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# Exposure of pre-stressed T91 coated with TiN, CrN and DLC to Pb–55.5Bi

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## Abstract

The aim of this work is the examination of different coatings in order to select the most suitable one for the use in lead bismuth eutectic (LBE) to protect a structural material. The three coatings we have focused on are: TiN + 2–3%Cr (CVD), CrN + W (PVD) and DLC (diamond like carbon; prepared by a developed low temperature process). Coated T91 specimens were exposed to flowing LBE at 350 °C and a static stress (0, 70, 150 and 200 MPa) in the CORRWETT loop. After 1000, 3000 and 6000 h of exposure the specimens were dismounted. Cross section cuts were made of the exposed specimens without removing the adherent solidified melt. Subsequently metallurgical examination, SEM and EDX analyses were carried out. Additionally the surfaces of the cleaned specimens were inspected by SEM and EDX analyses. All investigated coatings showed excellent results concerning their compatibility in LBE. The static stress influenced the stability of CrN and DLC coated specimens but not the TiN coated ones.

## 1. Introduction

The choice of using ferritic/martensitic steels as structural materials in lead and lead bismuth eutectic (LBE) facilities and future accelerator driven system (ADS) reactors is due to their good mechanical properties under irradiation up to 500 °C.

Compatibility of structural materials with lead alloys is essential for safe operation of such devices. Two different kinds of corrosion attack can happen. One is liquid metal corrosion which is a dissolution process of structural material in the liquid melt [1–3] and is less pronounced for ferritic/martensitic steels than for austenitic steels in consequence of the absence of the steel element nickel which has a higher solubility in LBE than iron and chromium. The other attack is liquid metal embrittlement (LME) which leads to very fast usually brittle intergranular and failure of a component [4–7].

One disadvantage of ferritic/martensitic steels is their sensitivity to liquid metal embrittlement (LME) in the presence of lead or lead-alloys under specific conditions [8–11]. One important requirement for LME is the direct contact of the liquid melt with the surface of the steel. One possibility to prohibit the failure by LME can thus be a protection of the components by formation of a natural oxide or by coating the surface with a corrosion resistant material.

The selection of a coating depends not only on its stability in LBE but also on a good adhesion

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on the basic material and the mechanical stability. The coating method should be an industrial process that generates reproducible uniform coatings and is able to coat even large and complex structures.

The aim of this work is the investigation of three different coatings suitable for the use in LBE and protecting the steel T91. The three coatings we have focused on are: TiN + 2–3%Cr (CVD), CrN + W (PVD) and DLC (diamond like carbon; prepared by a developed low temperature process). Coated T91 specimens were exposed to flowing LBE at 350 °C and a static stress (0, 70, 150 and 200 MPa) in the CORRWETT loop. In the paper the results are discussed and at the end the most suitable coatings are presented.

## 2. Experimental

### 2.1. Coated specimens

Martensitic steel T91 (produced by USINOR, Le Creusot, France; Heat No. 504/3) was chosen as base material. The chemical composition of T91 is listed in Table 1.

T91 sheets with the dimensions 48 × 10 × 1 $mm^3$ were heat treated to achieve the standard condition (1050 °C for 30 min, air quenching and 750 °C for 1 h). Before the coating process, the steel sheets were electro polished to produce smooth, uniform surfaces which are needed to achieve good adherence of the coatings on the basic material. Hence it was not necessary to add an adhesive intermediate layer. Electro polishing and the various coating processes were performed by IonBond AG, Olten, Switzerland. The experimental conditions chosen for each coating procedure are shown in Table 2. Additionally the thickness of the layers given are listed. The gases and metals used for producing the coatings had a purity of 99.99% in minimum.

### 2.2. CORRWETT loop

The LBE loop CORRWETT, manufactured of austenitic steel 316L, is used for CORRosion and WETTing experiments on different materials. The loop is filled with app. 10 l of Pb–55.5Bi which is pumped by a mechanical pump. The heat exchanger system consists of LBE–oil||oil–water circuits. The eutectic Pb–55.5Bi (44.8 wt% Pb and 55.2 wt% Bi) alloy used was supplied by Impag AG (Switzerland). ICP-OES analysis of the fresh LBE yielded the following impurities given in ppm: Ag 11.4, Fe 0.78, Ni 0.42, Sn 13.3, Cd 2.89, Al 0.3, Cu 9.8, Zn 0.2.

