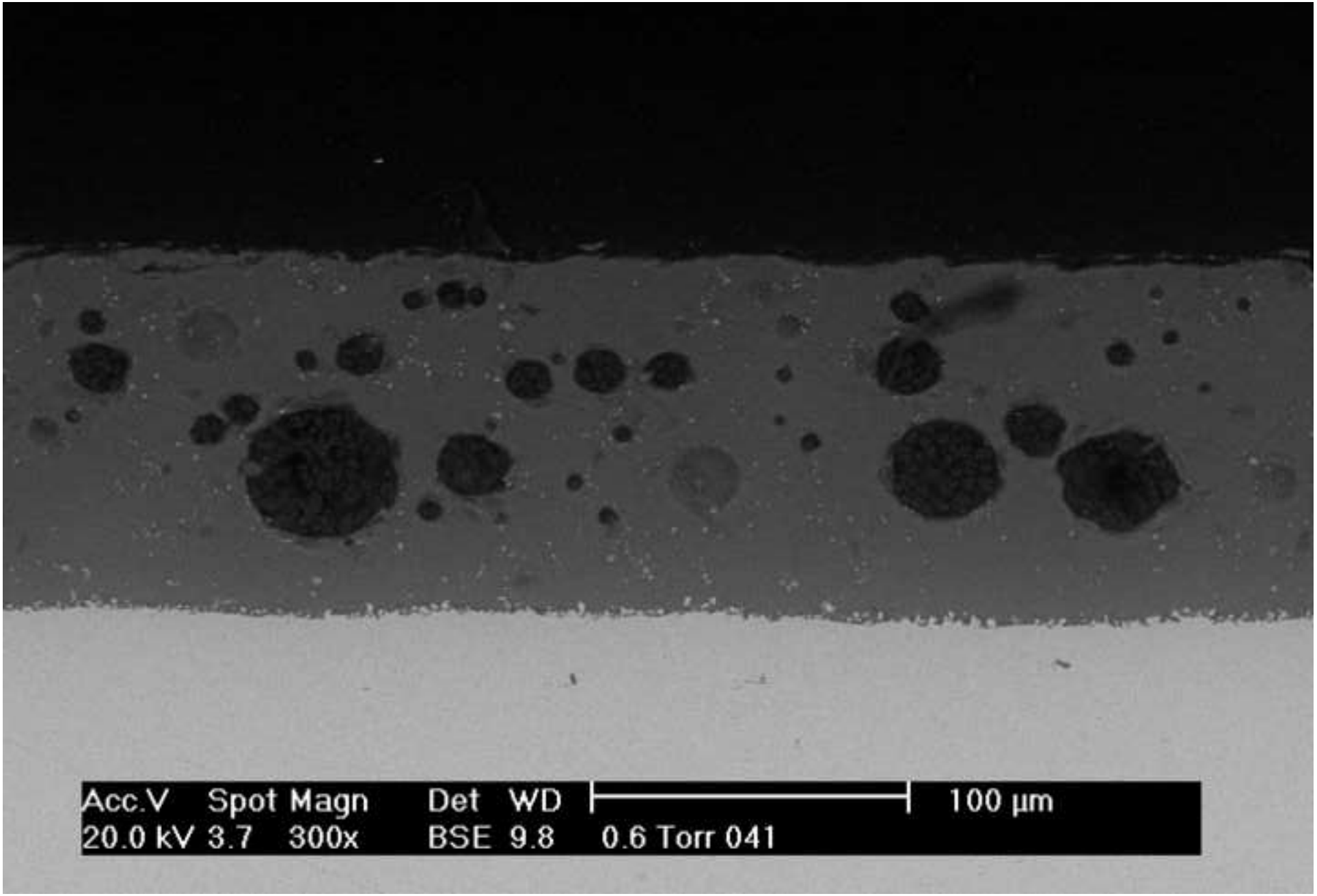

Figure1b

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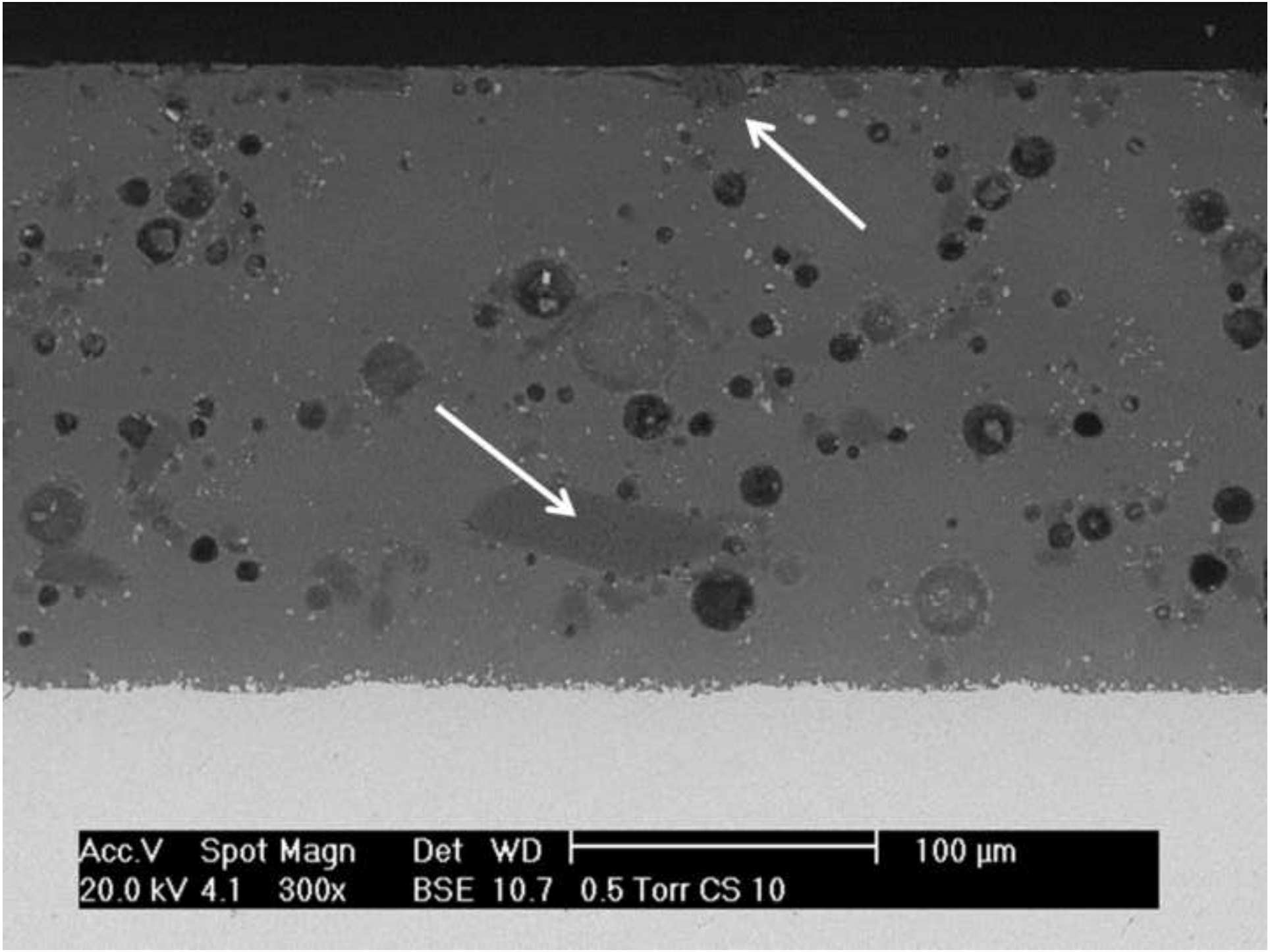

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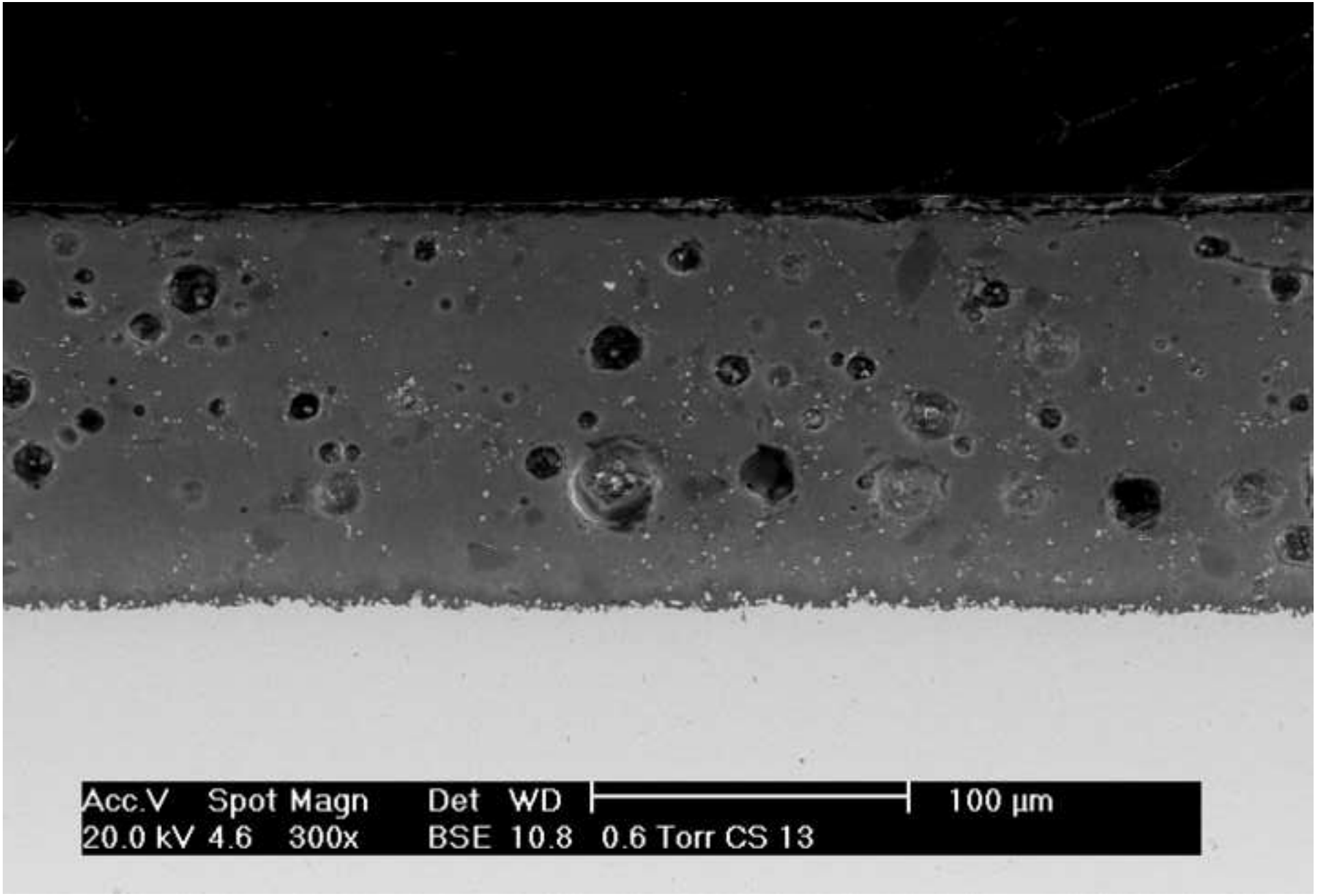

