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SEM/TEM INVESTIGATION OF DEGRADATION OF BI-LAYER (Cr,Al)N/Cr2N3 DUPLEX COATINGS EXPOSED TO ALSI ALLOY HIGH PRESSURE DIE CASTING CYCLES

High pressure die casting (HDPC) allows to produce aluminum parts for car industry of complicated shapes in long series. Dies used in this process must be robust enough to withstand long term injection cycling with liquid aluminum alloys, as otherwise their defects are imprinted on the product making them unacceptable. It is expected that nitriding followed by coating deposition (duplex treatment) should protect them in best way and increase intervals between the cleaning/repairing operations. The present experiment covered investigations of the microstructure of the as nitride and deposited with CrAlN coating as well as its shape after foundry tests. The observations were performed with the scanning and transmission electron microscopy (SEM/TEM) method. They showed that the bottom part of this bi-layer is formed by roughly equi-axed Cr_2N crystallites, while the upper one with the fine columnar (CrAl)N crystallites. This bi-layers were matched with a set of 7x nano-layers of CrN/(CrAl)N, while at the coating bottom a CrN buffer layer was placed. The foundry run for up to 19 500 cycles denuded most of coated area exposed to fast liquid flow (40 m/s) but left most of bottom part of the coating in the areas exposed to slower flow (7 m/s). The acquired data indicated that the main weakness of this coating was in its porosity present both at the columnar grain boundaries (upper layer) as well as at the bottom of droplets imbedded in it (both layers). They nucleate cracks propagating perpendicularly and the latter at an angle or even parallel to the substrate. The most crack resistant part of the coating turned-out the bottom layer built of roughly equiaxed fine Cr_2N crystallites. Even application of this relatively simple duplex protection in the form of CrAlN coating deposited on the nitride substrate helped to extend the die run in the foundry by more than three times.

Keywords: duplex coatings; CrN/Cr_2N/(CrN/CrAlN)/CrAlN; SEM; TEM; HPDC

1. Introduction

A high pressure die casting (HDPC) was developed for large scale production of aluminium alloys parts of relatively complicated shapes. It entails a stringent requirements on the dies used in such processes, i.e. they should be resistant to temperature cycling and wear caused both by fast flow of liquid aluminium and friction exerted by as solidified parts during their removal from the die. The early experiment with dies made of tool steel showed, that production need frequent breaks for die cleaning or even overlay welding of the most exposed areas. The improvement was sought in their surface improvement by heat treatment [1], nitriding [2] or additional deposition of ceramic coatings [3]. The most perspective among all of them seems to be the latter approach as it easily allows to increase surface hardness and form a barrier against reaction with liquid aluminium.

The coatings development of the coatings dedicated for dies used in high pressure casting of aluminium alloys went from CrN or CrAlN monolytic ones [3,4], through CrN/AlN multilayers [5] end eventually CrN/CrVN, CrAlN/VN, TiAlN/VN or their combination [6,7]. The former coatings helped to improve both surface hardness as well as protect the steel substrate from interaction of reactive aluminium liquid, while the latter not only helped to achieve even higher hardness (multilayers) but also introduce self-lubricating properties (obtain through step by step oxidizing of VN component). The latest modification of the coatings used for HPDC are aimed at their capping with the Al_2O_3 layer decreasing wetting and reactivity [5]. Most of them are deposited on heat treated nitrided tool steel inserts forming so-called duplex system. It agrees with a generally accepted rule known as "hard over hard", i.e. that harder is the support of the very hard coating the more successful is such combination [8], i.e. rises chances to keep them at the die surface through tens of thousands of injection cycles.

Deposition of coatings on the dies used in HPDC is mostly realized with the arc discharge systems, as they allow to cover

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substrates of relatively large size with metallic or ceramic material in relatively short time [9]. On the low side, such coatings carry a high density of in-flight solidified spherical particles called droplets. At their bottom – due to shadowing effect – form cavities, which may act as notches starting crack propagation parallel to the substrate [4]. Additionally, arc are characterized by a columnar or in case of nano-layers by pseudo-columnar microstructure, with a possible significant porosity at the column boundaries [10]. Presence of these defects might lead to through coating cracking and opening the steel substrate to the attack of the reactive liquid aluminium alloy. The significance of the latter defects was confirmed by immersion test, which showed that aluminium having access to the steel reaction front could fast propagate under otherwise untouched coating [5]. The ultimate assessment of the mechanism of deterioration of the coating systems elaborated for dies used during HP casting could be assessed only through detail microstructure investigation of inserts used in foundry runs. However such results are lacking even for simple monolithic or duplex coatings .

Therefore, the present experiment was planned to cover microstructure characterization of the arc CrN/Cr_2N/(Cr/AlN)/CrAlN coating on the part of the die in as deposited form as well as after casting cycles in the foundry. It was especially aimed at documenting its wear at areas of low and high flow of liquid aluminium. The investigations were performed with scanning and transmission electron microscopy (SEM/TEM) methods.