Table 2
Summary of the experimental conditions chosen for each coating procedure

| Coating | Method | Conditions[a] | Thickness[a] (μm) |
|---|---|---|---|
| TiN + 2–3%Cr | CVD | ~1000 °C for 5 h | ~5 |
| CrN + W | PVD | ~480 °C for 3 h | 8–12 |
| DLC | Special process | ~180 °C for 2 h | 2–3 |

[a] Specifications given by the supplier.

The LBE temperature in the test section unit was permanently measured by three thermocouples which were directly in contact with the liquid melt. They were placed on the inlet and outlet flow of LBE and in between the two test sections. The temperature showed that the set point of 350 °C was held constantly during the whole experiment (i.e. 6000 h).

### 2.3. Sample holder

Special sample holders to be installed into the CORRWETT loop were developed to apply a specific static stress. The specimens were pre-stressed in 3-point bending to a specific stress levels. As sample holder with installed steel sheet is shown in Fig. 1(a) as schematic and (b) as photograph display. Each sample holder (consisting of two parts) was fabricated of T91 steel.

The height of the centre part versus the support points defines the degree of bending and hence the stress applied.

Two stacks of 35 sample holders each were inserted into the CORRWETT loop. They were set together and fixed in position by two location plugs threaded into the two holes drilled into the sample

Table 1
Chemical composition of T91 in wt%; Fe in balance

| C | P | Si | Mn | Ni | Cr | Mo | V | Cu | Al | Co | Nb |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .088 | .019 | .317 | .597 | .099 | 8.76 | .862 | .186 | .054 | .021 | .019 | .073 |

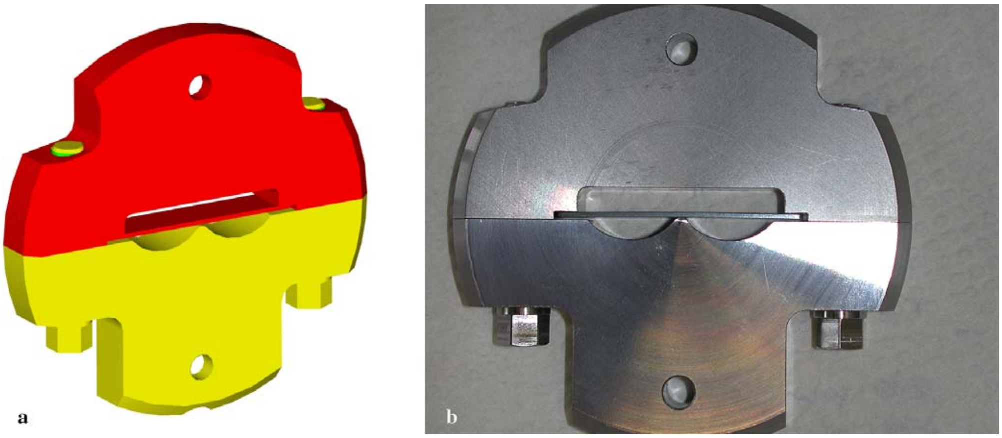

Fig. 1. Sample holder with installed steel sheet: (a) schematic and (b) photograph.

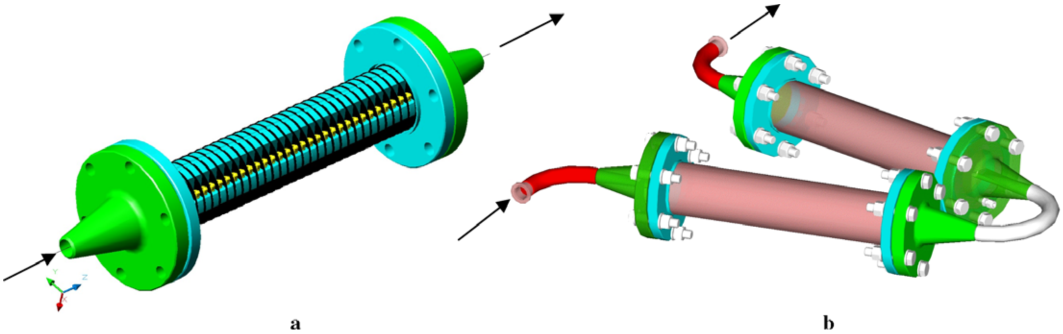

Fig. 2. Schematics of (a) installation of 35 sample holders in a row and (b) the two connected test sections.

holder (see as well Fig. 1). Scheme of one stack is shown in Fig. 2(a). The shape of the two test sections and the assembled positioning of them to each other in the CORRWETT loop are given in Fig. 2(b).

