M CrAlY bond coats are widely used as oxidation-resistant coatings on superalloys. The major phase is the thermally stable intermetallic β-NiAl phase. The addition of Cr increases the oxidation and corrosion resistance but leads to the formation of α-Cr precipitates. Both phases are brittle and limit the fracture toughness of these coatings. To study the influence of thermal exposure and the resulting chemical composition on the fracture properties, the fracture toughness of both phases is measured by notched microcantilever bending, after processing and after oxidation by thermal cycling. The fracture toughness of β-NiAl decreases during thermal cycling due to the depletion in Al, whereas the fracture toughness and the composition of α-Cr stay constant. As the fracture toughness of α-Cr is lower compared with β-NiAl, the formation of α-Cr precipitates is supposed to decrease the fracture toughness of the bond coat.

**1. Introduction**

Turbine blades are thermally high-stressed components. To protect the used nickel-based superalloys under cyclic load from oxidation in reactive atmospheres, protective coatings have to be applied. These consist of ceramic thermal barrier coatings (TBCs) with a high melting point as well as low thermal conductivity and intermetallic bond coats that assure the oxidation resistance of the substrate. The bond coats are exposed to even higher temperatures than the substrate. They need a sufficiently high ductility to prevent crack growth during thermal and mechanical cycling and they have to compensate the thermal expansion between the substrate and the TBC. Furthermore, they should be thermally stable for a long time although oxidation and diffusion between bond coat and substrate occurs. These M CrAlY (M = Co, Ni, or Co/Ni) coatings consist of different phases embedded in a β-NiAl matrix. β-NiAl (B2 crystal structure) features a low fracture toughness, but a high melting point, good thermal conductivity, and a high oxidation resistance, due to the formation of a protective Al2O3 layer. A high Cr content increases the protection against sulfidation, but leads to the formation of a body-centered cubic (bcc) α-Cr phase in the diffusion zone between substrate and coating, as shown in former investigations. α-Cr has a higher melting point and a lower coefficient of thermal expansion compared with β-NiAl, reducing thermal stresses. Furthermore, the fracture toughness is known to be higher for pure α-Cr and Cr alloys compared with β-NiAl. However, it is not yet clear, whether the α-Cr phase within the coatings has the same fracture toughness as pure α-Cr and if the formation of α-Cr precipitates has a beneficial effect for the lifetime of a M CrAlY bond coat. As the size of the α-Cr phase is in the micrometer scale, it cannot be measured by macroscopic fracture experiments. Hence, the aim of this study is to determine the fracture toughness of both phases in a M CrAlY bond coat by microcantilever bending experiments. In addition, the influence of the evolution of the chemical composition of α-Cr and β-NiAl phases during thermal exposure on the fracture toughness was investigated.

**2. Experimental Section**

**2.1. Materials**

Two different coatings were investigated, which were applied on the Ni-based superalloy IN100. The samples were provided by MTU Aero Engines AG, Germany, and were coated with two chemically different compositions A and B. Both coatings consisted mainly of β-NiAl with an excess of Al, but with a higher amount of Cr in coating A, as shown in Table 1. Cyclic oxidation experiments were performed to mimic the diffusion and oxidation during application. One cycle consisted of a 24 h heat treatment in normal atmosphere at 1100°C, followed by air cooling. This long holding time for eight cycles allowed diffusion between the substrate and the coating, as well as the formation of an oxide layer. Nanoindentation measurements by Webler et al. on these coatings revealed that cyclic oxidation reduces the hardness of the coating. Their microstructure and composition were analyzed with scanning electron microscopy (SEM, 1540Esb, Carl Zeiss, Germany) and energy-dispersive X-ray spectroscopy (EDX, Inca, Oxford, GB). Furthermore, their fracture toughness was determined by microcantilever bending tests, as described later.
2.2. Sample Preparation

Focused ion beam (FIB)-milled microcantilevers were used in this work to investigate the fracture toughness of the phases in the coating. An FIB milling system (Helios NanoLab 600i, Thermo Fisher Scientific, Massachusetts) was used to shape the notched cantilevers, as described in former studies,[14,15] with an acceleration voltage of 30 kV. The first step was to form the rudimental shape of a beam with currents higher than 2500 pA, which was afterward milled with finer currents of 780 pA. The initial notch was milled with a very low current of 7 pA to minimize beam radiation. This led to a crack tip radius of 10 nm, which was afterward milled with currents higher than 2500 pA, to remove the remaining roughness and achieve the rectangular shape, the beams were polished from all sides in a polishing step (80 pA). The dimensions of the final cantilevers were measured for each cantilever in the SEM. They had an aspect ratio length:width:thickness (L:W:T) close to 9:2:2 μm. The initial crack length \(a_0\) was in the range of 0.35–0.45 μm. An image of a cantilever for testing the α-Cr phase is shown in Figure 1. The cantilevers were always cut close to the interface between coating and substrate.

