Development of a thermal-barrier coating-system for rocket combustion chambers

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Abstract

To protect the copper wall of liquid-rocket combustion-chambers, thermal barrier coatings (TBC) may be applied. In this study, a state of art NiCrAlY/YSZO TBC-system as usually used in gas turbines is tested for the use in rocket engines by thermal cycling and laser shock experiments to gain more understanding on the basic failure modes. Based on these findings, new concepts for further coating design are developed, focusing on a modified bond-coat alloy and full metallic Ni-based or Co-Re-based top-coats.

1. Introduction

The combustion chamber in LOX/LH liquid-rocket engines is exposed to high thermal and thermomechanical loads. The process gas can reach temperatures of 3200 °C.[19] To cool down the combustion chamber wall, it consists of a copper liner with a high thermal conductivity and cooled on the inside using liquid hydrogen in cooling channels with temperatures of approximately -240 °C. The surface temperature of the copper liner can reach temperatures of up to 600°C[13] with large heat fluxes of more than 100 MW/m^2.[12, 17] The copper liner above the cooling channels has a thickness of 1 mm. Therefore, the thermal gradient and the large pressure difference between combustion chamber and cooling channel cause a high thermo-mechanical load. Typical failure mechanisms are ratcheting due to the high loads[14] or blanching, caused by cyclic oxidation and reduction in the oxygen/hydrogen atmosphere.[10]

To protect the combustion chamber against high thermal loads and oxidation, thermal barrier coatings may be applied. This has been investigated in several ways in the past, but no successful use in a rocket mission has been reported so far. For example, NASA recently developed Cu/Cr coatings for high temperature oxidation protection, applied with electron-beam PVD and ion-beam assisted deposition techniques, but only isothermal oxidation tests were reported.[22] Another coating investigated by NASA is a TBC-system with a NiAl top-coat and a Ni bond-coat, applied with low pressure plasma spray and vacuum plasma spray. The coatings had to be hot isostatically pressed after coating application. The coatings were successfully tested in blow-torch tests with a thermal gradient.[21] Nevertheless, for application of these coatings, vacuum chambers or high pressure containment vessels with an adequate size to handle combustion chambers are necessary. Coatings applied with atmospheric processes were investigated in the past: Immich et al.[20] reported extensive subscale-test-chamber experiments at Astrium with a zirconia TBC, applied with atmospheric plasma spray. The coatings showed no failure after 7 cycles. Zirconia TBC were also investigated at NASA,[14] applied with conventional flame spray techniques. The life time of the subscale test-chamber could be increased significantly with a 203 μm top coat, but it is mentioned, that ceramic TBC have to be much thinner in real rocket applications than applicable with this coating technique due to their low thermal conductivity.

The long-term aim of our work is to develop a TBC system for rocket engines applied with atmospherical processes. The coating development is divided in two steps: In a first step, a well-known thermal-barrier coating-system as usually used in gas-turbines is investigated for the use in rocket engines. The main goal is to gain more understanding of failure mechanisms on the different substrate material and under different service conditions compared to gas-turbine application. Furthermore, experimental tools are developed, and a micromechanical simulation-model is validated with data from the experiments and the literature. In a second step, new coating concepts will be developed based on the findings with the standard coating-system.

2. Experimental Details

2.1 Coating application

The coatings in this work were applied under atmospheric conditions by thermal spray processes. The standard TBC-system was applied with atmospheric plasma spray (APS) with an Oerlikon-Metco (formerly named Plasmatechnik) F4-Gun with a 6 mm torch diameter. An Ar/N_2-mixture was used for the bond coat, the ceramic top coat was applied with an Ar/H_2-mixture. For both coatings, argon was used as carrier gas. Before bond-coat application, the substrates were preheated to a temperature of 250 °C. The enhanced, metallic coatings were applied by high velocity oxygen-fuel spraying (HVOF) with a WokaStar-610 liquid-fuel gun from Oerlikon Metco with a 4-inch barrel. The gun was moved with a 6-axis manipulator in a translative path over the substrate. A preheating was not carried out, since the copper substrate would oxidise at higher temperatures and the bonding of the coatings was sufficient even without preheating.

