



Development of Oxide Dispersion Strengthened MCrAlY Coatings

K. Bobzin, T. Schläfer, K. Richardt, and M. Brühl

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MCrAlY materials are widely used as bond coats for thermal barrier coatings on turbine blades. The aim of this work is to improve mechanical properties and wear resistance of thermal sprayed NiCoCrAlY-coatings by strengthening the coating with hard phase particles. In order to retain the effect of the dispersion reinforcement at high temperatures, the use of temperature-stable oxide hard phases such as $ZrO_2\text{-}Y_2O_3$ is necessary. To realize this new material structure, the high-energy ball-milling process is applied and analyzed. The mixture ratio between NiCoCrAlY and $ZrO_2\text{-}Y_2O_3$ was varied between 5 and 10 wt.% $ZrO_2\text{-}Y_2O_3$. The influences of the milling time of the high-energy ball-milling process on the distribution of the hard phases in the metal matrix were analyzed. After spraying with a HVOF system the mechanical properties of the coatings are measured and compared with conventional NiCoCrAlY coatings.

Keywords coatings for gas turbine components, composite materials, feedstock, HVOF spray parameters, novel materials, production/preparation technology, wear, wear and corrosion

1. Introduction

MCrAlYs are among the most important protective coating materials applied to counteract hot corrosion and high-temperature oxidation in hot parts of turbine like blades or duct segments. Due to the particulate nature of the aspirated air and the high centrifugal force at the blades, a high mechanical strength and hardness are important features of the protective MCrAlY coatings. To increase the mechanical strength of coatings, metal matrix composites (MMC) were developed during the recent years (Ref 1). In most cases, carbides such as Cr_3C_2 or WC were used as strengthening hard phases. But these materials pyrolyze at temperatures of about 500-800 °C and therefore applications in turbines are very limited.

Because of that MMC with oxide hard phases were developed for high-temperature applications. The high-energy ball-milling technique is an effective method for

producing powders for MMCs (Ref 2, 3). In the milling process, for ductile/brittle material combinations like NiCoCrAlY and ZrO_2 , the particles of the brittle powder are broken into fine particles, cut into the metal matrix, and surrounded by the metal matrix.

In order to achieve a good hot gas corrosion and oxidation resistance for the MCrAlY coatings, a very dense coating is essential. Due to the high kinetic energy of the particles, the high velocity oxy-fuel (HVOF) process leads to dense coatings. Furthermore, it has been confirmed that MCrAlY coatings can be produced by HVOF spraying with equivalent mechanical properties to vacuum plasma sprayed MCrAlY coatings (Ref 4, 5). Therefore the developed powder will be sprayed by the HVOF system.

2. Experimental Procedure

2.1 Materials

For the production of the dispersion strengthened powder, a commercial spray powder (NiCoCrAlY -45 + 22.5 μm , H.C. Starck, Goslar, Germany) was used as starting matrix material. The basic material for the hard phases was a commercial yttria partially stabilized ZrO_2 (YPSZ) spray powder ($ZrO_2\text{-}Y_2O_3$ 93-7 wt.%/-45 + 10 μm , H.C. Starck, Goslar, Germany).

2.2 Dispersion Powder Preparation

The dispersion strengthened powder was prepared by a high-energy ball mill of type Simoloyer CM08 (Zoz, Wenden, Germany). The mixture ratio between NiCoCrAlY and YPSZ was varied between 5 and 10 wt.% YPSZ. Both powders were mixed and milled in air with various milling times. In order to achieve a high relative velocity between the stainless steel balls (100Cr6) within the mill, the revolution speed was varied during milling.

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The ground revolution speed was 900 rev/min and every 5 min the speed was reduced for 1 min to 500 rev/min. Based on the changing of the rotation rate, a balance between the balls can be avoided. The ball-to-powder ratio in mass relation of 10:1 was selected according to previous experiences (Ref 6). The stainless steel chamber, which was filled with 8 kg balls, was water cooled during the milling process in order to keep the powder temperature at approximately 37 °C. The progress of the milling process was measured by taking powder samples every hour. The maximum milling time was 10 h. The selection of the optimal milling time for the two different powders was based on particle morphology, particle size distribution, and homogenous distribution of the hard phase.

