Mechanically alloyed SiC composite powders for HVOF applications

B. Wielage[1], J. Wilden[1], T. Schnick[1], A. Wank[1], J. Beczkowiak[2], R. Schülein[3], H. Zoz[4] H. Ren[4]
[1] Inst. of Composite Materials, Chemnitz University of Technology, D
[2] Praxair Services GmbH, Wiggensbach D
[3] Euroflamm GmbH, Bremen, D
[4] Zoz GmbH, Wenden, D

HVOF sprayed coatings have reached a high standard with regard to wear and corrosion resistance in many industrial applications. The increasing surface demands concerning mechanical, thermal and chemical performance of thermally sprayed coatings lead to development tasks for the feedstock materials. As SiC combines excellent mechanical, thermal and chemical properties it is of great interest for spray applications. The decomposition of SiC at high temperatures and the reactivity with transition metals require the protection of the hard particles in metallurgically designed binder phases. The high energy ball milling process is an interesting and economic alternative for the production of SiC containing composite feedstock. Investigations with mechanically alloyed SiC-composites in different matrices are carried out and the results concerning microstructure and wear resistance are compared to conventional HVOF sprayed cermet coatings.

1 Introduction

In general component surfaces are exposed to a combination of detrimental mechanical, tribological, corrosive and thermal effects. The stress induced at the component surface causes a degradation of properties or in the worst case a complete failure.
Surface technologies enable the deposition of protective coatings. In many cases the complex surface demands can only be met by the application of composite materials.
HVOF spraying is actually one of the advanced surface technologies for the production of coatings against wear and corrosion with respect to process control and economic issues. Due to the flexibility of the process and the diversity of applicable feedstock HVOF has reached high acceptance for industrial applications.
In consideration of increased coating efficiency, the reduction of the weight of coated volume and cost saving leads to the effort to optimize the spray facilities and on the other hand to the development of new consumables for expanded applications.

2 State of the art

At present a variety of various feedstock materials as well as thermal spray processes are available for the production of protective coatings. By the knowledge that the particle velocity takes significant influence on the attainable coating quality HVOF processes have gained increasing market shares.
Besides the further development of spray facilities new material concepts offer a great potential for the thermal spray technology.
To achieve an improved wear resistance of technical surfaces the application of hard particle reinforced feedstock on the basis of WC is state of the art.
The wear resistance of composite coatings is influenced by various factors. The hard particle share, the distribution in the metallic binder the size, form and embedding of the hard particles in the matrix are decisive for the tribological characteristics of the coating.
Up to now it has been considered to be impossible to apply SiC for thermal spray applications. A new material concept, based on the application of adapted matrix alloys in composites, shows a high potential to overcome the decomposition and the reactivity of SiC in thermal spraying [1].
The difficulties for the application of SiC are based on the incongruent melting behavior as well as the strong reactivity with almost all transient metals even in solid state at elevated temperatures [2], [3]. The dissolution of SiC in the metallic matrix leads to undesirable formation of silicides.
Extensive examinations regarding the wetting and reactivity of SiC show, that the decomposition of SiC proceeds in the area of the primary crystallization of the metallic matrices. Adapted alloying of the metallic matrix outside the crystallization limiting eutectic permits to reduce the reactivity and promotes the wetting of the SiC particles in the composites.
Based on the new material concept Ni and Co based matrices were developed and applied for the production of SiC containing composites. The experimental results for the application of agglomerated as well as blended composites show the high potential to achieve high SiC containing composites for wear and corrosion protective coatings.
Besides the conventional feedstock facilities for composites the high energy milling (HEM) is an interesting and economic alternative method.
HEM was developed amongst other things for the production of oxide reinforced Ni-alloys. In connection with this, the process is widely described as mechanical alloying. The high energy ball milling is a process, in which the alloying is due to the repeated breaking and cold welding of the involved particles. A newly developed process permits the commercial production of composites for thermal spray applications under industrial conditions [4].
The successive breaking and milling leads to an increase of stack faults, imperfections and dislocations. The continuously created surfaces feature high activity and permit the manufacturing of metal-oxide and metal-carbide compounds of high strength [5], [6].