### 2.4. Experimental conditions

70 specimens in total were exposed to flowing LBE at a temperature of 350 °C and pre-stressed to 0, 70, 150 and 200 MPa. The exposure time to flowing LBE was 1000, 3000 and 6000 h reps. During unloading of the specimens, the loop was drained and cooled down.

Polished cross sections were prepared of the specimens without removing the adherent solidified remains of LBE. Subsequently metallurgical examination, SEM and analyses by EDX were carried out. Additionally the surface of the cleaned specimens was inspected by SEM and analysed by EDX. Cleaning was done in ethanol in an ultrasonic bath. In few cases it was necessary to immerse the specimens in a solution of hydrogen peroxide, ethanol and acetic acid to remove the LBE. The time needed for cleaning dependents on the amount of LBE adherent on the surface.

EDX surface analyses were carried out varying of the beam energy (10, 20 and 30 keV). For comparison as received coated specimens were investigated in parallel.

## 3. Results and discussion

### 3.1. CrN plus W (coating produced by means of PVD)

#### 3.1.1. As received material

SEM of the surface of the as received specimen revealed a very smooth surface with particles of CrN and W on top. Additionally there are some craters on the surface having a diameter less than 2 μm which may result from the loss of some of the particles.

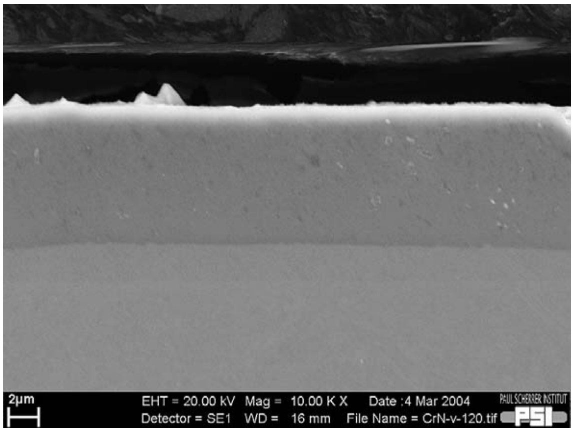

Fig. 3. Cross section of the as received CrN coated specimen showing a compact layer with some particles on top.

The cross section showed that the layer is homogenous in thickness and structure (see Fig. 3). There are neither in the layer nor in the interface any holes or cracks. Element analysis shows a uniform distribution of Cr, N, W and O the layer. The peaks on top belong to the CrN and W particles which were also observed on the surface by bird view. The thickness of the layer is about 8 µm, which is in agreement with the values quoted by the supplier. Depth profiles measured by point analysis in the layer indicated no gradient in composition. The main elements in the layer are Cr, N and W. A tiny amount of Fe was detected which most probably diffused from the steel into the layer during coating procedure. The element tungsten was detected up to a depth of about 7 µm measured from the surface which is an indication that diffusion between the elements of the coating and the steel has happened.

### 3.1.2. *After exposure*

After dissembling of the specimens tiny amount of solidified LBE was observed on some areas of the coating. In general CrN coated specimens were not or only slightly wetted and LBE could be easily removed in the US bath.

SEM analysis of the cleaned surfaces revealed the same over-all topography as observed on the as received specimen as it is shown in Fig. 4(a). There are still CrN and W particles and craters visible. This means that the particles stick quite well on the surface and were not dissolved by LBE. The element distribution is still homogenous and CrN did not react with oxygen which is present in the LBE melt to form $Cr_2O_3$. The standard free energy formation ($\Delta G_f$) is for $Cr_2O_3 = -927.7$ kJ/mol and $CrN = -61.6$ kJ/mol at 773 K [12]. The oxidation temperature of CrN is around 700–750 °C.