2.3 Particle Size Measurement

The particle size distribution was measured with an optical Particle Image Analyser Morphologi G2 (Malvern Instruments Ltd., Herrenberg, Germany). The Morphologi G2 particle analyzer provides repeatable and routine characterization of particle size. The system is equipped with a microscope coupled with a high-resolution digital camera for high definition aberration-free images. The diameter of single particles is measured in the following steps. The 3D image of the particle is captured as a 2D image and converted to a circle of equivalent area to the 2D image. The diameter of this circle is then reported as the diameter of that particle.

Table 1 HVOF spray parameters

Coating parameters	Mechanical alloyed NiCoCrAlY – YPSZ	Commercial NiCoCrAlY
Total gas flow, slpm	880	880
Stoichiometry (O ₂ /H ₂)	0.22	0.26
Shroud gas, slpm	300	300
Spray distance, mm	270	270
Powder feed rate, g/min	25	25

2.4 Microhardness Measurement

The microhardness of the powder and of the coating was measured by the Bühler Micromet 1 microhardness tester (Bühler GmbH, Düsseldorf, Germany). This system calculates the Vickers hardness (HV) from the quotient of the test load and surface of the quadrilateral diamond pyramid indentation left on the material. Within this work a test load of 25 g for the powder and 100 g for the coating was used.

2.5 Thermal Spraying

The YPSZ dispersion strengthened NiCoCrAlY powder, produced by using the deduced optimal milling parameter, was sprayed by the HVOF system Sulzer Metco Diamond Jet Hybrid™ DJ2600 (Sulzer Metco, Wohlen, Switzerland). Before spraying, the powder was sieved with a 45 and 20 µm sieve to achieve a suitable particle size distribution of -45 + 20 µm. The same commercial NiCoCrAlY powder, which was used as matrix material, was also sprayed as reference. The developed spray parameters are listed in Table 1. Due to the high-temperature analysis, the coatings were sprayed onto alloy 600 substrates, which were grit blasted and cleaned. The coatings were heat-treated for 6 h at 1050 °C in a vacuum furnace.

2.6 Wear Behavior

The wear resistance respectively the abrasive wear behavior of the coatings was measured by the pin-on disc test CSEM HT Tribometer (CSEM, Neuchâtel, Switzerland). The pin-on disc tests were performed at a temperature of 700 °C. As counter part an Al₂O₃ pin with 6 mm diameter was used. Prior to the testing, the coatings were ground to an 800-grit finish. The load force was 5 N and the total sliding distance 200 m. The sliding speed was adjusted to 5 cm/s. The surface line profiles of the wear track were analyzed by an UBM laser profilometer (UBM Messtechnik GmbH, Ettlingen, Germany). Based on the average of six profilometer measurements, the wear volume was calculated.

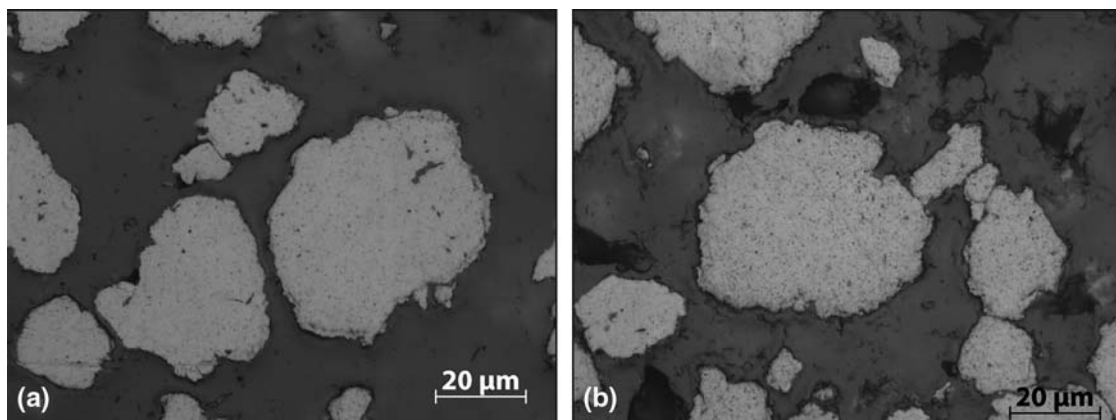


Fig. 1 SEM image of NiCoCrAlY + 5 wt.% YPSZ after 5 h milling (a) and NiCoCrAlY + 10 wt.% YPSZ after 4 h milling (b). The dark small points within the bright NiCoCrAlY matrix are YPSZ

