# Parameters Affecting TGO Growth and Adherence on MCrAlY-Bond Coats for TBC's

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## Abstract

Electron Beam - Physical Vapor Desposited Thermal Barrier Coatings (EB-PVD TBC) on the Ni-base superalloy IN 738LC were tested in respect to non-isothermal and cyclic oxidation resistance at 1100°C. Two types of MCrAlY's (M = Ni, Co), a Co-base and a Ni-base, were used as bond coats (BC) for the TBC's. Additionally, free standing MCrAlY specimens of 2 mm thickness were manufactured by vacuum plasma spraying. The results of the present studies strongly indicate, that an important life time governing factor of the TBC is the yttrium incorporation into the alumina based Thermal Grown Oxide (TGO) which results in an increase of the TGO growth rate and in parallel in a decrease of the yttrium concentration in the coating. If the yttrium concentration has been decreased beneath a critical level, its positive effect on TGO adherence is lost, resulting in TGO spallation. The time required for yttrium exhaustion will not only depend on the initial yttrium content but also on the yttrium reservoir, which is directly proportional to the BC thickness. The transport of yttrium into the TGO seems to occur slower in a Co-based than in a Ni-based coating, resulting in a longer life time for the TBC on the CoNiCrAlY-BC.

## 1. Introduction

In industrial gas turbines coatings of the MCrAlY type (M = Ni, Co) are commonly used as overlay coatings and as bond coatings (BC's) for ceramic thermal barrier coatings (TBC's) composed of yttria stabilized zirconia (YSZ) [1-4]. It is generally accepted that the TBC life crucially depends on the properties of the aluminium based, thermally grown oxide (TGO) which forms during high temperature service at the TBC/BC interface (see e.g. [1,5,6]). In case of TBC's produced by electron beam assisted physical vapour deposition (EB-PVD) failure is in most cases observed at the TGO/BC-interface. The growth rate of the TGO and its adherence to the metallic MCrAlY BC are therefore considered as crucial properties governing the life times of the TBC's during thermal cycling [7].

In the present study selected parameters which were expected to affect the growth kinetics and adherence of the TGO were investigated. Thereby, main emphasis was put on the effect of BC-type and the yttrium reservoir. The yttrium reservoir is defined as an effective amount of yttrium, available for the incorporation into the TGO. It is determined by the yttrium concentration and the volume to surface ratio of the coating (in first approximation coating thickness). For this purpose two types of test specimens (coatings on a superalloy substrate as well as free-standing MCrAlY coatings) were prepared for oxidation studies and TBC life time tests.

## 2. **Experimental**

Two MCrAlY-compositions were used in the present study, a NiCoCrAlY and a CoNiCrAlY with compositions typical for commercial MCrAlY-coatings, and an Y-content of around 0.5wt.-%.

The first type of test specimens consisted of plates of 3.5 mm in thickness of the nickel base superalloy IN738LC which were coated by vacuum plasma spraying (VPS) with a 200 μm layer of a NiCoCrAlY- and a CoNiCrAlY-coatings respectively. Subsequently the plates were coated with a 300 μm thick ceramic top layer of YSZ-TBC applied by EB-PVD. Before applying the TBC layer, the specimens were subjected to a conventional vacuum annealing for 2h at 1100°C and subsequently 24h at 850°C. After the annealing, the rough VPS coating surfaces were smoothened using a cut wire peening technique. For the oxidation tests, specimens of 20 x 20 mm in size were cut with a low speed saw from the coated plates.

The second type of specimens was produced by spraying NiCoCrAlY and CoNiCrAlY coatings of approximately 3 mm thickness on a steel substrate. From these plates, free standing MCrAlY coating specimens of 20 x 10 x 2 mm were prepared by spark erosion. The eroded specimens were ground down to 1200 grit surface finish to remove contamination related to the erosion process, and subsequently they were given the same vacuum heat treatment as described above.

All specimens were subjected to oxidation treatments at 1100°C with exposure times between 1 and 1580 hours in laboratory air. The exposures were interrupted after regular time intervals for weight measurements. After oxidation the specimens were analysed by optical metallography, scanning electron microscopy and Secondary Neutrals Mass Spectrometry (SNMS). The SNMS depth profiles were quantified in atomic percents according to ref. [19]

## 3. Discussion and Results

### 3.1 Life time of the TBC coatings

The TBC-specimens with the two different bond coats were oxidized in air at 1100°C. Macroscopic failure of the TBC occurred for the Ni-base BC after 740 hours, for the Co-base BC after 1230 hours. Fig. 1 shows cross sections of the TBC specimens, which were exposed in parallel and were removed after 111h oxidation at 1100°C. Fig. 2 shows the TGO thickness measured on the cross sections for the two BC types as function of time. It shows that the TGO reaches after 406h a thickness of approximately 3.1 µm above the NiCoCrAlY BC and a thickness of 3.8 µm above the CoNiCrAlY BC. An interesting observation is, that the TGO on the NiCoCrAlY coating consists of “purer” alumina than that on the Co-base BC, the latter exhibiting a minor amount of stringer-like Y/Al-oxide precipitates in the TGO (Fig. 1)

### 3.2 TGO formation on free-standing Bond Coats

Fig. 3 shows cross sections of the oxide scales on the free-standing Ni- and Co-base coatings of 2 mm thickness after different exposure times, i.e. 111 and 406 hours at 1100°C. The heating/cooling cycles were identical to those of the TBC coated specimens referred to in Fig. 1 in the previous section. The oxide scales appear to be substantially thicker than those observed in the case of the TBC coated specimens (compare Fig. 3 c,d with thickness values in Fig. 2). A further difference is that in the case of the free-standing coatings quite large amounts of Y-rich oxides are present in the scale as well as in the internal oxidation zone beneath the alumina scale (Fig. 3). The scale thickness and the extent of internal oxide precipitates after 111h exposure are far more pronounced for the Ni-base than for the Co-base coating. However, after 406h exposure the oxide scales on both coatings are very similar.

