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Al₂O₃ + Graphene Low-Friction Composite Coatings Prepared By Sol–Gel Method

Bożena Pietrzyk^{1,*}, Sebastian Miszczak¹, Ye Sun² and Marcin Szymański¹

- ¹ Institute of Materials Science and Engineering, Faculty of Mechanical Engineering, Lodz University of Technology, Stefanowskiego Str. 1/15, 90-924 Lodz, Poland; sebastian.miszczak@p.lodz.pl (S.M.); m.szymanski@mail.com (M.S.)
- ² Wanhua Research Institute (NERP), NO. 59. Chongqing Road, Yantai 264006, Shandong, China; sunye@whchem.com
- * Correspondence: bozena.pietrzyk@p.lodz.pl

Received: 15 July 2020; Accepted: 2 September 2020; Published: 4 September 2020



Abstract: In this work, Al_2O_3 + graphene coatings were prepared using the sol-gel method. The aim of the study was preliminary determination of the influence of size and amount of graphene nanoplatelets on morphology, chemical structure, and basic tribological properties of Al_2O_3 + graphene composite coatings. Two types of reduced graphene oxide (rGO) nanoplatelets with different lateral size and thickness were used to prepare the coatings. To characterize them, scanning electron microscope (SEM), glow discharged optical emission spectrometer (GDOES), Fourier-transform infrared (FTIR), reflectance spectrometer, and ball-on-disk tribological tests were used. It was found that the presence of graphene in the Al_2O_3 + graphene coatings did not fundamentally change the chemical transformation of ceramic Al₂O₃ matrix. Morphology examinations of coatings containing larger graphene nanoplatelets revealed a tendency to their parallel arrangement in relation to the coated surface. The tribological properties of Al_2O_3 + graphene coatings turned out to be strongly dependent on the size of graphene nanoplatelets as well as on the heat treatment temperature. The friction coefficient as low as 0.11 and good durability were obtained for the Al_2O_3 + graphene coating with larger nanoplatelets and heat-treated at 500 °C. The results of conducted research indicate the potential use of Al_2O_3 + graphene composite coatings prepared by the sol-gel method as low-friction ceramic coatings.

Keywords: ceramic coating; alumina coating; sol–gel; composite coating; graphene oxide; graphene nanoplatelets (GNP); rGO

1. Introduction

Alumina (Al₂O₃) as a technical ceramic is one of the most commonly used oxide materials [1]. Thanks to its good mechanical strength and high hardness, chemical stability, high thermal and very low electrical conductivity, and cost-effectiveness, alumina has been utilized for a large variety of applications, such as electric and electronic devices, reinforcing components, catalytic supports, medical implants, and thermal and wear resistant components, among others [2–8].

Aluminum oxide can also be used in the form of coatings produced by various methods: oxidation [9,10], thermal spraying [4,11], chemical vapor deposition [12,13], sputtering [14,15], sol–gel deposition [16,17], and so on. These coatings can also have a variety of applications, but among the most popular are the following: protection against electrochemical and high temperature corrosion [18–22], as well as reducing wear [23–25]. The latter application is justified by high hardness and thermal/chemical stability of Al₂O₃ coatings, despite the fact that achieved coefficients of friction

(COF) of pure alumina coatings are relatively high—between 0.65 and 0.9—regardless of manufacturing methods [11,26–30].