Exposure up to 1000 h did not have any effect on the surface structure. In contrary to this grooves in the surface appeared in the stressed areas after 3000 and 6000 h of exposure (see Fig. 4(b)).

SEM inspection of the cross section of the exposed coated CrN specimens (remember: LBE was not removed before embedding) gave the following results: Outside of the stressed areas the coating was not attacked by LBE up to 6000 h of exposure and structure and thickness of the layer stayed unaffected.

The middle part of the specimens, i.e. the area stress was applied to, was covered with solidified LBE. SEM analysis of the areas where tension was put on revealed no influence of the stress (70, 150, 200 MPa) to the structure and thickness of the coating. In contrary to this, compression had an influence on the structure of the coating. Already

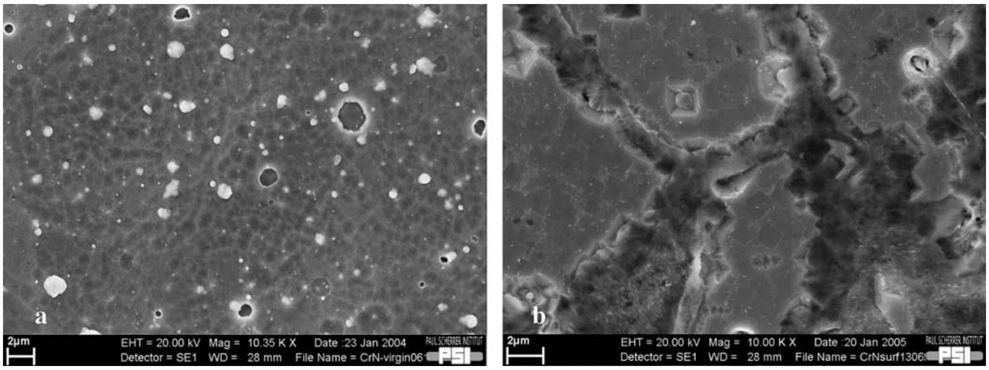

Fig. 4. After 3000 h of exposure and stressed with 150 MPa, the surface topography has changed in the stressed area by forming grooves (b) which were not present in the as received coating (a).

70 MPa produced cracks running parallel to the surface (Fig. 5).

Just beside the cracked area corrosion attack to CrN coating happened. EDX analysis on LBE penetrated into the coating (position marked with ∗ in Fig. 6) revealed the elements Cr, W, Pb and Bi, thus it seems that dissolution has already started. It is thinkable that a protecting surface scale prohibited corrosion attack of LBE to CrN and this protecting layer possibly was broken by compression i.e. attack of LBE to CrN could begin. EDX analysis revealed oxygen in the surface near region which might have formed a thin but very stable layer of $Cr_3O_4$ responsible for the protection. With our method used for analysis – EDX – an enrichment of oxygen on top of the surface was not detected but other more sensitive analysis techniques should be carried out on the surface of CrN to clarify this point.

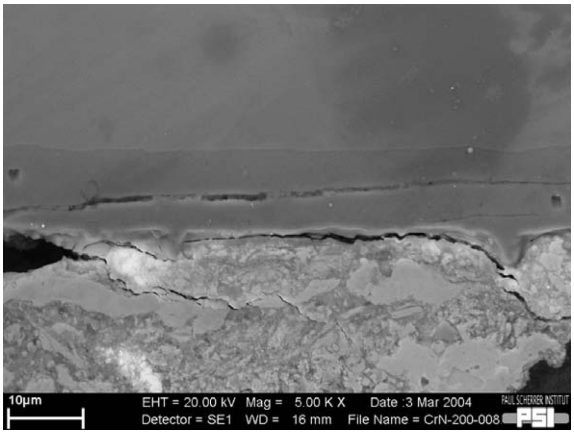

Fig. 5. Static compressive stress seems to affect the structure of the CrN coating. Cracks were formed at 200 MPa running parallel to the surface. Specimen exposed for 1000 h.