A Comparison of the results on the two types of free standing coatings, shows that the differences in growth rates of the TGO are caused by differences in the extent of incorporation of the reactive element (in the present case yttrium) into the surface oxide scale. This is in agreement with findings from other authors, not only observed for Ni(Co)CrAlY-systems but also for FeCrAl-type alloys [8,9]. The present microstructure data for the free-standing coatings show that yttrium incorporation occurs faster in the case of the Ni-base than in case of the Co-base coating. Also, substantially more yttrium incorporation occurs in case of the free standing coatings than in the case of the BC's beneath the TBC, this was determined by the amount of Y-rich phases (oxides and aluminates) observed in the oxide scale and in the sub-TGO regions of the bond coat.

The first mentioned effect seems to indicate a slower diffusion rate of yttrium in the Co-base than in the Ni-base coating. Considering results in ref. [8] The thicker TGO's on the free-standing specimens might be related to the differences in yttrium reservoir which is much larger in the free-standing coating of 2 mm thickness than in the 200 µm thick BC.

To check the latter hypothesis, vacuum annealed free-standing CoNiCrAlY coating specimens were ground to 1200 grit surface finish down to different thicknesses (0.15, 0.7 and 2 mm) and oxidized at 1100°C for a total exposure time of 120 hours. The metallographic cross sections (Fig. 4) after exposure demonstrate that the extent of Y/Al-oxide precipitates and the thickness of the oxide scale depend on the initial specimen thickness, the scale being thinner for the thinner specimens. Although a quantitative estimation of the remaining yttrium contents in the specimens after oxidation could not yet be obtained by EDX or WDX, the results strongly indicate, that during long term oxidation at 1100°C the incorporation of yttrium into the scale and thus also the growth rate of the alumina become for the thinnest specimen limited by the existing yttrium reservoir in the specimen. The oxide formed on the thinnest free standing coating specimen has a similar thickness, composition and morphology as that on the BC beneath the TBC (compare Figs. 1b and 4a). This, in combination with the fact that this BC has a thickness in the same range as the thinnest, free standing coating specimen, strongly indicates that the differences in oxidation rates between the BC beneath the TBC and the free standing coating specimens (Fig. 4) are mainly related to differences in the yttrium reservoir in the coating.

### 3.3. Oxide growth rate and scale adherence

After 406h of exposure the TBC specimen with CoNiCrAlY BC exhibited better TGO-adherence than the one with NiCoCrAlY coating, which showed TGO-delamination during mounting. These differences in the TGO adherence on the two coatings beneath the TBC may be related to intrinsic differences in the oxidation properties of the BC, however, they might e.g. also be related to differences in interdiffusion behaviour with the base material IN738. To obtain insight in the intrinsic differences in adherence of the TGO's on the two MCrAlY coating types, the 2 mm thick, free standing coatings shown in Figure 3 were subjected to extended cyclic exposure. First indications of macroscopically visible oxide spallation for the NiCoCrAlY specimen were observed after 950h. For the CoNiCrAlY specimen the exposures were continued till 1580h and then stopped. Until this exposure time no indications for macroscopically visible oxide spallation were found. This result shows that not only in case of the TBC coated specimens but also for the free-standing coatings the adherence of the alumina based TGO on the CoNiCrAlY- coating is better than that on the NiCoCrAlY-system. Also, the times for onset of spallation of the TGO are longer for the free-standing specimens than for the BC beneath the TBC. Considering the high oxide growth rates on the free-standing specimens this seems at first sight surprising, because it is generally accepted that the tendency to TGO spallation increases with increasing oxide thickness [10,11].

Although the differences in times to oxide spallation between free-standing coatings and TBC coated specimens might be affected by a number of factors (e.g. different stress generation and relaxation due to the presence of TBC and superalloy, interdiffusion processes, surface condition), the observed scale growth processes on the various specimen types indicate that the observed differences in adherence of the TGO’s are crucially dependent on the yttrium reservoir in the MCrAlY coating. A high yttrium reservoir leads to a high growth rate of the TGO which is, intrinsically detrimental for oxide adherence. In addition, the coarse Y/Al-oxide precipitates in the TGO which were discussed previously, are known to be crack initiation sites and thus may enhance spallation [12]. However, from a large number of studies [13-16,18] it is known that the presence of yttrium in the coating is crucial for TGO adherence. Exhaustion of the yttrium reservoir will therefore promote TGO spallation. Thus, for a given Ni(Co)CrAlY system, an optimum yttrium content exists to obtain a compromise between the beneficial effect on oxide adherence without extensively enhancing the growth rate of the oxide. A new finding from the present study is, however, that in defining this optimum yttrium content it is absolutely necessary to take into account the actual yttrium reservoir in the coating. In other words, the yttrium content for obtaining optimum TGO growth rate and adherence in a 100 μm thick BC layer will differ from that in a 200 μm BC.

Based on these considerations, the observed differences in times to TGO spallation for the various specimens can be qualitatively explained. The TBC on the NiCoCrAlY BC shows during the discontinuous oxidation tests earlier spallation (approx. 740h) than the CoNiCrAlY BC (1230h). A Comparison of the TGO composition/morphology (Fig. 1) with those of the free standing coatings of different thickness (Fig. 4) strongly indicates that the yttrium reservoir in the NiCoCrAlY coating was at the beginning of the oxidation exposure smaller than that in the CoNiCrAlY coating. A possible explanation for this effect could be that in the first BC more Y was lost during the vacuum annealing and subsequent surface smoothening prior to TBC deposition. This loss of yttrium, mainly due to the formation of Y/Al-garnet could be also demonstrated by cathode luminescence analysis of specimens after vacuum annealing [17]. The more rapid yttrium loss would be likely because of the observed faster yttrium diffusion in the NiCoCrAlY- than in the CoNiCrAlY coating. This assumption was verified by SNMS-depth profiles of the free-standing specimens after vacuum heat-treatment prior to oxidation. As can be seen in Fig. 5 a more extensive enrichment of yttrium at the surface is observed for the NiCoCrAlY- compared to the CoNiCrAlY-coating, indicating a more rapid Y-diffusion to the surface in the former material.

