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## INVESTIGATIONS ON THE DEPOSITION AND THE EFFICIENCY OF A MULTILAYER HIGH TEMPERATURE COATING SYSTEM FOR GAS TURBINE BLADES



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### ABSTRACT

The content of this work is the development and investigation of a high temperature coating system for gas turbine blades. On a single crystal CMSX4 substrate a thin CVD layer of alpha-alumina was deposited as a diffusion barrier coating. As a protection against high-temperature corrosion it was covered with a PVD NiCoCrAlY layer, which also performs as a bond-coat for the following thermal barrier coating deposited by Atmospheric Plasma Spraying. The surface preparation techniques and coating parameters for the multilayer coating were optimized with respect to the bonding mechanisms of the different deposition techniques. The samples were annealed at 1100°C for 100 h under a neutral atmosphere. Furthermore thermocycle experiments were carried out to investigate thermocycle behaviour. The coating system proved its efficiency: no cracks were observed except vertical segmentation cracks in the TBC, all layers showed good adhesion and the diffusion barrier remained intact suppressing any noticeable diffusion of Al, Cr, Ta, Re, W and Ti.

### INTRODUCTION

The work submitted here was carried out in the context of a collaborative research center, where the main objective is to compile mathematical models of different coating processes (CVD, MSIP-PVD, APS) and to verify these models by experimental data. Results of the numerical work concerning the coating processes are presented elsewhere (Lugscheider, 1997a; 1997b, 1998; Schierling, 1995). In this paper the latest experimental investigations on the deposition and testing of a multilayer high temperature coating system for gas turbine blades are presented.

Gas turbine research includes efforts to increase the turbine inlet temperature for better engine efficiencies. Besides the introduction of innovative cooling techniques, multilayer coating systems have become generally accepted to protect the blades against the high temperatures in the hot gas stream. Thermal insulation is obtained with help of a ceramic thermal barrier coating. In addition a metallic bond-coat is used to adapt the thermal expansion between blade and ceramic top-coat. This coating generally consists of a matrix material of Ni, Co and Fe and relatively high contents of Al and Cr. During thermal loading this coating promotes due to its high Al- and Cr- content the growth of an oxide layer underneath the TBC. This slowly growing oxide layer protects the NiCoCrAlY layer and the Ni-base alloy from further hot gas corrosion. If the temperature at the phase boundary

superalloy/bondcoat exceeds approx. 1080°C, interdiffusion between base-material and coating becomes noticeable. This can lead to the appearance of Kirkendall voids and thus to a premature failure of the coating system (Rhys-Jones, 1989). The application of a diffusion barrier between base material and NiCoCrAlY is a conceivable means to suppress these diffusion effects. Several coating compositions have been taken into consideration to prevent interdiffusion, e.g. TiN and TiC (Telama, 1986). The system Al-O-N showed promising properties as diffusion barrier at 1100°C (Knotek, 1993; Cremer, 1998). Cremer et al. examined sputtered Al-O-N coatings and a sputtered diffusion barrier of gamma-Al<sub>2</sub>O<sub>3</sub>, which could not prevent interdiffusion during annealing due to the transition to alpha-Al<sub>2</sub>O<sub>3</sub> (T > 1000°C). They supposed that the direct deposition of alpha-Al<sub>2</sub>O<sub>3</sub> would lead to better results. The use of an alpha-Al<sub>2</sub>O<sub>3</sub> layer as diffusion barrier is also proposed by Singheiser (Singheiser, 1993). The alpha modification of alumina meets all demands for the use as diffusion barrier, since it is the thermodynamically stable phase (hcp-crystal structure) and therefore undergoes no further phase transitions during use.

The coating system investigated consists of an alpha-Al<sub>2</sub>O<sub>3</sub> diffusion barrier deposited by CVD on single crystal CMSX4 samples with a thin TiN interlayer, a NiCoCrAlY coating deposited by MSIP-PVD as protection against hot gas corrosion and an yttria-stabilized ZrO<sub>2</sub> thermal barrier coating sprayed by Atmospheric Plasma Spraying. Figure 1 shows the cross-section of the coating system after production.

