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Cast Alloy Soldering Tendency and Corrosion Resistance of Duplex PVD Coatings for Application on Die Casting Tools for Aluminum Alloys Processing

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ABSTRACT

Wear resistance of die casting tools used for aluminum alloys processing is successfully increased by application of duplex PVD nitride coatings. However, their performance greatly depends on few surface characteristics which are often overlooked. These are coatings topography, growth defects morphology and variable nature of surface chemistry. This investigation concerned H11 steel, plasma nitrided steel, CrN and TiAlN PVD coatings deposited in the form of duplex layers, all prepared on different levels of surface roughness. Soldering and corrosion behavior in cast Al-Si-Cu alloy were evaluated by an ejection test performed on conventional and delayed alloy solidified samples. The coatings outperformed steel and nitrided treatments and exhibited no reaction with the cast alloy in both experimental configurations. By decreasing the coating roughness, the ejection force from the conventionally solidified castings considerably increased. However, the highest ejection force that was recorded for post deposition polished coatings, with delayed solidification, decreased as a consequence of coating oxidation. Corrosion of the nitrided substrate developed through the defects in the coatings, but the observed damage did not compromise coating integrity. In order to achieve the highest coating performance, besides selection of appropriate coating type, focus should be on the surface morphology and transformations of coatings during their use.

INTRODUCTION

The application of light alloys for complex structural automobile components is rapidly growing. Consequently, there are increasing demands for mass production of high pressure die cast parts. A highly efficient and economical production process which results in high quality castings is required to compete in this industry [1].

High pressure die casting is a mass production technology of light alloys in which the cast metal is under high pressures injected into a steel die (tool) and then allowed to rapidly solidify. In this process, tool surfaces are exposed to severe environment which causes tool wear. Due to wear, tool operation becomes difficult, production efficiency decreases, castings lose tolerances and quality of their surface finish deteriorates [1]. Continuous application of worn tools in production endangers integrity of both castings and tools. [1].

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Before every casting cycle, a protective die lubricant is applied on tool surfaces which serve as a barrier between tool material and liquid casting. However, in some areas it gets removed due to the impingement of high-velocity molten metal. The exposed surfaces easily wear by erosion, corrosion and by sticking and soldering of cast alloy. Additionally, the alternating heating and cooling cycles induce material fatigue (thermal fatigue) which manifests in network of cracks on tool surfaces [2]. These wear mechanisms act simultaneously and produce cavities, or built-up layers on tool surfaces which hamper the casting ejection. Nowadays, the cast alloy soldering becomes a major concern in high pressure die casting industry as it increases the production costs through increased tool maintenance [1].

To combat wear of high pressure die casting tools, diffusion layers, thin ceramic coatings and their combinations in form of duplex layers have been applied [2–4]. Coatings produced by physical vapor deposition (PVD) have a range of required mechanical properties, oxidation resistance and high chemical inertness in molten metals [1–3]. These coatings efficiently suppress different kinds of wear and especially erosion and corrosion caused by fast moving molten aluminum [2–4]. However, PVD coatings are also prone to formation of cast alloy built-up layer (mechanical soldering) on their surfaces [1,5]. Although not detrimental, such layer hampers castings ejection and increases tool maintenance costs [1].

Over the years, numerous investigations studied the performance of PVD coatings for high pressure die casting tools. However, few very important aspects are rarely considered in development of these layers. It is well known that surface roughness greatly affects coatings adhesion, casting surface quality and tool costs. Still, coating surface roughness is scarcely recognized as a property that essentially affects the high pressure die casting tool performance. Presence of growth defects and their influence on the protective function of coatings are often neglected. Also, coatings properties which change during their service (i.e. surface chemistry) are rarely systematically studied to understand their effects on the properties of high pressure die casting tools. Therefore, it is essential to further investigate coating deterioration mechanisms and to develop PVD coatings with properties specifically tailored for application on high pressure die casting tools.

This investigation addresses soldering and corrosion of H11 hot-working tool steel, plasma nitrided H11 steel, and CrN and

TiAlN duplex coatings by ejection test with conventional and delayed solidification. Effect of coatings surface roughness on their performance was also studied in the presented investigation.