2.2 Thermal cycling

Isothermal cycling experiments were carried out with up to 50 cycles at temperatures up to 800 °C and hold-times of 30 min. The coated samples were heated up in an oven under ambient air and cooled down with different cooling rates in air, icy water and liquid nitrogen. The fastest cooling rates were measured with icy water, but the lowest temperatures were reached in liquid nitrogen.[1]

For thermal cycling with high heating rates and a thermal gradient, a laser test-bed was designed.[1] It consists of a diode laser with a maximum power of 3 kW and a special optics to get a broad focal point, so that the whole specimen surface can be heated homogenously. The surface temperature is controlled by a high speed two-colour pyrometer. Surface temperatures of up to 1500 °C can be reached within 0.5 s with this set-up. Plate-shaped samples with a diameter of 20 mm and a thickness of 2 mm are heated only on the coated surface, while the uncoated downside is exposed to ambient air. Depending on the surface-temperature, the heating time and the thermal conductivity of the applied coating, thermal gradients of up to 500 K can be reached. Figure 1 shows for example the measured surface temperature and the downside temperature of a copper sample coated with an 80 μm Rene 80 coating, exposed to a 10 s, 1000 °C laser cycle. The thermal gradient reaches its maximum of approximately 500 K within the first second and reaches about 150 K after 5 s, which then stays nearly constant during the hold time at 1000 °C.

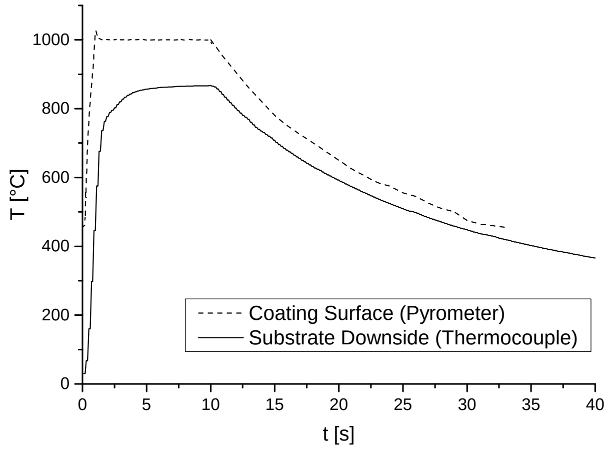

Figure 1: Measured temperatures of a 10 s, 1000 °C laser cycle with a copper-sample with an 80 μm Rene 80 coating.

2.3 Micro-mechanical modelling of the coatings

To determine thermal stresses in the coatings, a 2D finite-element micro-model of the laser-cycling experiments was set up. The model has been described in detail elsewhere.[4] The model represents a small strip of the laser-test specimen perpendicular to the coating surface. The interfaces between the substrate and the coatings are assumed to be sinusoidal in shape to model the typical interface roughness due to a thermal spraying process.[7] On the coating surface, the temperature-amplitude measured in the laser experiments was applied. The heat flux on the substrate downside was applied with a heat sink, which has been validated with the temperatures measured in the laser experiments.[4]

3. Results and Coating Development

3.1 Standard NiCrAlY/YSZO TBC-system

As a starting point for the coating development, a well known TBC-system consistsing of a NiCrAlY (Ni-22%Cr-10%Al-1%Y) bond coat and an Yttria stabilised Zirconia (YSZO, 8% Y_2O_3) top coat is investigated. This coating system has been well described in the literature and failure mechanisms in gas-turbine applications as well as material data are available. The coating is applied with atmospheric plasma spraying.

3.1.1 Isothermal Cycling

Coated copper samples were exposed to thermal cycling at temperatures up to 800 °C for 30 min.[1] At slow cooling rates, no damage of the coatings was observed after 50 cycles. The coatings showed a good protection of the copper substrate. Failure only occurred at high cooling rates at the edges of the specimens, where copper oxide undermined the coating and the bond coat delaminated (see figure 2). Thermally grown oxides (TGO) did occur not even after long time exposure,[1] although internal oxidation in the substrate near the substrate/bond coat interface was observed, caused by oxygen-diffusion due to the relatively high porosity of the bond coat and pre-oxidation during coating application. Segmentation cracks were only observed in the ceramic TBC. The cracks stopped at the TBC/bond-coat interface and did not influence the bond coat.[4]