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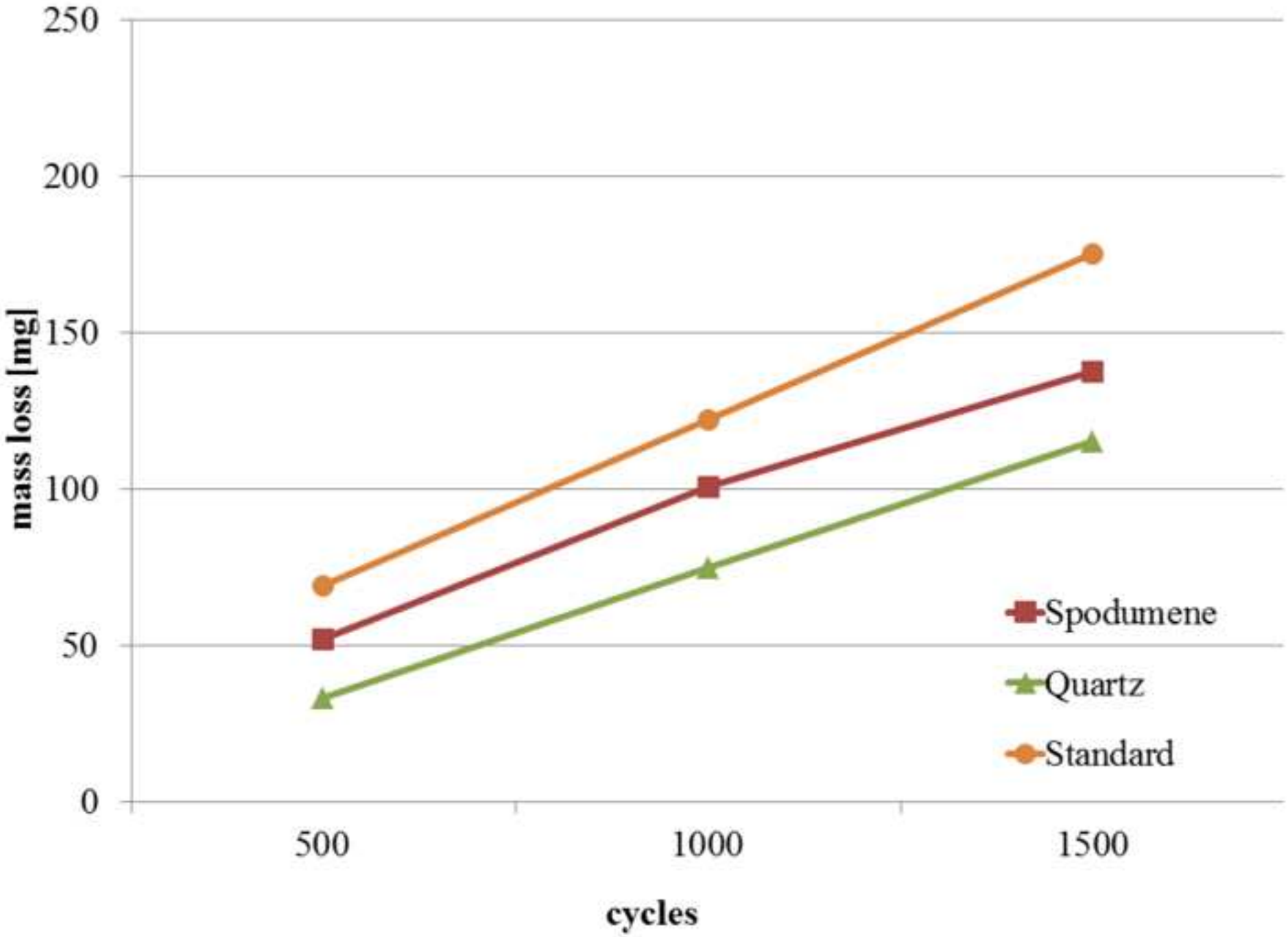

Figure 3a

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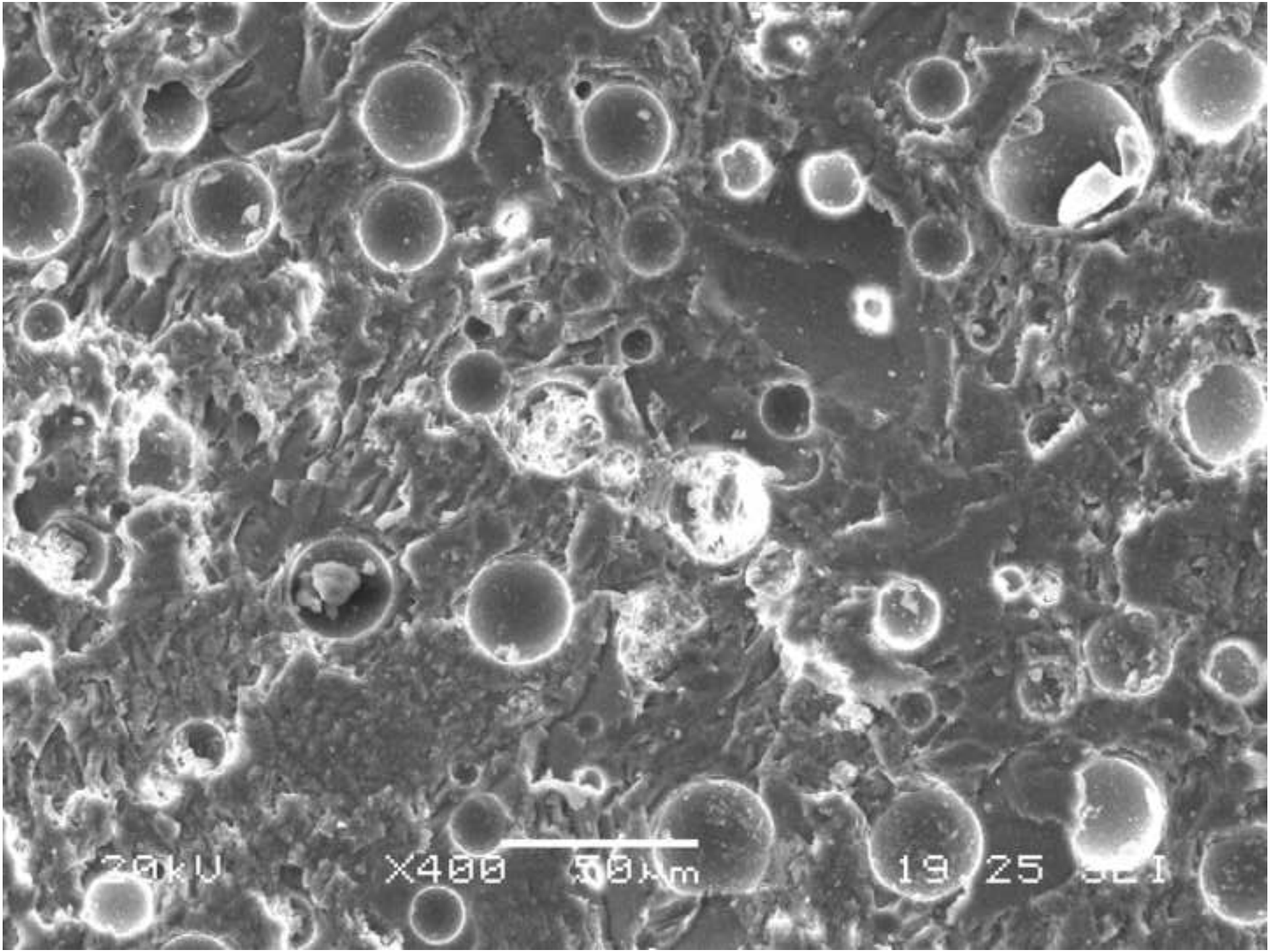

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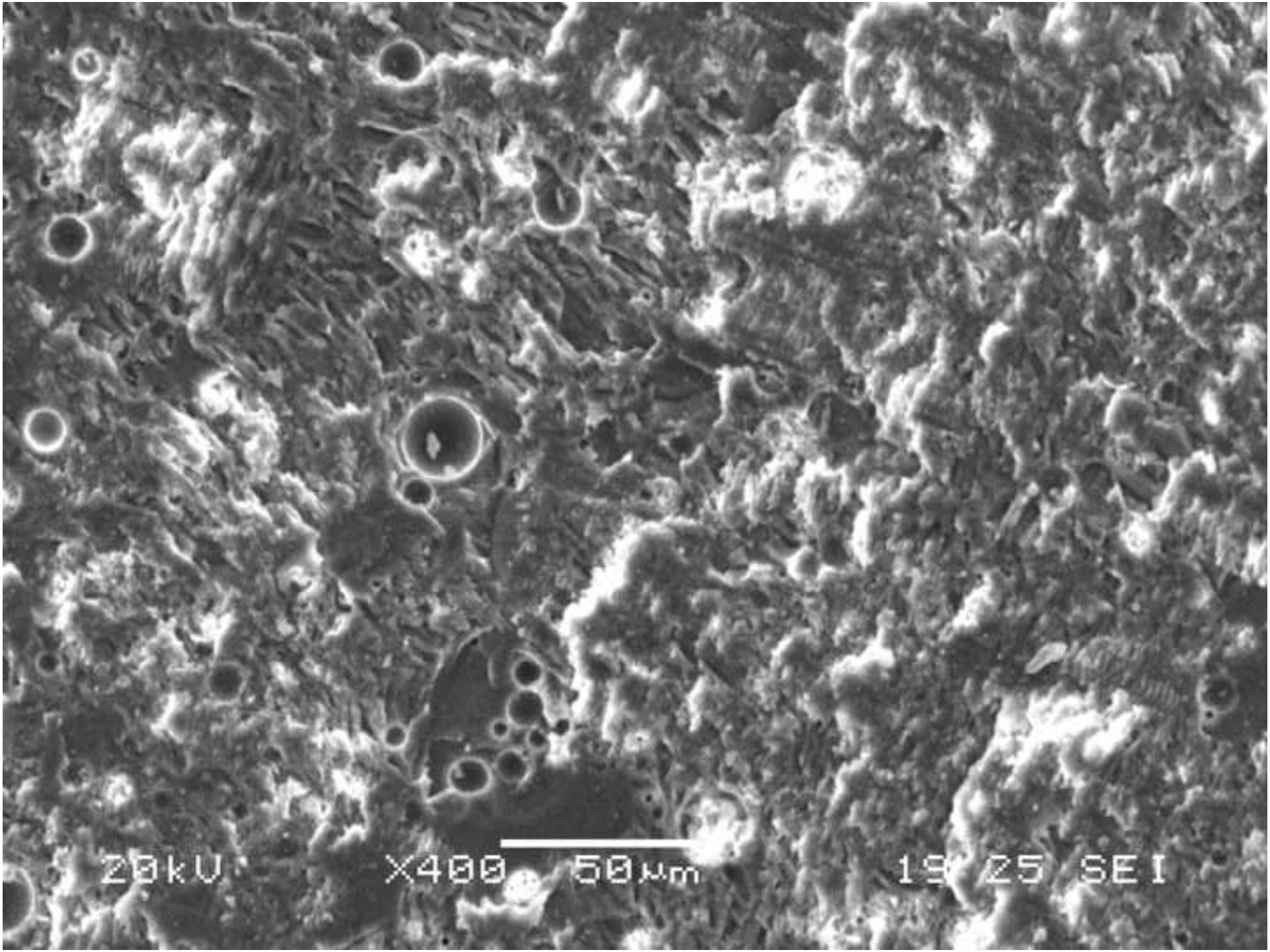