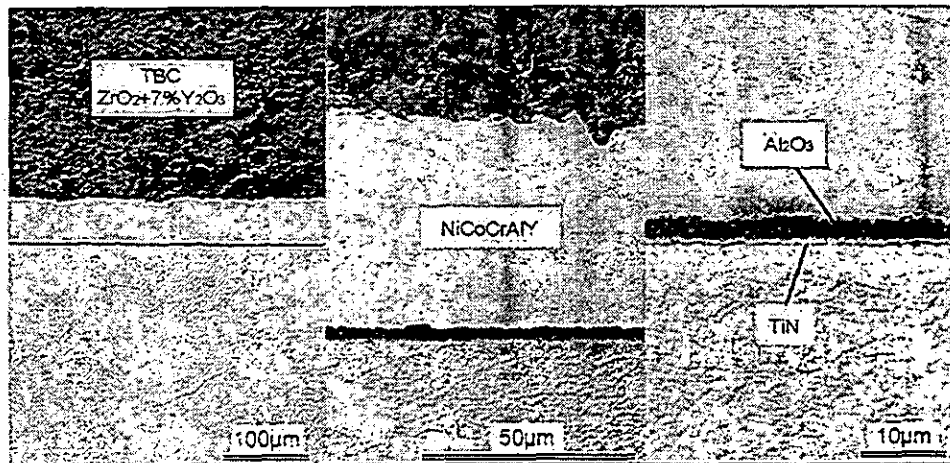


Fig. 1: Coating system before annealing

## TESTING PROCEDURES

The described coating system was deposited on single crystal CMSX4 substrates of the dimension 45x15x8mm. The sample size was limited due to the dimensions of the available CVD reactor. The performance of the diffusion barrier coating was examined by annealing tests with thermal exposure durations from 10 hours to 100 hours. The coated samples were exposed to 1100°C for 100hrs in an argon atmosphere. In order to verify the performance of the diffusion barrier reference samples without diffusion barrier were annealed at the same temperature for 10hrs.

Thermocycle experiments were carried out in a furnace that was heated up to 1000°C. The coated samples were exposed to the high temperatures within cycles of 10 minutes each. It could be expected that within that period of time the sample geometry was fully heated. After removing the sample from the furnace they were cooled down to room-temperature by compressed air from the front for two minutes time. A thermocouple fixed to the sample bracket was used to measure the sample temperature during the thermal cycling.

## PROCESSING AND COATING SYSTEM OPTIMIZATION

Due to the combination of different coating technologies significant problems turned out in optimizing the bonding mechanisms of the individual coating technologies and materials respectively. Efforts had to be made to define suitable preparation techniques for each process step.

### Deposition of alpha-Al<sub>2</sub>O<sub>3</sub> by CVD

The stable alpha-alumina phase can directly be obtained by thermal CVD at temperatures above 1000°C. The alpha-Al<sub>2</sub>O<sub>3</sub> film was deposited in a vertical hot wall reactor at 1050°C and a total pressure of 100 hPa from the system AlCl<sub>3</sub>-H<sub>2</sub>-CO<sub>2</sub>. The deposition of alpha-Al<sub>2</sub>O<sub>3</sub> on a substrate with high contents of Ni, Cr and Co may cause problems due to the growth of undesired whiskers (Colombier, 1986) (see fig. 2). To overcome this problem a CVD-TiN layer (835°C, 1013 hPa total pressure, system TiCl<sub>4</sub>-H<sub>2</sub>-N<sub>2</sub>) was used to seal the substrate. The approx. 2µm thin layer of TiN also serves as a buffer to reduce thermally induced stresses due to the mismatch in thermal expansion coefficients of CMSX4 and alumina. Figure 3 gives the XRD pattern of a coated sample proving the existence of the crystal structure of alpha-alumina. Coating thicknesses of up to 3µm alumina were realized. Prior coating the CMSX4 substrate was grinded and polished using a 1µm diamond-suspension. Afterwards a pre-treatment with nitric acid (34 weight%) followed by cleaning within an ultrasonic bath (methanol and acetone) was performed. After deposition of the TiN layer the deposition of the alpha-Al<sub>2</sub>O<sub>3</sub> was started immediately. For further details on the CVD deposition techniques can be found in the work of Mueller et al. (Mueller, 1999).