2. Experimental procedure

The DIN 1.2344 (EN X40CrMoV5.1) tool steel and thermomechanical treatment described in detail elsewhere [11] was used for fabrication of parts of the tested die. After hardening, they were polished, micro-shot blasted and tumbled. Finally, all working surfaces were plasma nitrided and immediately coated with the CrN-buffer/Cr_2N/(7xnano-CrN/AlN)/CrAlN layers (CrAlN). Schemes with arrangement of the individual layers within the coating and of the investigated pin with marked places of fast and low flow of the liquid AlSi alloy, i.e. 40 m/s and 7 m/s respectively were presented in Fig. 1, as well as its image taken after arc deposition process with the CrAlN is presented in Fig. 1.

The microstructure investigations were performed using XL30 (30 kV) FEI scanning electron microscope (SEM) (Eindhoven, Netherlands) and Tecnai G2 F20 200kV FEG transmission electron microscope (Eindhoven, Netherlands) equipped with High Angle Annular Dark Field (HAADF) detector for scanning-transmission (STEM) observations. The local chemical composition was determined with an integrated EDAX Energy Dispersive X-ray Spectroscope (EDS), (Berwyn, USA). The lamellas for TEM observations were prepared using FEI Quanta 200 3D Dual Beam Focused Ion Beam (FIB) (Eindhoven, Netherlands) equipped with Omniprobe (Dallas, Texas) lift out system.

3. Results

3.1. Foundry test-by-work

The as-coated pin covered with the CrN/Cr_2N/(Cr/AlN)/CrAlN layers shows a dull grayish color on all sides of slightly changing shades depending on the illumination conditions (Fig. 2a). The carrying out of a successive injection cycles resulted in its gradually increasing overlapping with thin layer of aluminium changing the surface hue to more whitish one (Fig. 2b). Therefore, every couple of thousands of cycles the accumulated material was removed with Emery paper restoring the pin to as-deposited conditions (under visual inspection). The above procedure was continued up to several tens of injections (on average ~20 000 cycles), after which a thicker layer of solidified aluminium started to accumulate at the pin face accompanied by irregular agglomerates at its sides (Fig. 2c). The above changes of the die working pieces negatively affected the produced castings up to the level necessitating a stop in their production. The

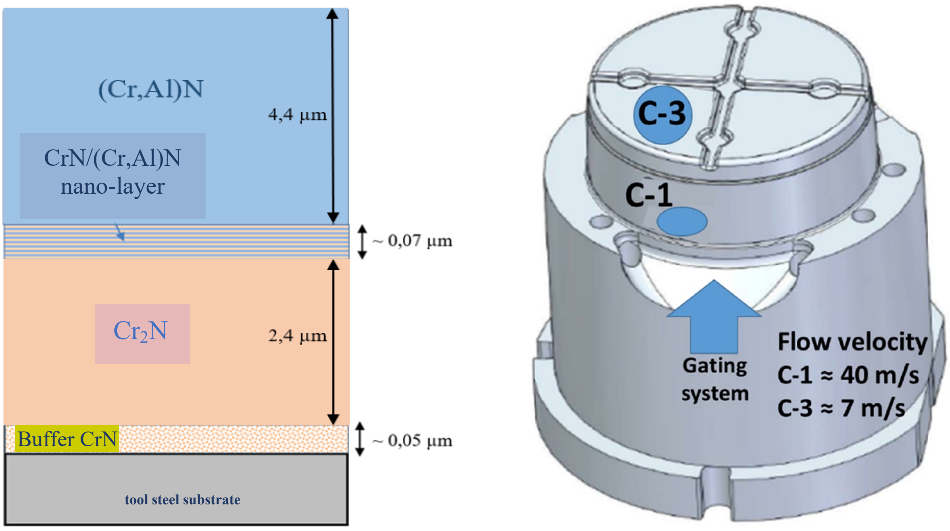

Fig. 1. Schemes of the CrAlN coating and of the investigated pin with marked places of the high (C1) and low (C2) flow of liquid aluminium alloy

