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A Novel Approach for Durability Evaluation of Metal Protective Coatings in Dynamic Interplay with the Liquid Alloy

P. Pałka [a,*], G. Boczkal [a], A. Hotloś [a], G. Mrówka-Nowotnik [b]

[a] AGH University of Krakow, Faculty of Non-Ferrous Metals
Al. Mickiewicza 30, 30-059 Kraków, Poland
[b] Rzeszów University of Technology, Department of Material Science
Al. Powstańców Warszawy 12, 35-959 Rzeszów, Poland
*Corresponding author. E-mail address: pawel.palka@agh.edu.pl

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Abstract

The article describes a new test method to quickly evaluate the durability of a protective coating to dynamic contact with liquid metal. The essence of the method is the movement of a drop of liquid metal inside a rotating ring, covered from the inside with the protective coating under test. The parameters determined in the test are analogous to the classic pin-on-disk tribological test. The method was tested for the system: liquid alloy 2017A vs. AlTiN coating on a copper substrate. The test temperature was 750°C, and exposure times ranged from 30 to 90 minutes. Sliding path equivalent for the metal droplet/coating system ranged from 31.6 to 95 m. The study, which included visual evaluation of the surface of the samples, followed by phase and microstructural analysis, showed the high efficiency of the method for assessing the lifetime of protective coatings on contact with liquid metal. The investigated issue was also analyzed from the model side taking into account changes in the diffusion coefficient at the contact of liquid metal with the substrate, occurring with the progressive degradation of the protective coating.

Keywords: Liquid impact erosion, Surface topography, PVD coatings, High temperature, Surface analysis

1. Introduction

Testing the resistance of protective coatings is a key element in the design of new materials with unique properties. The tribological methods currently used to test protective coatings are limited to contact of the coating with a counter-sample made of a material with a solid structure and known parameters. Most popular methods of tests are described in work [1] and [2]. In the work [3] authors concentrate on the wear tests of multilayer coatings. Such tests are carried out in direct contact with both elements. Sometimes an additional lubricating agent (lubricant) is added to reduce friction. The essence of the test is the interaction of two solid bodies and the wear consequences. A typical measurement uses a spinning disk sample and a spherical counter-sample made of hard material, most often steel or a hard intermetallic phase. Such tests are carried out on bearings, for example. In this case, the measure of the wear resistance of the substrate / coating system is the distance travelled by the ball pressed with a certain force against the substrate, without damaging the protective coating applied to the substrate surface. This parameter is called the sliding distance (SD). This classic test is defined by the norm DIN ISO 7148-1 – "Testing the tribological behavior of material for sliding bearings Part 1: Testing of bearing materials, test procedure A, pin on disk".

Studies using this method at room temperature for thin AlTiN coatings deposited on steel are described in [4]. Thickness of the layer was 2 mm. Sliding distances under 5N load were 126 m, 251 m and 377 m. Microhardness of these layers reach the range of 2100 HV0.05 to 2500 HV0.05.

In others work, AlTiN coatings were deposited on YT14 cemented carbide balls. The friction and wear behavior of the AlTiN-coated balls against SKD11 hardened steel was investigated at various temperatures from 25 to 700 °C in air [5]. The tested coatings were about 4 mm thick, sliding distance under 2 N load press was 31 m. The role of the sample was in this case a ball covered with a coating, and the counter-sample was a steel target.

Despite the possibility of carrying out tests at elevated temperatures, the limitation of this method is its applicability only to a system of two solid bodies.

The concept described in this article is to transfer the design of the above test to the test system in which the sample will still be a solid body but the counter-sample will be in a liquid state.

Existing methods for assessing the interaction of liquid metal with a substrate use the static solid-liquid-type effect, which consists of measurements of the contact angle. The static wettability measurement can use several approaches: the out-dropping of liquid metal onto the tested surface using a capillary [6-8], lowering the tested substrate from above onto a drop of molten metal (reverse test) [9], high-temperature capillarity (HTC) [10], direct melting of a piece of metal on the substrate surface [11,12].

To date, no methods have been described in the literature to investigate the impact of dynamic contact between the liquid metal and the substrate and to evaluate the durability of the coating under such conditions. Research of this type is carried out only as technological tests on already available stands. The choice of coating is then based on tabular data rather than direct testing. Other tests involve immersing a rotating element, with deposited of investigated layer, in liquid metal [13,14], but the results obtained in this way are difficult to interpret and compare.

The new method presented here allows to test the dynamic interaction of the substrate with liquid metal, while the interpretation of results is carried out in the same way as in a typical tribological test, i.e. by measuring the distance covered by the sample in relation to the counter-sample. The only difference concerns the state of matter of the counter-sample and the lack of pressure exerted on the counter-sample when it moves on the substrate. The sliding distance (SD) known from the classic tribology wear test was replaced by the ‘solid / liquid sliding distance’ (SLSD).

2. Methods

The tested materials were: copper ring (M1E grade electrolytic copper) protected inside with a protective AlTiN coating and drop of alloy 2017A as a counter-sample equivalent.