### PVD of NiCoCrAlY

The NiCoCrAlY coating was deposited by using the Magnetron-Sputter-Ion Plating (MSIP-PVD) process. The average thickness of the coating was approx. 50µm with a coating rate of 17 µm/h. Argon was used as process gas without any further reactive gases. The process-gas pressure during coating was fixed to 1 Pa. The coating was performed in dc-mode with a power of 600W, the potential of the target was -800V. We applied a bias voltage of -50V at the substrate. The substrate was heated before and during the coating process by contact heating up to approx. 300°C. Prior coating the samples were cleaned with propanol in an ultrasonic bath. The compositions of the NiCoCrAlY target (according to PWA 1386), which in former investigations turned out to be suitable for such applications (Beele, 1994), and the composition of the CMSX4 substrate are given in table 1.

	Ni	Co	Cr	Al	Ta	W	Re	Ti	Si	Y	Hf
CMSX4	63.62	9.71	7.53	12.7	2.00	1.97	0.97	1.26	-	-	0.03
NiCoCrAlY	40.35	18.27	16.08	23.9	-	-	-	-	0.87	0.38	0.11

Table 1: Composition (at.%) of the CMSX4 substrate and the NiCoCrAlY sputter target

### Deposition of TBC by APS

The TBC was sprayed by Atmospheric Plasma Spraying. For spraying a Plasmadyne system was used in combination with a Sulzer Metco F4 spray gun and a nozzle diameter of 6 mm. The gun was carried by an automated positioning system. For the experiments yttria stabilized zirconia (ZrO<sub>2</sub>+7%Y<sub>2</sub>O<sub>3</sub>) was sprayed with a powder fraction of -90 +16µm using a power of 40kW. As plasma forming gas a mixture of argon and hydrogen with a flow of 41,9 SLPM and 4,8 SLPM was used. The average coating thickness was approx. 400-450µm sprayed in 14 cycles with the average thickness of 30µm each. The substrate was preheated up to 600°C before spraying.

In order to optimize bonding between PVD-NiCoCrAlY and APS-TBC numerous experiments were carried out to investigate and compare different substrate preparation techniques. For the deposition of a ceramic spray-coating a certain surface roughness, i.e. a minimum surface activation, is needed. Steel samples had been grit

blasted with different pressures and materials to obtain different surface constitutions. The differently prepared samples had been coated by approximately 20 $\mu\text{m}$  NiCoCrAlY with varying process parameters. Aim of the investigation was to determine a minimum surface roughness to allow spraying of the TBC on top of the deposited sputter coating. However, the surface roughness is an important factor in the sputter process limiting the ability to deposit dense coatings. Figure 4 gives SEM-photographs of the substrate-surface prior and after sputter process. It can be seen that despite the fact the absolute value of surface roughness is about the same before and after deposition of the NiCoCrAlY in both samples, the coating covers all sharp edges and cavities and hence leads to a relatively smooth surface. The actual surface activation due to e.g. sharp edges could not be mirrored by the NiCoCrAlY coating. Better results have been obtained when sputtering on smooth surfaces and grit-blasting the NiCoCrAlY after deposition. Low air pressure during blasting and the use of fine grain material turned out to be sufficient for an activation the NiCoCrAlY-coating and good bonding properties.