EXPERIMENTAL METHODS

Samples and Preparation Methods

The investigation used quenched and tempered H11 (EN X27CrMoV51), hot-worked tool steel, plasma nitrided H11 steel, and CrN and TiAlN coatings produced as duplex layers on plasma nitrided samples of H11 steel. Cylindrical pin-shaped samples (ϕ15 mm × 100 mm) were produced by procedures regularly employed in production of high pressure die casting tool parts (Fig. 1 a). Surface finish was obtained by fine grinding and polishing using diamond paste of 6 µm and 3 µm granulation.

Plasma nitriding was performed by ION-25I (IonTech) unit in a 12-hour processing cycle. Coatings were deposited using two industrial deposition units. Under-stoichiometric CrN coatings were deposited in thermionic arc ion plating system BAI730 (Balzers) and TiAlN coating in CC800/7 (CemeCon), an unbalanced magnetron sputtering system. Plasma nitrided samples were polished prior to coating deposition to remove the compound layer and to enhance coating adhesion. In order to accurately compare performance of different materials, samples were produced applying the same surface finishing treatments. However, the coated samples were prepared with two additional degrees of surface roughness. The rougher group was prepared by fine grinding followed by polishing (6 µm), while the finest surface finish was obtained by post deposition polishing using diamond paste of 3 µm granulation. Denotations of samples are presented in Table 1.

Table 1. Denotations of samples used in experiments

	H11	PN	CrN	TiAlN
Rough samples (R)	-	-	CrN-R	TiAlN-R
Smooth samples (S)	H11-S	PN-S	CrN-S	TiAlN-S
Post polished samples (PP)	-	-	CrN-PP	TiAlN-PP

Evaluation of Soldering Tendency - Ejection Test

Cast alloy soldering (sticking) tendency was evaluated by ejection test. In this test, a pin sample is used as a core for production of a simple casting with a hole (Fig. 1 b and 1 c). After the casting process a pin-casting assembly is obtained (Fig. 1 c). A tensile testing machine ZDM 5/91 (VEB) was used for ejection of pin samples from castings. During ejection, a force-displacement curve was recorded (ejection curve). This test imitates the process of core removal from a casting produced by a high pressure die casting process. The force recorded during the test carries information about soldering tendency of cast alloy toward pin material. Production of pin casting assemblies were performed in two types of experiments, i.e. by conventional and delayed casting solidification. The conventional casting experiment was performed by gravity melt pouring of A380.0 (EN AC-46200) aluminum alloy, at temperature of 730 °C, into a specially designed steel die (Fig. 1 b), preheated to temperature of 320 °C. The experiments with delayed solidification were conducted using the same die, which was preheated to temperature of 600 °C. Upon filling the die cavity, the die was placed into furnace heated to 700 °C for 5 and 20 minutes in order to prevent casting solidification. After the predetermined time, the die was taken out and the casting was allowed to solidify. This experimental procedure was been developed to enhance the corrosion processes that occur between casting and pin sample. Abbreviations used for denotation of the experiments are: CS-conventional solidification, DS-delayed solidification (5 min, 20 min).

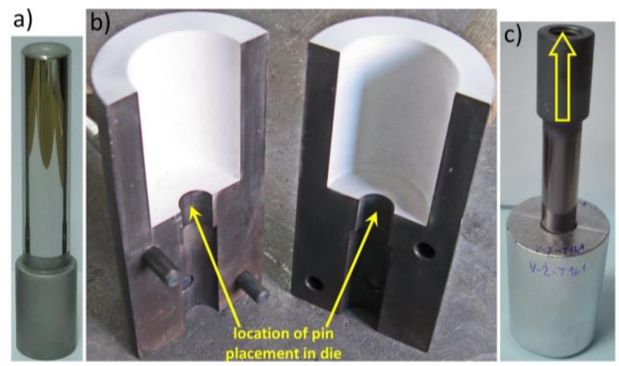

Figure 1. a) Pin sample, b) experimental casting die, c) pin-casting assembly

Characterization of Samples

Surface topography was acquired by 3D-profilometer (Taylor Hobson Talysurf). Instrumented hardness tester H100C (Fischerscope) was used for determination of mechanical properties of layers and thin coatings. During indentation, a load of 100 mN loads was applied. After the ejection tests, the sample surface morphology and cross section were examined. A confocal optical microscope was used (CFM), Axio CSM700 (Zeiss). A focused ion beam (FIB) was used for sample surface characterization. Also, a Helios Nanolab 650i (Fei) and a Scanning electron microscope (SEM), Ultra Plus (Zeiss) were used for characterization. Both instruments were equipped with energy dispersive spectroscopy (EDS).