The PVD method was used to produce the protective coating [15] using a Sulzer Metaplas PVD device. Coatings were made using recipes used by Ion Galenica. Parameters PVD process were: time 120 min. and temperature 400°C, time and voltage of ion etching polarization|: 60 min. and 300 V, pressure in a reaction chamber 8.5 10^{-2} mbar, voltage of polarization 40-80 V. The coatings were applied to the substrate without additional surface preparation by abrasive or blasting methods.

The proposed method uses the rotational motion of the substrate, however, due to the counter-sample in the liquid state (instead ball in pin-on disc method), a ring with double-sided plugs was used (instead of a classic target covered with the tested layer) [16].

The test samples have the shape of a ring, the inner surface which is covered with the tested coating, what is shown in Figure 1. The copper sleeve has flanges on both sides to prevent metal flowing out during the test.

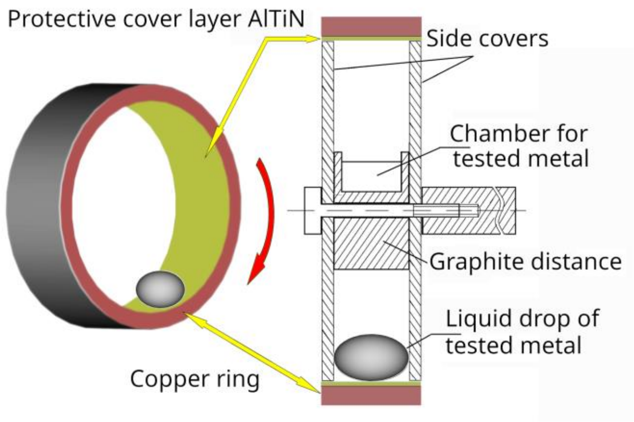


Fig. 1. The scheme of the method of the test

In the graphite distance located between the side covers there is a chamber to place the batch of metal. After loading the metal batch (counter-sample), the chamber is in the upper position. The system is then introduced into a furnace and heated to the target temperature. The metal in the chamber melts. When the preset temperature is reached, the rotation of the system is activated, and molten metal pours out of the chamber onto the inner surface of the sleeve covered with the tested coating.

Continuation of rotation makes the liquid metal drop (counter-sample) move on the tested coating. The force of gravity acting on the drop of metal keeps it in the lower part of the spinning ring throughout the test. This forces an interaction in the solid (sample) and liquid metal drop (counter-sample) system and is analogous to the classical solid-state tribological test.

In the described test, a copper sample was used in the form of a ring with an internal diameter of 50 mm, a ring width of 20 mm and a wall thickness of 1 mm. The inner part of the ring was covered with a 2.2 μm AlTiN phase layer. The ring rotation speed was 6.36 rpm, which corresponds to a linear speed of about of 1 m / min. Mass of liquid metal (2017A) was about 8 g and volume of liquid was ~3 cm^3. The entire system was closed in a chamber with an argon atmosphere. Temperatures 750 ºC and 720 ºC were applied.

To compare the wear resistance of individual variants, it was necessary to introduce a parameter linking the wear effect with the active movement of liquid metal along the tested coating. This working parameter named „solid/liquid sliding distance’ (SLSD) determines distance of direct interaction between protective coating and the liquid metal. With the known time of the tests t, the diameter of the ring and rotational speed w, it is possible to calculate the distance travelled by the liquid metal drop on the coating (Equation 1):

$$SLSD\,[m] = \pi \cdot d[m] \cdot \omega[rpm] \cdot t[min] \quad (1)$$

The time of the interaction of liquid metal with the layer on the internal surface of the sample will depend on the geometry of the sample. The rotational speed (ω) determined a dynamic of contact. In practice, faster w value consequences shorter time for contact diffusion processes. This parameter may be related to the speed of movement of the metal stream in the crystallizer.

The described method allows the test conditions to be standardized. The characteristic parameters are T, w and t. The w it is a parameter that determines the rate of movement of the drop relative to the ground. Increasing the rate of rotation reduces the time per unit contact between the liquid drop and the point on the path.

The proposed test can be carried out in several variants:

- specified SLSD and T parameters - after the test, the coating is subjected to wear analysis,
- under the specified conditions, the test continues until the coating fails, the result is the SLSD parameter needed for the coating to fail,
- the sample consists of two half-rings with different coatings. After the test, the resistance of both coatings can be directly compared under identical test conditions.

The test was carried out according to the first variant. One type of coating was tested at the same rate of ring rotation. Different exposure times were used, and in one variant the temperature was additionally lowered by 30 degrees, from 750 °C to 720 °C. Parameters for carried tests are listed in Table 1.