The ductility of the milled material is crucial for mincing, deformation and growth of particles. With increasing ductility the milled material tends to particle growth and flake formation due to the high deformation energy. Another parameter for the milling process is the size of the balls. The contact zone is in theory dot-like between the grinding balls. In reality Hertzian compression leads to a size depending on the contact area. With decreasing ball diameter the contact zone approaches the dot-like form which permits to produce high deformation energy per grist volume. The demand for small balls, which despite the small diameter feature a high kinetic energy lead to the development of the so called Simoloyer high energy ball milling technology.
The horizontal arrangement of the HEM device eliminates the influence of the gravity on the balls and the grinding media at operation rotary speed. By this way dead zones are avoided in the milling device. This configuration enables an uniform distribution of the balls and grinding media, which assure homogeneous allocation of the impact processes.
The advancement compared to conventional drum-mills consists of the fixation of the grinding chamber and the acceleration of the balls via a rotor shaft. As milling device a large quantity of steel balls with a small diameter are applied. In **Figure 1** the configuration of a HEM device is shown.

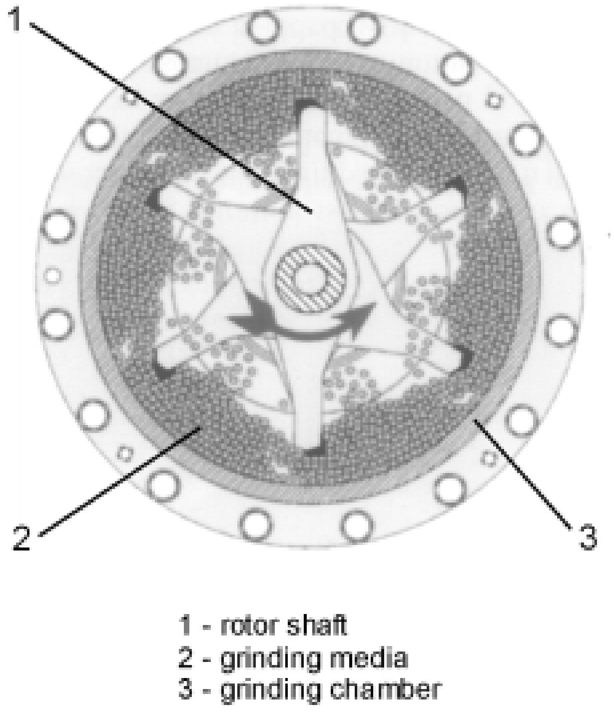

Figure 1. Cross-sectional view of the Simoloyer grinding unit with horizontal rotor shaft, milling balls and grinding chamber

The most stressed parts of the grinding units are the rotor shaft blade ends, where bulk wear parts transfer the kinetic energy. The selection of these parts must correlate to the grinding medium. Experience shows, that the major contamination is caused by the grinding medium. The quality of the grinding medium must be chosen with respect to the acceptable impurity in the mechanically alloyed composite.

3 Experimental

3.1 Mechanical alloying of SiC composites

Based on the considerations of SiC composites for HVOF applications different Ni and Co based matrix alloys are chosen for the production of mechanical alloyed SiC composites, **Table 1**.

Table 1. Chemical composition of the metal matrices

Element	1 [wt.-%]	2 [wt.-%]	3 [wt.-%]	4 [wt.-%]
Ni	72,2	83,4	-	-
Co	-	-	92,5	86
Fe	3,4	2,7	-	-
C	0,8	0,3	1,5	1
Cr	16	8,6	-	7
B	3,3	1,6	-	1.5
Si	4,3	2,9	6	4.5

For the preliminary investigations the mechanical alloying of the SiC-composites are carried out with a Simoloyer CM 01-2l, by variation of the rotary speed, processing time and SiC content. The milling is carried out under ambient conditions.
The analyses of the composite morphology show that with rising process time the morphology of the powder particles changes from spherical to irregular shape, **Figure 2**.