RESULTS AND DISCUSSION

Properties of Investigated Materials and Layers

Mechanical properties and thickness of investigated materials and layers are presented in Table 2. All samples were made of H11 steel, bare ones and ones which were additionally treated by plasma nitridng and duplex treatment had same starting mechanical properties. The nitriding process resulted in a 100 µm thick layer of high hardness. This layer is appropriate for both the direct application on die casting tools and as a support for CrN and TiAlN coatings produced in form of duplex composites. Properties of investigated duplex coatings are sufficient for achieving significant improvement in erosion wear resistance and suppression of thermal fatigue of high pressure die casting tools. Surfaces of produced coatings are characterized by typical growth defects, nodules, pinholes and craters.

Table 2. Properties of investigated materials and surface layers

	H11	**PN**	**CrN**	**TiAlN**
Hardness [HV_{kgf}]	455 HV_{30} ±41	1300 $HV_{0.01}$ ±76	2575 $HV_{0.0025}$ ±208	3600 $HV_{0.0025}$ ±655
Thickness [μm]	-	100 ±10	2.7 ±0.2	3.4 ±0.2

Ejection Tests

During the ejection tests, ejection curves which represent change in force with the traveled distance are recorded. At the beginning of the ejection process force increases until it reaches the maximum. After reaching the maximum, force constantly decreases until the pin is entirely ejected. The highest recorded force is the force required to start the pin ejection, and its value can be used as a single quantitative parameter defining the soldering tendency. Beside this parameter, a work of the ejection force can be calculated as the area under the ejection curve.

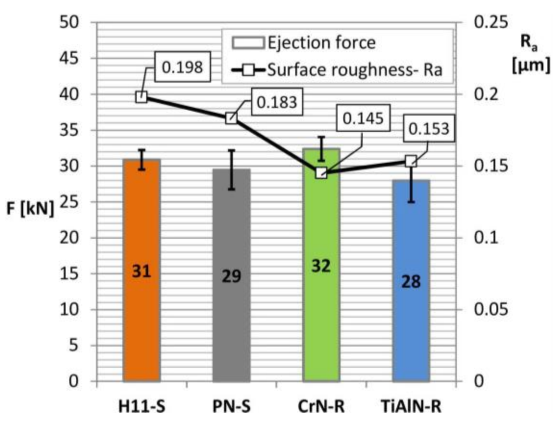

Figure 2. Average values of maximal ejection force obtained for various materials, with comparable arithmetic average roughness (R_a), in CS experiment, error bars represent ±1 measurement standard deviation (SD)

The average values of maximal ejection force recorded in the ejection tests of the conventionally cast samples are shown in Fig. 2. In order to make a relevant comparison between different materials, samples with approximately the same degree of roughness (R_a) were compared. A negligible difference in ejection force was observed between samples of different chemical composition. Mostly, these differences fall in the range of testing deviations, which did not exceed 10 % of the average value. The identified trend is not in agreement with the results published in earlier investigations [2,3]. In the cited studies, considerably higher force was recorded for H11 steel and plasma nitrided H11 steel than for samples coated with PVD nitride coatings. Disagreement with their results can be explained by the fact that the studies neglected the effects of surface topography on ejection performance. Considering that surface topography predominantly affects the initial mechanical pin-casting interlocking conditions, disregarding its influence can lead to inaccurate interpretation of results [1]. It will be seen in the following that for coated samples surface topography has more pronounced influence on the ejection process than chemical composition of sample materials.