Table 1.
Variants of conditions under which individual samples were tested

Sample	Temp. [°C]	Time [min]	SLSD [m]
A	750	30	31.6
B	750	60	63.3
C	750	90	95
D	720	90	95

An X-ray diffractometer Bruker Discover D8 Advance was used for the measurement. It was equipped with an Euler cradle with a radius of 300 mm and a copper tube with a wavelength l = 1.54 Å. Soller slits were used to form the primary optics, and the divergence slits of 0.6 mm on the side of the secondary optics were used. Additionally, the anti-scatter slits with the span of 0.6 mm and receiving slit with span of 0.2 mm were inserted. A nickel filter on the secondary optics side was used to obtain a monochromatic beam. The measurement was carried out with a step angle of 0.02° and a time of 4 s per measurement step. Diffractograms with intensity vs 2theta angle in in the range between 30° to 100° were obtained. After such measurements, the obtained spectra were subjected to initial numerical processing using the EVA software consisting of cutting off the background and reducing noise using the Fourier transform. The PDF-2 crystallographic data base was used to identify the phase.

Structural examinations were performed using Hitachi S-3400N scanning electron microscope (SEM) with an EDS Thermo Noran System Six chemical composition analyser in microregions.

Samples after various variants of wear were documented using a Nikon D7000 camera with a macroscopic lens. This corresponds to the assumption of the method, where one of the advantages is the possibility of visual evaluation of the sample after the test, without the need for advanced microstructural studies.

After macroscopic observation, the samples were subjected to microstructural and elemental analysis using SEM Hitachi S-3400N equipped with EDS (Energy Dispersive X-Ray Spectroscopy) microanalyzer. The test specimens were cut to reveal the cross-section of the AlTiN protective coating and then embedded in conductive resin. Preparation for the observation of the microstructure included grinding on abrasive papers with a gradation up to 4000. The end stage was polishing with diamond pastes from 3 to 1 µm and OPS (SiO_2 colloidal suspension from Struers).

Microhardness tests were carried out using the Knoop method with a load of 0.025 kG an Innovatest Nova 240 microhardness tester with a Knoop indenter was used. An area of 10x10 mm was tested with a step of 1 mm.

3. Results obtained during the test

The described measurement method was applied to samples with M1E grade electrolytic copper substrate, on which nitride protective coatings AlTiN (55/45 at. %) were applied by PVD method; deposition parameters are showed in Table 1. This type of the coating is well-known, thus it is convenient for testing the new method [4,5,18].

In Figures 2a, b cross section of the layer for initial state is presented. The mean thickness of coating was about 2.2 µm.
Analysis of the microstructure shows good bond with the substrate. The boundaries of the separation between the layers are blurred, which shows the effect of diffusion, and consequently, a large contact surface. The tested layer is uniform but includes a structural discontinuities. Its thickness is constant over the entire observed section.

Figure 2c shows the surface microstructure of the AlTiN layer. There are visible heterogeneities resulting from the PVD production process. Taking into account the high hardness of the tested phase, the changes of which are shown in Figure 2c, the observed surface defects may be the cause of microcracks and consequently, the formation of defects that contribute to the degradation of the protective coating.

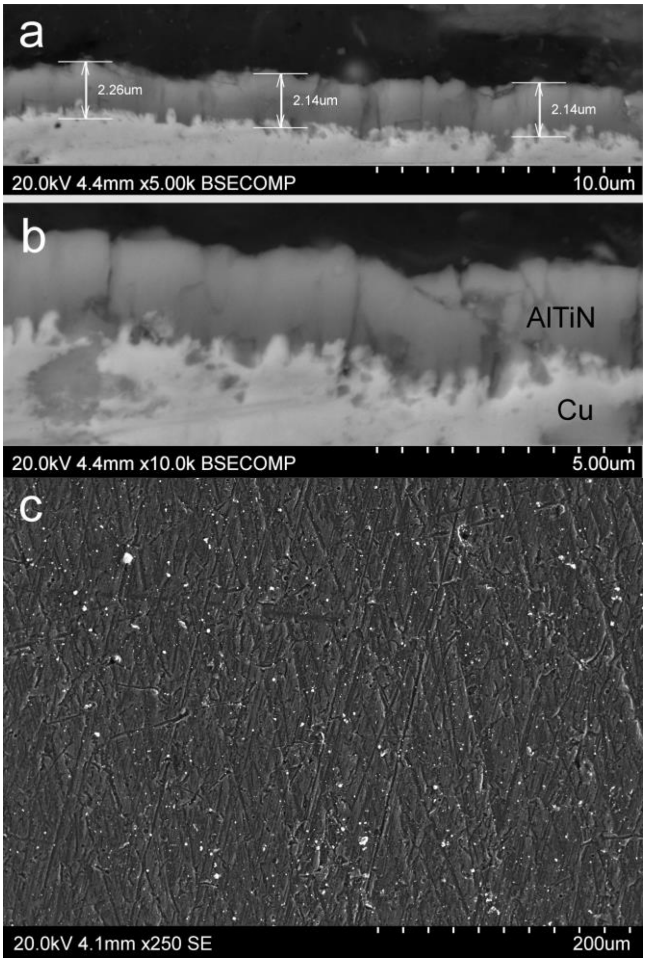


Fig. 2a b). Microstructure of the Cu/AlTiN layer (55/45 at%) ring cross-section, c) microstructure of the work surface of the AlTiN layer – internal surface of the investigated ring

The microhardness of the AlTiN phase (Figure 3) measured in the area of 10x10 mm with steps of 1 mm was in the range 1696-2037 HK0.025, with an average value of 1857 HK0.025 and a standard deviation of 78 HK0.025.