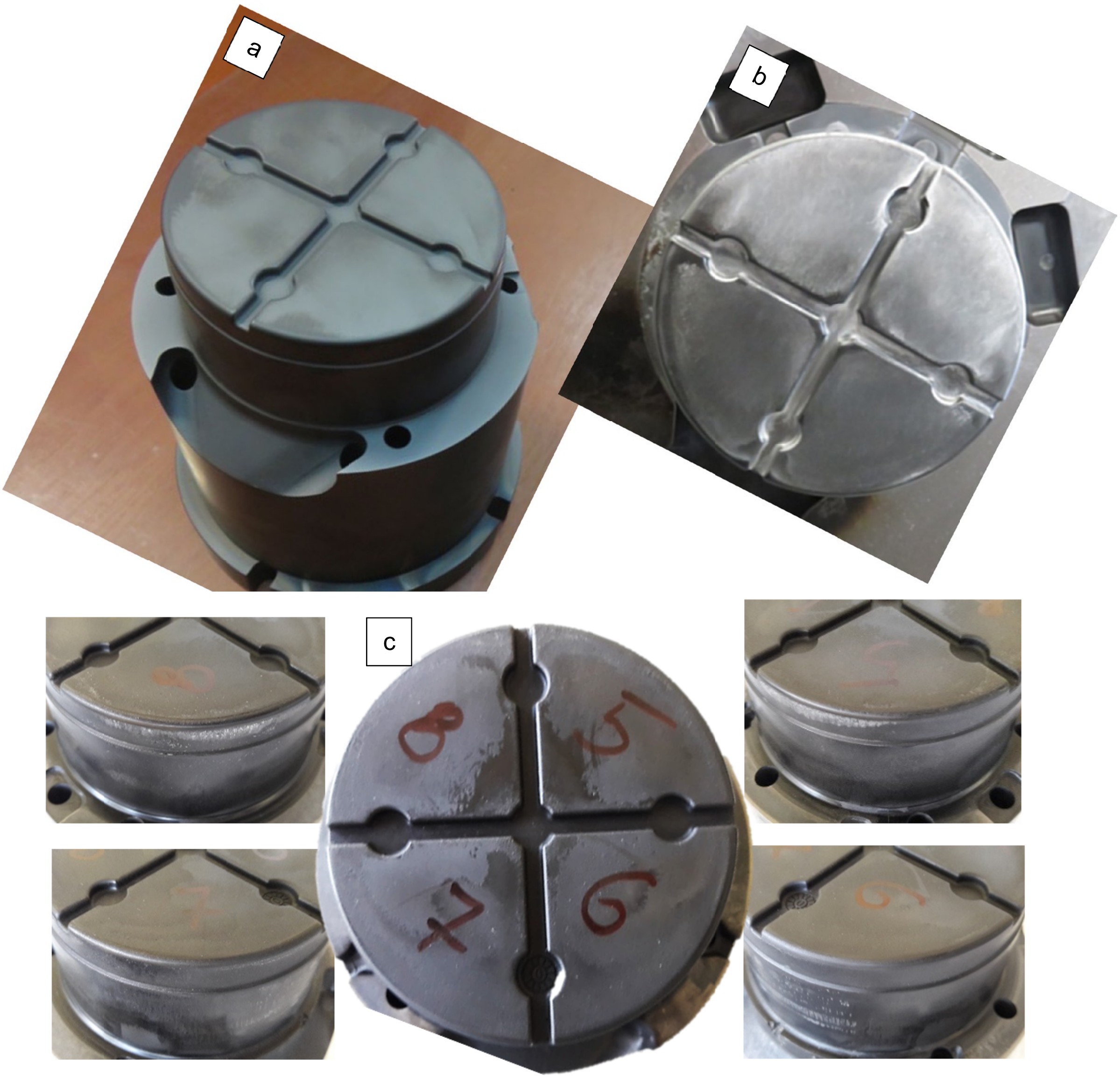

Fig. 2. Image of the pin: a) as-deposited with the Unicomp, b) after 150 injections and c) after 19 500 injections (please note thicker aluminium alloy accumulation at the pin edges)

removal of attached remnants of solidified aluminium from the pin showed that most of the pin face has changed color from dull gray to shiny metallic indicating. Such a change means that the coating at that area was already removed. Simultaneously, even more damage (local chipping/ crumbling-outs of the substrate) was noted at the edges of the pin (Fig. 3). Even so the coating allowed to extend the die lifetime up to 3.6 times as compared with quenched and nitride one.

Fig. 3. Images documenting small (a) medium (b) and large (c) chipping damage to the pin surface after 19 500 injections (please note cracks spreading from the latter one)

3.2. SEM/TEM microstructure observation of as-deposited and subjected to injection cycling CrAlN coating

The sections of the pin as-deposited with CrAlN coating observed using the SEM/BSE method showed, that the arc-deposition allowed obtain its full coverage with the denser layer at the bottom (Fig. 4a). It was despite the fact that the pre-deposition mechanical treatment of the substrate caused its strong roughening. Dark features present under the coating represent pieces of ceramic beads left from the micro-shots cleaning procedure.

The same type of observations of this pin after long term work approaching 1 950 injection cycles indicated, that even at the surfaces in contact with a slow flow of the liquid aluminium alloy (~7 m/s) most of the top layer of the coating is gone (Fig. 4b). However, the bottom layer of this coating still remained mostly untouched except for an occasional cracks passing through its full thickness (marked with white arrow). On the other hand at the areas of the pin exposed to a fast flow (~40 m/s) not only the upper layer was gone, but also the lower one was locally removed or at least punctured (Fig. 4c). The unprotected substrate turned out corrosion prone, as confirmed aluminium alloy penetrating small cracks extending toward the core (marked with black arrow).

