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Damage mechanisms of metallic HVOF-coatings for high heat flux application

Torben Fiedler *, Roland Groß, Joachim Rösler, Martin Bäker

Technische Universität Braunschweig, Institute for Materials, Langer Kamp 8, 38106 Braunschweig, Germany

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ABSTRACT

The copper wall of regeneratively cooled liquid fuel rocket-combustion chambers is exposed to high thermomechanical loads. Although it is cooled by liquid hydrogen in internal cooling channels, surface temperatures of more than 800 °C on the hot-gas side are reached. To lower this temperature and to protect the copper against oxidation, a metallic coating system is developed. It is applied with high velocity oxygen fuel spray (HVOF) and consists of a bond coat and a top coat. As top-coat materials, two candidates were tested in this study: A nickel-based and a cobalt-rhenium-based alloy. For the bond-coat, a new NiCuCrAl alloy has been developed previously.

The purpose of this article is to investigate the failure mechanisms of the new metallic coating systems. For this purpose, two tests are applied. On the one hand, laser-cycling experiments are conducted to test the coatings with a thermal gradient between top-surface and substrate and to investigate the influence of high heating rates. On the other hand, the coatings were tested isothermally in a furnace to investigate the coatings without any thermal gradient. Interface delamination, buckling, formation of vertical cracks and kirkendall porosity are identified as relevant failure mechanisms and the conditions under which they will occur are discussed.

1. Introduction

The combustion chamber wall of regeneratively cooled LOX/LH2 liquid-rocket engines like the Vulcain 2 or the Space Shuttle main-engine is exposed to hot combustion gas with temperatures of about 3200 °C [1]. To cool down the chamber wall, liquid propellant circulates in internal cooling channels and the chamber wall is made of a high thermal conductive copper alloy. However, the copper liner can reach temperatures of about 800 °C [2] and the cooling heat-flux is in the order of magnitude of 0.1 GW/m^2 [3,4]. The high temperatures may cause damage of the copper liner due to thermomechanic fatigue [5] and oxidation and reduction [6] of the surface. To avoid this, the combustion chamber could be protected by a thermal barrier coating (TBC).

In the past, several coating systems have been investigated. State of the art TBC consisting of a metallic bond coat and a zirconia top coat were tested for example at NASA [5] or within the European TEKAN research program [7]. But recent work shows that ceramic coatings with a thickness applicable to atmospheric processes lead to extremely high surface temperatures [8]. Furthermore, the very high thermal gradient even with thinner ceramic coatings will result in large differences in thermal expansion and therefore large thermal stresses in the coating. These disadvantages could be avoided, using a full metallic coating system with higher thermal conductivity than the ceramic coatings, yet substantially lower conductivity compared to the copper substrate. Additionally, a larger strain tolerance and robustness can be expected from a full metallic coating.

A metallic coating system was tested for example at NASA. They developed Cu/Cr coatings for oxidation protection [9] and a NiAl TBC [10], both applied with vacuum processes. A good oxidation resistance of the coatings is reported, but no information about the mechanical integrity with a thermal gradient is given. The tests with the Russian kerosene/oxygen driven RD-180 rocket engine show that a thermal gradient for coating qualification is of importance: A coating system consisting of a nickel bond-coat and a chromium top-coat was developed, but after hot firing tests, vertical cracks in the chromium top-coat were observed, which proceed into the nickel bond-coat with every further firing cycle [11,12].

A new coating system, consisting of a NiCuCrAl bond-coat and a top-coat of a Ni-based superalloy or a CoRe-alloy was developed recently [13–17]. The bond-coat has a copper content of 30% to lower the thermal and chemical mismatch between substrate and bond-coat, and the Ni- and CoRe-based alloys on the top account for the large thermomechanical loads. Detailed simulations were conducted to gain a better understanding of the mechanical loads in these coatings in high heat flux applications with a large thermal gradient. They show that high in-plane compressive stresses occur in the hot upper areas of the coating after heating, caused by the high thermal gradient. If

* Corresponding author.
E-mail address: t.fiedler@tu-bs.de (T. Fiedler).

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these stresses relax, high tensile stresses and vertical cracks may form after subsequent cooling [18]. Additionally, any heating cycle causes stresses normal to the interfaces due to interface roughness in conjunction with the thermal expansion mismatch across the interface [19,20]. This may lead to interface cracking and delamination and, finally, buckling in the presence of in-plane compressive stresses.

The main aim of the present study is to test the new coatings experimentally for the high heat flux application in liquid rocket engines and to identify possible failure mechanisms. Two different experiments are carried out: On the one hand the coatings are exposed to isothermal heating in a furnace. This kind of experiment is particularly well suited to study time dependent damage mechanisms caused by diffusion. On the other hand, a high power laser is used irradiating the coating surface in multiple cycles, thus providing a thermal gradient for a short time span. This type of experiment reflects more closely the situation in the rocket engine and allows to investigate the effect of large temperature gradients on the failure mechanisms.

2. Materials and methods

The coatings were applied via High Velocity Oxyfuel Spray (HVOF) with a kerosene/oxygen driven WokaStar 610 gun from Oerlikon Metco (former Sulzer Metco). Spray parameters are given in Table 1. The NiCuCrAl and CoRe feedstock powders were atomized in an argon flow at Nanoval, the Rene80 powder is obtained from Oerlikon Metco. The powders have a spherical shape, the chemical compositions and powder sizes are given in Table 2. For the copper substrate, an age-hardenable CuCr1Zr alloy (material number 2.1293) was used. The surface of the substrate was sand blasted with 60 μm to 120 μm alumina to increase the mechanical adhesion of the coating, and ultrasonically rinsed in ethanol.