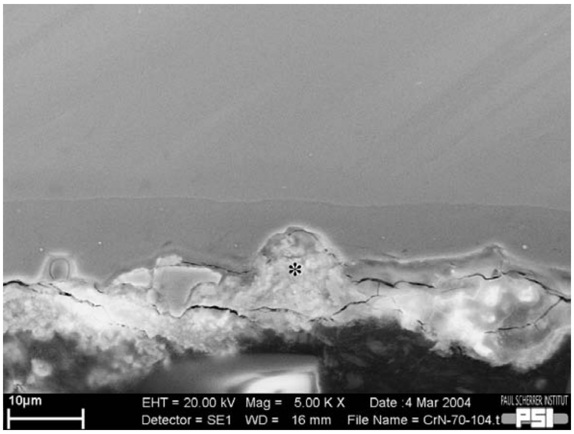

Fig. 6. Corrosion attack of LBE to CrN coated specimen. EDX point analysis (marked by ∗) revealed the elements Cr, W, Pb and Bi. Specimen exposed for 1000 h.

### *3.2. DLC (coating produced by means of low temperature process)*

#### *3.2.1. As received material*

Top view of the surface recorded by SEM with 10 keV shows the structure of the DLC layer and is given in Fig. 7(a). By increasing the accelerator energy to 30 keV the topography of the original steel surface is reflected. The reason for this is that the penetration depth of high energetic electrons (30 keV) is about 7 μm in C because the light element C is highly transmissible for electrons. Due to the fact that DLC layer is much thinner (∼3 μm) than the penetration depth most information is given from the steel. Spectra measured by EDX analysis with 10, 20 and 30 keV reveal information of different depth areas of the specimen. The results are summarised in Table 3.

The results can be explained as follows: Information gained by 10 keV is mainly coming from the DLC layer and hence the main component is C. The analysis of the 20 keV spectra revealed no C at all because DLC layer is transparent for the higher energetic electrons and no interaction has happened between DLC and the electrons. A relatively high content of N and Si beside steel elements Fe and Cr were analysed in the 20 keV spectra which indicates the presence of an intermediate layer. In the 30 keV spectra the amount of the elements N and Si has decreased whereas that of Fe and Cr has increased compared to the 20 keV spectra. The thickness of the intermediate layer between steel and DLC layer consists of Si and N. Element distribution measured on the cross sectional cut of the specimen confirmed that there is an intermediate layer containing Si and N between the DLC layer and the steel surface having a thickness less than 1 μm. The examination of the cross section by SEM revealed a uniform DLC layer with a thickness of 3–3.5 μm showing only little variation in thickness on very few areas (Fig. 7(b)). Cracks or holes have not been observed and the adhesion of the layer to the steel seems to be good.

#### *3.2.2. After exposure*

The SEM inspection of the cleaned surfaces of DLC layers revealed the same structure as observed

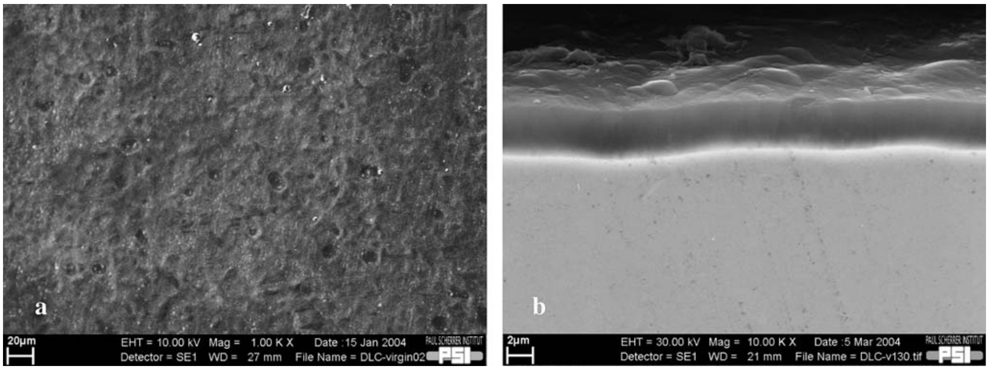

Fig. 7. SE images of the (a) surface and (b) cross section of the as received DLC coated specimen.