3. Results and Discussion

The powder was analyzed every hour concerning the particle size, powder morphology, and the homogeneous distribution of the oxide hard phases in the metal matrix. Every powder batch was embedded and analyzed by cross sections. Figure 1 shows the cross section of the powder NiCoCrAlY + 5 wt.% YPSZ after 5 h milling. It can be seen that the hard phases (dark phase) are fine and homogeneously dispersed in the metal matrix (bright phase). In the milled powder with 10 wt.% YPSZ, a homogeneous distribution of YPSZ in the metal matrix could be achieved after 4 h.

The particle size distribution of every powder batch was measured by using the optical analyzing system Morphologi G2 produced by Malvern Instruments Ltd. Figure 2 shows the distribution of the two powder batches at different states of milling. In this figure, two different lines for each powder are displayed. After 4 h milling, 90 vol.% of the powder NiCoCrAlY + 10 wt.% YPSZ is finer than 71 μm and 90 vol.% of the powder including 5 wt.% YPSZ is finer than 80 μm after 5 h milling. For the same milling times, half of the volume of the powder NiCoCrAlY + 5 wt.% YPSZ exhibits a particle size under 45 μm and 50 vol.% of the powder NiCoCrAlY + 10 wt.% YPSZ is below 38 μm . The powder was sieved to receive a fraction between 45 and 20 μm and the yield was approximately 40%. The leftover can be filled back into the mill for milling again.

The morphology of the powder is another important property for a suitable thermal spraying powder, as it influences the flowability of the powder. Figure 3 shows particles of the milled NiCoCrAlY + 10 wt.% YPSZ after 2 and 4 h milling. The powder after 4 h milling exhibited a more spherical shape than the powder after 2 h. In this way, the 4 h milled powder was more convenient for feeding. A suitable spherical shape for NiCoCrAlY + 5 wt.% YPSZ was achieved after 5 h milling.

Figure 4 shows Vickers hardness at room temperature measured on the three different powders. It can be seen that the dispersed strengthened powder owned drastically

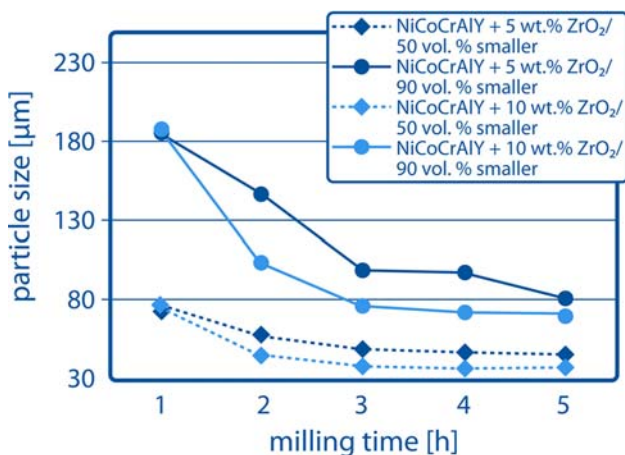


Fig. 2 Particle size of the powder at different milling times

higher hardness than the powder without hard phases. The hardness of the non-dispersed commercial NiCoCrAlY powder was approximately 420 HV0.025. The powder strengthened with 5 wt.% YPSZ exhibited with 660 HV0.025 a higher hardness than the commercial powder. An increase of the dispersion to 10 wt.% YPSZ did not