A cast alloy built-up layer was found on surfaces of all pin samples, regardless of applied experimental configuration (CS, DS). The morphology of built-up layers mostly depends on surface morphology (grinding marks, coating defects), while its thickness depends on surface chemistry. Thickness of built-up layer on H11 and PN samples was up to 45 μm, while for CrN and TiAlN coated samples built-up layer was only 12 μm thick. Built-up layer was easily dissolved by NaOH solution from all samples which were prepared in CS experiment configuration. No remnants were found after treatment by NaOH solution. On the other hand, after dissolving the built-up layer from H11 and PN samples which were prepared in DS experiment, corrosion attack was revealed on the sample. This means that CS experiments consider mechanical soldering, while DS experiments consider metallurgical soldering processes.

Figure 3 presents the results of the ejection tests obtained for CrN coatings of different roughness, submitted to both types of experiments. For the samples obtained in CS experiments the ejection force increases as the coating roughness decreases. Similar trend was also observed for TiAlN coating. In our previous study [1], it has been shown that the pin-casting contact is completely interlocked. Therefore, the observed trends can be explained only by different shearing phenomena and stress concentrations that develop on the pin-casting interfaces of samples with different roughness [1]. During ejection, the tops of the asperities of rough samples (CrN-R) facilitate casting material shearing at lower ejection forces. On the other side, post polished samples (CrN-PP) do not have stress concentrators (marks, nodular defects). Considering that cast alloy adhesion is high, shearing might develop only inside the casting material. Accordingly, the ejection force needed to start the shearing (ejection) is high. When it comes to the smooth coated samples (CrN-S), the ejection conditions lie in between the two conditions previously explained, and accordingly the values of their ejection force. As it can be seen from topographic image in Fig. 3, the surface of CrN-S sample is smooth but contains nodular coating defects which stand out from the rest of the surface and act as stress concentrators during the ejection. This effect is much more pronounced for TiAlN coating which is characterized by a higher density of nodular defects [1].

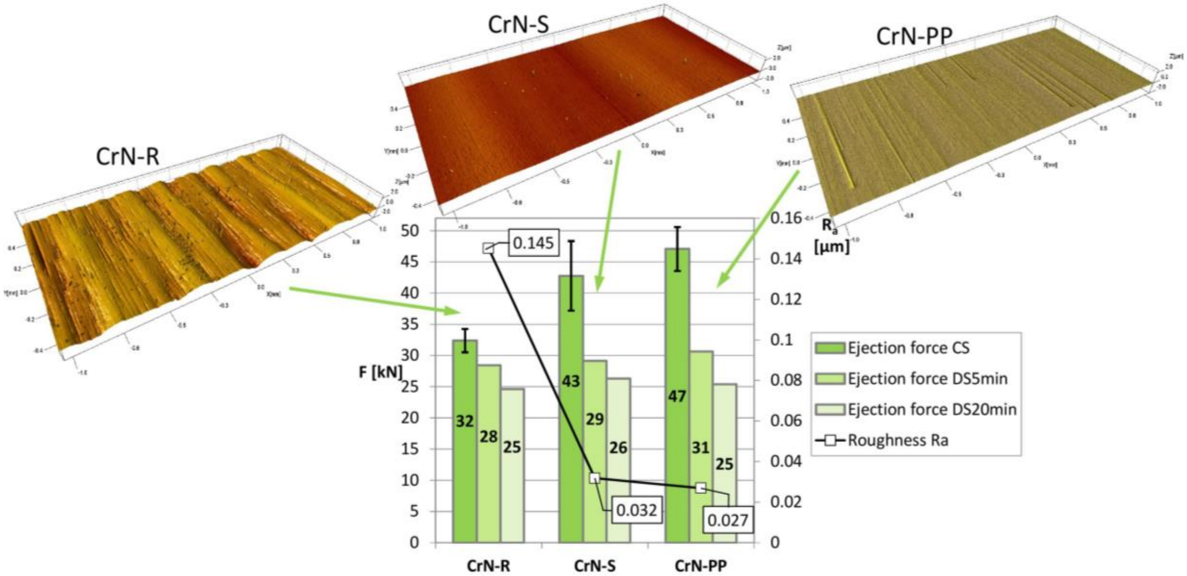

Figure 3. Ejection force values for CrN sample with different roughness, tested with different experimental configurations (CS, DS) error bars represent ±1 CF (confidence interval), images are representative surface topographic images of coated samples.