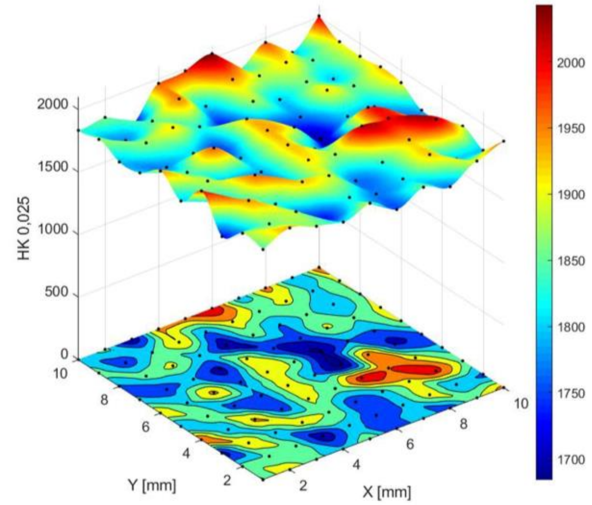


Fig. 3. Knoop microhardness HK0.025 distribution on the AlTiN surface, 10x10 mm area with 1 mm step

Phase analysis was also performed for the coating tested in its initial state. It is shown in Figure 4

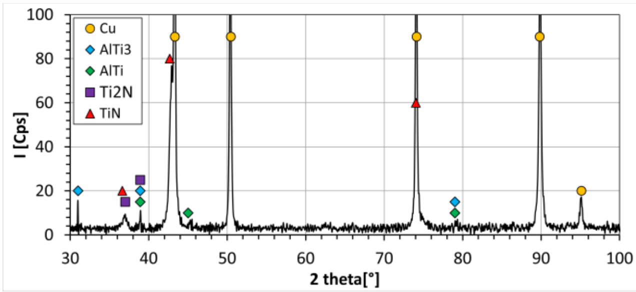


Fig. 4. The XRD diffraction for nitride protective coatings AlTiN (55/45 at.%) on the copper substrate, using copper lamp with a wavelength l = 1.54 [Å]

The analysis showed 4 different phases and a copper signal from the Cu substrate. The phases were: AlTi tetragonal (03-065-5414), $AlTi_3$ hexagonal (03-065-7534), Ti_2N tetragonal (01-076-0198) and TiN face centre cubic (03-065-5774).

The analysis of the Al-Ti phase diagram allowed us to conclude that the tetragonal AlTi phase should be the dominant in terms of quantity. The adjacent $AlTi_3$ phase is the result of microsegregation of components during the layer application. Moreover, both discussed phases are characterized by a wide range of possible concentrations, which in their immediate vicinity may lead to structural differences in their separation zone [17].