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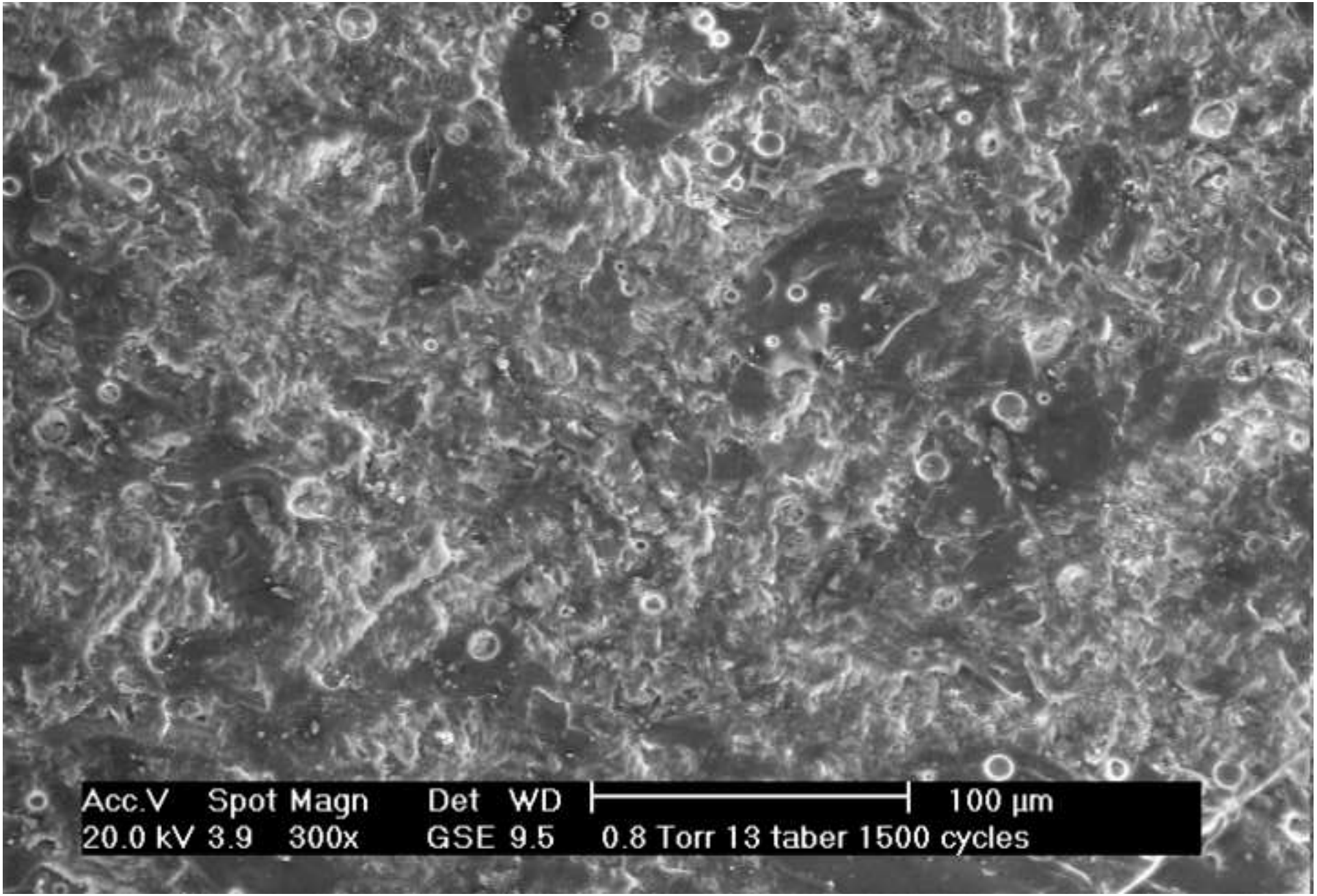

Figure 4a

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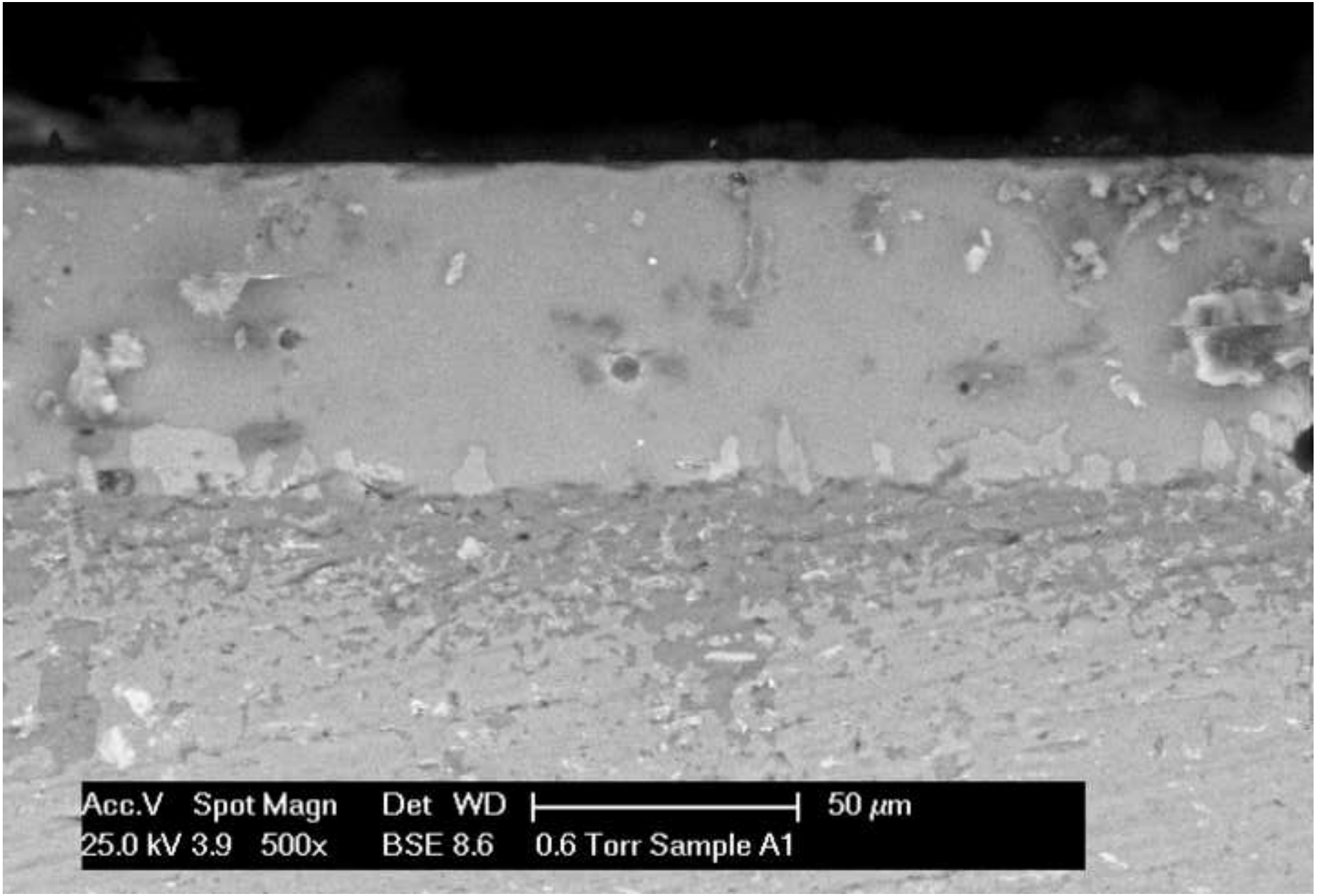

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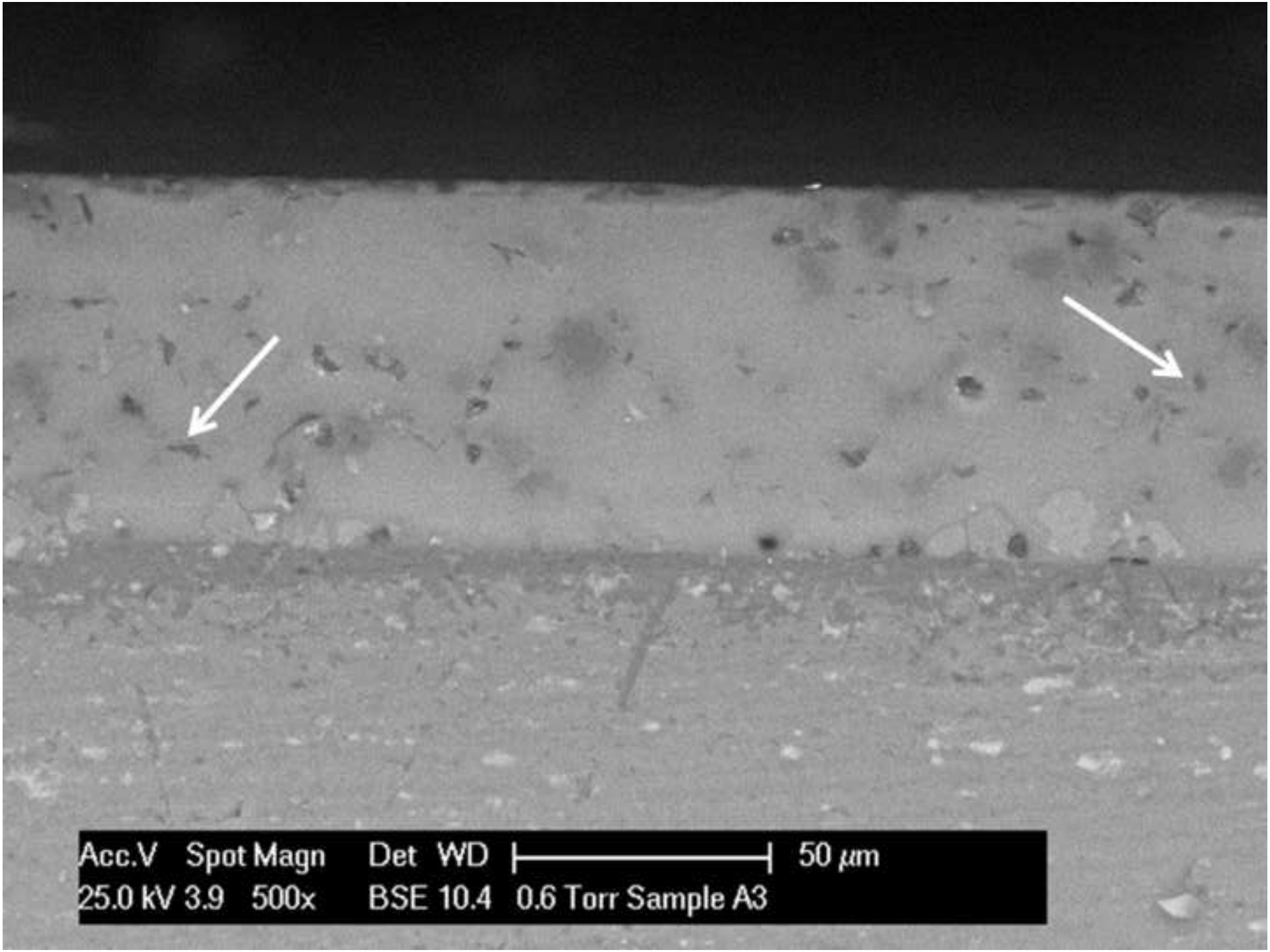