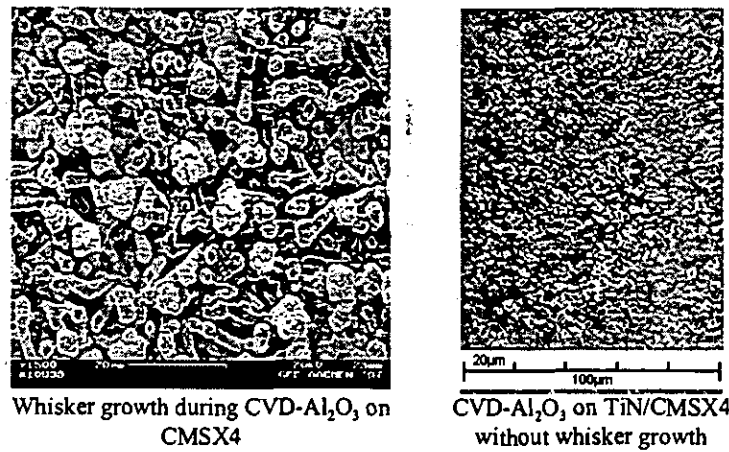


Fig. 2: Effect of TiN on CVD-Al<sub>2</sub>O<sub>3</sub> coating growth

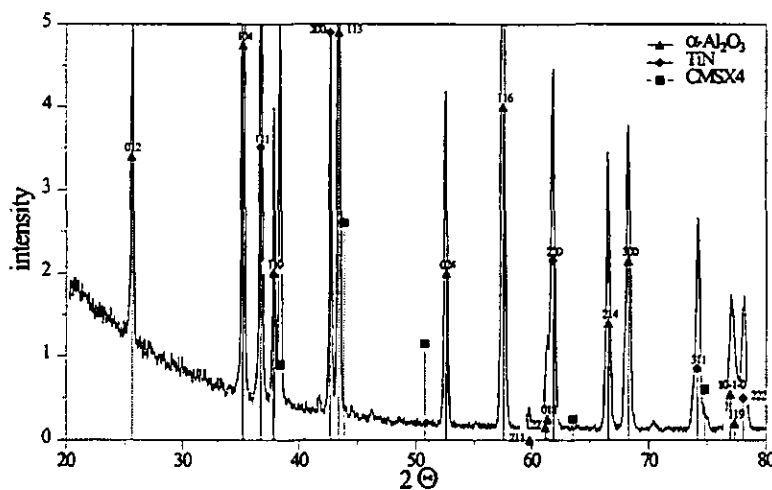
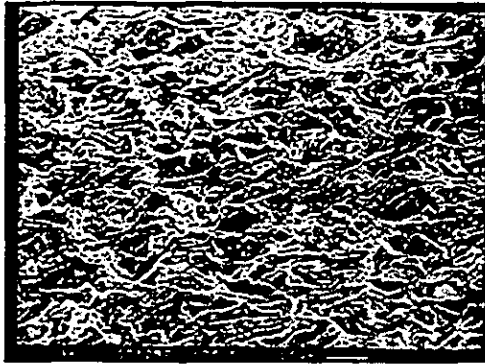
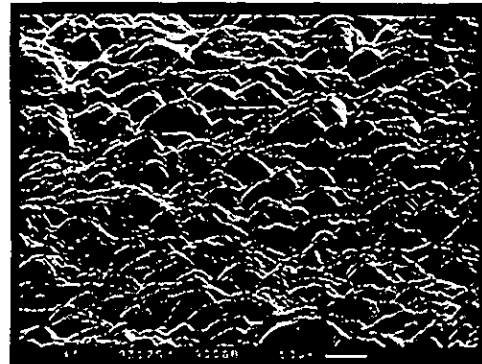


Fig. 3: XRD-analysis of a reference-sample ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>/TiN multilayer on CMSX4) peaks according to JCPDS chart42-1468 ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) and 38-1420 (TiN)



Surface morphology of steel AISI.304 grid blasted with  $\text{Al}_2\text{O}_3$  (+53-90 $\mu\text{m}$ ) at 5bar, 30s



Surface morphology of steel AISI.304 grid blasted with  $\text{Al}_2\text{O}_3$  (+53-90 $\mu\text{m}$ ) at 5bar, 30s, after coating with 20 $\mu\text{m}$  NiCoCrAlY at 600W, 1Pa

Fig. 4: Surface morphology modification by MSIP-PVD coating

## RESULTS

All samples were characterized by optical microscopy, scanning electron microscopy (SEM), energy dispersive x-ray- (EDX) and thin film x-ray diffraction analysis (XRD).

No heat treatment was performed after deposition. The microstructure of the NiCoCrAlY after deposition showed a homogeneous distribution of elements, no formation of different phases could be observed. The CVD- $\text{Al}_2\text{O}_3$  and -TiN layers showed a homogeneous and dense structure.

Metallographic examination of both, the thermocycle samples as well as the annealed samples, revealed the presence of beta- and gamma-phases in the NiCoCrAlY coating. It was confirmed by EDX-mappings (fig.5) and EDX-composition analysis (table 2) that these phases were the beta-(Ni,Co)Al and the gamma-(Ni,Co)Cr phases. The appearance of that kind of a two-phase microstructure is known and expected for this type of NiCoCrAlY and could be confirmed, it also has been observed by Boudot et al. (Boudot, 1998) for vacuum plasma sprayed NiCoCrAlYTa coatings and by Leyens et al. (Leyens, 1996) for electron beam physically vapour deposited NiCoCrAlY coatings.