## Summary and conclusions

From numerous publications in literature a large number of parameters are known which affect the life time of EB-PVD TBC's on MCrAlY bond coats during thermal cycling. The results of the present studies strongly indicate, that a further important life time governing factor is the rate of yttrium depletion in the MCrAlY coating due to yttrium incorporation into the alumina based TGO. The yttrium incorporation results in an increase of the TGO growth rate and in parallel in a depletion of the yttrium concentration in the coating. If the yttrium concentration has been decreased beneath a critical level, its positive effect on TGO adherence is lost, resulting in TGO spallation accompanied by TBC failure. The time required for yttrium exhaustion will not only depend on the initial yttrium content but also on the yttrium reservoir, which is directly proportional to the BC thickness. The transport of yttrium into the TGO seems to occur slower in a CoNiCrAlY- than in a NiCoCrAlY-coating, resulting in a longer life time for the TBC on the CoNiCrAlY-BC. The critical yttrium level required to retain TGO adherence needs further quantitative investigations.

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## Figure Captions

Fig. 1 – SEM cross sections of TBC specimens after 111h discontinuous air oxidation at 1100°C; a) specimen with NiCoCrAlY bond coat, b) specimen with CoNiCrAlY bond coat.

Fig. 2 – TGO growth during air exposure at 1100°C of the TBC specimens with NiCoCrAlY and CoNiCrAlY bond coat.

Fig. 3 – SEM cross sections of free-standing MCrAlYs after exposure to air at 1100°C; after 111h: a) NiCoCrAlY and b) CoNiCrAlY; after 406: c) NiCoCrAlY and d) CoNiCrAlY.

Fig. 4 – SEM cross sections of free-standing CoNiCrAlYs with different thickness after 120h exposure to air at 1100°C; a) 0.15 mm; b) 0.7 mm; c) 2 mm.

Fig. 5 –Yttrium-Concentration profiles (measured by SNMS) of free-standing NiCoCrAlY and CoNiCrAlY coatings (thickness 2 mm; ground surfaces) after 2h heat-treatment at 1100°C plus 24h at 845°C in vacuum of $10^{-3}$ Pa.

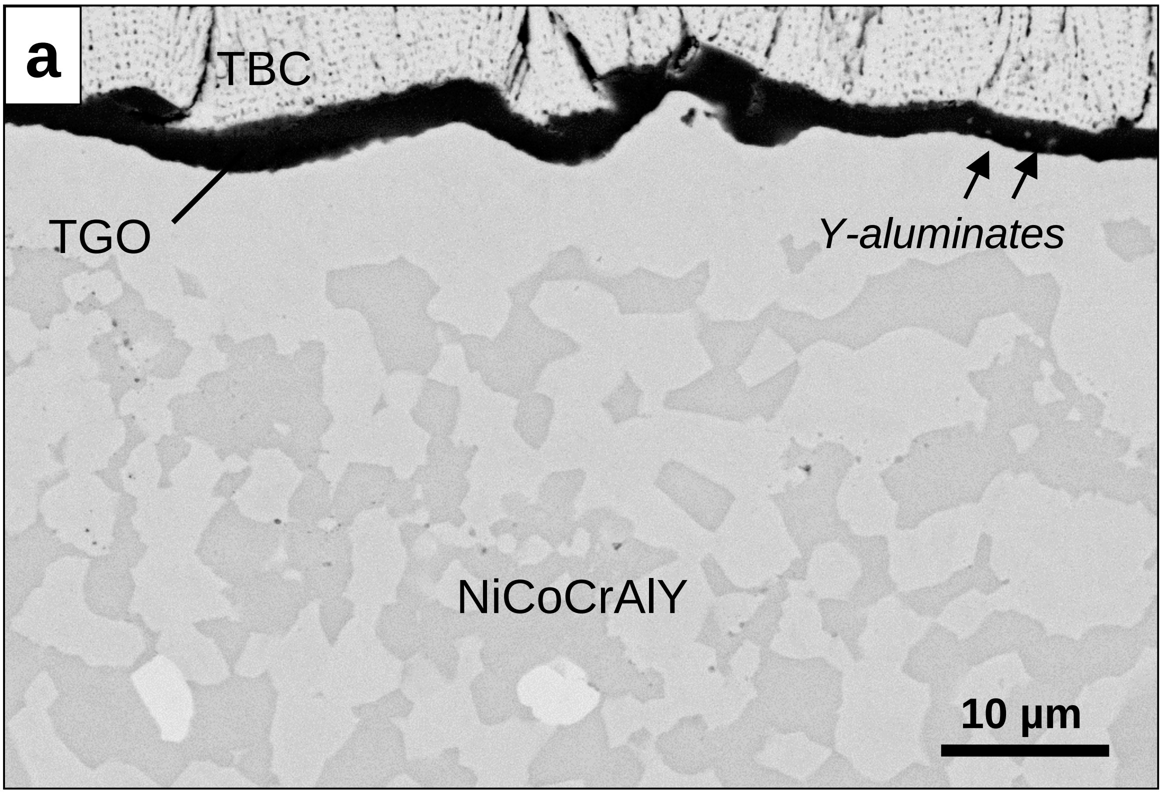

Fig. 1a

Fig. 1 – SEM cross sections of TBC specimens after 111h discontinuous air oxidation at 1100°C; a) specimen with NiCoCrAlY bond coat