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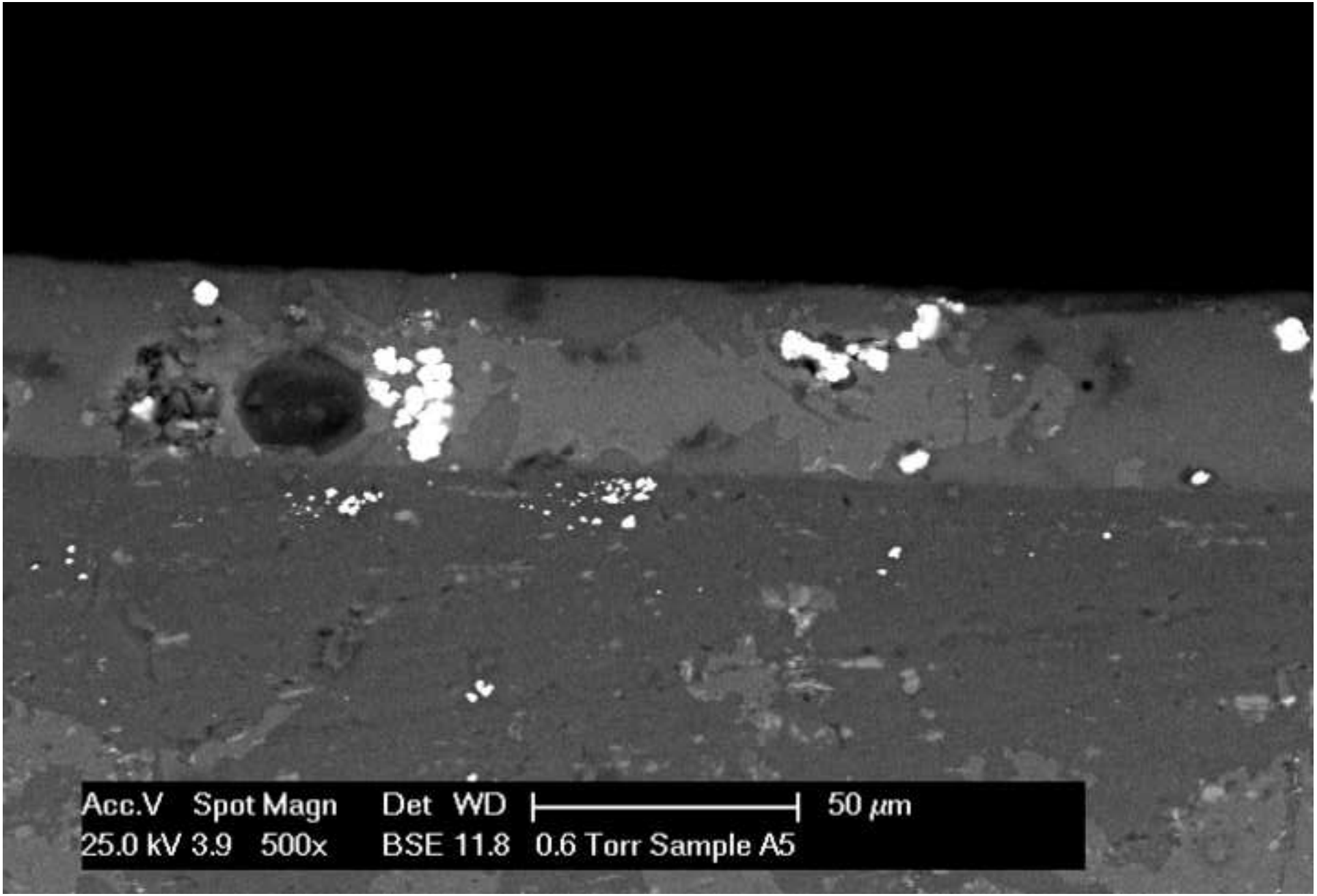

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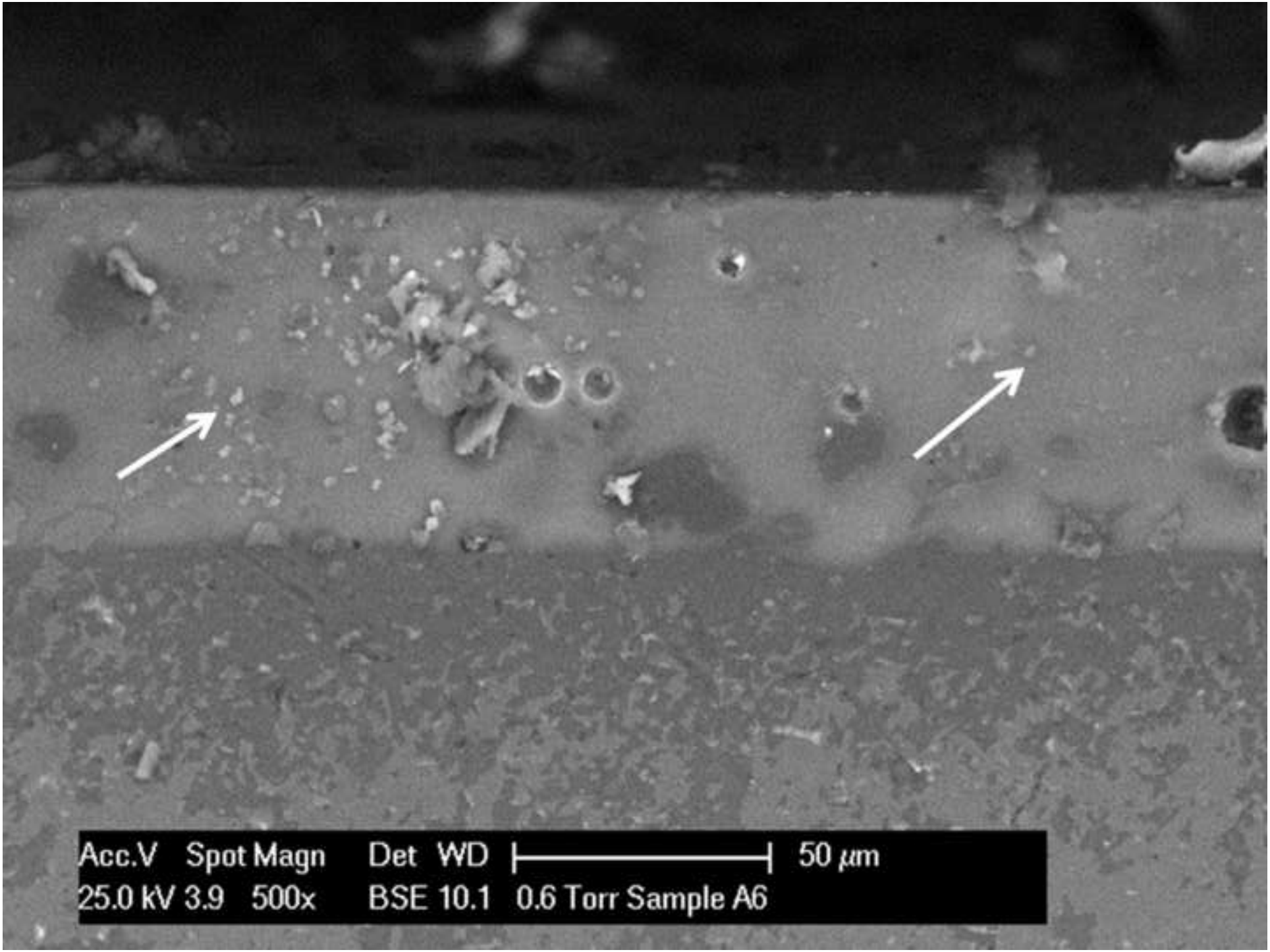

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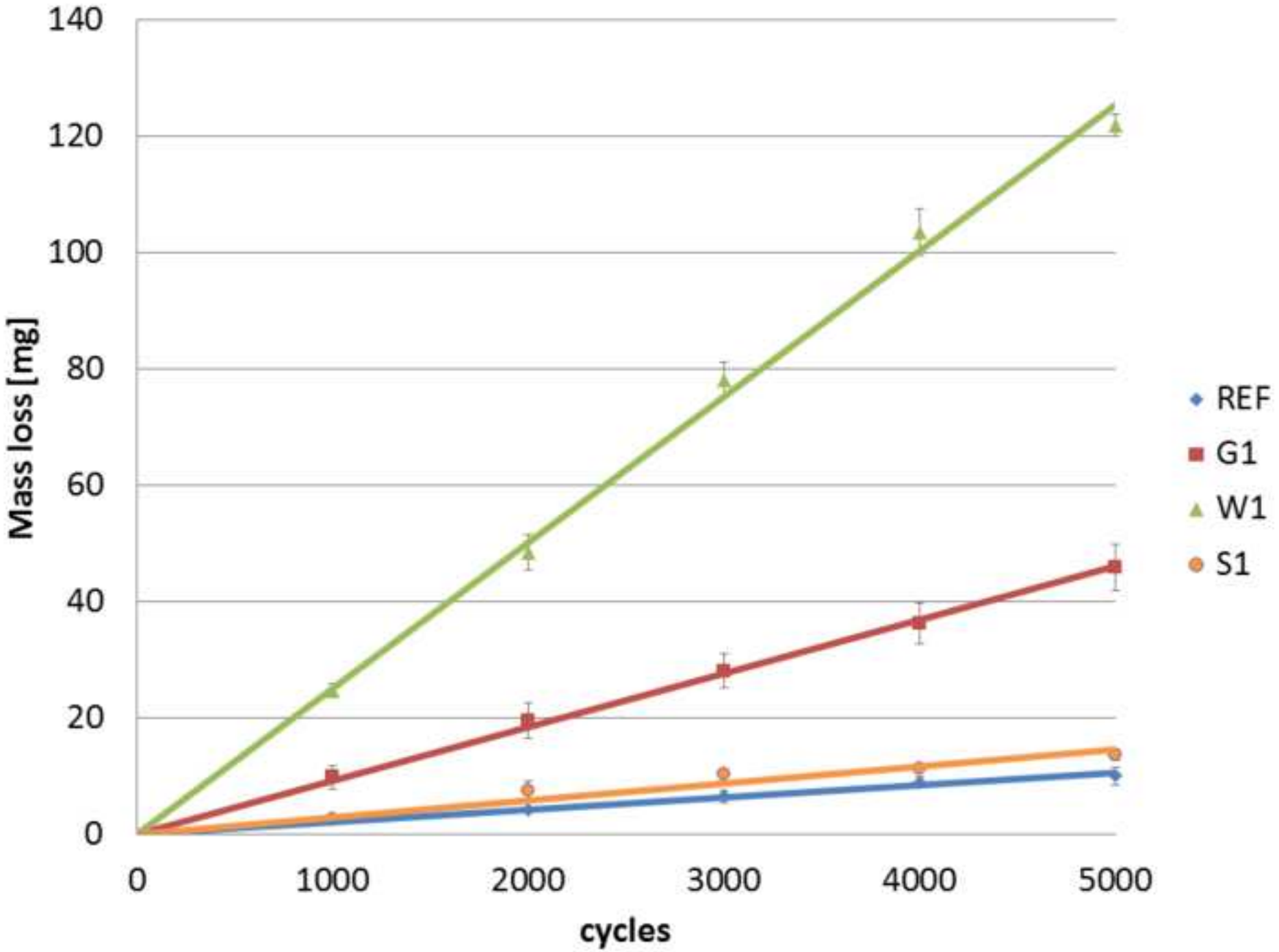