As lowering the COF is crucial for durability and wear resistance of coatings, efforts are being made to reduce it. The basic direction of modification is the implementation of additives in the coating, for example, particles of oxides [17,31], sulphides and fluorides [32–34], carbon nanotubes [35–37], graphite [38,39], or recently graphene [40–42]. Graphene, a two-dimensional allotropic form of carbon consisting of hexagonally arranged atoms in the form of a single flat layer [43], aroused great interest thanks to its excellent physico-chemical, electrical, and mechanical properties and resulting applications [44–47]. The tribological properties of graphene justify its use to reduce wear [48,49], provided that it has been effectively introduced into the volume of the coating in an appropriate amount. In case of alumina + graphene coatings, despite the efforts, the results of incorporating graphene into alumina vary. In most cases, the improvement of wear resistance can be seen, but with the use of commonly used production methods (mainly plasma spraying and complex CVD methods), a large spread of the friction coefficient is obtained, fluctuating between 0.3 and 0.7 [40–42]. It can be presumed that the reason for this may be insufficient control over graphene dispersion and/or the adverse effect of the physico-chemistry of the deposition processes itself. Considering the above, the sol-gel method may be an interesting alternative for the production of alumina + graphene composite coatings. The sol-gel method is a well-known and well-established technique of obtaining ceramic materials [50,51], which can also be used for the production of ceramic coatings [52]. The method is a simple, convenient, and low-cost chemical route for preparation of high quality coatings, including alumina [53]. The most important advantage of the sol-gel method is the presence of the liquid phase stage-sol, which can be deposited on substrates using various methods [54], and allows the introduction of specific additives into the coating, for example, particles of other phases, such as graphene.

In this study, Al_2O_3 + graphene coatings were prepared using a simple three-step sol-gel method: (1) preparation of Al_2O_3 + graphene sols, (2) dip-coating deposition of prepared sols onto the substrates, and (3) furnace heat treatment of obtained coatings at various temperatures. The aim of the study was preliminary determination of the influence of amount and type (size) of graphene nanoplatelets on surface morphology, chemical structure, and basic tribological properties of Al_2O_3 + graphene composite coatings.

2. Materials and Methods

2.1. Preparation of Sols

An alumina sol was prepared by dissolving aluminum isopropoxide (Sigma-Aldrich, >98%, Steinheim, Germany) in boiling water. During mixing, nitric acid solution (1 mol/L) was added to the precursor solution as a hydrolysis catalyst. The concentration of precursor in the sol was 0.7 mol/L.

Two kinds of reduced graphene oxide (rGO) in the form of graphene nanoplatelets (GNPs) with different size and thickness were used for the preparation of composite coatings:

- G1 graphene with average GNP thickness of 12 nm and average lateral size 4500 nm (AO-3, Graphene Laboratories Inc., New York, NY, USA);
- (2) G2 graphene with average GNP thickness of 1–5 nm and average lateral size less than 2000 nm (0540DX, SkySpring Nanomaterials, Inc., Houston, TX, USA).

The suspensions of both G1 and G2 graphenes were prepared using Tween 20 (Sigma-Aldrich, \geq 40%, Steinheim, Germany) as surfactant. For the preparation of each suspension, the surfactant (0.02 mL) was dissolved in 50 mL of water and then added to the proper mass of graphene powder. These solutions were sonicated using an ultrasonic bath for 15 min to prepare suspensions of both G1 and G2 graphene with 2 and 4 wt.% concentration. Subsequently, the same volumes of the prepared graphene suspensions and the alumina sol were mixed and sonicated in an ultrasonic bath for 15 min. As a result, Al₂O₃ + graphene sols were obtained—the final concentrations of each type of graphene

were 1 wt.% and 2 wt.%. The final concentration of alumina precursor in Al_2O_3 + graphene sols was about 0.35 mol/L. The sedimentation processes of graphene flakes in alumina sol were observed: for suspensions of G1 in alumina sol, the layer of graphene was visible on the bottom of the vessel in a few minutes after mixing; the suspension of G2 in alumina sol was much more stable. For homogeneity of suspension, the 2 min of sonication of each Al_2O_3 + graphene sols was carried out directly before each deposition process.

For deposition of Al_2O_3 coatings without GNPs, the obtained alumina sol was diluted using distilled water to the concentration of precursor of 0.35 mol/L in order to maintain the same deposition conditions as for the rest of the coatings.