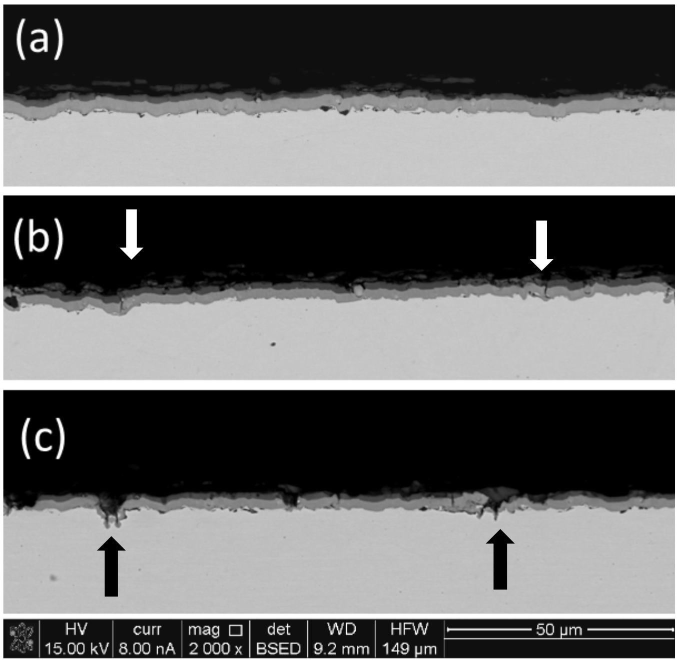

Fig. 4. The SEM/BSE images of as-deposited CrAlN coating (a) and after 1 950 injection cycles in the areas of slow (b) and fast (c) flow of liquid aluminium alloy

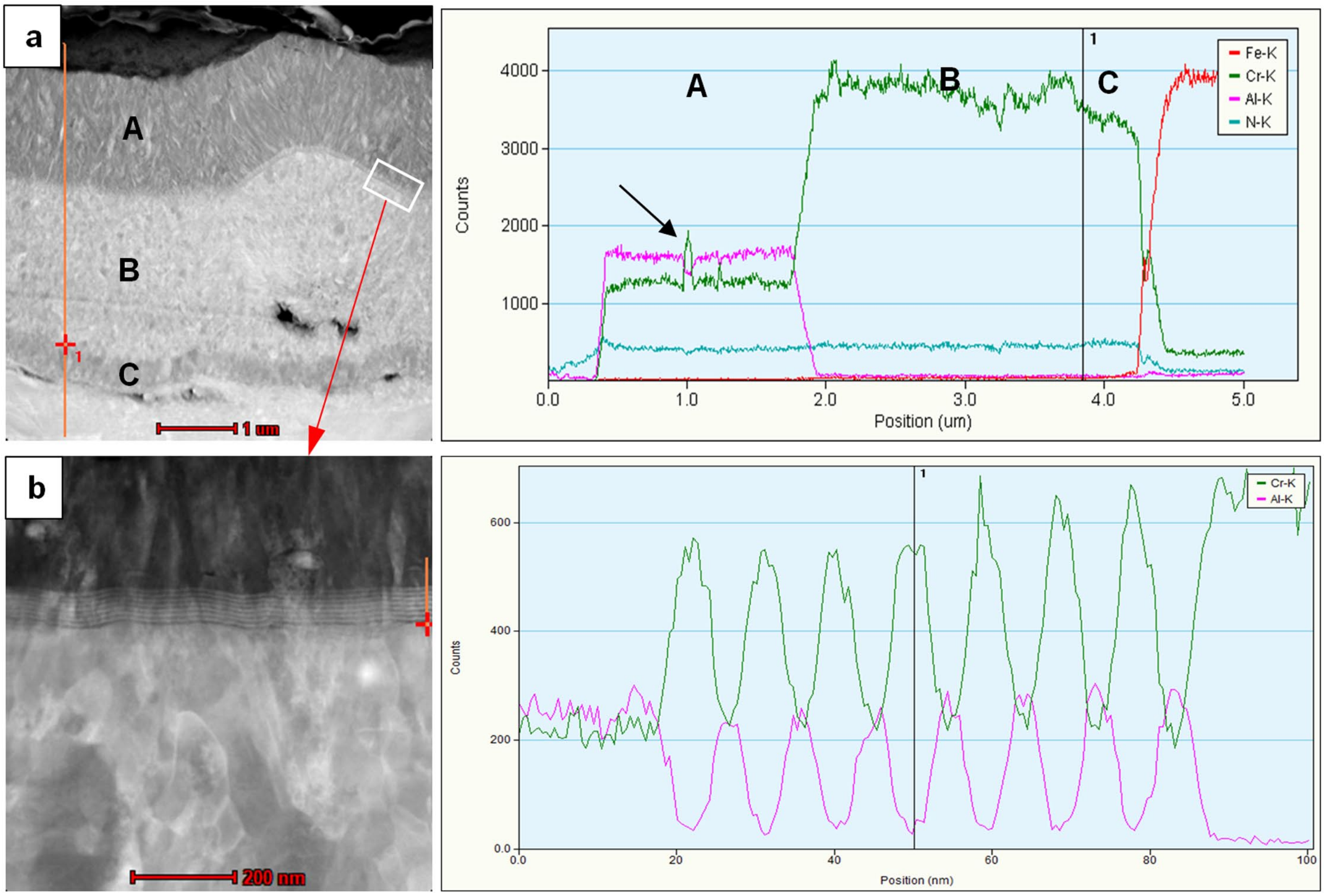

Fig. 5. STEM/HAADF image of cross-section of as deposited coating and accompanying profiles at medium (a) and high magnification of the bi-layer interface with adjoining profiles presenting distribution of N, Al, Cr and Fe along the line marked on the image. Position of the cross on this line is tied with that of the vertical line on the eft marking the buffer/bottom layer interface. Black arrow pointing to local maximum in chromium concentration pinpointing position of chromium droplet buried in CrAlN layer