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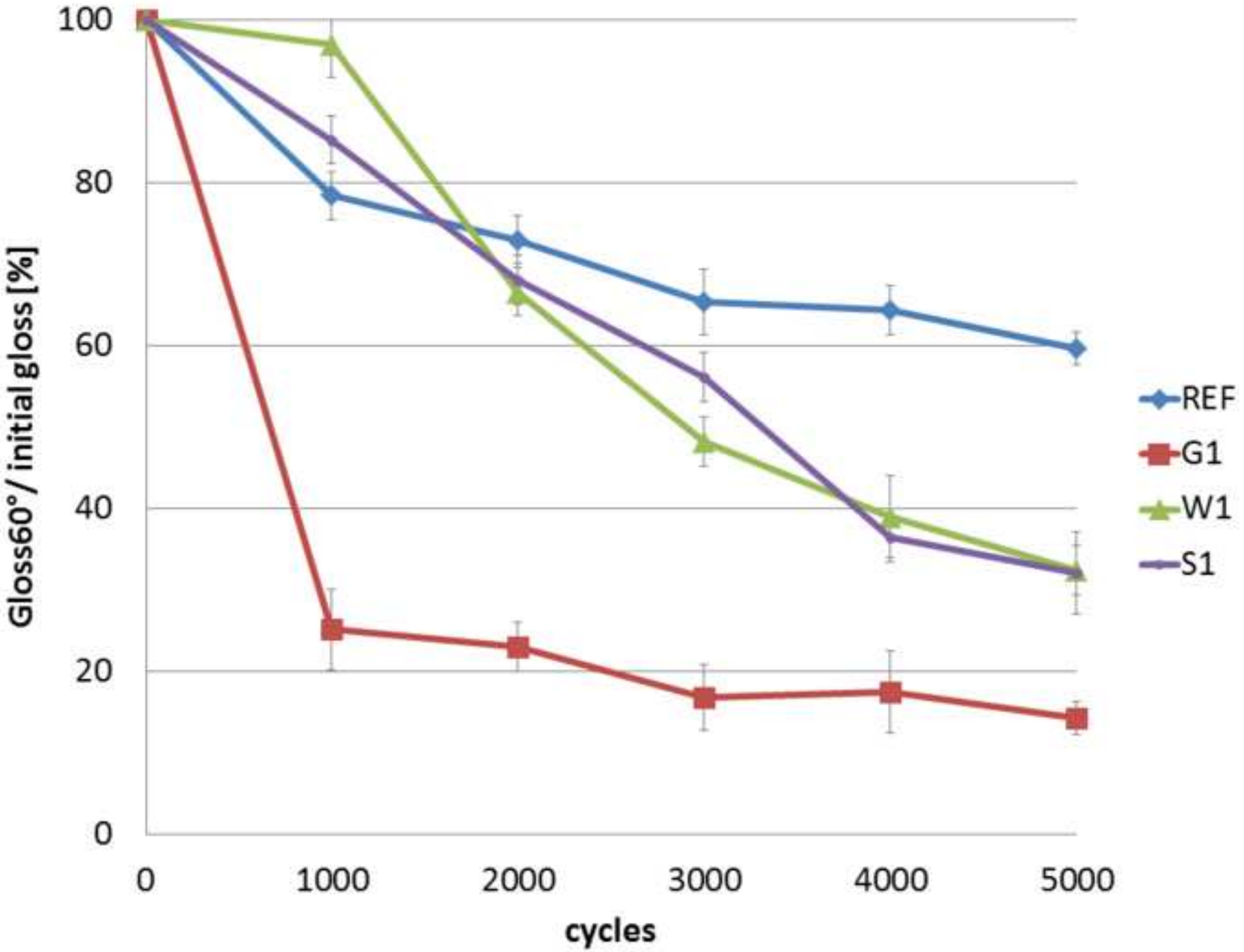

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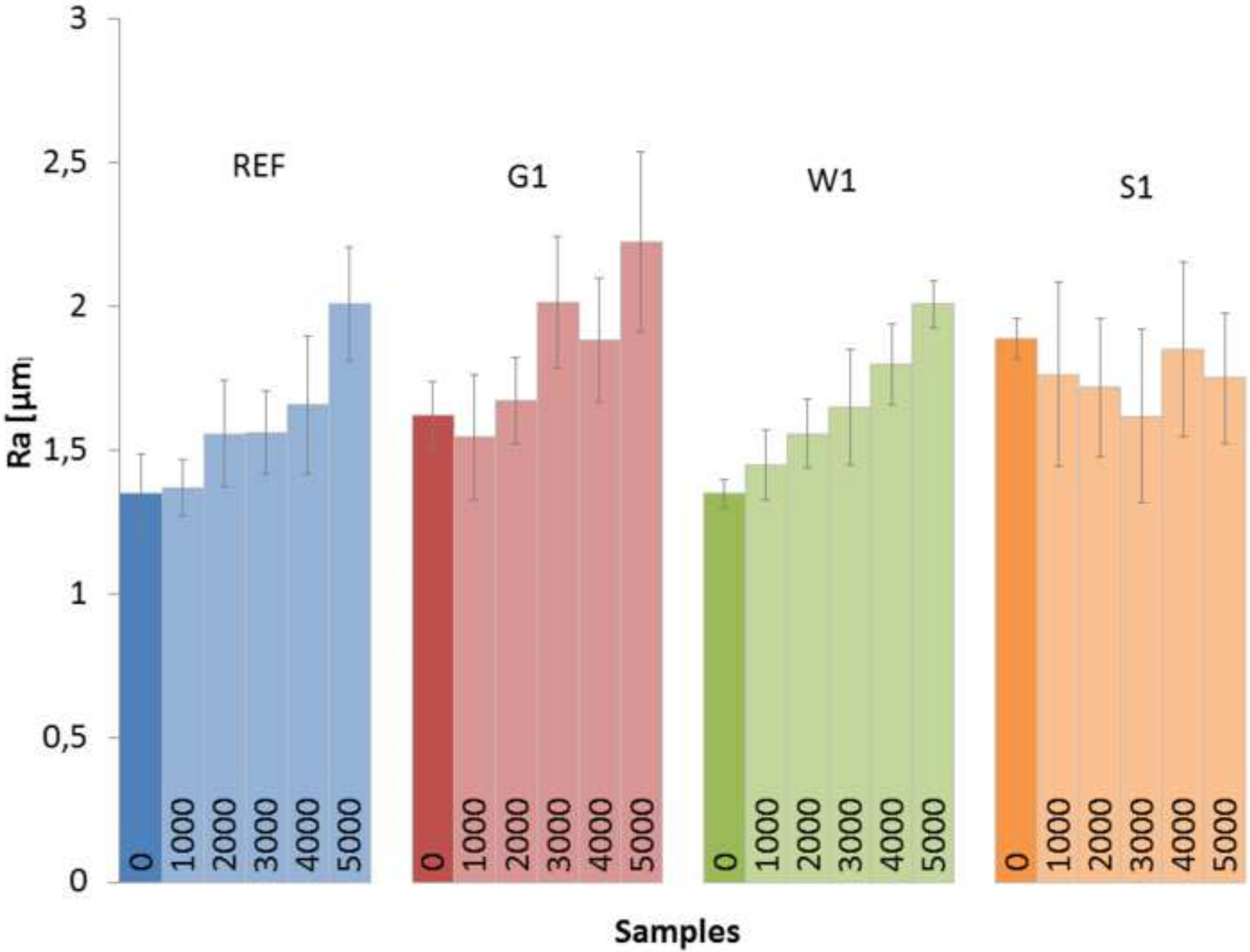