During annealing and during the thermocycle experiments an  $\text{Al}_2\text{O}_3$  layer was grown on top of the NiCoCrAlY coating. This  $\text{Al}_2\text{O}_3$  was also found in the annealed samples although no oxygen was in the atmosphere of the oven. It can be concluded that because of the fact that  $\text{Al}_2\text{O}_3$  is thermodynamically much more stable than zirconia the Al in the NiCoCrAlY reduced the  $\text{ZrO}_2$  in the TBC. This causes a depletion of the beta-(Ni,Co)Al phase underneath the grown  $\text{Al}_2\text{O}_3$  layer. No depletion of the beta-phase occurred at the NiCoCrAlY - CMSX4 interface, which indicates that the deposited CVD-coating performed as diffusion barrier. This was also verified by EDX linescans for the elements Ni, Co, Cr, Al, Ti, Re, Ta and W across the entire coating system and by composition analysis right above and underneath the diffusion barrier. The performed linescan for the annealed samples for selected elements is shown in fig. 6.

Diffusion barriers of two different thicknesses were tested. EDX measurements were done after annealing to prove their performance. Whereas the thicker  $\text{Al}_2\text{O}_3$  coatings of approx. 3 $\mu\text{m}$  showed no interdiffusion: the elements Ta, Re, W and Ti could be detected right underneath of the  $\text{Al}_2\text{O}_3$  coating in the substrate expected concentration, right above the diffusion barrier none of these elements could be found. Thin  $\text{Al}_2\text{O}_3$  coatings of approx. 1.5 $\mu\text{m}$  turned out to be unstable during high temperature exposure. With the optical microscope (fig. 7) it can be seen that the  $\text{Al}_2\text{O}_3$  diffusion barrier was no longer dense. The beta-phases were heavily depleted, which was caused by the diffusion of Al to the CMSX4 substrate. In addition we observed at the NiCoCrAlY-CMSX4 interface an approx. 10 $\mu\text{m}$  deep zone where the structure of the CMSX4 was altered. With EDX-linescans we found that the aluminium concentration peak at the diffusion barrier was much lower than before, whereas the Ti peak for the TiN bonding was still sharp and high. The TiN was obviously thermally stable, but did not suppress

the interdiffusion between substrate and NiCoCrAlY. The aluminium content in the NiCoCrAlY was reduced, but a significant increase of aluminium in the CMSX4 could not be found. The concentrations of Re, Ta and W appeared no longer as a step at the diffusion barrier, but followed a smooth slope. Diffusion of Co and Cr showed a different behaviour with both elements diffusing approx. 10µm into the CMSX4. This diffusion depth correlates well with the thickness of the diffusion zone as seen in the optical microscope. As it can be seen when comparing figures 7 and 9, the depletion of the beta-(Ni,Co)Al towards the TBC interface was much stronger in the annealed samples than in the thermocycled samples. In case of the thermocycled samples we observe a more pronounced segregation between beta-gamma two-phase microstructure on the one hand and a pure gamma microstructure on the other hand. The beta-phase concentration gradient in case of the annealed sample was much more homogeneous. This was caused by the higher temperatures and longer annealing times leading to higher diffusion activity within the NiCoCrAlY. If we compare the EDX-linescans of two samples coated with NiCoCrAlY on CMSX4 (without TBC and diffusion barrier), one exposed for 10hrs at 1100°C in argon atmosphere and the other as coated, it can be seen that even after the short time of exposure a large interdiffusion zone appears (fig 8).

The thermocycle behaviour of the tested coating systems turned out to be quite promising. No delamination of the TBC occurred during thermal cycling during tests up to 500 cycles which corresponds to 125 hrs testing with 83 hrs thermal loading. A formation of few vertical segmentation cracks within the TBC could be observed. Figure 10 gives an example of the largest developed crack within the investigated cross-section. It can be seen that no damaging of the NiCoCrAlY and the diffusion barrier occurred. Moreover, the formation of segmentation cracks leads to more strain-tolerance of the TBC-toplayer without any losses in thermal barrier performance. As described above, the typical formation of the two-phase microstructure within the NiCoCrAlY could be demonstrated. Within the test-run of 500 cycles no cracking in the NiCoCrAlY occurred and hence it can be stated that thermal cycling at the investigated degree of loading means no limitation for the performance of the NiCoCrAlY and the diffusion barrier.

	at. %			
	Al	Cr	Co	Ni
gamma-(Ni,Co)Cr	8.57	23.83	27.31	40.27
beta-(Ni,Co)Al	32.98	4.37	10.54	52.02

Table 2: Elemental analysis of two-phase microstructure in NiCoCrAlY after heat exposure