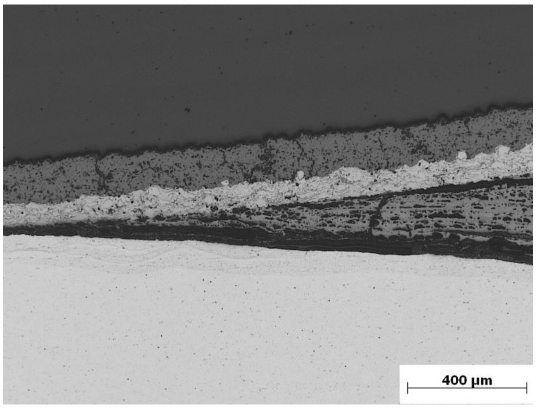

Figure 2: Micrograph of the cross-section of a NiCrAlY-coating after 50 cycles at 800 °C: copper-oxides undermined the coating at the edges of the sample.[4]

3.1.2 Laser cycling

To exacerbate the conditions in thermal cycling tests and to account for the high thermal loads in real service, the coatings were tested in the laser test bed. In these cycling experiments, the coatings failed completely after the first cycle (2s holding time) at temperatures above 1250 °C (figure 3). At surface temperatures of 750 °C, the coatings survived 8 cycles, compared with 50 cycles in the thermal cycling experiments. The coatings failed by delamination between bond coat and substrate over the whole specimen, no partial failure was observed.[1]

Oxidation of the substrate seems to have no influence on the delamination since no oxidation at the substrate/bond coat interface could be observed. Furthermore, the delamination of the bond coat is not influenced by the thermal barrier coating: Samples with only bond coat and no TBC showed delamination even at surface temperatures of 500 °C.[4]

3.1.3 Diffusion heat treatment

To enhance the adhesion of the bond coat, diffusion heat treatments were carried out at 700 °C for 14 h.[4] After heat treatment, an overall interdiffusion zone of more than 10 μm was observed at the bond coat/substrate interface. Laser

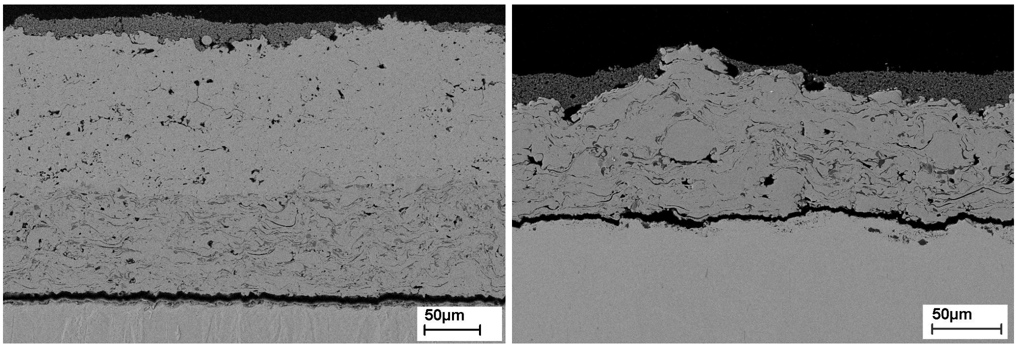

Figure 3: SEM-image of the cross section of the standard coating-system after laser cycling.[4] Left: full system, 2 cycles at 1250 °C, 1 s. Right: Without YSZO top coat, 1 cycle at 500 °C, 1 s. Both coatings failed by bond-coat delamination.

cycling experiments showed a lifetime of more than 30 cycles at surface temperatures of 1250 °C and a heating time of 1 s, while the not heat treated samples failed after only one cycle at the same conditions. This lifetime improvement might be caused on the one hand by lowering the chemical gradient at the interface by diffusion of copper from the substrate into the bond-coat as well as diffusion of nickel from the bond-coat into the substrate. On the other hand, it can be expected that the coefficient of thermal expansion in the bond-coat diffusion-layer is increased due to the increased copper-content. Summing up, the diffusion heat-treatments show that lowering the chemical and thermal mismatch between substrate and bond coat will increase the lifetime of the coating.