The STEM/HAADF observations of FIB lamella prepared from as-deposited coating helped to establish that the thickness of the bottom one (marked as B) is close to 2 mm, while of the upper one (marked as A) only ~1.5 mm (Fig. 5a). In between both layers an intermediate thin (<100 nm) nano-layer was inserted, while at the interface with the substrate a visibly thicker buffer layer (~0.5 mm) was deposited. A darker features at the buffer/substrate interface might be either pieces of glass beads imbedded in to it during the cleaning procedure or just some close porosity. The adjoining profiles presenting distribution of the elements of coating confirmed that starting from the substrate side it consist of Cr lean chromium nitride followed by Cr rich chromium nitride and finished with aluminium-chromium nitride. The local changes of chemical composition, like the one pointed by the arrow on the profile adjoining the Fig. 5a, are caused from presence of droplets imbedded in the layers. The high magnification STEM/HAADF image obtain from the interface between both the bi-layers showed that they are connected by a packet of nano-layers (Fig. 5b). The accompanying EDS profile helped to establish that the nano-layer composition changes accordingly to (Cr,Al)N/CrN formula.

TEM/ BF microstructure observations showed that the lower layer of the coating is built mostly of relatively fine (~100 nm) roughly equiaxed crystallites, while the upper one of columnar crystallites (Fig. 6a). The latter ones usually nucleate at the bottom of the packet of nano-layers and extend up to the top of the coating (please note porosity at their bounder Fig. 6b). It is the buffer layer, which is formed with large fraction of very fine (<50 nm) rounded crystallites (Fig. 6c). Selecting areas with diffraction aperture (marked with broken circles in Fig. 6a) allowed to prove the coating is separated from the substrate with the CrN buffer (Fig. 7a). The layer directly above the buffer was identified as the CrN$_2$ phase, while the top one (of (Cr, Al) N chemical composition) was found to be of CrN type (Figs. 7b and 7c, respectively).

HREM observation of the CrN/(Cr,Al)N stack performed in two beam mode and presenting arrangements of 200 lattice planes confirmed that neighboring nano-layers are semi-coherent (Fig. 8). It explains the through layer growth of pseudo-columnar grains. The inset obtain by masking all intensities in Fast Fourie Transform (FFT) except the diffracted beams and building from them the invers FFT confirms that in-between the nano-layers

The STEM/HAADF investigations of the of the CrAlN coating in places where it was still present at the pin surface after 19 500 injection cycles confirmed the previous SEM observations, i.e. that after such a large number of cycles most of the upper layer was removed (Fig. 9a). It also showed that removal of this layer is progressing by breaking out material along the columnar grain boundaries (Fig. 9b). On the other hand the bottom layer is sustaining more damage from cracks propagating at an angle or parallel to the substrate. The first punctures passing through the whole coating are usually forms at largest barbs at the substrate, as marked with arrows in Fig. 9a. The TEM observation of this partly damaged coating helped to establish, that aside of the cracks at columnar grain boundaries they also tend to