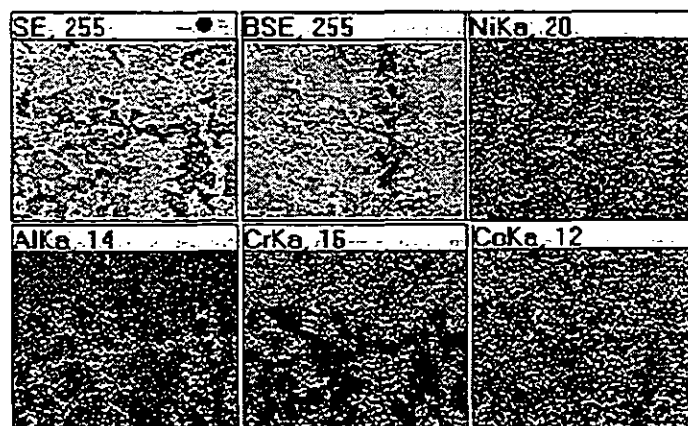


Fig. 5: Secondary electron -, backscattering electron photograph and element distribution of Ni, Al, Cr and Co in MCrAlY after annealing

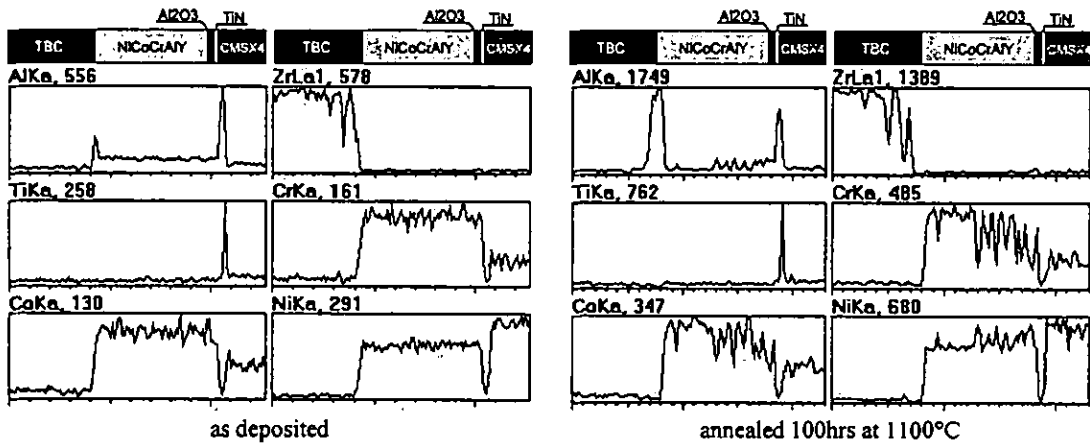


Fig. 6: EDX line-scaas of a multilayer coating before and after annealing

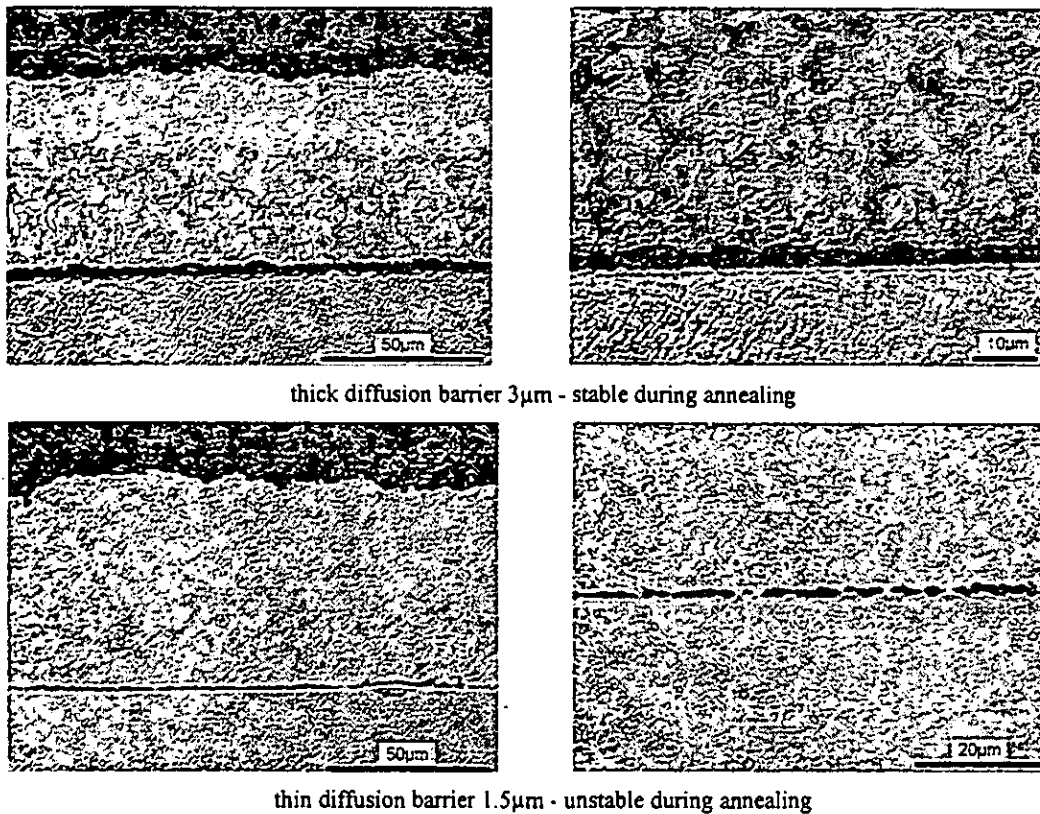
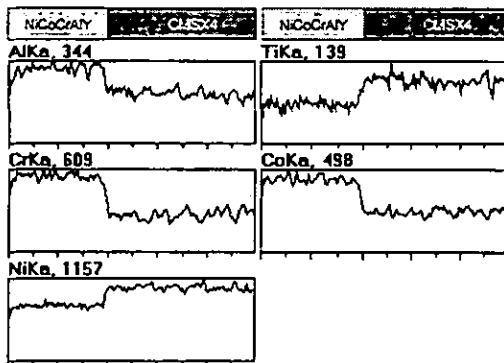
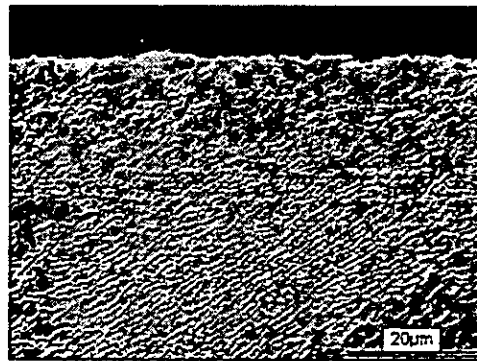
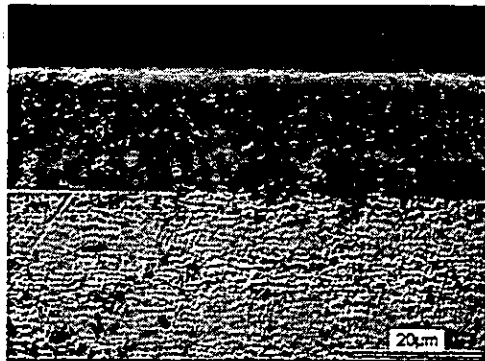