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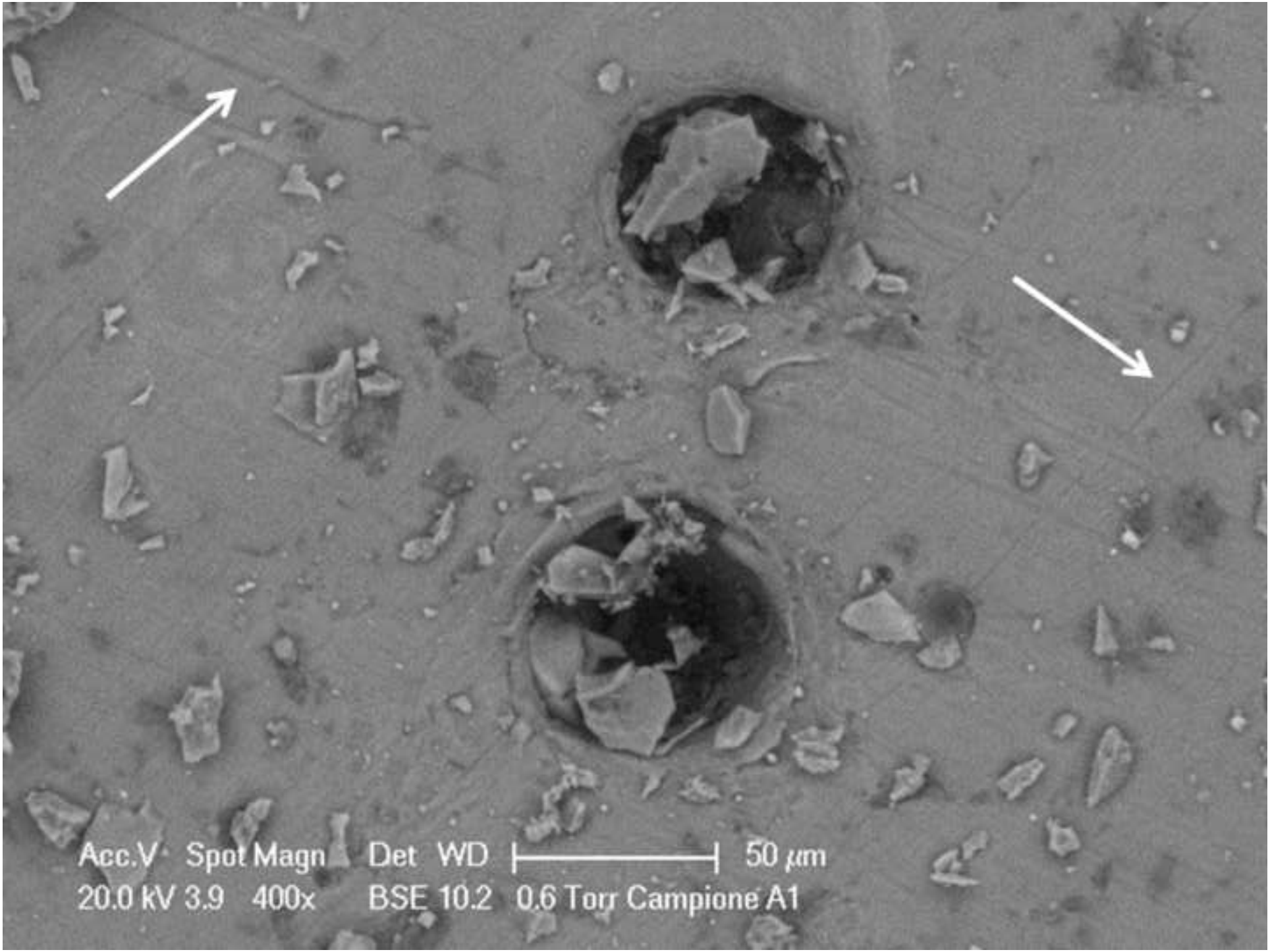

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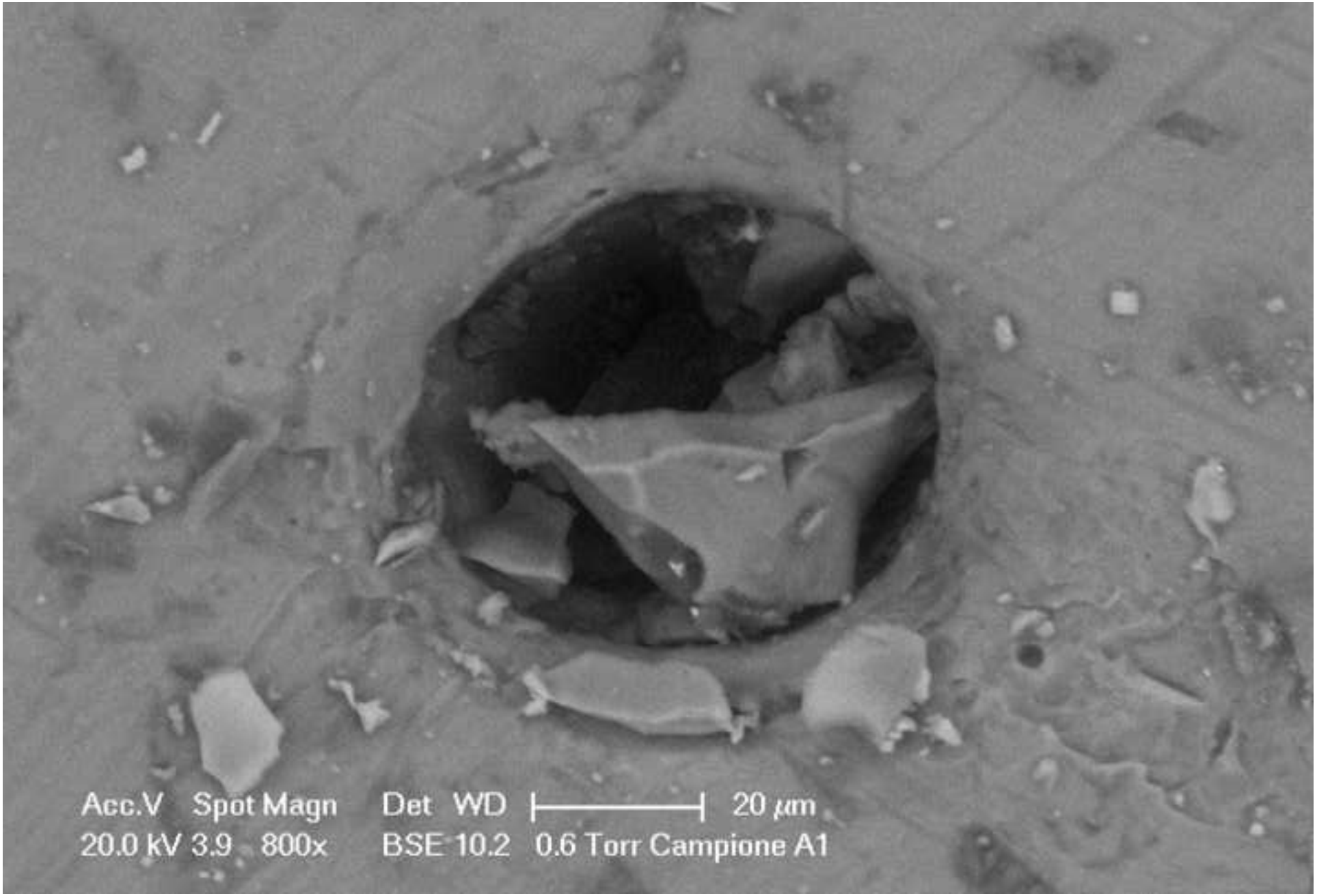

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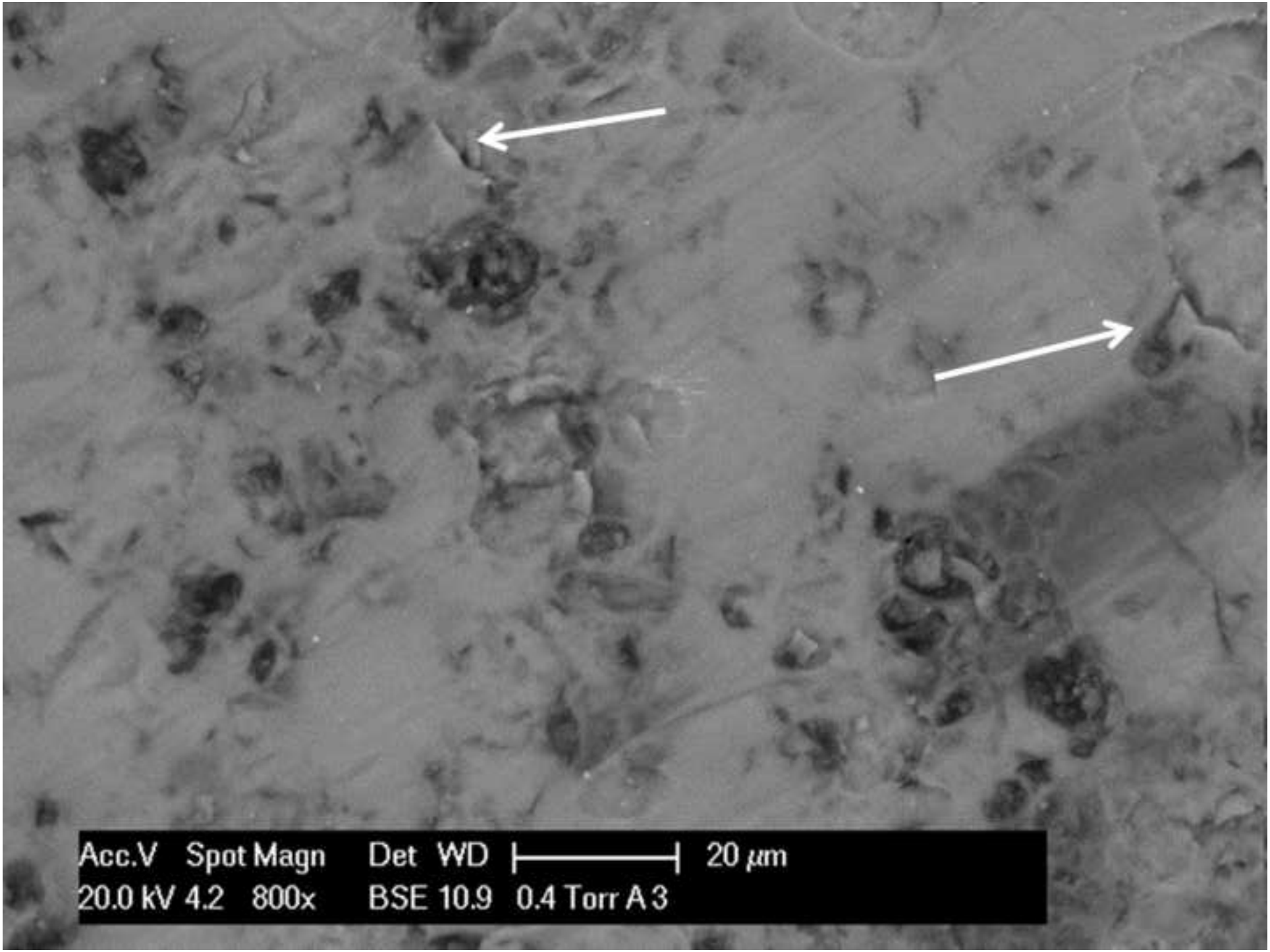