Figure 4 presents the values of ejection force obtained for different materials in all testing configurations. Results are shown only for some of the most interesting groups of surface finishes (roughness). The values of ejection force for H11 sample increase as the time in contact with molten aluminum increases. This occurs due to progression of corrosion and formation of intermetallic compounds between pin and casting material that create strong bonds. The surface of PN samples were seriously corroded, however the intermetallic layers on these samples are brittle and do not form strong pin-casting bonding. Accordingly, the ejection force of PN samples is nearly the same for all experimental configurations.

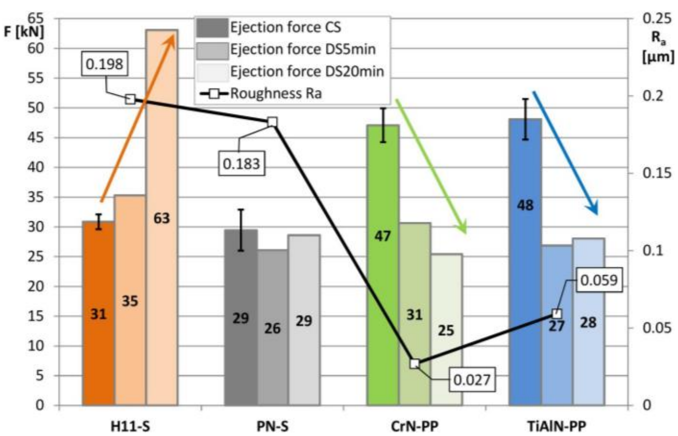

Figure 4. Average ejection force recorded for different materials subjected to CS and DS experiments; arrows indicate the trends of ejection force.

Completely different trend was found for coated samples. As can be seen from diagrams in Fig. 3 and Fig. 4, the force required for ejection of CrN and TiAlN samples which were obtained in DS experiments was significantly lower (around 35 %) than for samples obtained in the CS experiments. In the experiments with DS outer layers of coatings underwent some changes which induced a large decrease of ejection force, even for the post polished samples. Beside changes in color, the macroscopic and CFM analysis did not reveal any substantial changes of coating layers. Further surface characterization was performed by SEM, FIB and EDS.

Characterization of Surface Layers after the Ejection Tests

FIB-SEM cross-sectional image and results of EDS analysis of CrN-R sample obtained in DS-20 min experiment are presented in Fig. 5. These analyses revealed several changes of CrN coating. On the outer CrN layer oxidation is revealed, and both the outer and interfacial-substrate layer increased their nitrogen content. In Fig. 6 cross sectional image of fractured CrN-R sample with remained cast alloy built-up layer is shown. Here the changes in microstructure that occurred during DS experiments on the outer and interfacial-substrate layer are evident. In the regions with increased nitrogen content pronounced columnar grains of CrN formed. Furthermore, in the close-up insert of Fig. 6 the arrows point on the oxide layer of CrN coating, which has a fine-grained microstructure and thickness of about 150 nm. Analysis performed on the oxidized surfaces, not presented herein, revealed a polygonal shape of a fine-grained oxide products. Formation of very thin oxide layer was also detected for TiAlN coating submitted to 20 minute DS experiment.

The oxidation of under-stoichiometric (Cr_2N) coating occurred by a well-known mechanism. Oxidation develops at high temperatures by outward diffusion of Cr and inward diffusion of O, where Cr_2O_3 oxide layer forms with underlying nitrogen enriched layer [6]. On the other side, oxide layer that forms on TiAlN coating is usually Al_2O_3 or a double oxide layer of both

Al_2O_3 and TiO_2 [7]. Considering that oxides were only formed on coated samples that were subjected to delayed solidification, the reduction of ejection force with the time samples stay in molten alloy can be linked to formation of those oxides. This link might be explained by high inertness of Cr_2O_3, Al_2O_3 and TiO_2 oxide layers in contact with molten aluminum and thus weaker adhesion of cast alloy [2]. Additionally, lower shear strength (low coefficient of friction [4]) and polygonal shape of oxide products will decrease friction during pin release and sliding over casting surfaces.