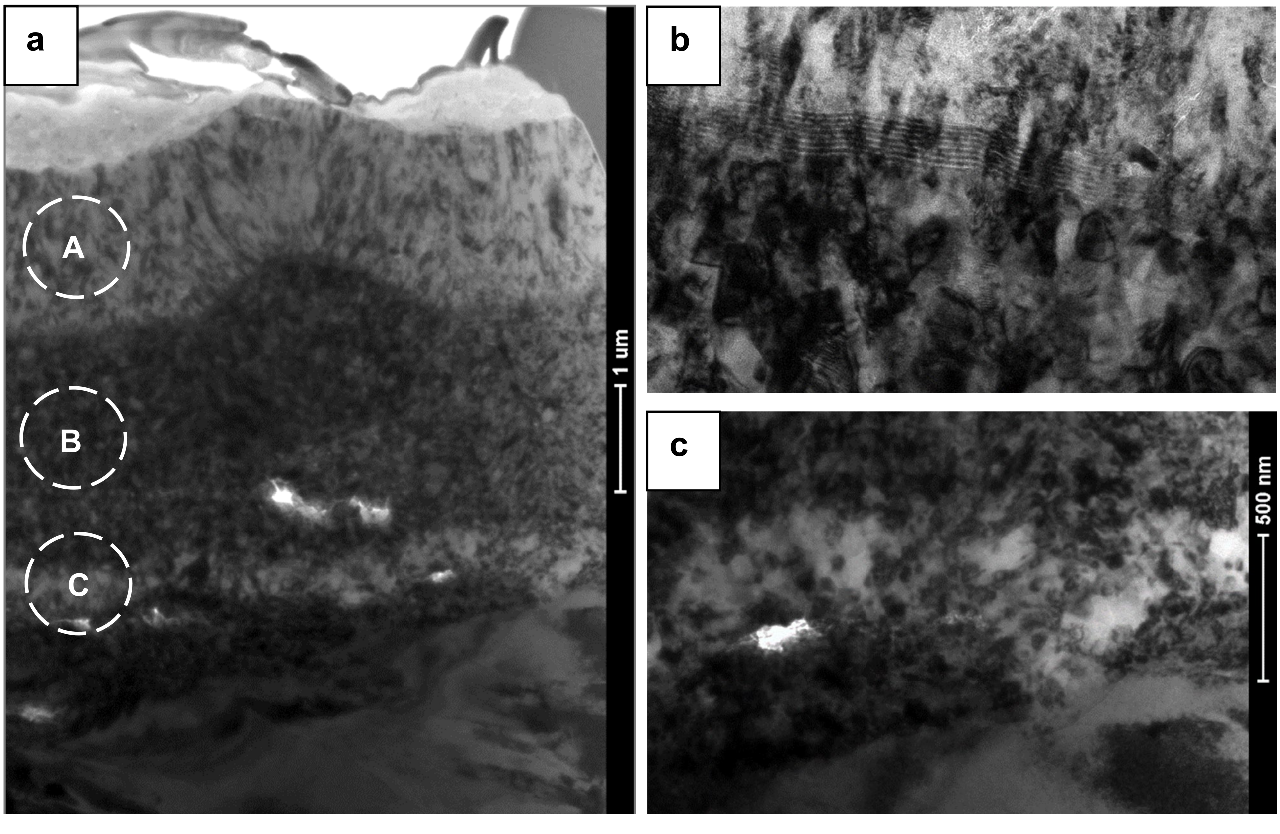

Fig. 6. TEM/BF image of cross-section of as deposited coating (a), magnified images of stack of nanolayers located between bi-layers (b) and buffer layer between coating and substrate