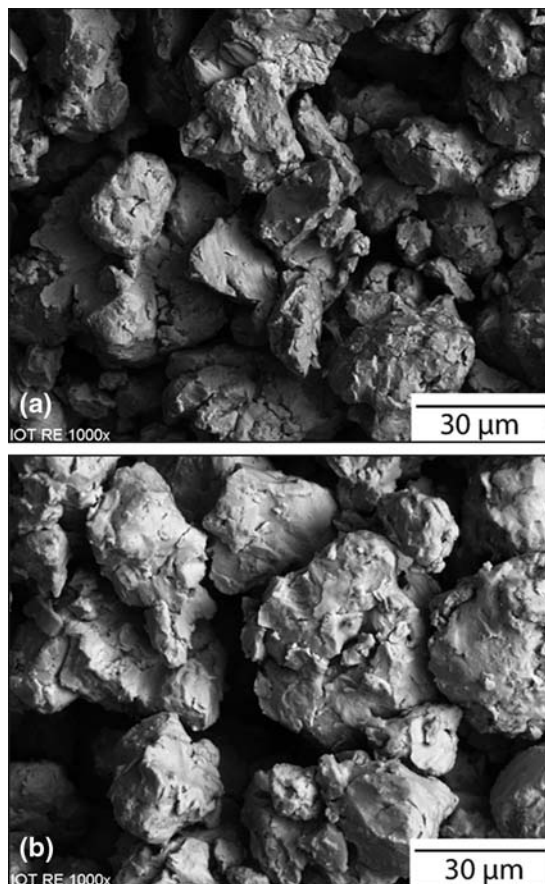


Fig. 3 Milled NiCoCrAlY + 10 wt.% YPSZ after 2 h (a) and 4 h (b) milling time

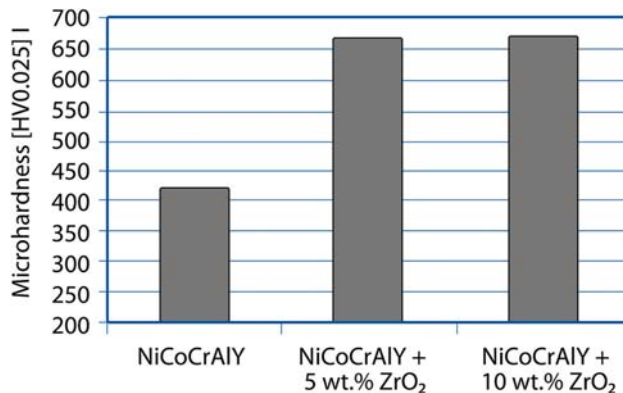


Fig. 4 Vickers hardness at room temperature for the three different powders

lead to a difference in the microhardness of the powder in comparison to the powder strengthened with 5 wt.% YPSZ.

Cross sections of the HVOF sprayed coatings after heat treatment are displayed in Fig. 5. Apart from the coating with 10 wt.% YPSZ, the coatings show a dense structure after diffusion process. The unstrengthened coating possessed a low porosity with 1.15% and the coating strengthened with 5 wt.% YPSZ had a porosity of 2.59%. In contrast to this, the coating with 10 wt.% YPSZ exhibited a porosity of 7.9%.