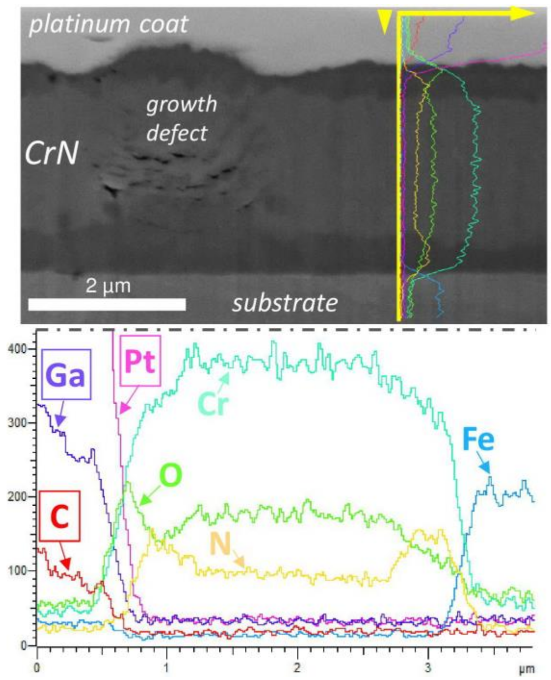

Figure 5. FIB-SEM and EDS cross-sectional analysis of CrN-R sample after the DS experiment of 20min

The intensive die pre-heating process in experiments with delayed solidification (600 °C) can certainly induce oxidation of sample surfaces. On the one side, this could be regarded as a defiance of the experimental method. On the other side, such condition considers the oxidation process that develops during longer service of a coating in a real production, in a period after the running-in stage [8].

On surfaces of all coated samples subjected to the 20 minutes DS experiments typical corrosion sites appeared. One of the most representative sites, presented in Fig. 7 a, was detailly evaluated by FIB-SEM and EDS analysis (Fig. 7 b). These corrosion sites typically appear in form of craters filled with cast alloy and porous material. Cross sectional analysis revealed that these sites are craters formed by wrenching or flaking of typical nodular defects. Bottom of these craters mostly establishes direct contact with the underlying substrate.

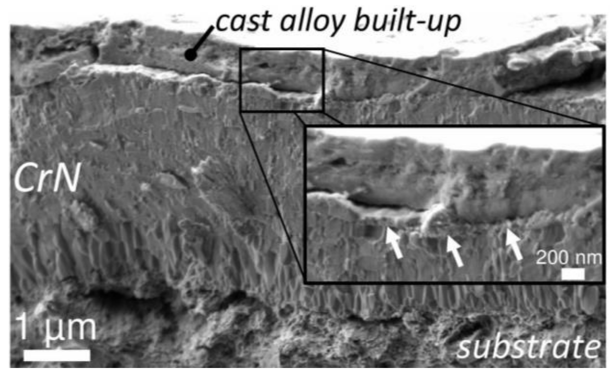

Figure 6. Cross sectional analyses of CrN-R sample after the ejection test with20 minute DS experiment, arrows in the insert of close-up image point on oxide layer of CrN coating

In the analyzed site, material from the crater is in direct contact with the underlying porous region of the substrate. The EDS analysis revealed that material contained in the crater is a corrosion product that formed by dissolution of Fe and Cr from the substrate material. The porous region of the substrate contains Al and Si from the cast alloy, possibly in form of their oxides. This analysis shows that cast alloy induced corrosion and dissolution of nitrided substrate through crater defects present in the coatings. However, the observed stage of damage does not endanger coatings integrity. For application, it is important that in all investigated cases the volumetric change caused by formation of intermetallic phases, between the cast alloy and substrate material, does not induce coating spallation. The observed corrosion phenomena are the most frequently detected on the post deposition polished coatings, as these samples have the largest density of crater defects.

CONCLUSIONS

The presented investigation employed ejection test for the evaluation of Al-Si-Cu alloy soldering tendency toward H11 hot-working tool steel, plasma nitrided H11 steel and CrN and TiAlN duplex coatings. Experimental examination was conducted employed conventional and delayed solidification of Al-Si-Cu cast alloy in contact with experimental pin samples. Additionally, the performance of duplex coatings is evaluated on samples prepared to a range of surface roughness.

The mechanical characteristics of investigated plasma nitrided layer and duplex CrN and TiAlN coatings are appropriate for the application on high performance high pressure die casting tools.