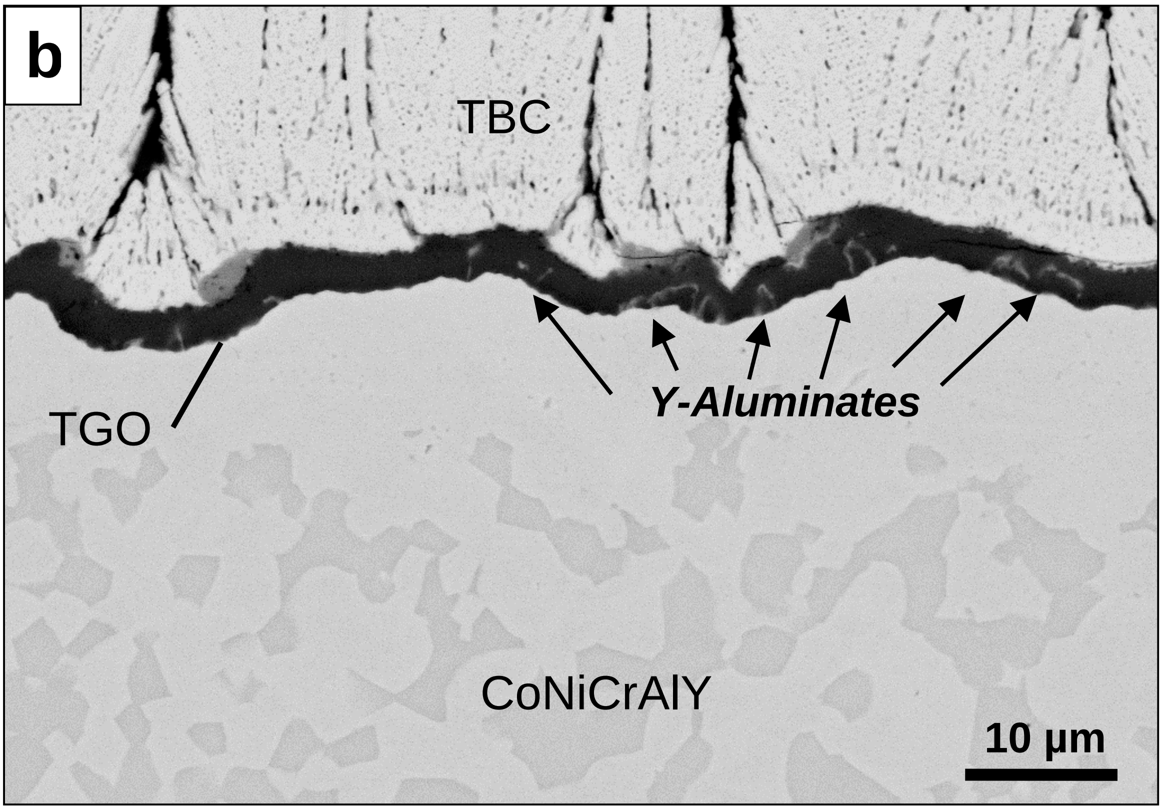

Fig. 1b

Fig. 1 – SEM cross sections of TBC specimens after 111h discontinuous air oxidation at 1100°C; b) specimen with CoNiCrAlY bond coat.

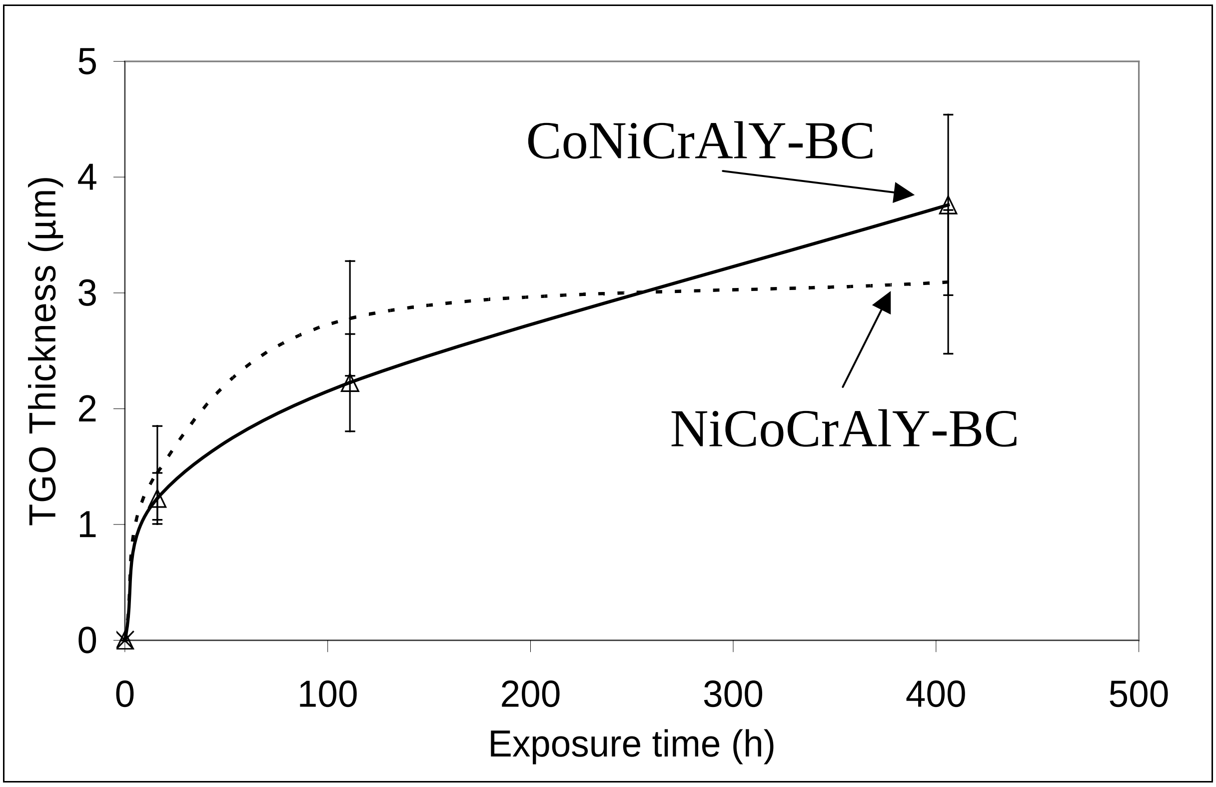

Fig. 2

Fig. 2 – TGO growth during air exposure at 1100°C of the TBC specimens with NiCoCrAlY and CoNiCrAlY bond coat.