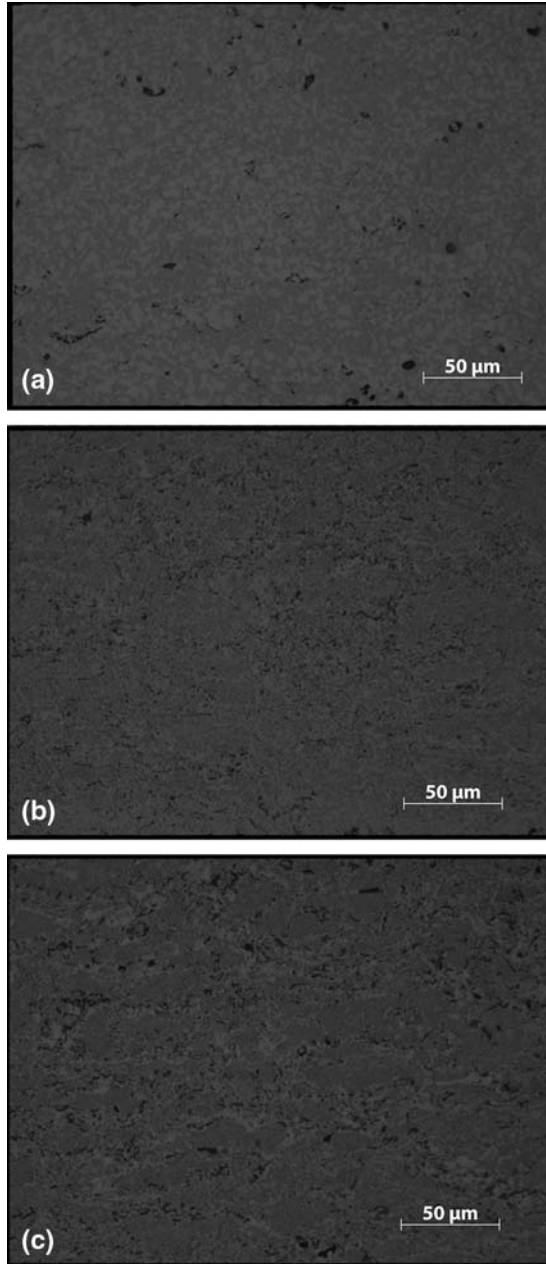


Fig. 5 Cross section of the conventional NiCoCrAlY coating (a), the strengthened NiCoCrAlY coatings with 5 wt.% YPSZ (b), and with 10 wt.% YPSZ (c)

Figure 6 shows the Vickers microhardness of the three different coatings. It can be observed that the microhardness of the unstrengthened conventional NiCoCrAlY coating is 100 HV0.1 lower than dispersed strengthened coatings. The microhardness of the 5 wt.% YPSZ coating and the 10 wt.% YPSZ coating slightly differs.

For the coating strengthened with 10 wt.% YPSZ, the microhardness did not correspond to the values for the abrasion rating of the coating. The abrasion rating of this coating was nearly the same range as the unstrengthened coating. Both coatings exhibited a volume loss of $3.7 \times 10^{-4} \text{ mm}^3/\text{Nm}$ (Fig. 7). In contrast, the coating strengthened with 5 wt.% YPSZ had just the half of the abrasion rating than the other two coatings ($1.75 \times 10^{-4} \text{ mm}^3/\text{Nm}$). A picture of the sliding track is shown in Fig. 8. Due to the high temperature, the pin ploughed through the coating without larger disruptions. In Fig. 8 it can also be observed that only less of the coating material was adhered on the pin after the sliding test. Another indication for this wear behavior can be seen in Fig. 9, which shows the track profile of the same coating. At the edge of the sliding track the material was plastically deformed and extruded outside of the sliding track.

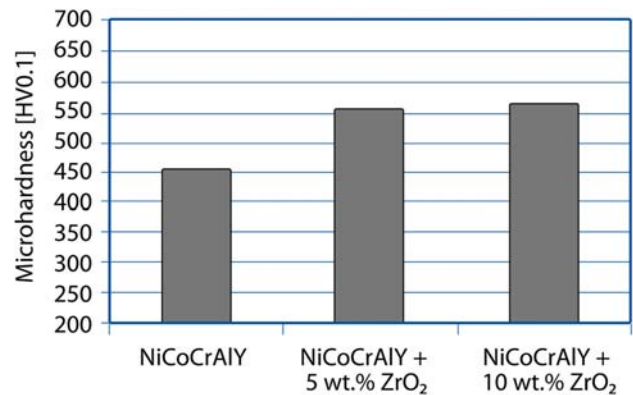


Fig. 6 Vickers hardness at room temperature for the three different coatings

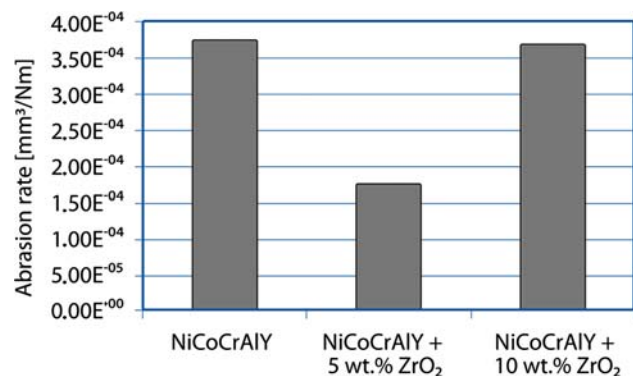


Fig. 7 Abrasion rating of the coating during the pin-on disc test at 700 °C. The testing parameters were sliding speed 5 cm/s, sliding distance 200 m, and load force 5 N. The counter part was an Al₂O₃ pin