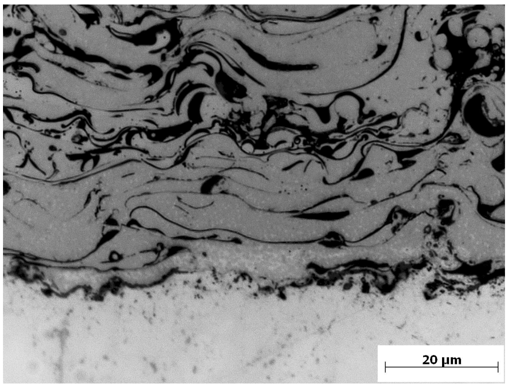

Figure 4: Micrograph of the substrate/bond coat interface after 14 h diffusion heat treatment at 700 °C. Coating: NiCrAlY, APS.[4]

3.1.4 Simulations

As seen in the above section, laser-cycling experiments lead to a delamination of the bond-coat. This delamination usually occurs by crack formation parallel to the substrate/bond coat interface, so the stress component perpendicular to this interface has to be elucidated. Therefore, simulations with a micromodel were carried out to evaluate the thermal stresses in the coatings.[4, 25] For a first estimation, the simulations were carried out elastically and no creep or yield was considered so far. Figure 5 shows the calculated perpendicular stress after heating from room temperature to 1000 °C: Large tensile-stresses in the valley of the surface roughness-profile can be observed, which are caused by the different coefficient of thermal expansion between substrate and bond-coat. These tensile stresses may cause delamination of the bond coat, as observed at high heating rates in the laser-cycling experiments (section 3.1.2). For slower heating rates like in the isothermal cycling experiments, the coating and substrate are expected to creep. Therefore, the interface stresses are much smaller than in the laser-experiments, and do not delaminate.

To estimate the maximum temperatures in the chamber wall, fluid-structure interaction (FSI) simulations of a rocket combustion chamber with the standard coating-sytsem were carried out by Kowollik et al.[2] They show, that ceramic coatings with coating thicknesses applicable with atmospheric spray processes will have too high surface-temperatures due to their low thermal conductivity. To lower the high surface temperatures with applicable coating thicknesses, the top-coat must be made out of a material with higher thermal conductivity, so further research may

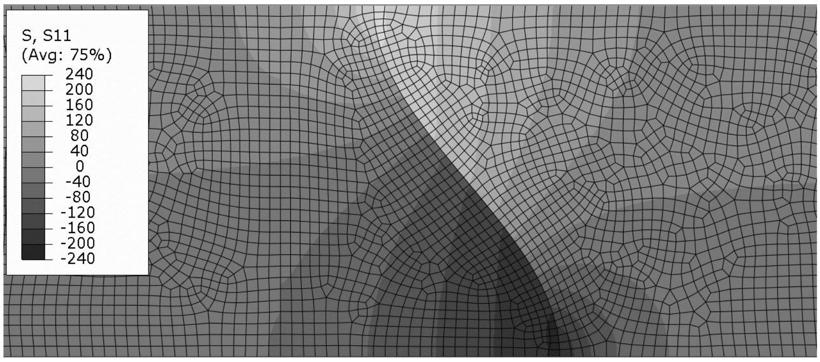

Figure 5: Calculated stress perpendicular to the surface at the interface between substrate (left) and bond coat (right) after heating from room temperature to 1000 °C.[25]

focus on metallic top-coats. Full metallic coating systems may also reduce the substrate temperature sufficiently while the coating temperatures have an adequate level also at higher coating thicknesses.[4]

3.1.5 Summary

The experiments with the standard NiCrAlY/YSZO coating-system showed that thermal cycling without a thermal gradient is not sufficient to test thermal barrier coatings for rocket engine application. Laser cycling experiments seem to be a suitable method to qualify thermal barrier coatings for rocket engine application because they produce damage and even delamination by thermal stresses. This delamination occurs only at the substrate/bond-coat interface, the main reason is the difference in thermal expansion and the chemical dissimilarity between copper-substrate and NiCrAlY bond-coat. Oxidation seems to play a minor role in the failure mechanisms, although substrate-oxidation was observed after long time heat exposure. But this oxidation is caused by the high bond-coat porosity and pre-oxidation, and could be prevented by more dense coatings.

