

PUBLICATION VI

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In: Proceedings of 16th International Plansee Seminar.
May 30–June 3, 2005. Reutte, Austria 2005. 12 p.
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Process optimization and performance of nanoreinforced HVOF-sprayed ceramic coatings

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Summary

Improved mechanical properties have widely been demonstrated for bulk nanocrystalline materials. Especially with ceramic materials decreasing of grain size has been found to be favourable. Nanocrystalline materials offer better thermal shock resistance, lower thermal conductivity and better wear resistance than their conventional counterparts. For nanostructured bulk composites with nanosized metal precipitations in the nanocrystalline ceramic matrix improved fracture toughness properties have also been reported. An increasing effort has been made to transfer such improvements also into thermal sprayed ceramic coatings. Mainly work has been carried out with plasma spray systems, but recently it has been shown that HVOF (High Velocity Oxy-Fuel) process can produce much denser coatings and hence better environmental protection capacity. In this paper we describe the development of HVOF sprayed nanocrystalline Al_2O_3 -composite coatings, where the grain size of Al_2O_3 has been decreased and a few percents of alloying elements has been added in order to toughen the coating.

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Keywords

Thermal spraying, HVOF, process optimization, alumina, nanostructure

1. Introduction

Thermal spraying is an effective and low cost method to produce thick coatings and change surface properties of the component. Because the coating is built-up from the melted or semi-molten droplets via fast cooling, thermal spraying offers an ideal means to produce coatings from a wide range of the materials. Thermal sprayed coatings are often used as environmental (wear, corrosion and/or thermal) or electrical barriers.

Ceramic coatings offer an interesting alternative to produce a protective layer over a steel structure due their excellent chemical, corrosion and thermal resistance. Plasma spraying is the mainly used method to produce a thick ceramic coating. Recently it has been shown that HVOF process can produce much denser coatings and hence better environmental protection properties than plasma sprayed coatings [1,2,3].

Even though HVOF coatings are much denser as compared to ordinary plasma sprayed coatings, the coating properties are inferior as compared to bulk ceramics because of pores and microcracks, which influence adversely the coating properties, i.e. toughness, hardness and wear resistance. The denser the coating is, the more limitations are observed due to the residual stresses and mismatches in CTE compared to the steel structure.

One strategy to improve the properties of the coatings is to decrease the grain size of the ceramic phase and to add toughening elements to the microstructure. Nanocrystalline material have been found to offer better thermal shock resistance, lower thermal conductivity and better wear resistance than their conventional counterparts. There are several recent reviews on mechanical properties of nanocrystalline materials [4,5,6]. For bulk materials also better fracture toughness is reported for nanostructure composites having nanosized metal precipitations in the nanostructured alumina matrix [7,8].

Thermal spraying is a complex process including a number of variables. Particle melting stage and possible phase transformations during its flight in the flame must be controlled as well as coating buildup mechanism including splat interface and stress

development. In order to produce a coating with desired properties, e.g. with high fracture strength, it is not sufficient to control material structure only inside one lamella. Also interactions between lamella, stress stages of the final coating, its adhesion to the substrate and cracking must be controlled. These different phenomena influencing on the final quality of the coating are depicted schematically in Figure 1.