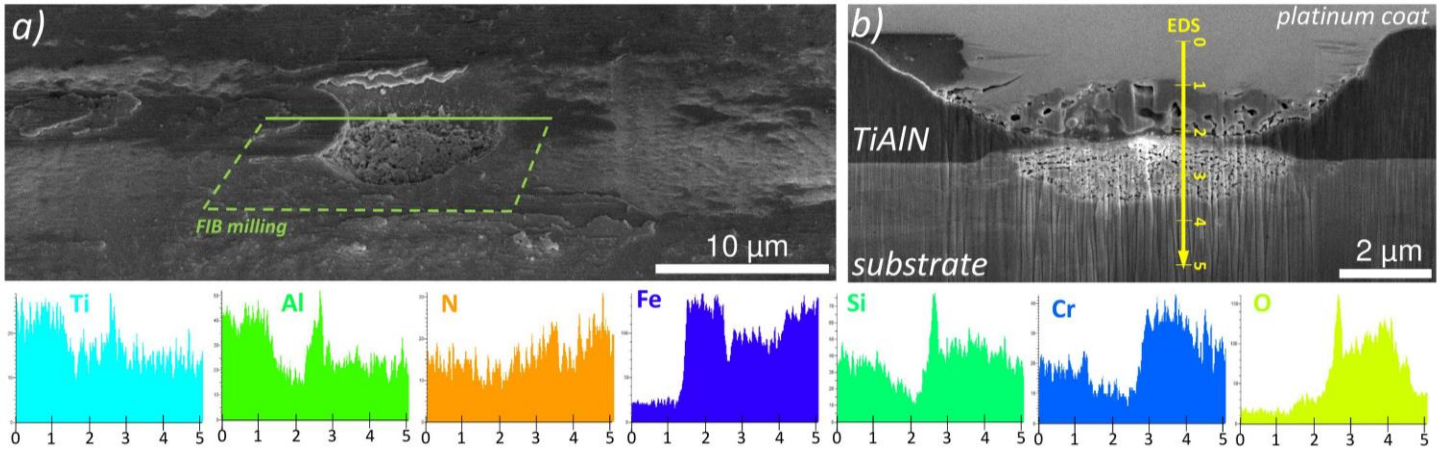

Figure 7. Analysis of corrosion process in crater of TiAlN-R sample submitted to 20 minute DS experiment, a) FIB-SEM image of the examination area, b) FIB-SEM image of cross-sectional area with indication of EDS line analysis, on the bottom - EDS line spectra.

In conventional solidification experiments, all investigated materials displayed a susceptibility to mechanical soldering by Al-Si-Cu alloy. In all cases the identified cast alloy built-up layer formed only by effects of mechanical soldering. The ejection performance of samples coated with CrN and TiAlN in conventional casting solidification experiment greatly depends on their surface roughness. By decreasing their roughness, the ejection force increased. For both kinds of coatings, the highest values were recorded for post deposition polished surfaces. Therefore, it is suggested that efficient application of coatings on high pressure die casting tools require special consideration of surface roughness and topography.

In delayed solidification experiments H11 steel and plasma nitrided steel undergone serious corrosion and H11 steel exhibit very high ejection force. CrN and TiAlN coated surfaces remained intact but corrosion of the underlying plasma nitrided substrate occurred on a micro level through crater coating defects. However, all coated samples tested over a range of surface roughness displayed much lower ejection force in delayed solidification experiments than in conventional solidification experiments. In experiments with delayed solidification on surfaces of CrN and TiAlN coating formation of oxide layers are detected. Due to the formation of these inert oxides (Cr_2O_3 on CrN; Al_2O_3 and TiO_2 on TiAlN coating) cast alloy adhesion is reduced and consequently the ejection force decreased. Therefore, besides selection of appropriate coating type, consideration should be also focused on the transformations of the coatings during exploitation. Additionally, intentional formation of oxide layers on nitride PVD coatings should be also considered as a technique for the elimination of coatings running in-period.

Concerning the corrosion resistance of PVD coatings, their further development for high pressure die casting tools should be directed toward elimination of the negative effects of coatings growth defects.

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