Considering the top-coat, no failure could be observed in the experiments, but simulations showed, that ceramic top-coats with an applicable thickness will lead to very high surface temperatures beyond the maximum service temperature of about 1200 °C.[5]

3.2 Enhanced Concepts

Development of a new bond-coat alloy

The studies of the standard NiCrAlY/YSZO coatings shows that the interface between the substrate and the bond coat has to be optimized. The thermal stresses, which lead to delamination, could be reduced by diffusion heat treatments and the failure of the coatings could be prevented. To avoid extensive heat treatments of the coated combustion chamber, one idea is to modify the NiCrAlY bond-coat material by adding copper.[4] The main requirements on this new bond-coat material are an intermediate CTE in the range between Cu-substrate and possible top-coat materials as well as chemical similarity to the copper substrate. The development of a new bond-coat alloy fulfilling these requirements has been described elsewhere.[3] This alloy has the composition Ni-30%Cu-6%Al-5%Cr. The difference in the coefficient of thermal expansion (CTE) between the new alloy and the copper-substrate is less than between the NiCrAlY-alloy and the copper-substrate (see table 1) and will therefore cause lower thermal stresses at the substrate/bond-coat interface. Furthermore, the high copper-content will lower the chemical gradient at the substrate interface.

Table 1: Coefficient of thermal expansion for different alloys at 800 °C.

Alloy	**CTE / 10^{-6}K^{-1}**
Copper[15]	19.5
Ni-30Cu-6Al-5Cr[3]	17.0
Rene 80[24]	15.0
Co-17Re-23Cr[16]	15.0
NiCrAlY[9]	14.5

Possible Candidates for Top Coat

The simulations showed that even a metallic top-coat will reduce the temperature of the copper-substrate sufficiently, while ceramic top-coats will become too hot on the coating surface (see above section). Hence, a full metallic coating system was choosen for further studies. Possible metallic top-coat alloys need a high maximum service temperature. Furthermore, the top coat needs a lower CTE than substrate and bond coat to reduce the high strain differences due to the thermal gradient in the coating. Possible candidates are for example Ni-based superalloys or Co-Re alloys.[4]

Ni-based superalloys have service-temperatures of up to about 1100 °C,[5] high oxidation resistance and a high thermal strength and are commercially available even as powders for thermal spraying. For further studies, the alloy Rene 80 (Ni-14%Cr-9.5%Co-5%Ti-4%Mo-4%W-3%Al) was used as one top-coat candidate. This material is commercially available as spherical powder in the required particle size, has a solidus temperature of about 1220 °C and an adequate strength at high temperatures as well as an improved resistance against hot corrosion.[6, 24]

Co-Re alloys are developed for application beyond Ni-based supperalloys.[11, 23] Melting temperatures of up to 1700 °C are possible.[11] For high temperature oxidation protection, chromium is added to the alloy to form a Cr_2O_3-layer. The formation of dense oxide-layers can be enhanced by adding silicon.[18] The experimental-alloy Co-23%Cr-17%Re-2%Si was chosen for first coating experiments.

The CTE of both alloys is in the range of NiCrAlY alloys and therefore lower than the CTE of the NiCuCrAl bond coat and the copper substrate (see figure 1).

Coating Process

The delamination at the substrate/bond-coat could be prevented on the one hand by reducing the thermal stresses. On the other hand, the bonding of the coating could be enhanced, for example by changing the application process. Therefore, the enhanced coatings were applied with high velocity oxygen-fuel spray (HVOF). The main advantages of this process compared to APS is on the one hand the higher particle speed, which will lead to more dense coatings and less porosity at the substrate/bond-coat interface. On the other hand, the HVOF flame temperatures are much lower than the plasma-flame temperatures. This will cause less heating of the substrate during coating application and therefore less oxidation.[4]

3.2.1 Laser testing

The new NiCuCrAl (HVOF) bond-coat was tested without a top coat by laser cycling experiments at a surface temperature of 1000 °C with a heat exposure time of 1 s and 2 s. No damage could be observed (figure 6). Furthermore, laser-cycling experiments on HVOF NiCrAlY were carried out to compare the HVOF coating process to the APS process. In this case, no delamination could be observed even at temperatures of 1000 °C, while APS NiCrAlY bond-coats showed delamination even at surface temperatures of 500 °C (see section 3.1.2).