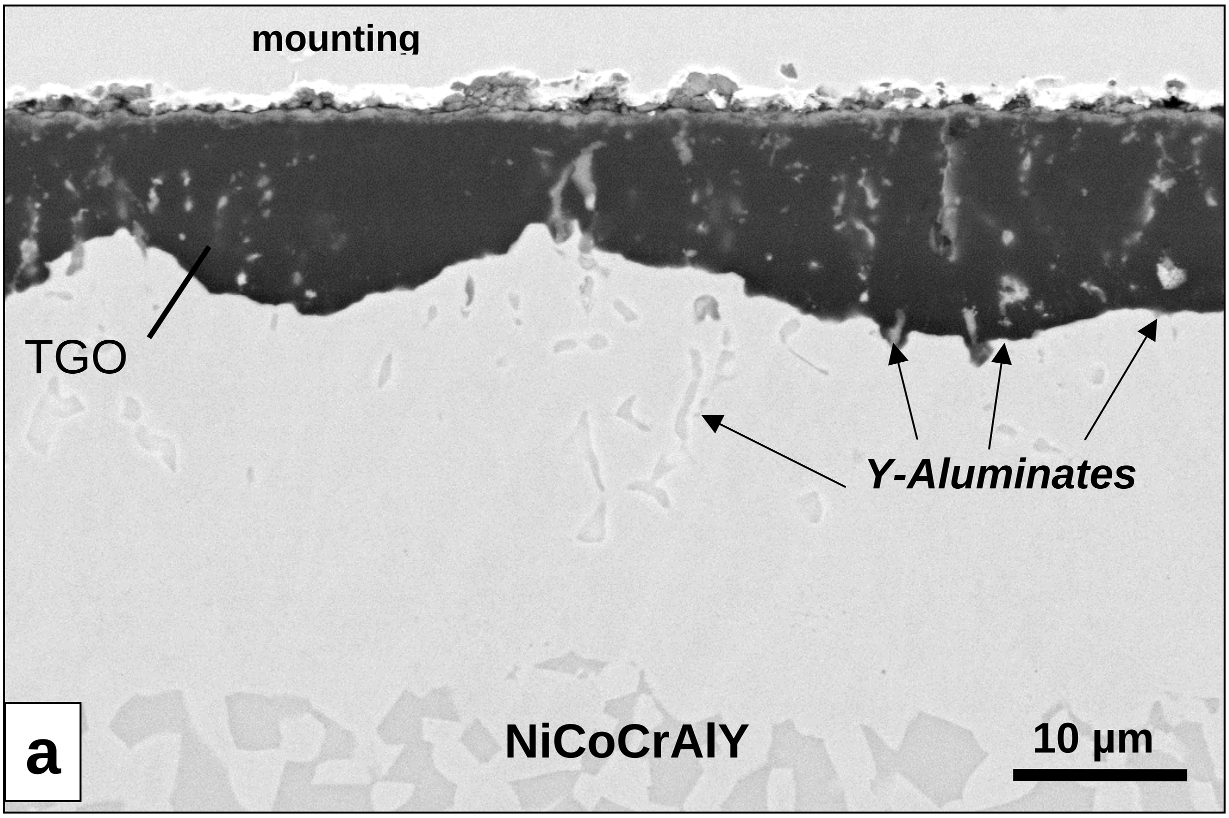

Fig. 3a

Fig. 3 – SEM cross sections of free-standing MCrAlYs after exposure to air at 1100°C; after 111h: a) NiCoCrAlY

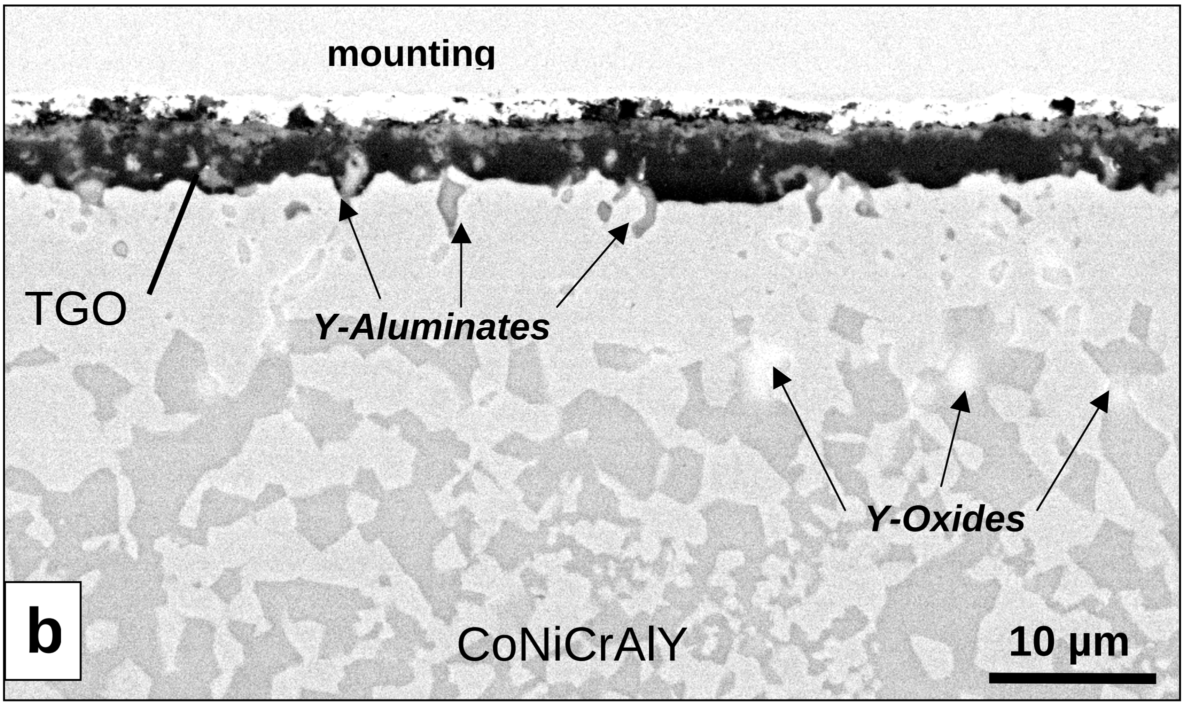

Fig. 3b

Fig. 3 – SEM cross sections of free-standing MCrAlYs after exposure to air at 1100°C; after 111h: b) CoNiCrAlY