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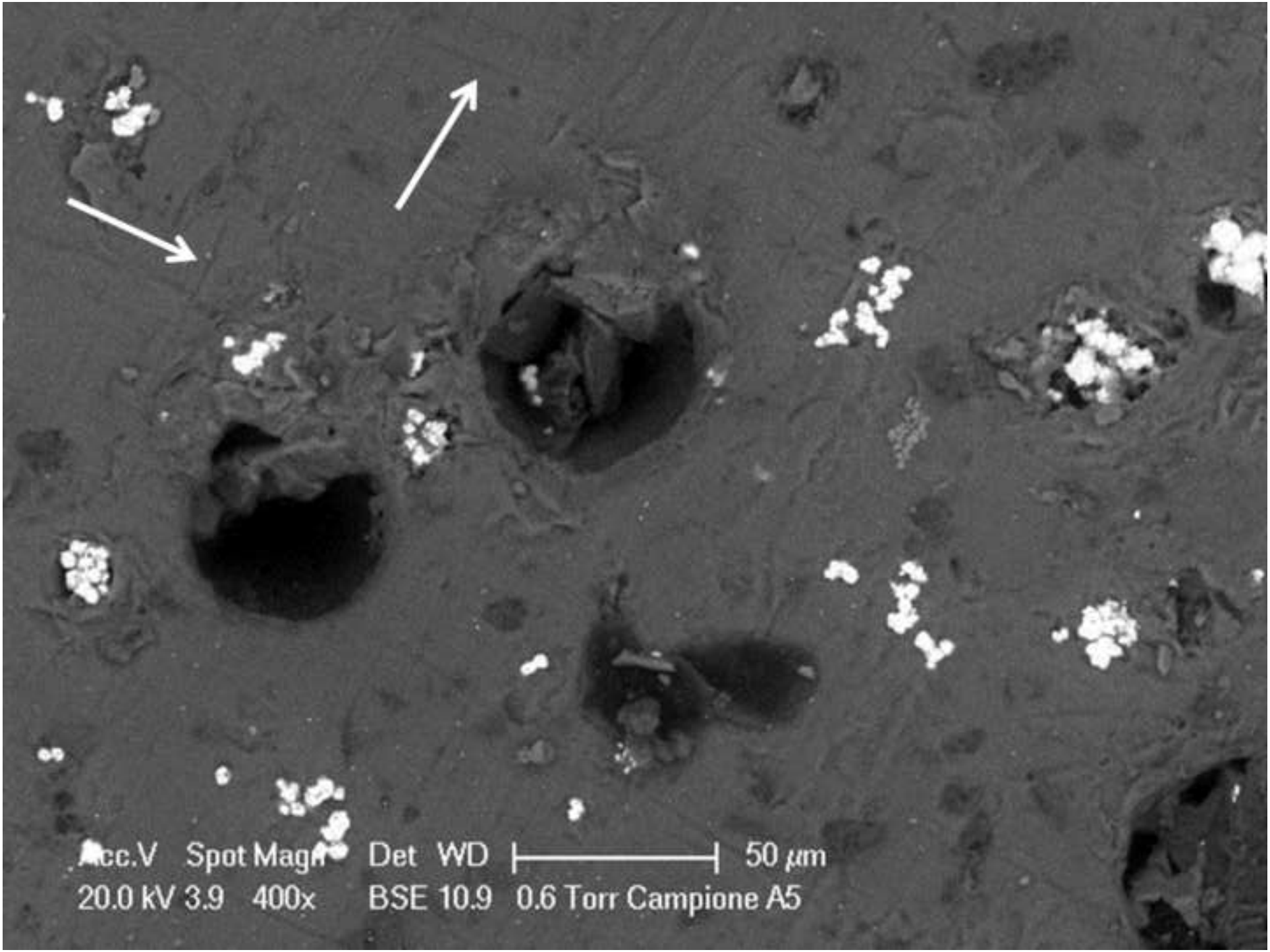

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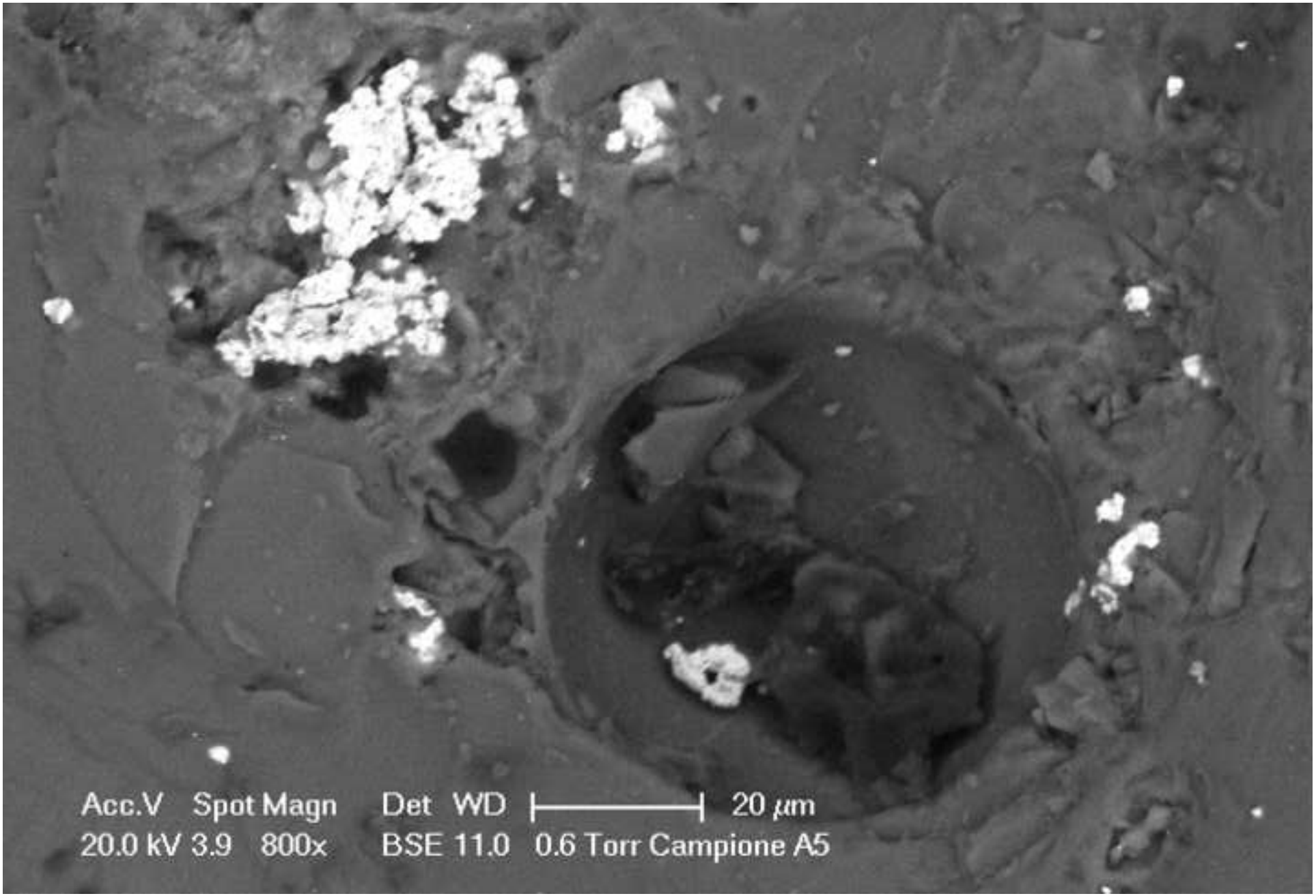

Figure 8f

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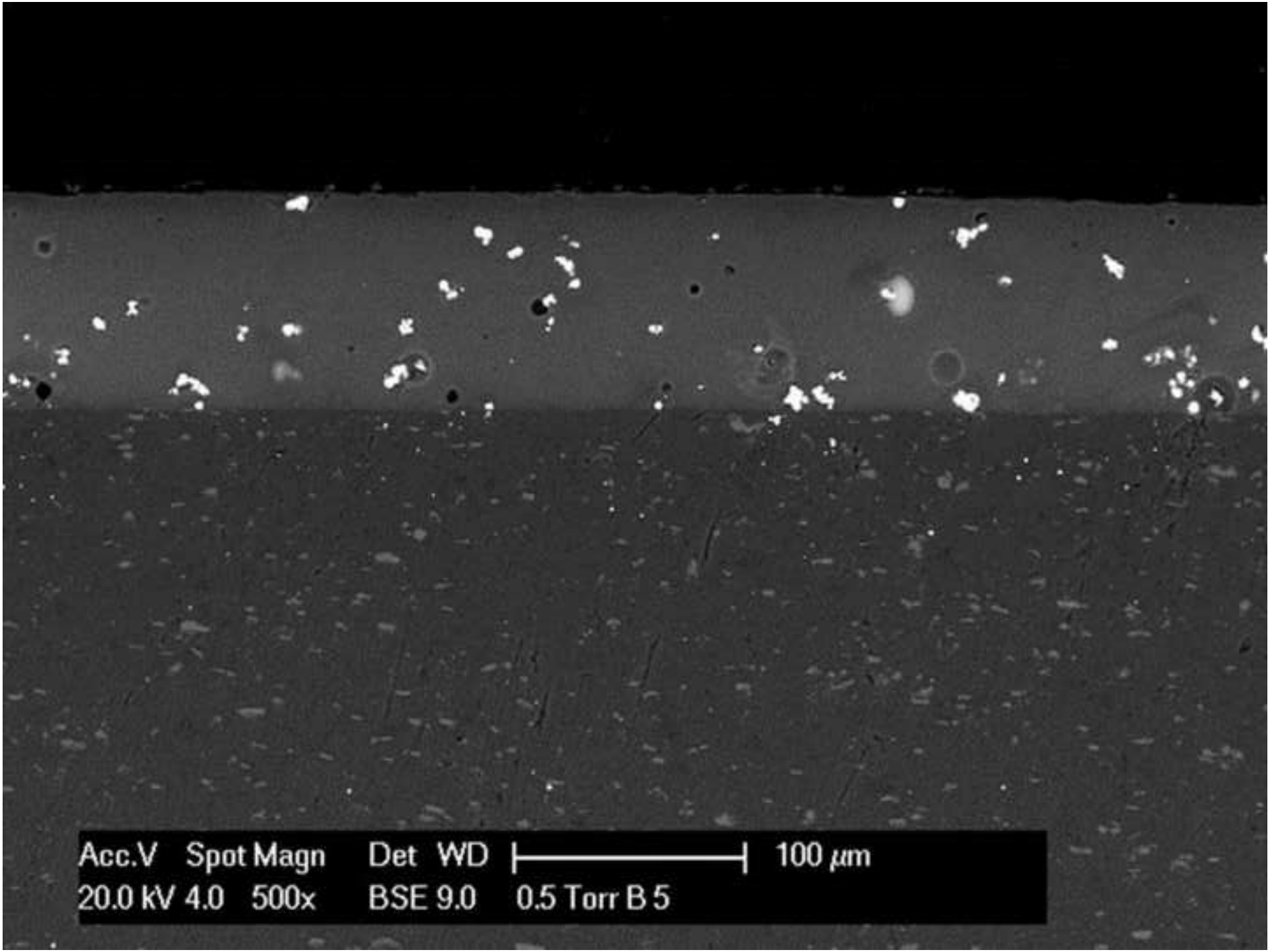