2.3. In situ Testing

The fracture toughness of the microcantilevers was measured using an in situ force measurement system (Kleindiek Nanotechnik, Germany) inside an SEM, explained in detail by Ast et al.[16,17] A description is also given in Supporting Information. By in situ testing, the cantilever deformation as well as the crack propagation were observed. The displacement of the tip on the cantilever was tracked by digital image correlation (Software: VEDDAC 6.0, Chemnitzer Werkstoffmechanik, Germany). With the combination of both signals, it was possible to evaluate the force–displacement behavior. After the tests, the fracture surfaces of the cantilevers were imaged in the FIB. If the crack path showed a phase transition or a change to the phase interface, the tests were excluded from the results.

2.4. Fracture Toughness Evaluation

The fracture behavior of the microcantilevers was classified in two categories. For brittle materials, sudden fracture occurs and the maximal force in the force–displacement curve is directly taken as the critical force initiating fracture. The fracture toughness \(K_Q\) for this linear–elastic behavior is described by linear–elastic fracture mechanics (LEFM) and was calculated by

\[
K_Q = \frac{F_{\text{max}} L}{W^2 \eta f (a/W)}
\]

with \(L\) being the span length between the loading point and the notch, the beam thickness \(T\), the beam width \(W\), and \(a\) as the crack length. \(f(a/W)\) is a dimensionless geometry factor of the tested specimens determined by Iqbal et al.[17] from FEM simulations and \(F_{\text{max}}\) is the force at failure. The subscript “Q” is used for \(K_Q\), as the definition of the plane strain fracture toughness \(K_{IC}\)[18,19] requires different conditions, which cannot be fulfilled by the cantilevers (e.g., a fatigue precracking). Hence, it describes the fracture toughness as a “conditional” value.

If the force–displacement curve intersects with 95% slope of the initial loading, the material behavior is elastic–plastic. Accordingly, the intersection point \(F_{0.95}\) is taken as the critical force. Then the \(J\)-Integral according to ASTM 1820[19] was evaluated.

\[
J(i) = f_i^\text{pl} + f_i^\text{el} = \frac{(K_{IQ,i})^2 (1 - \nu^2) - K_{IQ,i} f_i^\text{el}}{E} + \left[ f_i^\text{pl} + \frac{\eta (A_i^\text{pl} - A_i^\text{el})}{T(W - a_{i-1})} \right] \left[ 1 - \frac{a_i - a_{i-1}}{W - a_{i-1}} \right]
\]

Then the critical \(J\) value \((J_{0.9})\) was determined by taking the whole area under the curve to account for \(A^\text{pl}\), as the force–displacement curve never reached a force plateau and no crack growth was observed during the experiments. The fracture toughness \(K_{IQ,J}\) was then calculated.

\[
K_{IQ,J} = \sqrt{\frac{J_{0.9} E}{(1 - \nu^2)}
\]

As the orientation of the cantilevers was not determined prior to the experiments, the isotropic Young’s moduli and Poisson’s ratios were used for the calculations. Young’s modulus of α-Cr was 286 GPa with a Poisson’s ratio of 0.22. The properties of β-NiAl were 171 GPa and 0.315, respectively.[20]
3. Results

3.1. Microstructure and Chemical Composition

Figure 2 shows the microstructure and distribution of the main elements across the substrate and the coating B in the initial state. The substrate has a $\gamma/\gamma'$ microstructure with a sharp interface between the substrate and the coating. The coating consists mainly of a $\beta$-NiAl zone with a thickness of $22.3 \pm 0.3$ $\mu$m, whose composition changes from the substrate to the surface. The Al concentration increases, whereas the Ni concentration decreases toward the surface. This creates an Al-enriched $\beta$-NiAl area at the surface, which is $7.6 \pm 0.8$ $\mu$m thick and precipitate free. Furthermore, additional phases were observed in the coating. Bright $\alpha$-Cr phases are located in regions close to the superalloy substrate. They mainly consist of Cr and Mo, while all other element concentrations are reduced. They have an elongated shape, with a mean size of $1.1 \pm 0.7$ $\mu$m vertical and $0.7 \pm 0.4$ $\mu$m parallel to the surface. The size distributions of the $\alpha$-Cr phases for all states are shown in Supporting Information. In addition, some oxides (black inclusions) are formed above the interface, as described by Webler et al.\[13\]