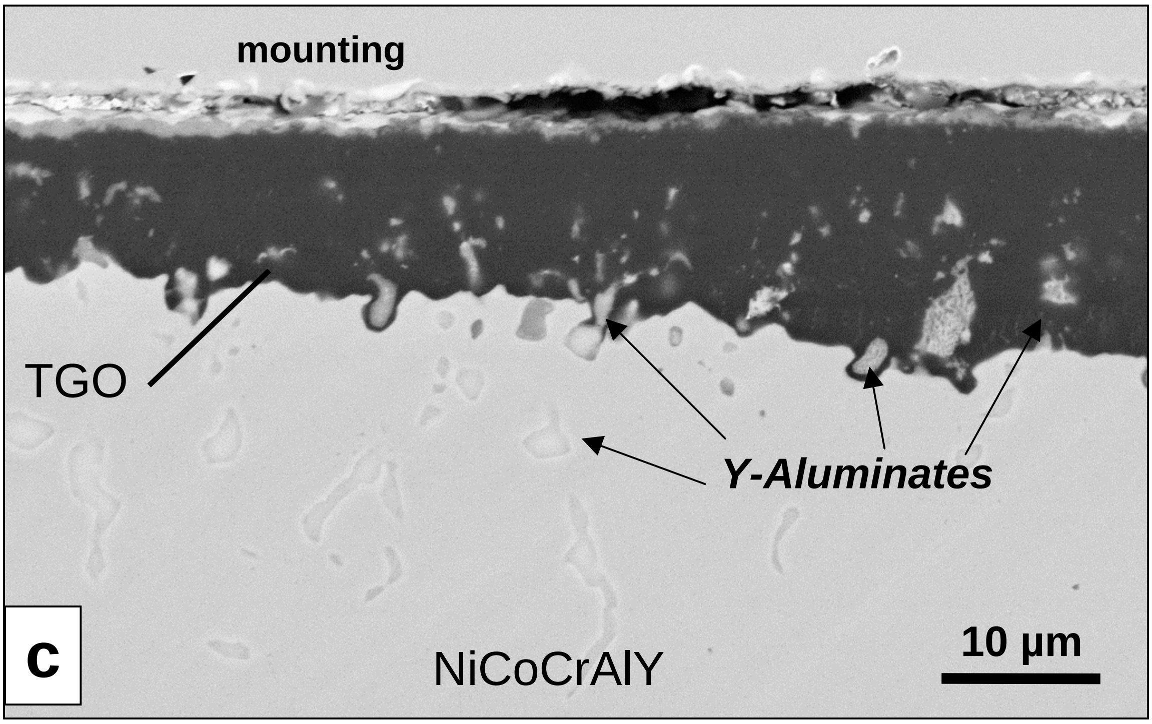

Fig. 3c

Fig. 3 – SEM cross sections of free-standing MCrAlYs after exposure to air at 1100°C; after 406h: c) NiCoCrAlY

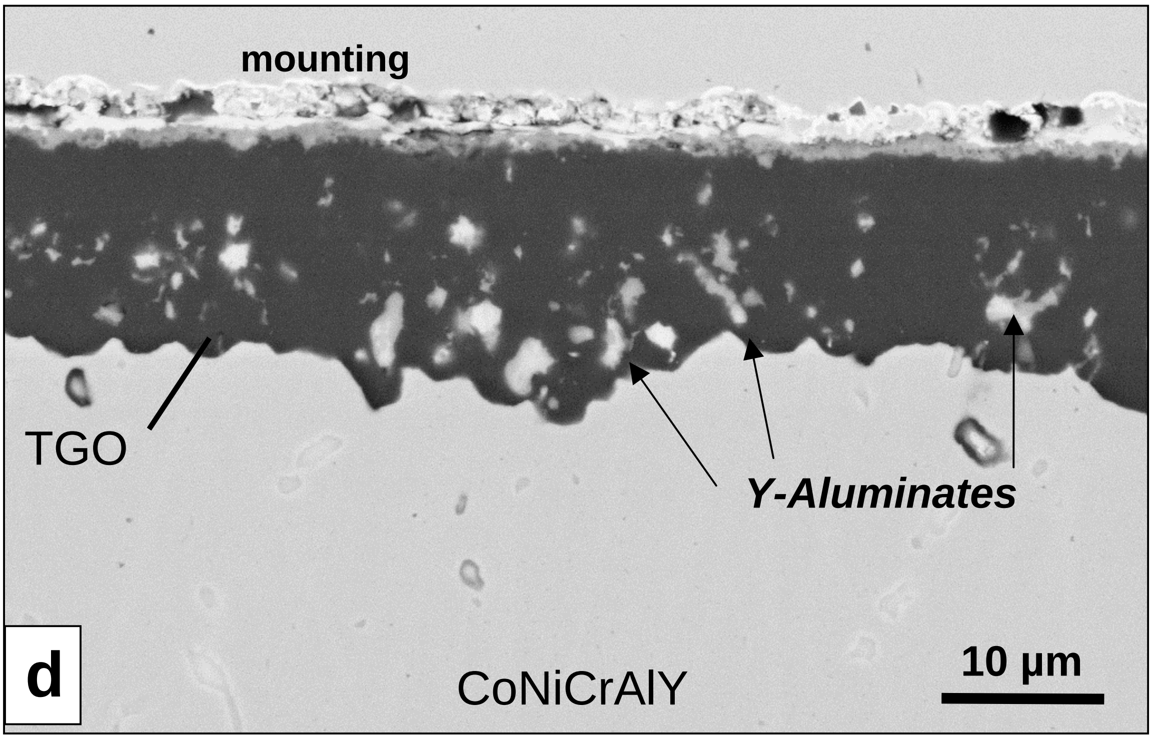

Fig. 3d

Fig. 3 – SEM cross sections of free-standing MCrAlYs after exposure to air at 1100°C; after 406h: d) CoNiCrAlY.