2.2. Deposition of Coatings

 Al_2O_3 and Al_2O_3 + graphene coatings were deposited by the sol-gel dip-coating method. The discs of 316 stainless steel with diameter of 16 mm and height of 5 mm as well as monocrystalline silicon wafers (100) were used as substrates. The surface of stainless steel substrates was ground on abrasive paper with grade 800 up to 2000. Before the deposition, substrates (both stainless steel and silicon) were washed in ethanol for 15 min using ultrasonic cleaner and dried in compressed air.

The substrates were immersed in previously prepared alumina sols as well as in suspensions of graphene in alumina sol, and withdrawn at a controlled constant speed of 120 mm/min using dip-coater (TLO 0.1 MTI Corporation, Richmond, CA, USA). After deposition, coatings were dried at ambient temperature in air for 30 min and heat-treated in the furnace at the temperature of 300 °C or 500 °C for 15 min. The same technological process of coatings production was the basis for comparing their properties.

2.3. Characterization of Coatings

The evaluation of Al₂O₃ and Al₂O₃ + graphene coatings morphology was performed using scanning electron microscope (SEM) (S-3000M, Hitachi, Tokyo, Japan) for coatings deposited on silicon.

The elemental analysis of coatings was carried out using glow discharged optical emission spectrometer (GDOES) (LECO GDS850A, St. Joseph, MI, USA) for coatings deposited on silicon.

The thickness as well as the refractive index of coatings deposited on stainless steel substrates were determined with use of reflectance spectrometer (Thin Film Analyzer UV20, Filmetrics, San Diego, CA, USA), using the Cauchy model.

The chemical structure of the coatings was studied using a Fourier-transform infrared (FTIR) spectrometer (Nicolet iS50, Thermo Fisher Scientific, Waltham, MA, USA) in the range of 4000–400 cm⁻¹. The study was carried out in transmission mode, recording the absorbance of IR radiation passing through coatings deposited on silicon or through graphene powder.

2.4. Tribological Tests

Friction tests were performed for Al_2O_3 and Al_2O_3 + graphene coatings deposited on the 316 stainless steel using a ball-on-disk tribometer (CSM THT, Needham, MA, USA) in rotary mode. The tribological tests were performed at room temperature, linear speed was 0.1 m/s, and radius was 5 mm. The applied normal load was 1N and sliding distance was fixed at 100 m. The alumina (α -Al₂O₃) testing ball measuring 6.35 mm in diameter was used as static element. The friction coefficients were automatically measured and recorded in real time by computer system of the tribometer.

3. Results and Discussion

3.1. Morphology and Thickness of Coatings

Figure 1 presents the morphology of Al_2O_3 coating heat treated at 500 °C and Al_2O_3 + graphene (both G1 and G2) coatings after drying at ambient temperature as well as after heat treatment at 500 °C. SEM observations revealed that the surface of coatings was free of cracks, delamination, or other

discontinuities. The surface of Al₂O₃ coating was smooth (Figure 1a), while Al₂O₃ + graphene coatings contained uniformly distributed particles whose shape and size depended on the type of graphene used. In the Al₂O₃ + G1 graphene coating (Figure 1b,c), the shape of particles was rather flat and their size was mostly between 2 and 5 μ m, corresponding to the size of G1 graphene nanoplatelets. Al₂O₃ + G2 graphene coating (Figure 1d,e) contained spherical particles that looked like small agglomerates of G2 GNPs with different sizes, but mostly smaller than 2 μ m. The particle size was roughly correlated with the size of each type of graphene.



Figure 1. Scanning electron microscope (SEM) images of Al_2O_3 and $Al_2O_3 + graphene$ coatings with 1% of graphene in sol suspension: (a) Al_2O_3 coating heat treated at 500 °C; (b) $Al_2O_3 + G1$ coating dried at ambient temperature; (c) $Al_2O_3 + G1$ coating heat treated at 500 °C; (d) $Al_2O_3 + G2$ coating dried at ambient temperature; (e) $Al_2O_3 + G2$ coating heat treated at 500 °C.