Table 3
The results of the three spectra measured with different energies

| Energy (keV) | C/in wt% | N/in wt% | Si/in wt% | Fe/in wt% | Cr/in wt% |
|---|---|---|---|---|---|
| 10 | 94 | 5.6 | – | – | – |
| 20 | – | 19.9 | 23.3 | 48.4 | 6.4 |
| 30 | – | 12.8 | 11.1 | 65.9 | 7.7 |

on the as received material. An interaction (corrosion attack) between DLC layer and LBE was not visible. The examination of the cross section exposed to LBE at 70 MPa confirmed no affect of corrosion attack was as well not promoted up to 6000 h.

In contrary to this static stresses of 150 and 200 MPa seem to have an impact on the mechanical stability of the DLC layer. On the compressive side of the specimen the coating is affected by stress which is demonstrated in the SE images of the cross sections in Fig. 8(a) after 1000 h and (b) after 6000 h of exposure. EDX point analysis was performed on several areas on specimen shown in Fig. 8(b). The intermediate Si–N layer that was primarily between steel and DLC coating is on some areas completely missing and an intensive interaction between LBE and steel had started. The surface structure of the DLC layer after 6000 h of exposure has changed as well in the stressed area and adjacent to it.

Beside the stressed area no detachment of the layer or change in structure or thickness was observed, i.e. the adhesion of the coating on the steel is very good and seems to be no problem and DLC showed corrosion resistance up 6000 h at 350 °C.

The mechanical stability of the coating can maybe be improve by changing coating parameter(s) like time, temperature, pressure, gas mixture or by adding suitable elements. Further development should be done because it is expected that the chemical stability and corrosion resistance of DLC in LBE is achieved also at high temperatures.

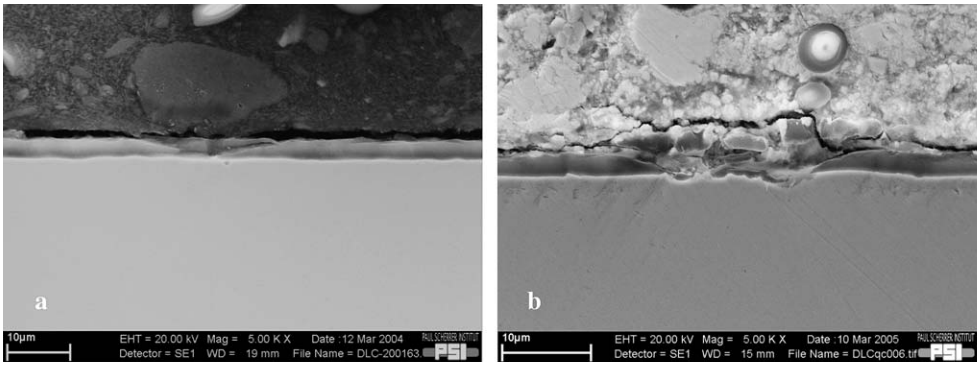

Fig. 8. Cross section of the DLC coated specimen after exposure in LBE and in the presence of 200 MPa showing slight degradation of the layer (a) after 1000 h and (b) after 6000 h on the compressive side.

### 3.3. TiN (coating produced by means of CVD)

#### 3.3.1. As received material

The very specific colour of TiN coatings is a golden shining one. The SEM analysis showed that the surface is uniformly covered by square-edged TiN grains having a size of about 2 μm in maximum. There are no uncertainties visible all over the specimen. The EDX analysis performed with 10, 20 and 30 keV of accelerator energy did not reveal enrichment of any element and only the elements Ti and N could be clearly detected homogenously distributed in the most outer part of the layer. The supplier IonBond has mentioned the addition of about 2–3% of chromium to the TiN layer, but with our analysis technique this was not detectable. Two explanations for this are thinkable: firstly the EDX analysis is not so sensitive to detect a small amount of Cr and secondly, which is the more likely one, is that during coating procedure the element Cr is ablated of the source material.

SEM inspection of the polished cross section of the as received specimen reveals a thin, uniform layer which follows the surface topography of the steel (Fig. 9(a) ×1000; (b) ×10 000). The roughness of the layer itself is negligible. The thickness of the layer is around 3 μm all over the specimen which is thinner than intended (expected thickness according to the prediction given by the supplier is 5 μm). Cracks in the layer or even delaminating of the layer were not detected. Some small uncertainties were observed on rare areas of the specimen which might have been produced during the preparation process (e.g. cutting and/or polishing).