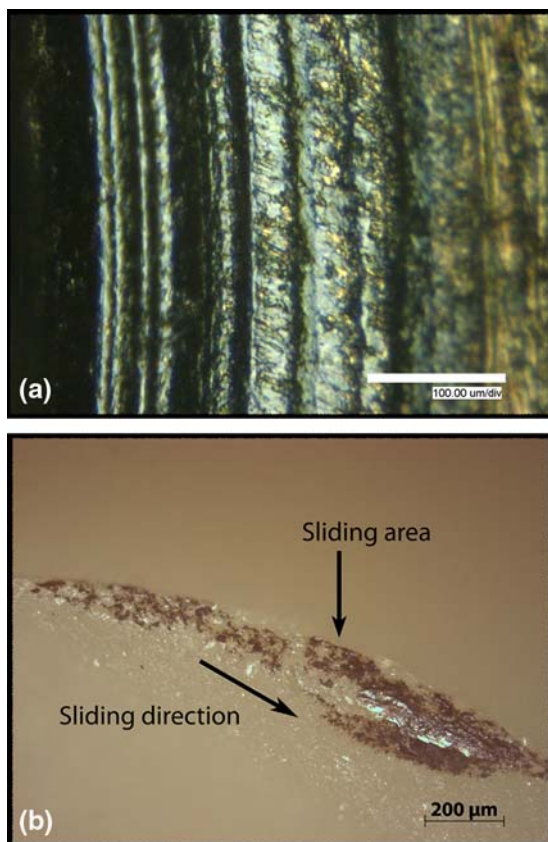


Fig. 8 Sliding track of the coating strengthened with 5 wt.% YPSZ (a) and the sliding area on the Al₂O₃ pin (b)

The higher abrasion rating of the strengthened coating with 10 wt.% YPSZ can be explained by the higher coating porosity after heat treatment. The higher porosity led to a lower cohesion between the particles within the coating in comparison to the other strengthened coating.

4. Conclusion

The presented study has demonstrated that oxide dispersion strengthened NiCoCrAlY powder can be prepared by using a high-energy ball-milling process. A homogeneous dispersion of the oxides can be achieved after 5 h milling for 5 wt.% YPSZ and after 4 h milling for 10 wt.% YPSZ. After this milling time, the powder has a suitable morphology for thermal spraying. By using oxide hard phases, the hardness of the powder can be increased from 420 HV_{0.025} for the commercial NiCoCrAlY powder to approximately 660 HV_{0.025} for the strengthened powder.

The powder can be thermally sprayed with a HVOF system. After heat treatment, a dense structure can be achieved. The microhardness of the strengthened coatings

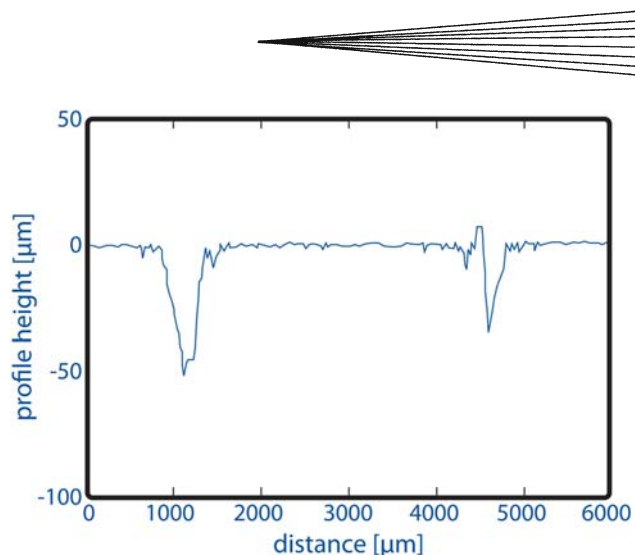


Fig. 9 Track profile on the coating NiCoCrAlY + 5 wt.% YPSZ

is 100 HV_{0.1} higher than that of the coating produced with the commercial NiCoCrAlY powder.

By strengthening the coating with oxide hard phases, the wear resistance can be improved. The abrasion rating of the coating produced with the NiCoCrAlY + 5 wt.% YPSZ powder is half of the rating of the commercial NiCoCrAlY coating. These results lead to the supposition that the strengthened coatings exhibit better erosion resistance than the commercial coatings. But this has to be investigated by further measurements.

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