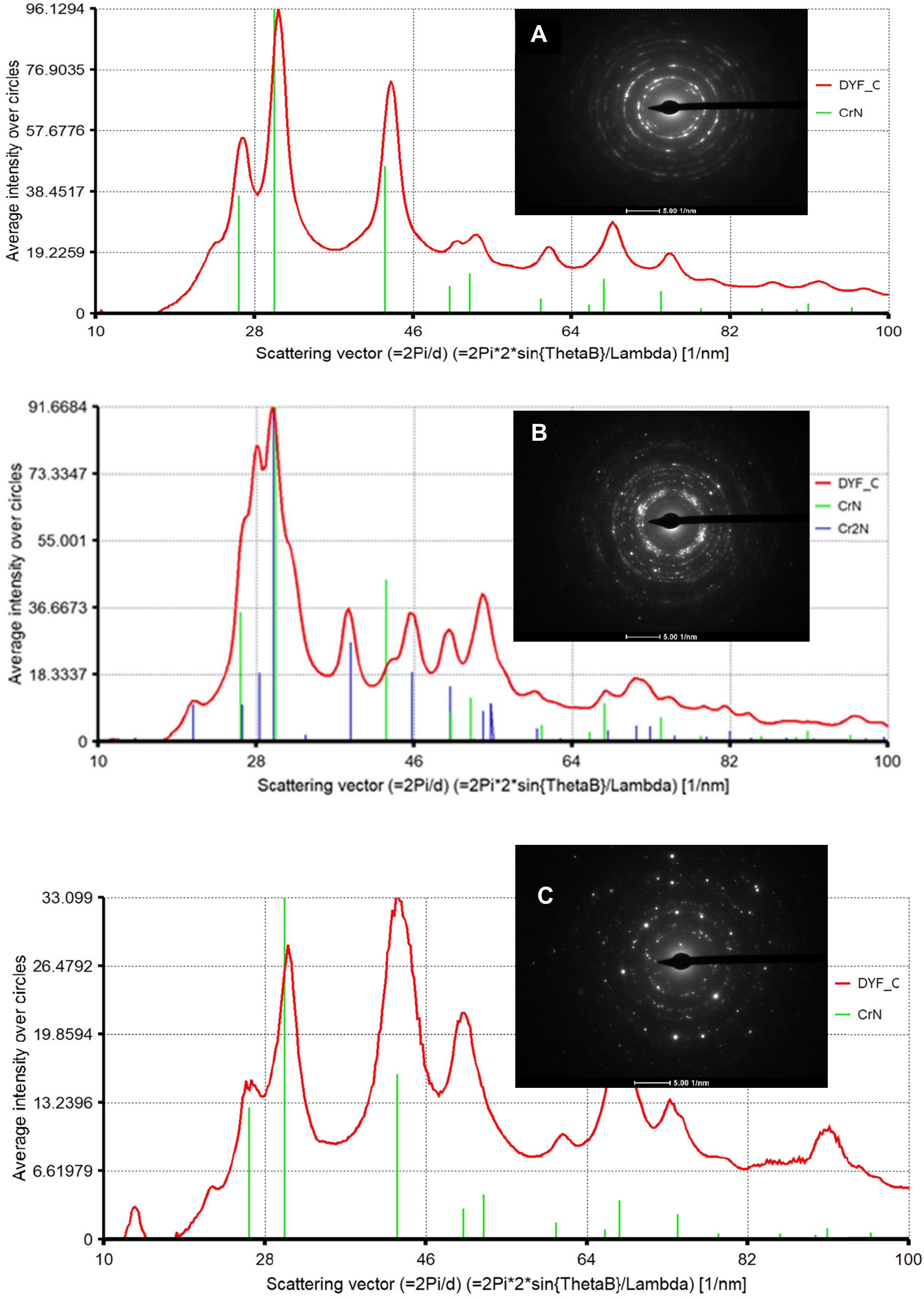

Fig. 7. SAEDP acquired from the areas marked on the Fig. 6 and the intensities integrated along the radi extending from the diffraction centre

nucleate in on the "winglets", i.e. porosity at the sides of droplets imbedded in the deposited material of both bi-layers (Fig. 10). These cracks run predominantly parallel to the interface with the substrate. These type of defects are masked in the bottom layer by presence of numerous grain boundaries characteristic for this layer, but they are practically equally numerous in both of them.

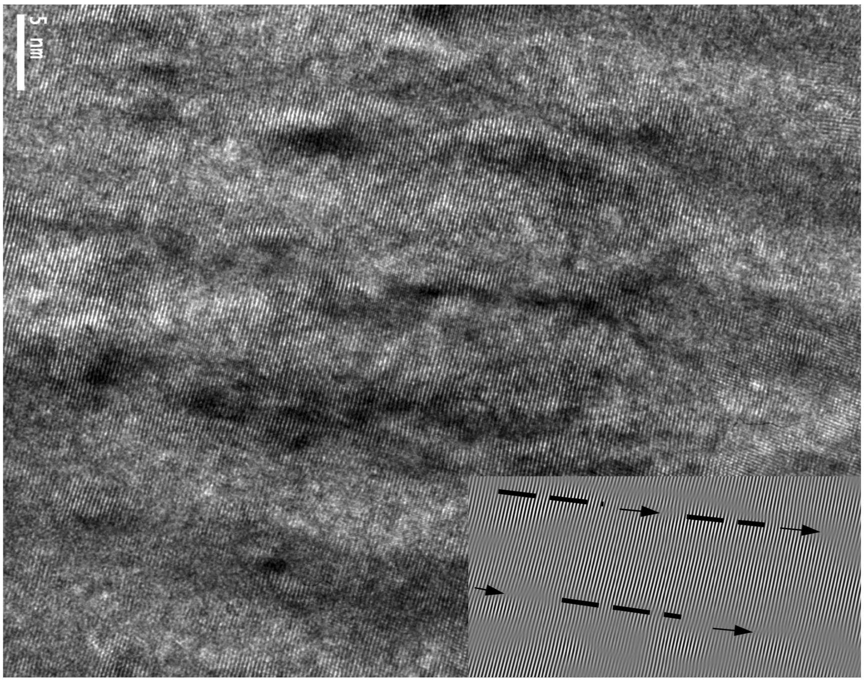

Fig. 8. HR TEM image of arrangements of 200 lattice fringes within the stack of CrN/(Cr,Al)N nano-multilayers (broken lines indicate position of the interfaces between individual nano-layers, while arrows point toward position of matching dislocations)