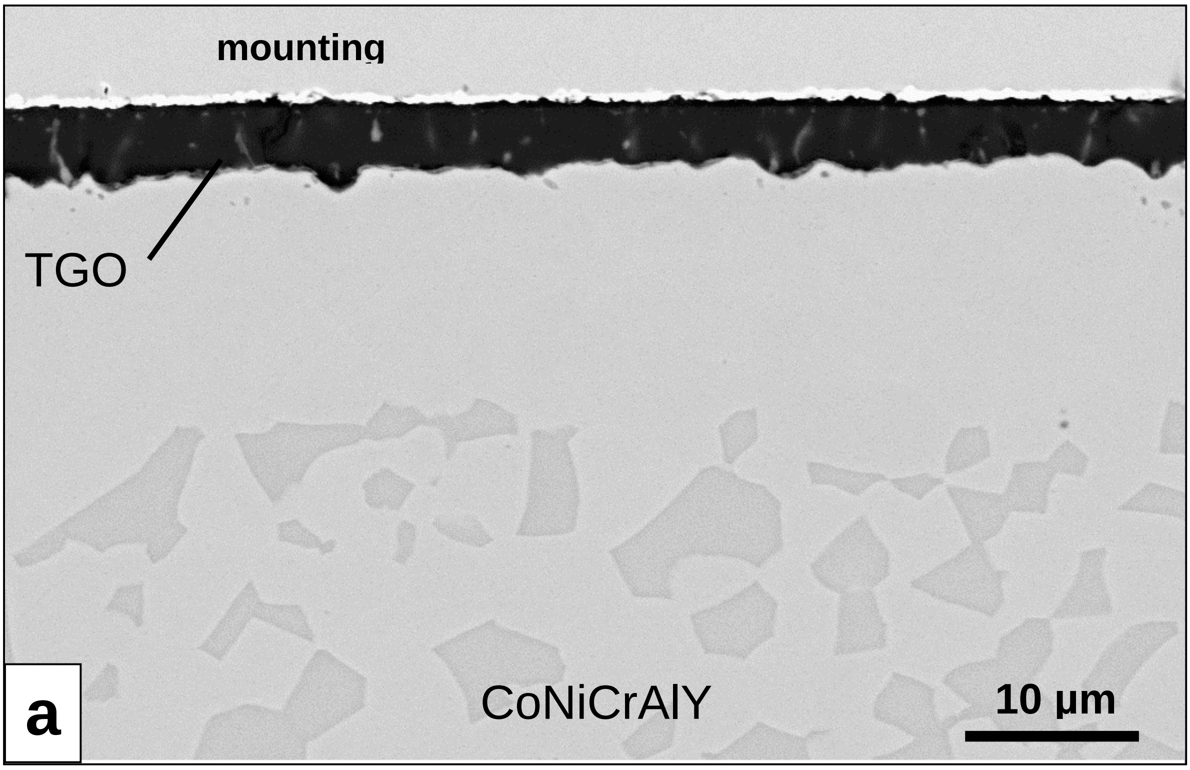

Fig. 4a

Fig. 4 – SEM cross sections of free-standing CoNiCrAlYs with different thickness after 120h exposure to air at 1100°C; a) 0.15 mm

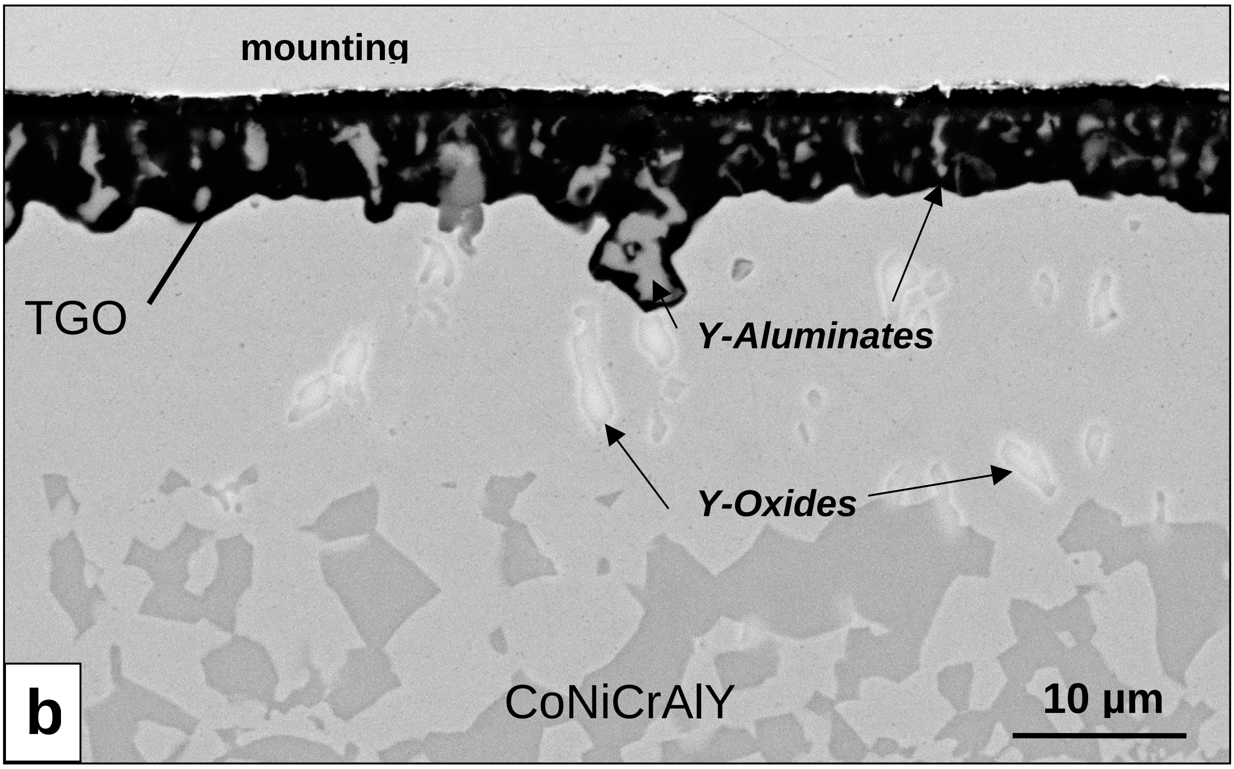

Fig. 4b

Fig. 4 – SEM cross sections of free-standing CoNiCrAlYs with different thickness after 120h exposure to air at 1100°C; b) 0.7 mm;