It should be pointed out that, whether coatings were heat treated or not, particles of both G1 and G2 graphene could be observed up to the temperature of 500 °C and did not change their shape and average size.

Figure 2 shows SEM images of $Al_2O_3 + G1$ and $Al_2O_3 + G2$ graphene coatings taken at an inclination of approximately 75 degrees. The analysis of the $Al_2O_3 + G1$ coating image (Figure 2a) indicates that the G1 graphene particles are in the form of thin nanoplatelets stacks located under the surface of the coating within the oxide matrix as well as protruding slightly above the surface (scheme in Figure 2c). In the image obtained at higher magnification (Figure 2b), the flat nature of the G1 nanoplatelet stack and its arrangement parallel to the surface of the coating and substrate is clearly visible.



Figure 2. SEM images of Al_2O_3 + graphene coatings with 1% of graphene in sol suspension: (**a**,**b**) Al_2O_3 + G1 coatings; (**d**,**e**) Al_2O_3 + G2 coatings, and proposed schemes of their internal structures (**c**,**f**).

The images of the $Al_2O_3 + G2$ coating (Figure 2d,e) show a large number of bulges protruding above the coating surface. Taking into account their varied size and height (up to 1 μ m), they can be identified as agglomerates of G2 graphene nanoplatelets of different lateral size and spatial orientation with respect to the substrate plane. These agglomerates consist of nanoplatelets (scheme in Figure 2f) surrounded by an oxide matrix, and their size significantly exceeds the thickness of the coating. The analysis of the shape of graphene agglomerates shows that G1 graphene (larger lateral size and thickness) forms agglomerates with GNPs oriented parallel to the surface, while G2 graphene (smaller lateral size and thinner) forms agglomerates with a globular shape and more random arrangement.

Figure 3 shows depth profiles of GDOES elemental analysis carried out for Al_2O_3 and Al_2O_3 + graphene coatings deposited on silicon from a suspensions with 2% of G1 and 2% of G2 graphene and heat treated at 300 °C. The results indicate that both the actual carbon content and the thickness of the coatings depend on the type of graphene. The Al_2O_3 coating had a carbon content of approximately 6%, which comes mainly from remnants of organometallic precursor. The carbon contents in Al_2O_3 + graphene coatings were higher: approximately 11% in the Al_2O_3 + G1 coating and approximately 20% in the Al_2O_3 + G2 coating. Despite the same original concentrations of G1 and G2 graphene in the suspensions, the carbon content of Al_2O_3 + G2 coating was much higher than that of Al_2O_3 + G1. This is a consequence of the observed sedimentation of G1 graphene particles in the suspension, so that its effective amount (by weight) in the coating is lower compared with G2 graphene.



Figure 3. Elemental analysis of Al_2O_3 (**a**), $Al_2O_3 + G1$ (**b**), and $Al_2O_3 + G2$ (**c**) coatings with 2% of graphene in sol suspension, heat treated at a temperature of 300 °C.

On the basis of the profiles obtained, it is also possible to estimate the thickness of the coatings: approximately 200 nm for the Al_2O_3 coating, approximately 110 nm for the $Al_2O_3 + G1$ coating, and approximately 200 nm for the $Al_2O_3 + G2$ coating.

Similar dependence of thickness on the type of graphene was observed for coatings deposited on a steel substrate. The results of the thickness measurements of these coatings are shown in Table 1.

		Constant's set		
Type of Coating	Temperature of Heat Treatment (°C)	Graphene in Suspension (%)	Thickness (nm)	n (Refractive Index)
Al ₂ O ₃ + G1	300	1	134 ± 2	1.49 ± 0.005
		2	130 ± 1	1.50 ± 0.01
	500	1	125 ± 3	1.46 ± 0.03
		2	123 ± 2	1.43 ± 0.01
Al ₂ O ₃ + G2	300	1	184 ± 1	1.55 ± 0.01
		2	171 ± 1	1.56 ± 0.01
	500	1	152 ± 1	1.50 ± 0.01
		2	147 ± 1	1.55 ± 0.005
Al ₂ O ₃	300	-	163 ± 8	1.56 ± 0.06
	500	-	152 ± 1	1.58 ± 0.005

Table 1. The thickness of coatings deposited on steel substrates.