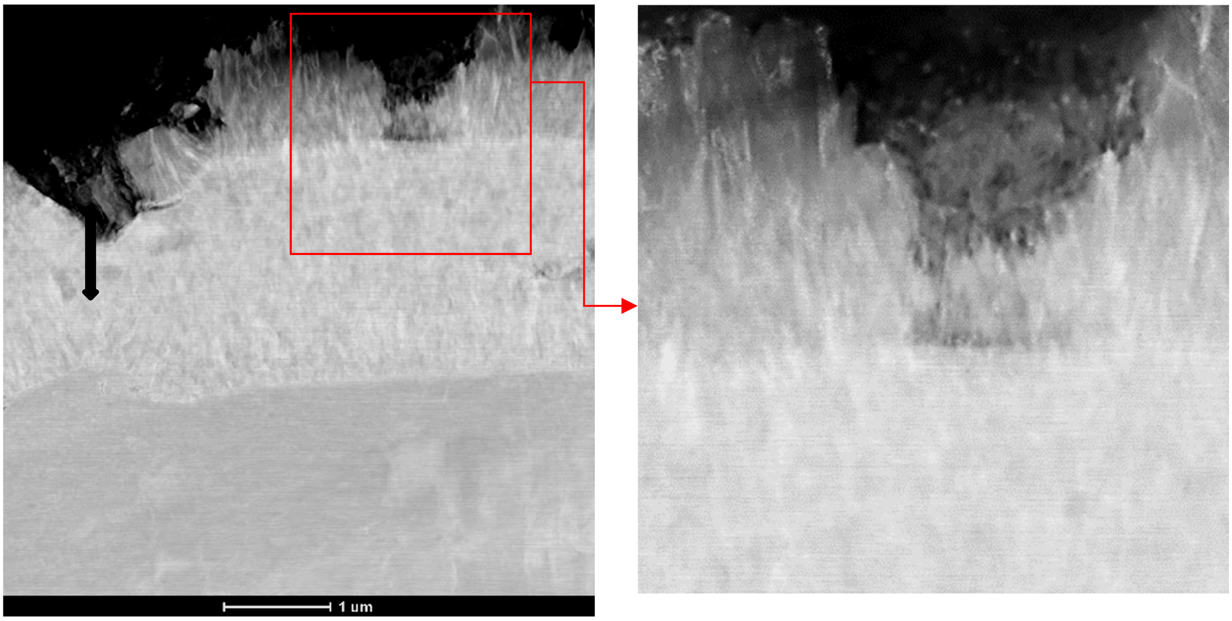

Fig. 9. STEM/ HAADF image of the coating after 19 500 injection cycles and adjoining magnified cut-out presenting steps formed along the columnar grain boundaries (area of interest marked with arrow)

4. Summary

The foundry test proved that the application of relatively simple CrAlN/ Cr_2N bi-layer with the proper intermediate spacer with stack of CrN/(CrAl)N nanolayers and the CrN buffer improving adhesion with the substrate applied to steel die helped to significantly extend its lifetime (>3x). The SEM/ TEM investigations of as-deposited coating as well as the same one after foundry tests helped to establish that, the main weakness of such protection is the porosity present both at the columnar grain boundaries as well as at the bottom of droplets imbedded in it. The former nucleate cracks propagating perpendicularly and the latter at an angle or even parallel to the substrate. The most robust part of the coating stopping numerous cracks turned-out the bottom layer built of roughly eqiaxed fine Cr_2N crystallites. The higher flow rate of liquid Al alloy was responsible for denuding larger areas of the covered substrate, while at lower flow most of the lower layer of the coating was retain (after the same extended injection cycling).

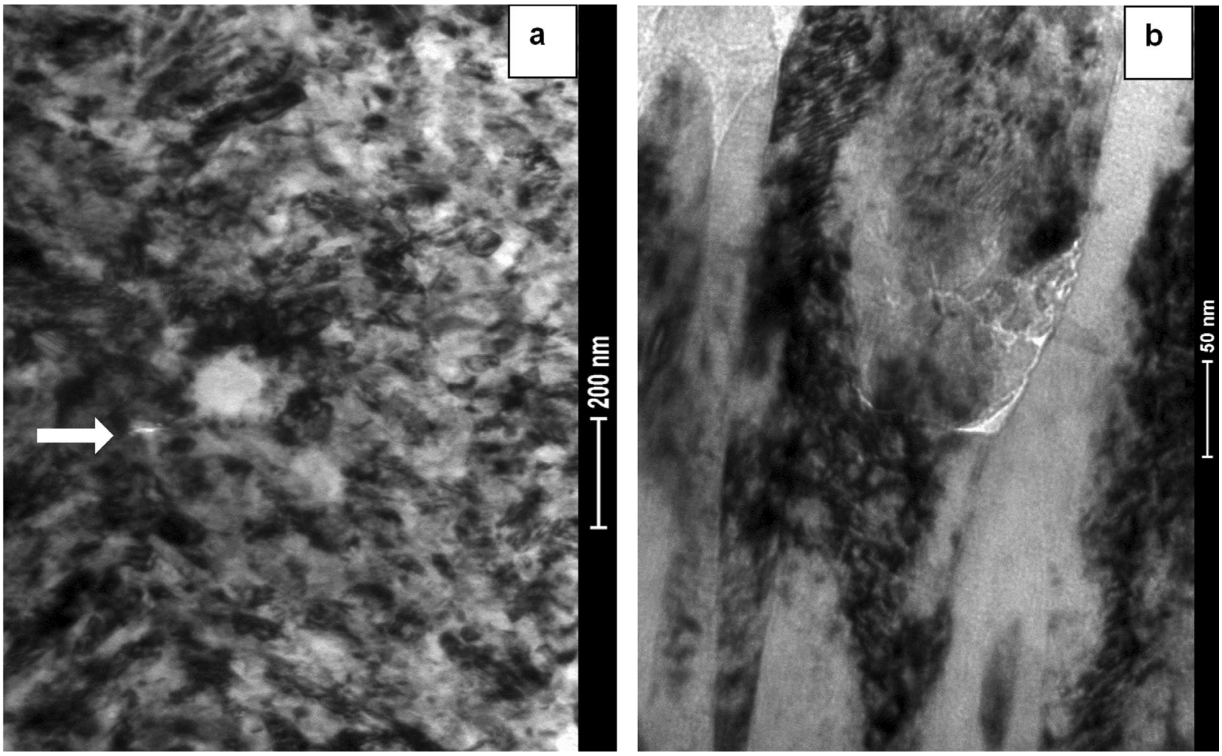

Fig. 10. TEM/ BF image of cracks caused by droplets in lower (a) and upper (b) layer formed in coating after 19 500 injection cycles

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