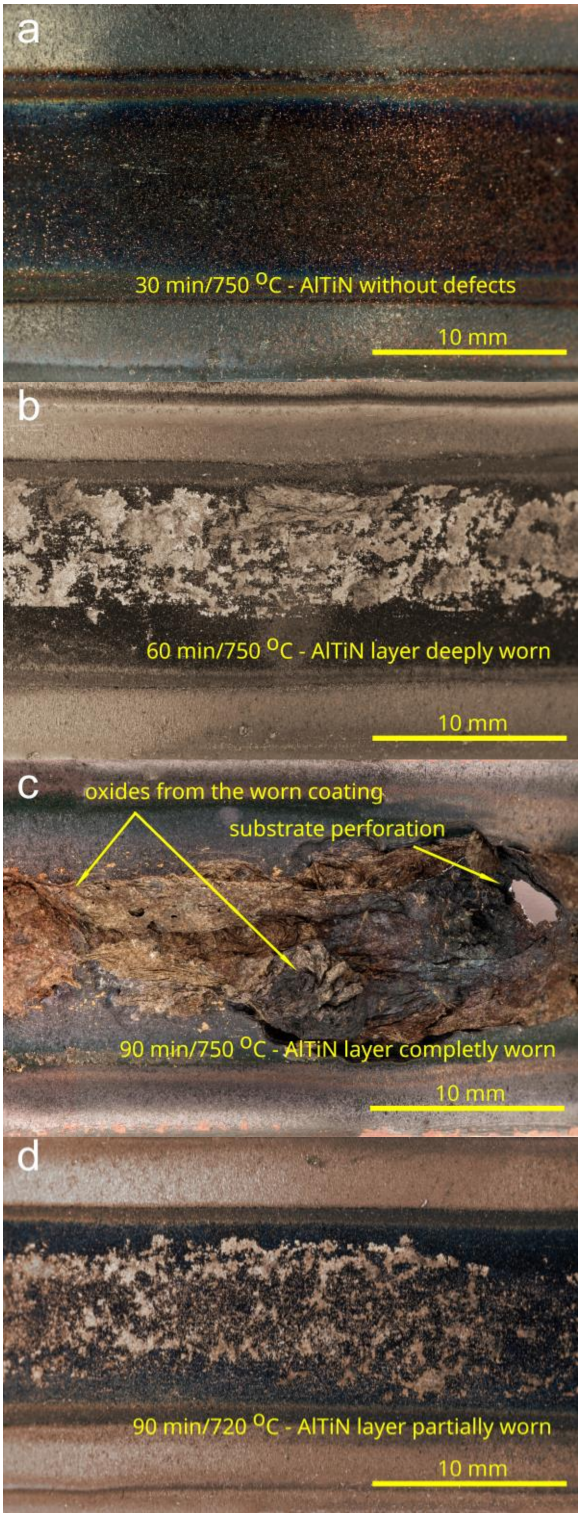
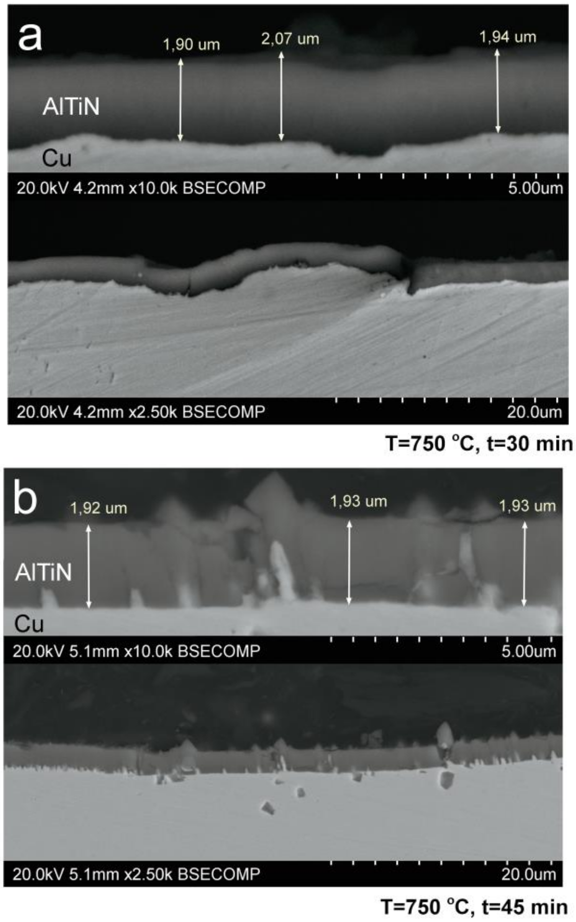


Fig. 5a). AlTiN cover after 30 min./750 ˚C, SLSD = 31.6 m, b) AlTiN cover after 60 min./750 ˚C, SLSD = 63.3 m, c) AlTiN cover after 90 min./750 ˚C, SLSD = 95 m, d) AlTiN cover after 90 min./720 ˚C, SLSD = 95 m

Next, two identified phases were formed as titanium nitrides. According to the equilibrium system Ti-N , the dominant phase in this case is TiN. The Ti_2N phase is formed as a result of the phase transformation of the TiN phase. Moreover, its area of occurrence is very limited [18].

After the initial state of the tested samples was defined, the layer/liquid metal interaction test began. The tests were done in an argon purge atmosphere. The liquid metal in contact with the coating was a 2017A alloy [19]. The tests were carried out for samples composed of two halves. The internal diameter D of the tested ring was 50 mm; width was 20 mm and 1 mm thickness of the wall was 1mm. The rotation speed during the test was 7 rpm. During 1 rotation cycle, the road of liquid metal drop relative to the inner surface was 0.15 m. Tests variant conditions are presented in the Table 1. Macrostructures observed on the surface of the samples after different test parameters are shown in Figure 5. Microstructural tests were also performed on the cross-sections of individual variants. They are presented in Figure 6.