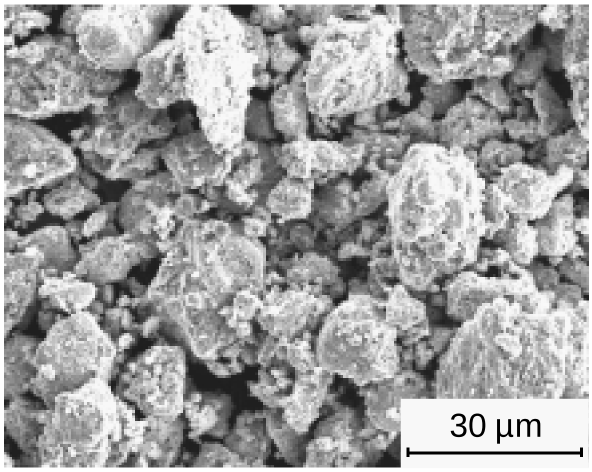

Figure 2. Morphology of the mechanically alloyed composite particles.

By optimization of the process parameters it was possible to manufacture SiC composites with a homogeneous distribution of the SiC particles. The detailed SEM examination of the cross section documents a meshed SiC structure with two SiC particle sizes. On the one hand SiC particles with an average diameter of 0.5 µm and on the other hand particles with an average particle size of less than 200 nm are observed, **Figure 3**.

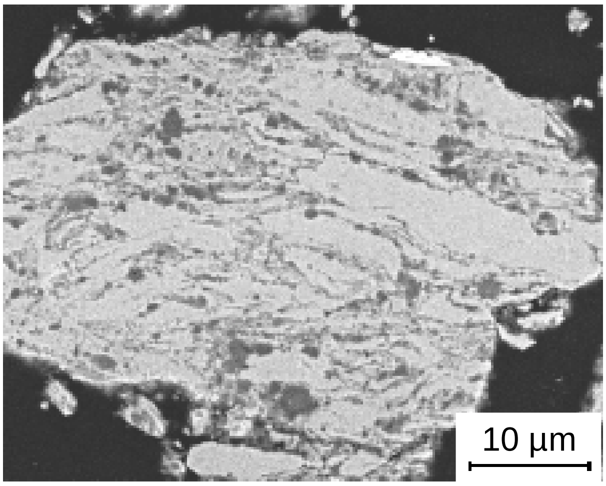

Figure 3. SEM image of a powder particle cross section, Ni-based SiC composite matrix type 1, SiC content in the composite powder type 1: 50 vol.-%, Simoloyer CM 01-2l.

The production of the mechanically alloyed SiC consumables for thermal spray applications is carried out with a Simoloyer CM 08-08l, with a grinding chamber volume of 8l. Parameter optimization permits to obtain comparable results like in the laboratory scale milling. In **Figure 4** a Co-based mechanically alloyed composite is shown.

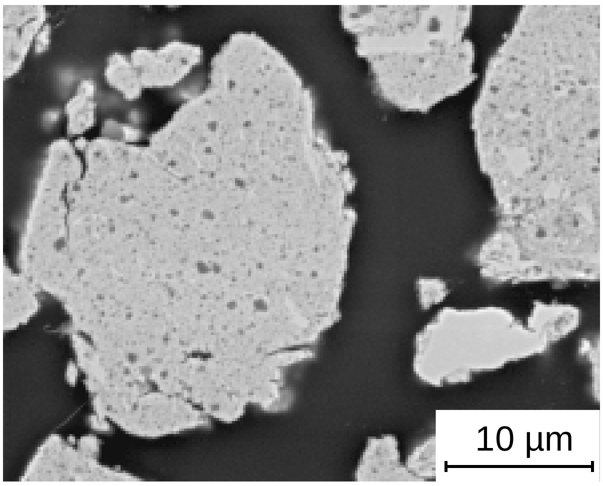

Figure 4. SEM image of a powder particle cross section, Co-based SiC composite matrix type 3, SiC content in the composite powder: 70 vol.-%,Simoloyer CM 08-08l.