Figure 3 shows the microstructural changes of sample B after the cyclic oxidation by EDX mappings. One of the major changes is that the coating thickness increases to $78.4 \pm 3.5$ $\mu$m after oxidation. This is accompanied by the growth of a $24.7 \pm 3.7$ $\mu$m-thick $\gamma$-Ni diffusion layer between the $\gamma/\gamma'$ substrate and the $\beta$-NiAl-containing outer layer. This is a result of the diffusion at high temperatures during cyclic oxidation. The Al concentration in the $\beta$-NiAl phase close to the surface is lower in contrast to the initial state, which results in $\gamma$-Ni precipitates. This is a result of Al consumption due to the outward diffusion for the formation of the oxide layer. The $\alpha$-Cr phase coarsens to a more spherical shape with a mean diameter of $4.7 \pm 3.1$ $\mu$m, while small precipitates dissolve. The biggest ones are still closer to the former interface, whereas some precipitates are formed beneath the surface. Besides the growth of the coating, the area fraction of the $\alpha$-Cr phase remains constant with $\approx 33.7\%$.

The microstructural changes in coating A are almost identical to the ones of coating B and are therefore not shown here, but can
be seen in the Supporting Information (Figure S1/S2). Coating A has an initial thickness of 55 $\pm$ 1.8 μm, which increases by thermal cycling to 92.4 ± 4.0 and a 21.9 $\pm$ 3.7 μm-thick γ-Ni diffusion layer. The main difference is that the higher Cr content leads to the formation of larger α-Cr phases in the initial state of coating A, which has a mean length of 2.5 ± 1.4 μm vertical and 1.3 $\pm$ 1.0 μm parallel to the surface. Those increase to 5.2 ± 3.9 μm after cyclic oxidation. However, the area fraction of the α-Cr phases in coating A is just slightly higher than in B with 35.4%. Nevertheless, it also leads to a change in the composition of the different phases, which were analyzed by EDX-point measurements, as seen in Table 2. The β-NiAl composition was determined close to the interface between substrate and coating. The measurement does not include the oxide concentration, as it was always lower than 0.5 at.-%.

These measurements show that during cyclic oxidation the composition in the β-NiAl zone changes to an Al-depleted state in coating B, whereas coating A is already depleted in the initial state, due to the lower Al concentration in the coating process. α-Cr instead has a high Cr and Mo content. The concentration of Cr is slightly higher for coating A, as the nominal concentration of Cr is higher than in B. After oxidation, the Cr content is almost equal in both coatings. Nevertheless, the high deviation in the measured compositions of the precipitates has to be taken into account. The incident electron beam always interacts with the surrounding β-NiAl matrix and thus the signal depth of the EDX is bigger than the precipitates. However, the composition after thermal cycling seems to be nearly identical in both coatings.

### 3.2. Fracture Toughness Measurements

The load–displacement data were recalculated by the method of Ast et al.,[16] to compensate dimensional effects of the cantilevers. The γ-axis represents the linear stress intensity factor (Equation (1)). Figure 4 shows the representative results of coating A and B before and after oxidation. All microcantilever fracture toughness measurements are shown in Supporting Information in Figure S4 and S5. While α-Cr is nearly perfectly brittle, as seen by the linear behavior, the β-NiAl curve flattens, which indicates plasticity. Hence the $J$-integral method was used for the ductile β-NiAl, as shown in Equation (4). The fracture toughness of α-Cr increased from 2.6 ± 0.4 MPa$\sqrt{m}$ to 3.1 ± 0.4 MPa$\sqrt{m}$ during oxidation, whereas the fracture toughness of β-NiAl decreased slightly from 5.2 ± 1.4 MPa$\sqrt{m}$ to 4.5 ± 0.4 MPa$\sqrt{m}$. The same tendency was observed for coating B, with a fracture toughness increase in α-Cr from 2.3 ± 0.2 MPa$\sqrt{m}$ to 3.2 ± 0.7 MPa$\sqrt{m}$ and a drop in β-NiAl from 4.2 ± 0.4 MPa$\sqrt{m}$ to 3.6 ± 0.2 MPa$\sqrt{m}$ due to thermal exposure.