Examination of the cross section of TiN layer is performed by EDX point analysis. Beside the element Cr also Fe is detected. The Fe/Cr ratio is with around 7 lower than that in the steel with about 10.8. In the surface near region of the steel just beneath the TiN coating a slightly enrichment of Fe versus Cr is measured (Fe/Cr about 11.7). It is likely that these two elements were not additionally added but they are diffused from the steel into the TiN layer during coating procedure which lasted for 5 h at about 1000 °C. The diffusion rate of Cr might be higher in TiN than that of Fe but this still has to be proved. With increasing depth the amount of the steel elements Fe and Cr increases in the layer. A relatively small amount of Ti and N has even diffused into the steel matrix up to a depth 2 μm. Hence the chemical boundary of the layer to the steel is not sharp but steadily although the SEM inspection gives a converse impression. This intermixture of the steel elements Fe and Cr and the elements of the coating Ti and N in the intermediate steel – layer has of course a positive effect on the adhesion.

#### 3.3.2. After exposure

Before surface examination by SEM and EDX started the exposed TiN coated specimens were cleaned with a mixture of ethanol, hydrogen peroxide and acetic acid to remove remaining of LBE which was solidified on the surface. The inspection revealed no big change of the structure and size of the grains and the same topography is found as on the as received TiN coated specimen. It only seems that the sharp square-edged TiN grains of the as received material got smoother by increasing exposure time which might be an erosion effect (for comparison see Fig. 10). By a magnification of 20 000 small particles could be visualised on some TiN

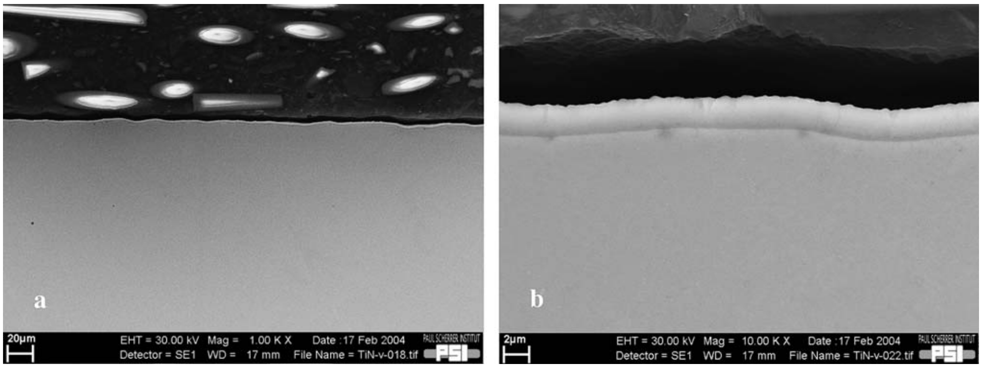

Fig. 9. A smooth TiN coating with good adherence to the steel surface is shown on SE images in different magnifications: (a) ×1000 and (b) ×10 000.

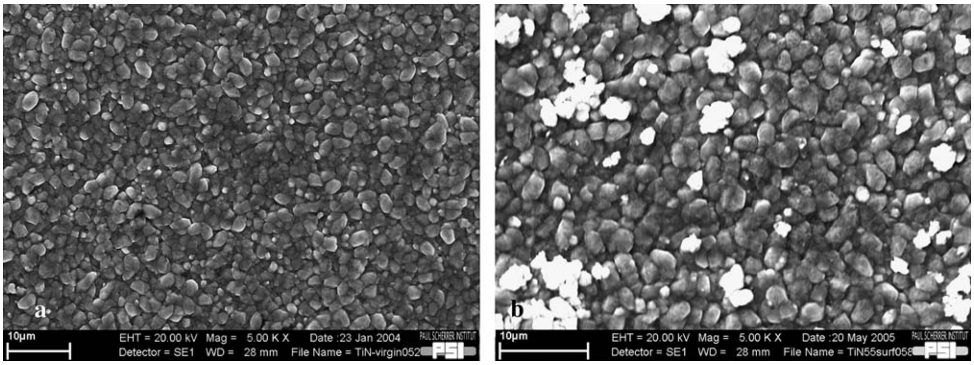

Fig. 10. Surface is uniformly covered with square-edged TiN grains having a size of about 2 μm in maximum; (a) as received material with the sharp edges and (b) the smoother edges after 6000 h of exposure.