In detailed SEM examinations of the SiC composites a minimum size of the alloyed SiC particles of 100 nm is observed, whereas SiC particles of an average size of 1 µm in the composites are detectable. With optimization of the grinding parameters the ratio of not alloyed starting matrix is negligible.

3.2 Thermal spraying of mechanical alloyed SiC-composites

Before the thermal spraying of the mechanically alloyed SiC composites, the powders are fractioned for the spray processes by sieving. The irregular shape of the mechanically alloyed SiC-composites complicates the flowability.
To realize short interaction time and moderate temperature regimes different HVOF processes are applied, **Table 2**.

Table 2. HVOF spray parameters

Diamond Jet Standard	
Propane	34 – 37 [Scale]
Oxygen	34 – 40 [Scale]
Compressed air	42 – 54 [Scale]
Spraying distance	150 – 300 [mm]
Top Gun K	
Kerosene	14 – 20 [l/h]
Oxygen	750 – 950 [SLPM]
Spraying distance	150 – 350 [mm]
JP 5000	
Kerosene	16 – 22 [l/h]
Oxygen	600 – 950 [SLPM]
Spraying distance	200 – 400 [mm]

Subsequent to thermal spraying the coatings are characterized metallographically with respect to the coating morphology by use of optical microscopy and SEM. Additionally XRD and element analyses via spectroscopy are carried out. The wear resistance of the sprayed coatings is determined by an oscillating wear test.

3.3 Coating characterization

In **Figure 5** a Diamond Jet sprayed coating of composite powder type 2 is shown. The maximum coating micro hardness amounts to 730 HV 0.05. Depending on the process parameters the coating porosity results in 5 vol.-% on average.
Due to the high process temperature HVOF systems, using propane as combustion gas, decomposition of the SiC particles could not be prevented. EDX analyses of sprayed coatings show an increase of the Si content in the metallic binder, which can be related to the decomposition and reaction of the metallic binder with the SiC particles.
In further investigations a SiC composite powder with a ductile matrix and a SiC content of 65 vol.-% in the starting powder was processed with the kerosene HVOF system, Top Gun K. The micro hardness of these coatings is 770 HV 0.05 with a minimum porosity of 2.5 vol.-%. In **Figure 6** a SEM image of the cross section is shown.

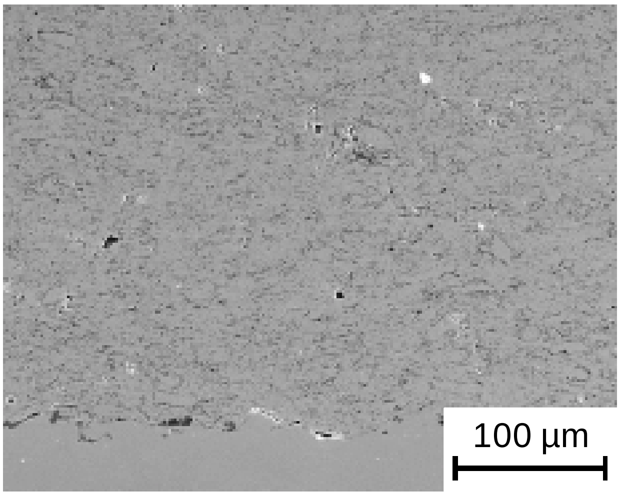

Figure 5. Cross section of a Ni-based SiC composite coating type 1, SiC content in the composite powder: 50 vol.-%, Diamond Jet Standard.