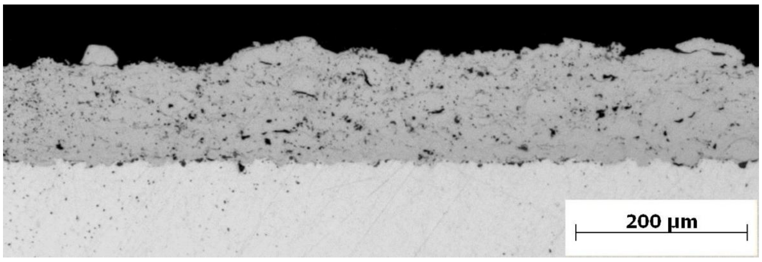

Figure 6: Micrograph of a cross-section through a NiCuCrAl (HVOF) coating after 15 Laser cycles (1000 °C, 2 s, Air cooling), no failure observed.

To exacerbate the testing conditions, the heat exposure time was increased to 10 s and the samples were quenched in icy water after each cycle. The NiCrAlY and the new NiCuCrAl coating applied with HVOF did not show any damage after 20 cycles at 500 °C, but at higher temperatures, segmentation cracks perpendicular to the surface were observed. These cracks seem to start at the outside of the edges of the sample and run radial into the inner areas (figure 7). For the NiCrAlY coating, a much higher crack density and longer cracks are observed compared to the NiCuCrAl coating. It is assumed, that the cracks form due to stress relaxation at high temperatures and subsequent formation of tensile stresses at the coating upon rapid cooling. The different crack densities might be caused by the different coefficient of thermal expansion of the coatings as well as different creep behaviour and different ductility. Further research will be carried out to evaluate the reason for this behaviour.

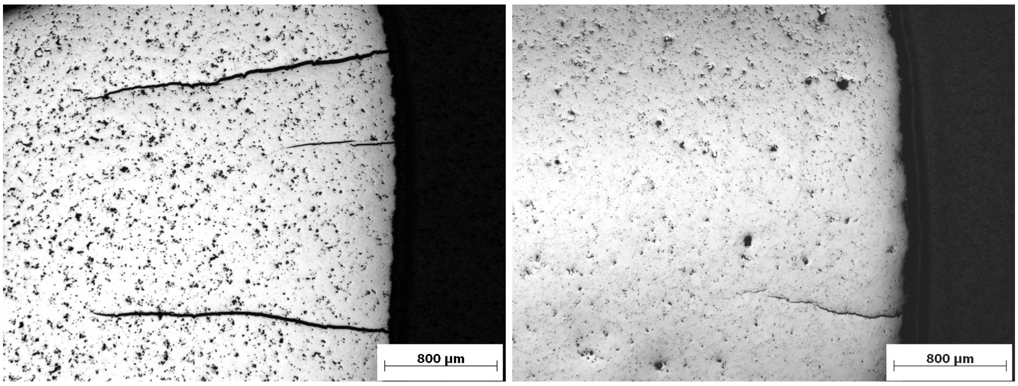

Figure 7: NiCrAlY bond coat (left) and NiCuCrAl bond coat (right) after 20 cycles at 1100 °C, 10 s, both applied with HVOF: Cross-section parallel to the coating surface.

4. Conclusions and outlook

In this work, state-of-the-art TBCs as usually used in gas turbines were investigated for their use in rocket engines. Testing methods and a simulation tool for TBCs in rocket combustion chambers were developed. With these methods, the main failure mechanisms of the coatings were defined. Furthermore it turned out, that the different loads and the different substrate make a modification of the bond coat and a new concept for the top coat necessary. Based on these findings, new coating concepts for further research were developed. They consist of a NiCuCrAl bond coat and a Ni-based or a Co-Re based top coat.

Further work will focus on the one hand on comparing the new top-coat candidates in the laser-shock experiments. On the other hand, mechanical and thermal material parameters will be measured as input for a more elaborate modelling of the coatings.

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