It was found that the thickness of Al_2O_3 coatings was similar to the thickness of coatings with G2 graphene. In contrast, the thickness of coatings with G1 graphene was lower than the corresponding coatings with G2 graphene or without any graphene. This may be owing to the shape and size of G1 graphene nanoplatelets, which, owing to the tendency to orientate parallel to the surface of the substrate, affect the transition between capillary and draining mechanisms characteristic for dip-coating deposition [55] and change the thickness of the wet layer formed during pulling out from the sol.

Analyzing the data in Table 1, it can also be seen that the thickness of the coatings decreases as the heat treatment temperature increases. This is a consequence of sintering of the Al_2O_3 matrix. The change of thickness is typical for sol–gel coatings below the temperature of obtaining a stable, dense crystal structure [52].

3.2. Chemical Structure

In order to determine the chemical structure, FTIR spectra of graphene powder as well as Al_2O_3 and Al_2O_3 + graphene coatings deposited on silicon substrate from a suspensions with 2% of G1 or 2% of G2 graphene, heat treated at different temperatures, were recorded.

FTIR spectra of G1 and G2 graphene, demonstrated in Figure 4a, were found to exhibit several absorption bands of carbon and oxygen-containing groups characteristic for graphene oxide: the absorption band around 1000 cm⁻¹ for C–O stretching vibration bonds, band around 1200 cm⁻¹ for C–OH stretching, and band around 1600 cm⁻¹ for carbon–carbon bonds conjugated with carbon–oxygen bonds [56,57]. The broad peak at 3400 cm⁻¹ was characteristic for stretching vibrations of -OH groups. The small peak at 2930 cm⁻¹ in the spectra was attributed to the C–H stretching vibration. The FTIR spectra of G1 and G2 graphene were similar, but the most characteristic bands for graphene oxide, visible at 1200 cm⁻¹ and 1600 cm⁻¹, exhibited higher intensity in G2 spectrum.

In the spectra of the Al_2O_3 coatings shown in Figure 4b, three main ranges of absorption bands can be distinguished: 2900–3700 cm⁻¹, 1300–1700 cm⁻¹, and 400–1100 cm⁻¹.

In the range of 2900–3700 cm⁻¹, the absorption bands for hydroxyl groups deriving from water absorbed in the coating were visible. The intensity of these bands decreased as the heat treatment temperature increased, which can indicate the removal process of absorbed water.

In the range of $1200-1700 \text{ cm}^{-1}$, bands of chemically bonded –OH groups ($1200-1500 \text{ cm}^{-1}$) as well as C–O and C–H bonds ($1300-1700 \text{ cm}^{-1}$) originating from the aluminum isopropoxide precursor were visible. The intensity of bands in this region also decreased with the increasing temperature, but some of them were visible even in the spectrum of coating heat treated at 500 °C.



Figure 4. Fourier-transform infrared (FTIR) spectra of (**a**) G1 and G2 graphene powders and (**b**) Al₂O₃ coatings heat treated at different temperatures.

The range of 400–1100 cm⁻¹ was characteristic for bands derived from Al–O bonds. The typical boehmite (AlOOH) band system (482, 620, 740, 1070, and 3090 cm⁻¹) [16] was visible in the spectrum obtained at room temperature as well as heat treated at 300 °C. In the spectrum of coating heat treated at 500 °C, one can observe that the discussed band became wider and showed maxima at 560 cm⁻¹ and 800 cm⁻¹, which indicated the transformation of the matrix structure from AlOOH to Al₂O₃ [16].

In the spectra of Al_2O_3 + graphene coatings (Figure 5), the characteristic bands of graphene were hardly visible because they overlapped with the bands present in the spectrum of the Al_2O_3 coating in the range 1000–1700 cm⁻¹ (Figure 4b).