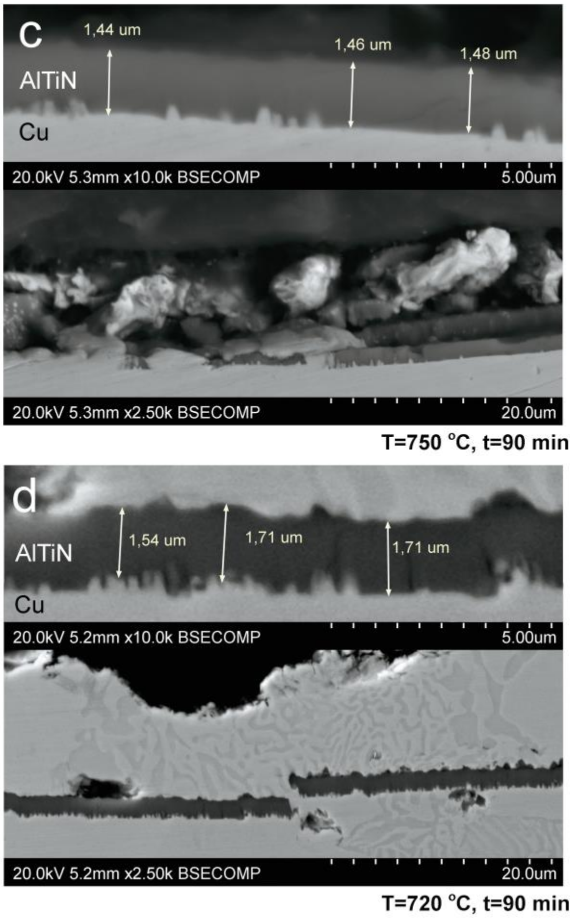


Fig. 6a). Cross-sections of Cu/AlTiN after 30 min. / 750 °C contacts with liquid phase of 2017A, b) cross-sections of Cu/AlTiN after 60 min. / 750 °C contacts with liquid phase of 2017A, c) cross-sections of Cu/AlTiN after 90 min. / 750 °C contacts with liquid phase of 2017A, d) cross-sections of Cu/AlTiN after 90 min. / 720 °C contacts with liquid phase of 2017A

AlTiN layer on a surface of samples tested at 750 ˚C are destroyed after 90 min. This is illustrated on Figure 5c, 6c and 8b. Then, a complete degradation of the surface was began. Then, as a result of the interaction of the liquid aluminum alloy with the copper substrate, a eutectic reaction occurs. The eutectic temperature in the Al-Cu system is only 548.2 °C [17]. At a test temperature of 750 °C, this leads to perforation of the copper substrate. This effect is shown in Figures 5c and 8b. Shorter exposure times at the same temperature cause only a gradual wear of the coatings, manifested by a decrease in their thickness and local losses. This can be seen in the Figures 5a, and 5b. However, the presence of the AlTiN layer prevents the substrate from reacting with the liquid metal. Moreover, decrease of the temperature at 30 degrees, strongly limited degradation of AlTiN cover. This effect is visible on Figures 5d and 6d. The same exposition time, 90 min at lower temperature prevents damage of the sample.

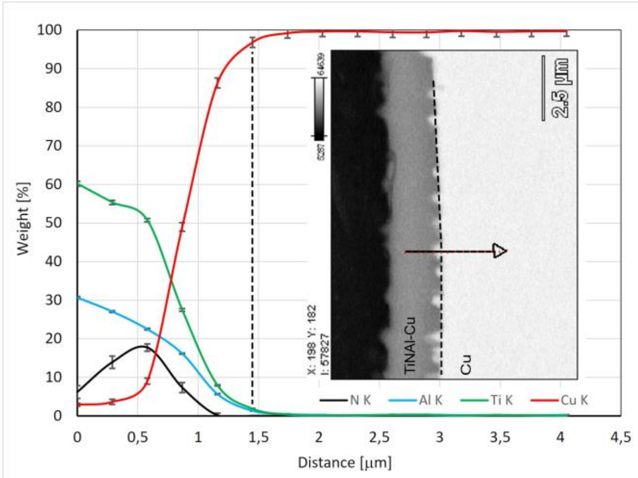


Fig. 7. Linear chemical composition for AlTiNCu/Cu boundary after 60 min / 750 °C, correspond to Figures 5b and 6b

The structure of the substrate/coating interface was also analyzed for the 60 min / 750 °C variant. for changes in chemical composition. This is shown in the Figure 7. From the side of the copper substrate, a copper diffusion-enriched area can be observed. It is formed as a result of contact diffusion accelerated by high temperature. This change is linear, indicating a constant rate of diffusion. The top layers of the coating, which are in direct contact with the liquid metal, show a chemical composition consistent with the structure of the AlTiN phase, with a trace content of copper from the substrate. Only a long time of exposure to temperature can result in diffusion of copper up to the surface layers. Then there is a weakening of the protective coating and the process of its degradation begins. After the appearance of defects in the continuity of the protective coating, the Al-Cu eutectic reaction occurs and the perforation of the substrate appears in Figure 5d.

4. Discussion of the results

The parameters of the AlTiN coating in the initial state corresponded in thickness and hardness to the values obtained by other authors. A comparison of the microhardness results to the data of authors [4] were done. Tests carried out on an pure AlTiN layer of similar thickness, on a steel substrate, with using the Vickers method gave results on in the range of 2100 HV0.05 to 2500 HV0.05 with tolerance about 200-300 HV. In [5] authors reported microhardness about 33.3 GPa, for a multilayer AlTiN /AlCrN. After recalculated this value correspond to 3400 HV.

Surface microhardness in this paper (Figure 3) were carried out using the Knoop method give a mean value 1857 HK0.025, using a penetrator with an high opening angle of 172.3°. This allows for a much smaller impression depth than with the classic Vickers method. Based on the analysis of the relationship between hardness of Vickers and HK the authors [20] noted that the results of hardness of Knoop values compared to HV are lower. After recalculating from Knoop to HV, according [20], mean value of microhardness from Figure 3 is an equivalent of about 2200 HV.

The observed scatter of results are a consequence of the inhomogeneous thickness of the measured layer. The lowest results obtained may be a result of the layer being too thin locally and interacting with the substrate.

The samples were subjected to successively longer test cycles. For variant SLSD = 31.6 m (30 min / 750 °C) (Figures 5a and 6a), the surface of the AlTiN phase shows signs of exposure to temperature and contact with liquid metal. However, no pitting, chipping or other signs of mechanical wear were observed.