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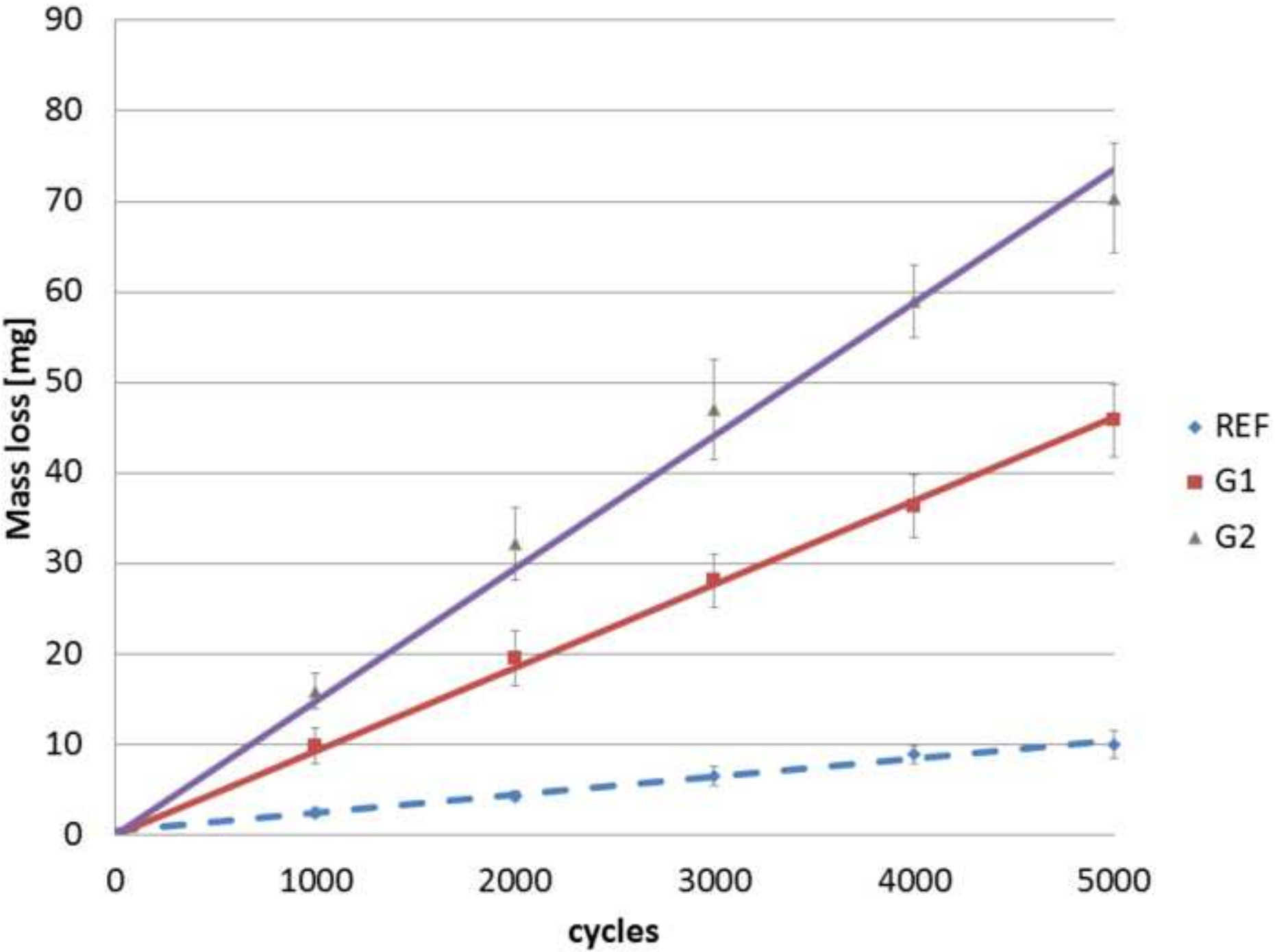

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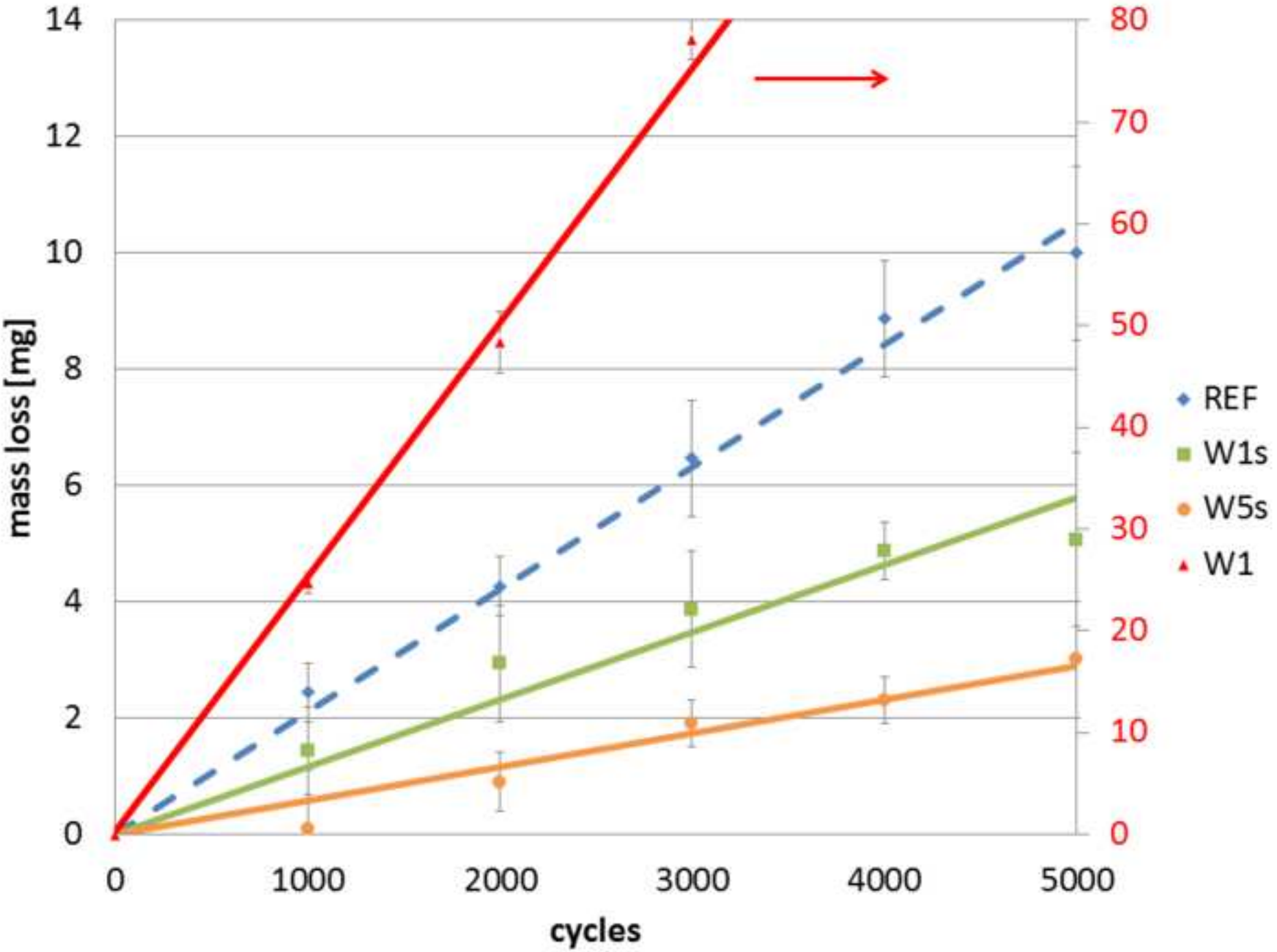

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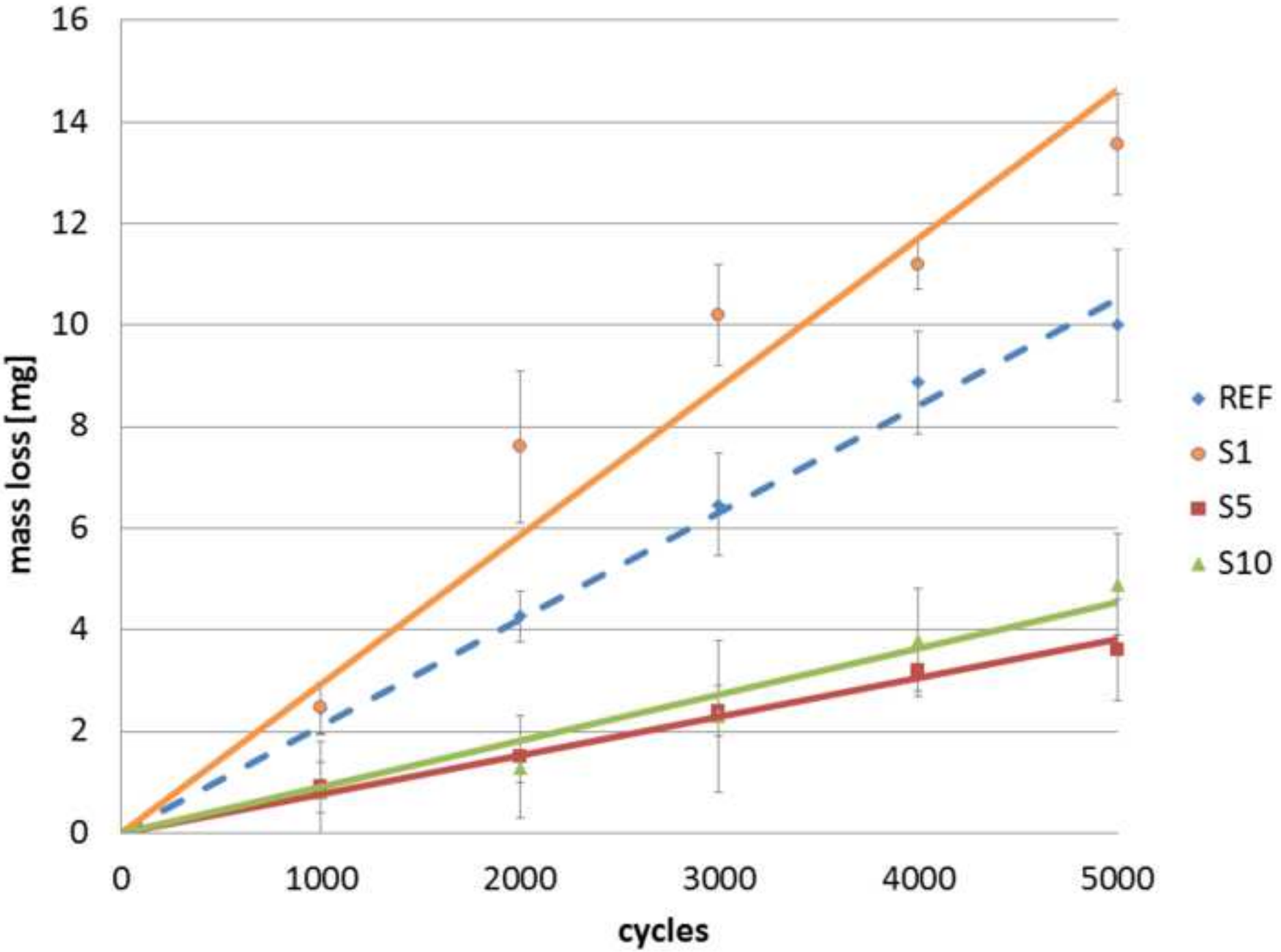

Table

Table 1: studied samples of second set.

Sample name	particles	vol%	sonication	Roughness R_a µm
REF	---	---		1.35 ± 0.14
G1	graphite	1%		1.62 ± 0.12
G2	graphite	2.5%		1.53 ± 0.09
W1	WC	1%		1.33 ±0.05
W1s	WC	1%	X	0.77 ± 0.13
W5s	WC	5%	X	0.76 ± 0.08
S1	SiC	1%		1.89 ± 0.07
S5	SiC	5%		1.56 ± 0.13
S10	SiC	10%		1.63 ± 0.05

highlights

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