The fracture surfaces after testing are shown only for coating B, as they are similar to A, in Figure 5. The crack in the α-Cr phase propagates straight down to the end of the cantilever without being deflected. While α-Cr has a smooth and plain breaking surface, β-NiAl reveals a very rough and faceted fracture surface. The upper part of the fracture surface is rather smooth, representing the area where the plastic crack growth is supposed to take place. However, the elastic anisotropy of β-NiAl being higher compared with α-Cr has to be considered[20] which also affects fracture toughness.[16] According to literature, the crack deflection in β-NiAl and the formation of facets is common for soft oriented planes. The difference of the fracture surfaces between the initial and the oxidized state is neglectable and therefore cannot describe the change in fracture toughness.[16]

### 4. Discussion

In this study, the fracture toughness of α-Cr and β-NiAl in two different oxidation-resistant MCrAlY coatings was determined. After the coating process, α-Cr phases were already present in the coating. These quite small precipitates grow during the oxidation cycles by a factor of two to three, but the ratio of α-Cr to β-NiAl stays constant in this coarsening process. α-Cr phases are located close to the interface to the substrate and move during the oxidation cycles with the growing β-NiAl matrix of the coating. The higher Al concentration at the surface in the initial state leads to an inward diffusion and expansion of β-NiAl. The reduced Al concentration in the β-NiAl layer leads to destabilization of the original α-Cr + β-NiAl equilibrium. It transforms into α-Cr + γ-Ni at the interface to the substrate, as shown in similar studies.[21,22] Those changes deplete the Al content in the coating, as shown by the EDX measurements in both coatings. This directly influences the composition of the β-NiAl phase, leading to a reduction of the fracture toughness of β-NiAl.

However, one should keep in mind that also other factors, such as the crystal orientation, FIB damaging, or varying

### Table 2. Chemical composition of the α-Cr and β-NiAl phases close to the interface between substrate and coating A and B before and after cyclic oxidation in at.-% by EDX measurements.

| Phase   | Coating | Condition | Cr     | Mo     | Ni     | Al     | Co     | Ti     |
|---------|---------|-----------|--------|--------|--------|--------|--------|--------|
| α-Cr    | A       | Initial state | 81.3 ± 1.7 | 6.6 ± 0.7 | 6.2 ± 0.5 | 1.2 ± 0.4 | 3.6 ± 0.7 | 1.2 ± 0.1 |
|         | B       | Oxidized   | 85.5 ± 1.5 | 4.9 ± 0.9 | 5.1 ± 0.9 | 0.5 ± 0.4 | 3.4 ± 0.4 | 0.7 ± 0.2 |
|         | B       | Initial state | 80.0 ± 8.0 | 8.2 ± 1.7 | 6.1 ± 5.7 | 3.9 ± 3.7 | 2.4 ± 1.7 | 0.5 ± 0.2 |
| β-NiAl  | A       | Oxidized   | 85.9 ± 0.3 | 5.5 ± 0.4 | 5.2 ± 0.2 | 0.2 ± 0.1 | 3.1 ± 0.3 | 0.3 ± 0.1 |
| B       | A       | Initial state | 8.3 ± 2.2  | 0.5 ± 0.3 | 46.2 ± 1.8 | 273 ± 2.4 | 11.0 ± 0.2 | 6.8 ± 0.9 |
|         | B       | Oxidized   | 7.1 ± 0.2  | 0.2 ± 0.1 | 53.1 ± 0.3 | 28.0 ± 0.4 | 8.9 ± 0.1 | 2.7 ± 0.1 |
|         | B       | Initial state | 5.5 ± 2.3  | 0.2 ± 0.1 | 44.9 ± 3.5 | 32.2 ± 3.0 | 10.9 ± 0.2 | 6.5 ± 3.3 |
|         | A       | Oxidized   | 7.2 ± 0.3  | 0.2 ± 0.1 | 55.2 ± 1.1 | 28.0 ± 1.2 | 7.7 ± 0.1 | 1.8 ± 0.1 |
cantilever geometries, could affect the determined fracture toughness, too. Here, the influence of different crystal orientations on the fracture toughness was not considered. As the fracture surfaces showed no indication of a hard orientation and the determined fracture toughness was close to values of the soft orientation, as measured in former studies, this effect is considered to be negligible. Furthermore, the results are consistent with those of Webler et al., who showed a similar trend for the Ni-to-Al ratio. In addition, the zone under the notch is embrittled by the Ga ions of the FIB milling. The affected zone is known to be smaller than 30 nm and it was shown that it has only a small influence on the measured fracture toughness. As the geometries of the measured cantilevers were consistent and they differ just slightly among each other, no influence on the fracture toughness is expected as in other studies with varying cantilever geometries. Consequently, the fracture toughness of the β-NiAl matrix decreases during oxidation.