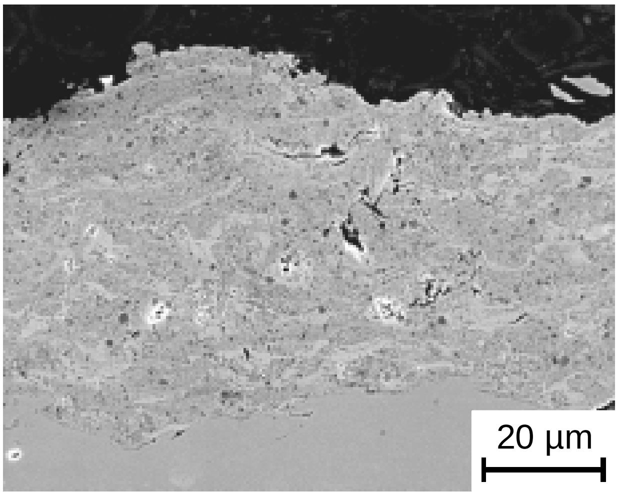

Figure 6. Cross section of a Co-based SiC composite coating type 3, SiC content in the composite powder: 65 vol.-%, Top Gun K.

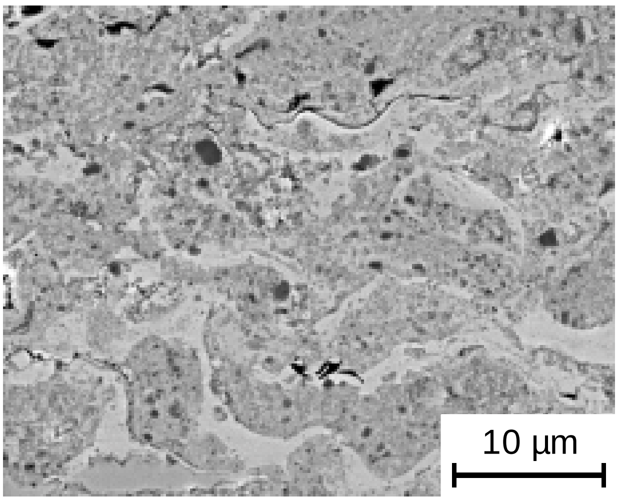

Figure 7. SEM detail image of a Co-based SiC composite coating type 3 cross section, SiC content in the composite powder: 65 vol.-%.

In detailed SEM investigations different grey scales are visible. In correlation to the starting SiC composites regions of not alloyed matrix, nano-structured SiC composite and SiC particles with an average SiC particle size of 1 µm are detectable.
In addition to the morphological examinations of the sprayed coatings XRD and spectroscopic analyses are carried out.
In **Figure 8** the XRD pattern of a Ni-based SiC composite coating of type 2 is shown. In addition to the starting phases of Ni, SiC and Cr_5B_3, the formation of the phases Cr_3C_2 and Ni_2Si is detected.

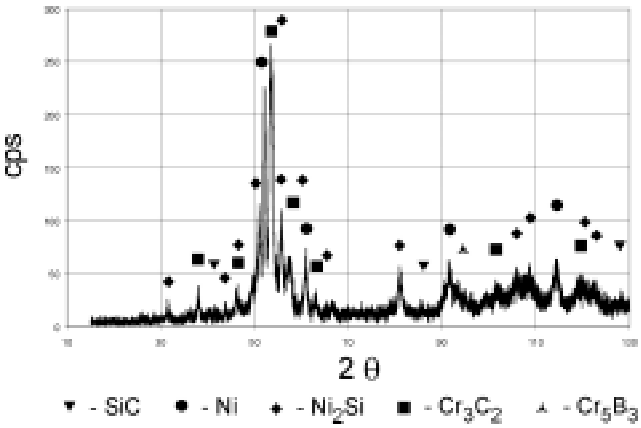

Figure 8. XRD pattern of a Ni-based nano-structured SiC composite coating, SiC content in the composite powder: 65 vol.-%, Top Gun K.