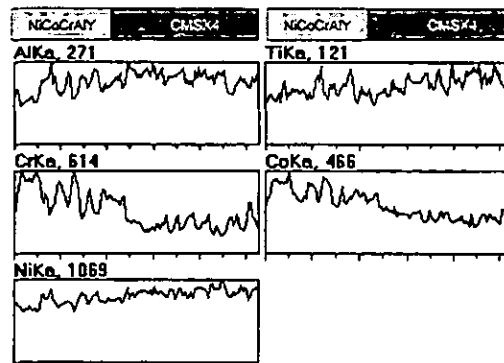


Fig. 7: Cross-sections of multilayer coating after annealing for 100hrs at 1100°C under argon atmosphere



as deposited



annealed 10hrs at 1100°

Fig. 8: EDX line-scan of coating system without diffusion barrier before and after annealing

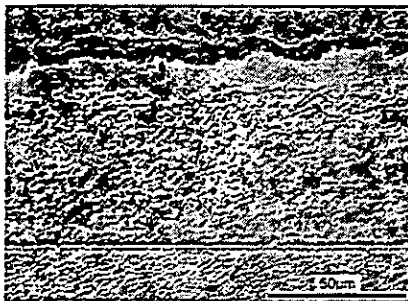


Fig. 9: NiCoCrAlY coating after thermal cycling



Fig. 10: Segmentation cracks due to thermal cycling

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