Figure 5. FTIR spectra of Al_2O_3 + graphene coatings with (**a**) G1 graphene and (**b**) G2 graphene, heat treated at different temperatures.

The similarity of the $Al_2O_3 + G2$ coating spectra (Figure 5b) to that of Al_2O_3 coating in the range of 400–1100 cm⁻¹ indicated no effect of the addition of graphene G2 on the changes taking place in the Al_2O_3 matrix during its heat treatment. The conversion of AlOOH into Al_2O_3 was analogous to that in the alumina coating. In the spectra of the $Al_2O_3 + G1$ coatings treated at 20 °C and 300 °C (Figure 5a), bands in the range of 400–1100 cm⁻¹ were less intensive and broadened. This may indicate a lower ordering of Al–O and Al–OH bonds structure caused by the presence of G1 graphene. However, in the spectrum of the coating treated at 500 ° C, further broadening of the bands and their shift towards higher wavenumbers, typical for the structure of the Al_2O_3 coating, were observed. Similarly as for the Al₂O₃ coating, for both (G1 and G2) types of the analyzed Al₂O₃ + graphene coatings, the intensity of absorption band of hydroxyl groups in the range of 2800–3700 cm⁻¹ decreased as the heat treatment temperature increased. It can be noticed that the intensity of this band for coatings with G2 graphene was higher than for coatings with G1 graphene. This was especially visible in the spectra of Al₂O₃ + G2 coatings obtained at lower temperatures: 20 °C and 300 °C. This may be owing to the adsorption of –OH groups on GNPs, whose amount in Al₂O₃ + G2 coatings was greater than in Al₂O₃ + G1 coatings.

3.3. Tribological Properties

To investigate the effects of graphene on the friction and wear of Al_2O_3 + graphene coatings, ball-on-disc tribological tests were performed for Al_2O_3 and Al_2O_3 + graphene coatings deposited on 316 steel substrates.

The results of the friction tests of uncoated 316 steel substrate and Al_2O_3 coatings heat treated at different temperatures are shown in Figure 6. In a test carried out on uncovered steel substrate, the COF quickly reached 0.88 and remained at this level (steady state) until the end of the test. A very similar shape of COF changes was obtained for the Al_2O_3 coating heat treated at 300 °C. The increase of COF over a short sliding distance to values typical for uncovered substrate is the result of rapid destruction of the coating. In the case of coating heat treated at 500 °C, the increase of COF was slightly slower and the destruction process was prolonged, which is probably the result of a better densification of the coating.



Figure 6. The ball-on-disc tests of uncoated 316 steel and Al_2O_3 coatings heat treated at 300 °C and 500 °C. COF, coefficient of friction.

Figure 7 shows the friction curves of $Al_2O_3 + G1$ coatings heated at 300 °C and 500 °C. Analyzing changes in the friction coefficient as a function of the friction path, significant differences can be observed. Compared with alumina coatings, no rapid initial increase/decrease of COF can be observed, regardless of the amount of graphene addition or heat treatment temperature. This may indicate a rapid development of a tribofilm containing graphene originated from the upper layer of the coating. The coating containing 1% of G1 graphene and heat treated at 300 °C lost its anti-friction properties over a sliding distance of over 12 m (~500 laps) and was destroyed, which is indicated by a rapid increase in COF to a value close to that of an uncovered steel substrate. Similar behavior was observed for the coating heat treated at 500 °C, except that the loss of anti-friction properties occurred over sliding distance of about 41 m (~1700 laps). In both cases, despite initially very low COF, the G1 graphene content appears to be too low to achieve and maintain a satisfactory self-lubricating effect. A slightly higher durability of the coating heat-treated at 500 °C compared with that of 300 °C may be a

consequence of better densification of alumina matrix, which is typical for thermal processing of sol–gel derived coatings [52,58].