The fracture toughness of the α-Cr phase was determined to be lower compared with β-NiAl and can be described as brittle. As the fracture toughness of pure α-Cr and its alloys is supposed to be higher than β-NiAl, it must be lowered by additional effects. The most tremendous embrittlement is supposed to be caused by the formation of nitrides at high temperatures in normal atmosphere. Those nitrides were probably formed during the coating process. Nevertheless, the nitrogen concentration was too low to be detected by EDX. However, nitrogen concentrations below 0.1 at.% already cause tremendous embrittlement, an influence by nitrogen cannot be neglected. Furthermore, the embrittlement in α-Cr could be caused by the elements of the coating, like Al, Ni, Co, or Ti. Several studies reveal a detrimental effect of concentrations with at least 1 at.% on the fracture toughness. In comparison, studies on the eutectic NiAl–Cr(Mo) in situ composites, which were produced with vacuum melting, showed less embrittlement of α-Cr. This is presumably a result of the absence of nitrogen and a lower content of soluted alloying elements.

Due to the flat cleavage planes and the brittle breaking behavior, the influence of the orientation is negligible. Nevertheless, it was proven that the change in the composition of α-Cr has only a small effect on the fracture toughness and it does not decrease during the oxidation.

The results indicate that the presence of α-Cr solid solution in oxidation coatings of superalloys has two major drawbacks. On the one hand, this phase has lower fracture toughness than the main component of the coating, β-NiAl. On the other hand, the size of the α-Cr phases and their stretched morphology makes crack growth even easier. This is accompanied by the effect that the interface between α-Cr and β-NiAl is prone to oxidation. These effects would suggest that α-Cr shortens the lifetime of a coating. Recent studies oppose that the main failure mechanism of the thermally loaded bond coats is crack growth along oxide protrusions and oxide spallation. Therefore the formation of stable α-Cr phases, which have a thermal expansion coefficient close to the oxides, increases the lifetime by reducing the thermal stresses. However, if the crack growth exceeds the oxidation limited regime, the α-Cr precipitates reduce the fracture toughness of the system. As the oxidation is less important for the crack growth at lower temperatures, thermal cycling will also favor an earlier failure by the brittle α-Cr. Hence, the amount of α-Cr phases in a coating should be reduced to prolong the lifetime at cyclic loading. Also, further studies should study the source of the embrittlement and how an
increase of the fracture toughness might influence the performance of the coating.

5. Conclusion

Two different MCrAlY coatings consisting of the main constituent β-NiAl phase and interspersed α-Cr precipitates were investigated. The oxidation experiments showed that the formation of alumina at the surface and the diffusion of aluminum into the substrate reduce the concentration of Al in the coating. The coating grows to more than two times its size during cyclic oxidation and the α-Cr precipitates coarsen from \( \approx 1 \) to \( 5 \) μm. With microcantilever experiments, it was possible to measure the fracture toughness of α-Cr and β-NiAl individually at their small scale. The determined fracture toughness of α-Cr is \( 2.3 - 2.6 \text{ MPa} \sqrt{\text{m}} \) lower than that of β-NiAl with \( 4.2 - 5.2 \text{ MPa} \sqrt{\text{m}} \) in the initial state. While the enrichment of Ni in β-NiAl decreases, its fracture toughness to \( 3.6 - 4.5 \text{ MPa} \sqrt{\text{m}} \) during oxidation, the fracture toughness of α-Cr stays nearly constant at \( 3.1 - 3.2 \text{ MPa} \sqrt{\text{m}} \) and is still below the fracture toughness of β-NiAl.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

bond coats, fracture toughnesses, intermetallics, microcantilever bending

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