Increasing the test time to 60 min in variant SLSD = 63.3 m (Figures 5b and 6b) resulted in a clear disturbance of the surface of the protective coating. The first cavities and surface irregularities on which aluminum oxides are deposited are visible. The item is not perforated.

In the case of variant SLSD = 95 m (90 min / 750 °C) (Figures 5c and 6c), the interaction time of the metal drop with the AlTiN coating was so long that the coating was destroyed. Moreover, there was a perforation of the substrate without protection. After the protective coating was damaged, the 2017A liquid alloy came into direct contact with the copper substrate.

According to the work [21], the formation of Ni/Al phases and the complete disappearance of the liquid aluminium phase took place after only 2 minutes. This high reaction rate is confirmed for the AlTiN/Cu vs. 2017A system, where rapid perforation of the substrate by the liquid metal is observed when the protective coating is damaged.

The high affinity of the metals that contact the substrate, supported by rapid diffusion in the liquid phase, led to the formation of low-melting phases as a result of the perforation of the substrate, showed in Figure 8.

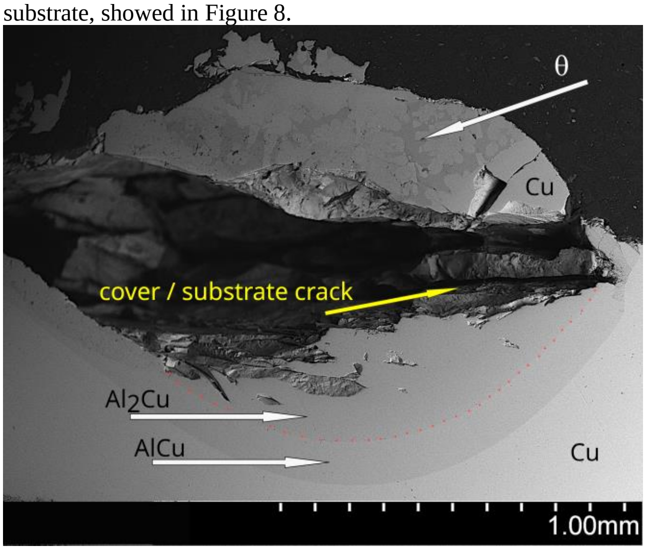


Fig. 8. Surface of the sample after 750 °C / 90 min. Protective coating AlTiN not exist and results of the eutectic reaction are visible

The last variant SLSD = 95 m (90 min / 720 °C) (Figures 5d and 6d) of the test was carried out under the same conditions as the previous SLSD = 95 m (90 min / 750 °C), but with a temperature lower by 30°. It turned out that the degree of wear of the coating was similar to that of variant SLSD = 63.3 m (60 min / 750 °C). The coating was partially damaged, but it was not perforated. XRD analyse showed in Figure 9 was not detected continuous AlTiN cover on the copper surface. Despite significant destruction (cracking) of the coating, its fragments still act as a separating element between the 2017A liquid alloy and the copper substrate (Figure 6d). The lower temperature also reduced the reactivity of the metals in contact. This allows us to conclude that even a slight reduction in temperature can significantly extend the service life of protective coatings.

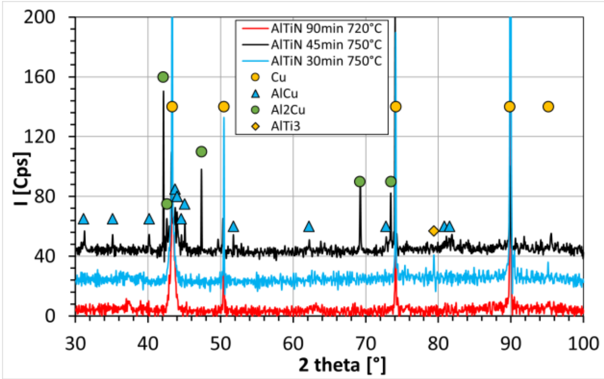


Fig. 9. The XRD diffraction on surfaces of the tested samples after exposure to different conditions, using copper lamp with a wavelength l = 1.54 [Å]

Another phase analysis of the surface composition of the samples was performed after exposure to various conditions. The summary results are shown in Figure 8 and Figure 9.

The phase diagram analysis shows that the $AlTi_3$ phase still exists on the surface for the samples given 30 min. of exposure to 750 °C (SLSD = 31.6 m). It also proves the highest corrosion and temperature resistance of this phase. At the same time, no phases are observed resulting from the reaction of the 2017A alloy with the copper substrate. The only additional phase identified for this sample was the copper substrate, which generates a signal as a result of the thin coating.

Extending the exposure time to 60 min. (SLSD = 63.3 m) while maintaining the same temperature has already resulted in a coating deterioration, as evidenced by the peaks of the AlCu and Al_2Cu phases. These phases were created as a result of the direct contact of the tested alloy with the substrate, and their presence proves that the protective coating was broken.