Figure 7. The ball-on-disc test of Al_2O_3 + G1 graphene coatings heat treated at 300 °C and 500 °C.

Different behavior was observed for coatings containing 2% of G1 graphene. Regardless of the heat treatment temperatures, these coatings showed a practically constant and very stable course of friction curves. The average COF of steady state for coatings heat-treated at 300 °C and 500 °C were 0.13 and 0.11, respectively. This behavior indicates the rapid development and maintenance of a tribofilm containing graphene nanoplatelets, the content of which was sufficient to provide a very low COF until the end of the test. Slightly lower average COF of coating heat-treated at 500 °C may again indicate the beneficial effect of better densification of Al₂O₃ matrix.

Comparison of the friction curves of coatings containing 1% and 2% of G1 graphene (Figure 7) showed major differences. Coatings with 1% of G1 graphene quickly lost their anti-friction properties (rapid increase in COF) and were destroyed. Despite initially very low COF, the 1% of G1 graphene content appears to be too low to achieve and maintain a satisfactory self-lubricating effect. Meanwhile, coatings containing 2% of G1 graphene showed a low and stable COF to the very end of the friction test distance. This indicates that, regardless of other parameters, the amount of graphene is crucial for proper friction properties of $Al_2O_3 + G1$ coatings.

Figure 8 shows friction curves of $Al_2O_3 + G2$ coatings heat treated at 300 °C and 500 °C. In the case of a coating containing 1% of G2 graphene and heat treated at 300 °C, the sliding distance before wearing out was 47 m (~1900 laps), while the coating treated at 500 °C showed almost immediate growth of COF towards values above 0.8, characteristic for uncoated steel substrate. Similarly, the coating containing 2% of G2 graphene and heat treated at 300 °C had better durability than the coating treated at 500 °C. The coating with 2% of G2 graphene heat treated at 300 °C revealed low, stable COF of around 0.17 throughout the test, while the coating with 2% of G2 graphene heat treated at 500 °C showed a progressive increase of COF above 0.8 over a sliding distance of 70 m. The observed behavior is the opposite of that for coatings with the addition of graphene G1. Assuming a similar effect of higher heat treatment temperature on the densification of Al₂O₃ matrix, the difference in the behavior of the $Al_2O_3 + G1$ and $Al_2O_3 + G2$ coatings may be owing to the shape and spatial orientation of graphene nanoplatelets in the coating matrix. For $Al_2O_3 + G1$ graphene coatings, SEM images (Figure 2a,b) indicate parallel arrangement of the GNPs relative to the surface of the substrate and the coating. The shape and spatial arrangement of GNPs seem to be extremely conducive to the formation of graphene tribofilm. In work by Cheng et al. [59], it is proposed that "under high normal stress and localized heat during friction test, graphene sheets from nanoplatelets are pulled under shear and become welded with overlapping areas to form an ultrathin graphene

tribofilm". This type of confinement is indicated as crucial in the frictional behavior of graphene, provided the thickness of the GNPs is maintained [60]. Graphene sheets attached to sliding surfaces facilitate their movement because graphene shears easily owing to the weak van der Waals forces at the sliding contact interface [61–63]. This phenomenon can be particularly effective when the GNPs are parallel to the plane of sliding surfaces—in combination with the multilayer structure of GNPs, it would allow to effectively use the slip mechanism proposed in the literature [64–66].



Figure 8. The ball-on-disc test of Al₂O₃ + G2 graphene coatings heat treated at 300 °C and 500 °C.

In the case of G2 graphene, there is a visible tendency to coagulate into small agglomerates (Figure 2d,e) without a clear spatial orientation. Owing to the smaller size, the spatial orientation of graphene flakes inside agglomerates is more random, which can deteriorate the utilization of slip mechanisms between them. As a result, despite the seemingly better dispersion of G2 graphene, its lubrication capabilities are worse than that of G1 graphene.