Thermal testing was done on the one hand isothermally in a furnace, on the other hand with a thermal gradient in laser-cycling experiments. For the isothermal tests, 5 mm thick copper sheets were coated with a 45 μm NiCuCrAl bond coat and a 45 μm CoRe or Rene80 top coat. The coated copper sheets were cut in small, 10 mm × 10 mm specimens. These specimens were exposed to heat in ambient air in a furnace for 6 h, since this is a reasonable accumulated service time in rocket engines. Subsequently, they were quenched in water to ensure a rapid cooling of the coating and therefore a defined time of heat exposure.

The laser-cycling experiments were carried out with 2 mm thick coin-shaped copper samples with a diameter of 20 mm. The coated surfaces were heated up by a 3.3 kW diode laser. The laser is equipped with a special optics to produce a broad focal point with the same size as the coated surface. A more detailed description of the setup can be found in [21]. With this experimental setup, it is possible to heat up the surface in less than 1 s (depending on the heat conductivity and heat capacity of the material) up to temperatures of 1500 °C. Due to the short heating time, a high thermal gradient in the samples is achieved. In the beginning of each laser cycle, the laser operates on its maximum power level, until the desired surface temperature is reached. The power is controlled by a two-colour pyrometer to keep the temperature constant. The total cycle time including the heating phase is 2 s. Subsequently, the samples were quenched automatically in water to simulate high cooling rates like in rocket engines after shutdown. This procedure is repeated up to 20 times for each sample.

Table 1
Coating parameters.

Material	Fuel flow, l/h	Oxygen flow, slpm	Combustion chamber pressure, MPa	Spray distance, mm
NiCuCrAl	16.2	650	0.50	400
CoRe	17.5	680	0.54	300
Rene80	18.0	680	0.55	300

Table 2
Coating materials used in this study.

Material	Chemical composition (weight-%)	Powder size	Median size
NiCuCrAl	Ni-30%Cu-6%Al-5%Cr	+20/−50 μm	29 μm
CoRe	Co-23%Cr-17%Re-2%Si	+20/−90 μm	31 μm
Rene80	Ni-14%Cr-9.5%Co-5%Ti-4%Mo-4%W-3%Al	+11/−45 μm	not specified

The laser samples were coated with a NiCuCrAl bond coat and a CoRe or Rene80 top coat. An overall coating thickness of 90 μm was chosen, where the combustion-chamber wall temperature in the rocket engine will be lowered sufficiently, but the maximum service temperature of the Rene 80 top coat is not exceeded [18]. Bond coat thicknesses of 20 μm, 45 μm and 70 μm were tested. To account for the higher service temperatures of CoRe, a larger coating thickness was also tested. This was realized with a 45 μm NiCuCrAl bond coat and a 255 μm thick CoRe top coat.

After the tests, the samples were cut in cross-section and observed microscopically. Delaminations at the substrate/bond coat interface were quantified by summing up the measured length of all delaminations along the cross section over the whole sample diameter and dividing this value by the overall length of the interface to get the fraction of delaminated interface.

For the investigation of the diffusion zone, electron dispersive X-ray measurements were performed on the samples. Spots of 15 μm diameter were scanned and the mean composition was calculated for each spot. Several spots were analysed every 8 μm along the cross section to obtain a composition profile perpendicular to the diffusion zone.

3. Results and discussion

In the thermal tests, four different damage mechanisms were observed: Delamination of the coating at the substrate/bond-coat interface (Fig. 1a), buckling of the whole coating system (Fig. 1b), vertical cracks (Fig. 1c) and Kirkendall porosity at the interfaces between substrate, bond coat and top coat (Fig. 1d). In the following, the conditions for these failure mechanisms to occur are discussed.

3.1. Delamination

Delamination of the coatings was only observed in the laser-cycling tests at the interface between substrate and bond coat after multiple cycles. Table 3 shows the delaminated fraction of the substrate/bond coat interface, where delamination occurred, versus the top-surface temperature during laser testing, the data are visualized in fig. 2. All samples were tested for 20 cycles with a hold time of 2 s each. The coatings consisted of a NiCuCrAl bond-coat and a Rene 80 or CoRe top-coat. The overall coating-thickness is 90 μm, the bond-coat thickness varies between 20 μm and 70 μm. Since no systematic influence of the top-coat material and the bond-coat thickness was observed, all measurements were put into one chart. Although the measured values scatter, a critical surface temperature of approximately 900 °C leads to a maximum in the delaminated interface fraction.

As mentioned before, delamination is caused by thermal stresses perpendicular to the coating surface due to different thermal expansion of substrate and bond-coat material. CuCr1Zr substrate has a coefficient of thermal expansion (CTE) about $2\cdot10^{-6}\,K^{-1}$ to $5\cdot10^{-6}\,K^{-1}$ higher than the CTE of the NiCuCrAl bond-coat, depending on the temperature [22,17]. Due to the rough interface, this mismatch leads to compressive stresses in the peaks and tensile stresses in the valleys of the interface roughness-profile, which can lead to cracking and a delamination of the coating. These stresses increase with increasing interface temperature.

The exact interface temperature during a laser cycle is not known yet, but simulations [18] and temperature measurements at the