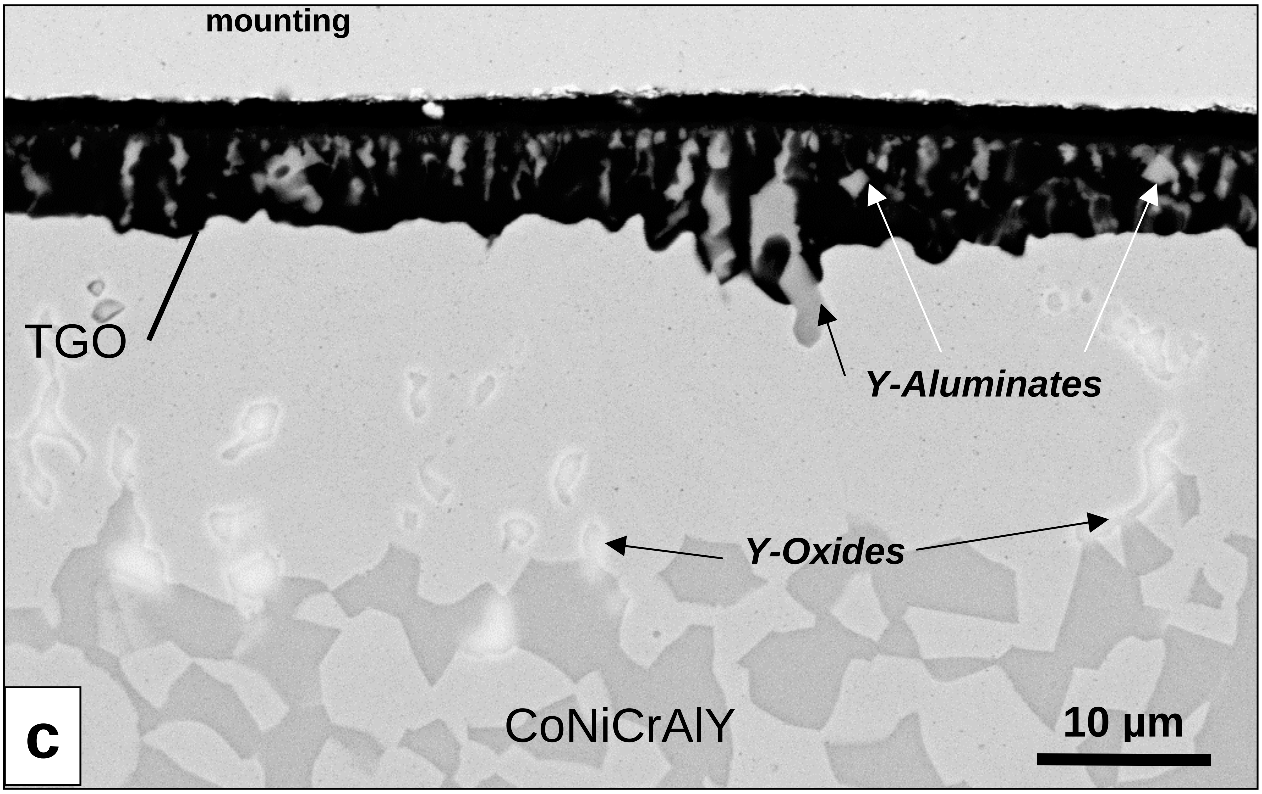

Fig. 4c

Fig. 4 – SEM cross sections of free-standing CoNiCrAlYs with different thickness after 120h exposure to air at 1100°C; c) 2 mm.

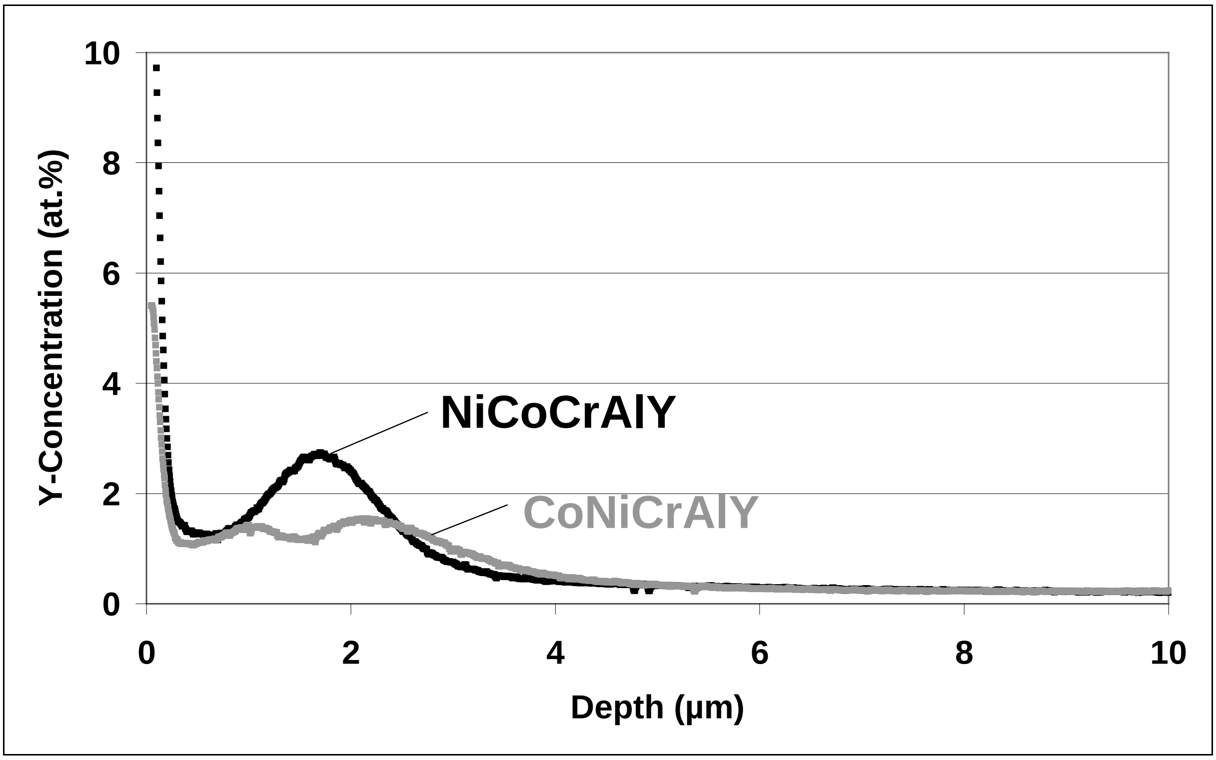

Fig. 5

Fig. 5 –Yttrium-Concentration profiles (measured by SNMS) of free-standing NiCoCrAlY and CoNiCrAlY coatings (thickness 2 mm; ground surfaces) after 2h heat-treatment at 1100°C plus 24h at 845°C in vacuum of $10^{-3}$ Pa.