Sample 90 min / 720 °C showed in Figures 5d, 6d and Figure 8b was exposed by the longest time on the contact with 2017A liquid alloy. The variant used in this case had a duration of 90 min. (SLSD = 95 m), with the temperature reduced by 30 degrees, that is, 720 °C. In this case, the phase analysis shows only the peaks originating from the copper substrate. The presence of aluminum-copper phases was not found, which proves the alloy lack of contact of the tested with the substrate. There are also no signals from the AlTiN protective coating. Fragments of the protective coating were covered by products of the eutectic reaction, which took place in the places where the protective coating was destroyed. This situation can be observed on a Figures 5d, 6d. Direct contact of the liquid 2017A alloy with the copper substrate led to the formation of a low-melting eutectic phase, which began to cover the surface with an even layer as a result of the swirling motion of the sample. The contact of both components, limited by the remains of the coating, limited the rate of this reaction, thanks to which there was no perforation of the sample. This proves that the occurrence of the limit moment, the protective coating in the middle zone of the sample, has practically ceased to exist.

The coating destruction is favored by microstructural inhomogeneities that can be observed on the surface of the AlTiN coating (Figure 2c). These places are the weakest points, and there may be mechanical losses (chipping) as well as a strongly developed surface, which leads to corrosion.

The proposed method allows performing tribological tests in the substrate / metal drop system. Despite the analogy to the classical method used in tribology, attention should be paid to the much greater role of the test temperature. In the case of contact of two solids, the temperature affects the friction coefficient, however, the role of diffusion processes is very limited. The working mechanisms are based on adhesion. On the other hand, the test in the solid / liquid system introduces diffusion processes into the system and consequently, intensive mass transport from the substrate to the metal drop. The diffusion coefficient D is given by the formula [22]:

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \qquad (2)$$

Where:
D is the activation energy of diffusion Q [kJ/mole]
D_0 is the preexponential constant [m^2/sec]

The key parameter for diffusion processes is the value of the diffusion activation energy Q. It decreases with increasing temperature, which in turn translates into a high intensity of matter-exchange processes.

The introduction of an additional protective coating into the system, as shown in Figure 9b, causes a strong limitation of atomic exchange due to the existence of a boundary with high-energy diffusion activation [23]. Only destruction of this layer can lead to an intensive atomic exchange reaction at the substrate / liquid metal interface. This method is best suited for testing the resistance of high-temperature protective coatings designed to protect the substrate from reacting with liquid metal. The tests showed that after the protective coating of the substrate was broken, the material quickly degraded, leading to perforation, as shown in Figures 10a and 10b.

The experiment shows how much the applied conditions affect the durability of protective coatings. A slight reduction in the process temperature can significantly extend the service life. In the tested case, lowering the temperature by 30 degrees extended the life of the coating by more than two times.

The path of the liquid metal droplet relative to the AlTiN layer on the copper substrate amounts to SDSL=37 ... 95 m, depending on the adopted variant, is of the same order as for pin-on-disk tests. The SD parameter in the work [4] reached values of 126 m, 251 m and 377 m, while it was 31 m during high temperature tests [5]. The comparison of these results shows that the proposed test method can complement the classical pin-on-disk test [1,2] by measuring interactions in the solid-liquid system. The SDSL parameter in this case is equivalent to the SD parameter from the classical test in the solid/solid interaction system.

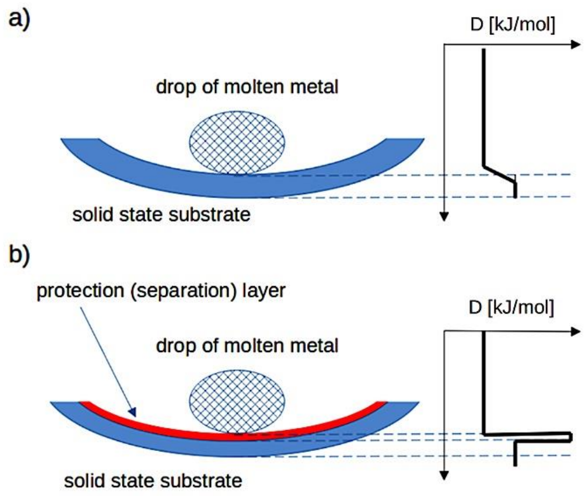


Fig. 10. Relationship of diffusion coefficient for a) direct contact of two metals at different states of matter and b) system with interlayer from high melting point phase

5. Summary

The investigated AlTiN coating provides substrate protection against liquid alloy 2017A by 90 min at 720 °C. It is equivalent to the path of contact equal 95 m. Temperatures higher than 30° reduce a protection time more than 2 times.

The presented method allows the solid / liquid contact wear test to be carried out. The parameter introduced ‘solid / liquid sliding distance” (SLSD) is an analogy to the sliding distance (SD) in typical tribological tests carried out in the sample / counter-sample system and may be the basis for direct comparison of the results obtained for different samples.

The described method enables an immediate visual assessment of the tested materials. This is a very useful feature for industrial research, where the time to get a result is important. Depending on the needs, a more sophisticated but also time-consuming e.g. SEM or XRD analysis can be applied.

Acknowledgments

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