The formation of Ni_2Si can be related to the thermally induced decomposition of parts of SiC, and reactions between the SiC and the matrix at elevated temperatures.
In addition to the XRD analyses spectroscopic examinations of thermally sprayed SiC composites are carried out. These investigation aim at the determination of the oxygen and carbon content in the coatings with respect to the adjusted process parameters, **Table 3**.

Table 3. Determination of the oxygen and carbon content for the SiC composite powder with type 2 matrix, SiC content in the powder: 65 vol.-%.

Sample	wt-%	
	oxygen	Carbon
Composite powder	0.682	7.042
Coating (oxygen-kerosene ratio 3.8)	4.263	6.874
Coating (oxygen-kerosene ratio 5.2)	3.588	6.369

A minor oxygen content is detected for the oxygen-kerosene ratio of 5.2 compared to a ratio of 3.8. With respect to the lower process temperatures for a ratio of 5.2 it can be deduced, that the decomposition of the

SiC particles decreases whereas a higher loss of carbon is detected. An oxygen-kerosene ratio of 3.8 which is quite near to the stoichiometric composition leads to high process temperatures in the HVOF process which promotes the formation of carbides in the sprayed coating.

3.4 Wear test results

For the oscillating wear test mild steel specimens (1.0503) are coated by the HVOF system Top Gun K. The parameters for the oscillating wear test are summarized in **Table 4.**

Table 4. Oscillating wear test parameters

Counter body	Al_2O_3, ∅ 9 [mm]
Load / frequency	20 [N] / 20 [s^{-1}]
Amplitude	1 [mm]
Duration	60 [min]
Temperature	Ambient

The results of the oscillating wear test are shown in **Figure 9**. The results of the nano-structured SiC composites are compared to the values of uncoated mild steel as well as to conventionally manufactured (agglomerated and sintered/blended) SiC composites and state of the art cermets (WC-CoCr).

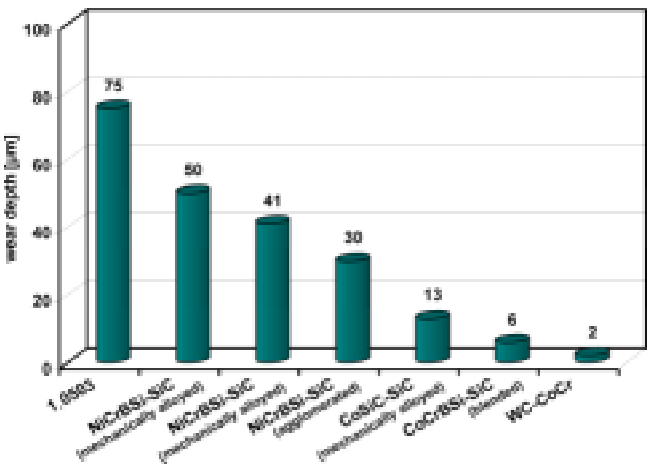

Figure 9. Oscillating wear test results of the nano-structured SiC-composites.

The examinations of the oscillating wear test show, that the wear resistance of WC-CoCr is nearly reached. The difference may be attributed to the lower micro hardness of the nano-structured SiC composites. In consideration at the high SiC content in the Ni-based mechanically alloyed composites the low wear resistance can be related to tearing out of SiC-particles under the complex tribological contact and their contribution as additional abrasive medium. The application of composites with adapted composition according the phase theory approach of saturated primary crystals lead to significant improvement of the wear resistance.

4 Summary and conclusions

The investigations show that the Simoloyer technology is a suitable production process for mechanical alloying of SiC-composite feedstock material.
The application of HVOF permits to reduce the thermally induced decomposition and reaction of the SiC with the metallic matrices, which enables to achieve high SiC containing thermally sprayed composite coatings.
The wear test results show the high potential for mechanically alloyed SiC composites under medium wear stress with respect to the costs. Further investigations will aim for examination of mechanical alloyed SiC composites for erosion resistance applications.

5 References

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