Another factor that may affect tribological efficiency of G2 graphene in $Al_2O_3 + G2$ coatings is its size and susceptibility to oxidation during heat treatment. The sol–gel method, based on the aqueous hydrolysis of organometallic precursors, is characterized by the presence of a large amount of hydroxyl groups derived from water absorbed in a coating. During heat treatment, a significant amount of them is still present in the coating. The atmosphere of air and presence of hydroxyl groups create favorable conditions for thermal oxidation of previously reduced graphene (rGO). High temperature oxidation of rGO can occur at a temperature of about 400 °C [67], and the increase in temperature can lead to a loss of lubricating properties of multilayer graphene [68]. Because the oxidation process occurs mainly at the edges of graphene flakes and in their defects, it will be more intense in the case of flakes with a smaller diameter—because of the worse circumference to the flake surface ratio. The smaller size of the G2 graphene flakes may make them more susceptible to this phenomenon, which may hinder or even prevent the formation of tribofilm, and—as a consequence—deteriorate tribological properties of the $Al_2O_3 + G2$ coating compared with the $Al_2O_3 + G1$ one.

4. Summary and Conclusions

Composite Al_2O_3 coatings containing 1% and 2% of GNPs were successfully prepared by the sol–gel method. The coatings were of good quality—free of cracks and discontinuities. The morphology of coatings containing G1 graphene revealed a tendency to parallel arrangement of GNP in relation to the coated surface, while in the coatings with smaller size G2 graphene, no spatial organization was observed. GDOES chemical analysis showed lower carbon content and lower thickness of $Al_2O_3 + G1$ graphene coatings compared with the Al_2O_3 and $Al_2O_3 + G2$. This is the result of a different dispersion of G1 graphene-flat arrangement of thin nanoplatelets during dip-coating deposition of the coatings.

The graphene nanoplatelets in Al_2O_3 + graphene coatings do not fundamentally change the nature of the chemical transformation of ceramic Al_2O_3 matrix. Regardless of the presence or absence of graphene, these changes rely on elimination of precursor functional groups and OH groups from the structure of the coatings during increasing of the temperature [16]. However, this process appears to vary depending on the size of the graphene nanoplatelets.

Tribological tests conducted on coatings showed different behavior depending on the type and quantity of GNPs. For both (G1 and G2) types of graphene, a content of 1% was insufficient to obtain and/or maintain a self-lubricating effect. Coatings with 2% of graphene had better properties. In the case of $Al_2O_3 + G1$ coatings, regardless of heat treatment temperatures, the coatings showed low COF (0.11 \div 0.13) and were not destroyed until the end of the tests. $Al_2O_3 + G2$ coatings behaved differently—only the coating heat treated at a lower temperature (300 °C) showed a satisfactory COF (0.17) and durability, while the coating heat treated at 500 °C showed a progressive increase of COF up to 0.8 and above, indicating its destruction. This is most likely associated with the random spatial orientation of G2 GNPs compared with G1, hindering the use of slip mechanisms between its layers, as well as the adverse effect of higher heat treatment temperature, which contributes to faster degradation of G2 graphene lubricating properties.

The results of this study show that, using the sol-gel method, it is possible to produce ceramic composite coatings in which graphene can act as a solid lubricant significantly reducing friction. The observed dependencies between manufacturing parameters (type, amount and dispersion of graphene nanoplatelets, heat treatment temperature) create opportunities to control the properties of graphene containing alumina composite coatings, which will be the subject of further research.

Author Contributions: B.P.: concept, methodology, investigations, data and results analysis, discussion, writing and editing; S.M.: concept, investigations, results analysis, discussion, writing and editing, Y.S.: methodology, investigations, results analysis, discussion, writing; M.S.: investigation, data analysis. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: The authors acknowledge Anna Sobczyk-Guzenda for recording of FTIR spectra, Krzysztof Jakubowski and Paulina Kowalczyk for GDOES tests, and Marek Klich for tribological investigations.

Conflicts of Interest: The authors declare no conflict of interest.

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