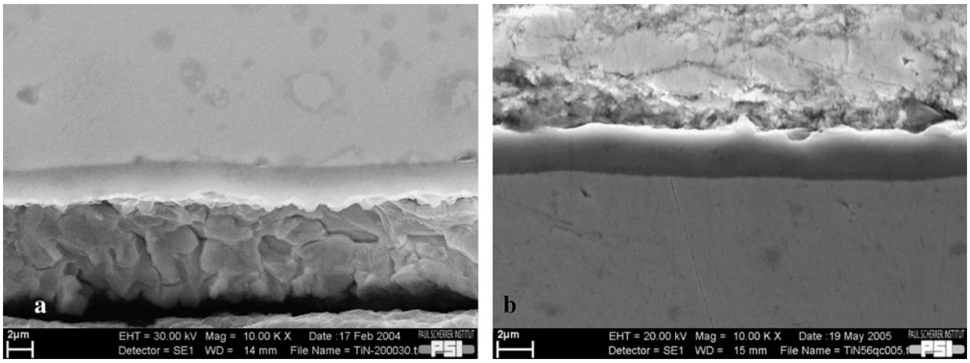

Fig. 11. TiN coated specimen after exposure to LBE in the presence of 200 MPa; (a) EDX point analyses were performed on positions 1 and 2 marked with stars and (b) showing the same area with magnification of 10 000.

grains. EDX point analysis has revealed that these particles concern to LBE which was not completely removed by the cleaning procedure chosen. The size in maximum of the LBE spots is about 900 nm, but most of them are much smaller (down to a size of 100 nm). EDX analysis was also performed over a large area on the surface by using accelerator energies of 10, 20 and 30 keV to see if titanium oxide was formed on the surface during exposure. Only the compound TiN was analysed on top; at 350 °C the compound TiN is stable and will not react with oxygen to form an oxide.

The specimens used for preparing cross sectional cuts were not cleaned before embedding, i.e. adherent LBE was still present on the surface. Anyhow most of the specimens were only very sparely covered by solidified LBE. No change in structure or thickness of the layer was observed thus the static stress (up to 200 MPa) and the hot, flowing LBE (350 °C) seems not to affect the TiN coating up to 6000 h. Stressed area of TiN coatings plus solidified LBE sticking on the surface are presented in Fig. 11(a) after 1000 h and (b) after 6000 h and underline the stability of the coating. The thickness and structure of the coating did not change. Tiny irregularities in the layer were as well visible as in the as received specimen and hence we think that this is not a corrosion effect but formed during coating procedure and EDX point analysis revealed neither Pb nor Bi in the TiN layer. We believe that no corrosion attack has happened under the conditions chosen and due to the fact that there was never measured any interaction between steel and LBE by EDX.

## 4. Summary

All investigated coatings showed excellent results concerning their compatibility in LBE at 350 °C up to 6000 h. Hence the composition of the selected coatings was appropriate for their use in LBE. Differences were observed by the behaviour of the coatings in the presence of static pressure. In the following the outcome achieved on each coating is summarised:

- Static load on CrN promoted the corrosion attack by LBE which was not the case when the exposure tests were carried out without any static pressure. Hence the compressive stress has a negative influence to the compatibility of this layer.
- There seems to be no chemical interaction between LBE and DLC layer. But already at a static stress of 150 MPa a degradation of the layer and change in thickness had occurred whereby the compression seems to be more urgent than tension. In the areas with the destroyed layer the specimen was affected by LBE.
- The exposure of TiN coated specimen up to 6000 h in LBE revealed the most promising results. This coating seems to be not influenced neither by LBE nor static stress up to 200 MPa.

TiN coating performed as best under the experimental conditions chosen. It is planned to expose TiN coated specimens at higher temperatures and to investigate the compatibility at high and low oxygen content in LBE.

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