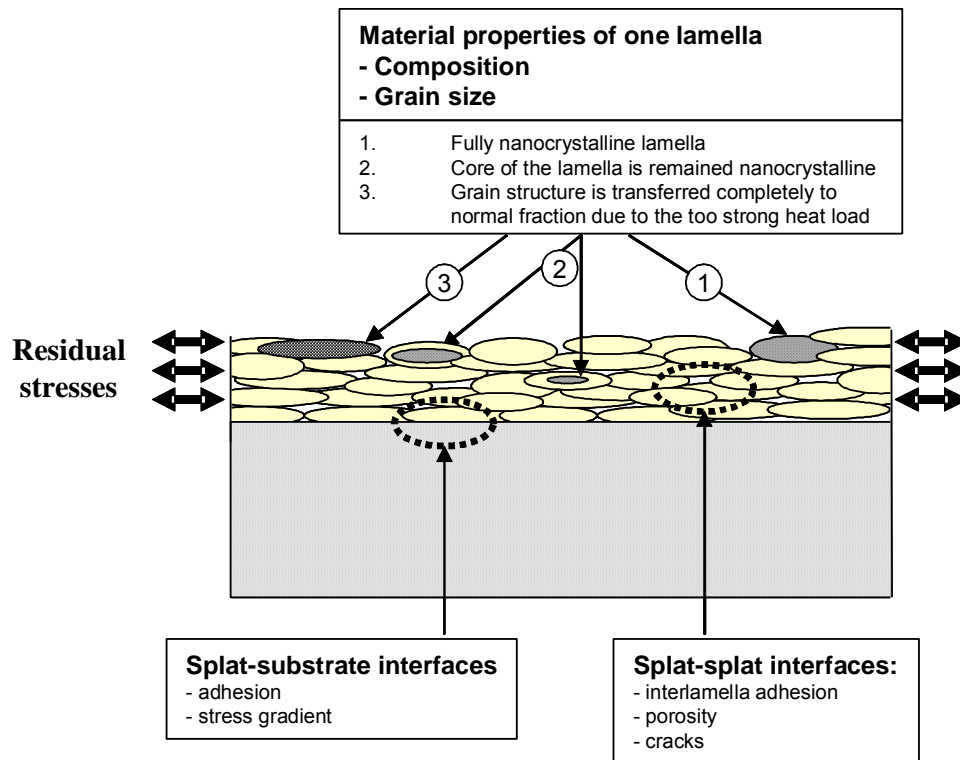


Fig. 1. Factors influencing the properties of thermally sprayed coating.

In this paper we describe the development of HVOF sprayed nanocrystalline Al_2O_3 -coatings, where the grain size of Al_2O_3 has been decreased and a few percents of alloying material has been added in order to toughen the coating. Raw material development, process optimisation for HVOF process and coating properties for different composite coatings including 5-vol% alloying of nickel, nickel oxide, zirconium oxide, and silicon carbide is discussed.

2. Experimental Details

2.1. Spray Powder Development

Different alloying elements were selected to obtain different melting temperatures. The used alloying elements were Ni, NiO, SiC and ZrO₂ having melting temperatures of 1455 °C, 1957 °C, 2500 °C and 2800°C, respectively. Melting temperature for alumina is 2054 °C.

There is a number of ways to produce ceramic nanocomposite powders. In the present work the synthesis of Al₂O₃ powder with and without Ni-nanoparticles was carried out using boehmite (AlO(OH)) as a starting media. The process is initiated by diluting Ni(NO₃)₂ to ethanol and then adding AlO(OH). After drying the resulting powder is calcinated at 500 °C to obtain NiO - γ-Al₂O₃. Both oxides in the powder (nickeloxide and alumina) are in the form of nanosized particles.

After calcination the nanopowder mixture was agglomerated into larger particle agglomerates by spray drying. After agglomeration the powder was heat-treated to reduce NiO to metallic nickel and to transform γ-alumina to α-alumina and to sinter particles loosely together. In the case of n-Al₂O₃ -5% NiO material the powder was manufactured in the way described above, but it was further heat treated in air at 700 °C to transform nickel into nickel oxide.

The n-Al₂O₃ -5% SiC powder was processed by first making dispersions of SiC powder and boehmite. These were mixed in a propeller agitator, spray dried and sintered. Mixture of n-Al₂O₃-5% ZrO₂ was made from nanosized yttria stabilized zirconia that was ball milled in water together with boehmite. Also this mixture was spray dried and sintered to obtain the desired powder for thermal spraying.

Pure nanostructured alumina powders were manufactured from boehmite. Boehmite was agglomerated by spray drying, heat treated to alumina and finally sintered. Praxair Al-1110HP Al₂O₃ powder was used as reference material having grain size in the micron range.

2.2. Thermal Spray Test Setup

Coating deposition and spray diagnostics were accomplished with a Praxair HV-2000 spray gun, fitted with 22mm combustion chamber allowing for varying process

parameters. Nitrogen was selected for a carrier gas, along with hydrogen as fuel gas. A two-axis traverse unit was used to manipulate the gun during coating deposition. Thermico CPF-2HP powder feeder was used to ensure sufficient powder feed rate also for experimental powders having a non-optimal size distribution and flow capability. *On-line diagnostics* by using the Spraywatch 3i equipment were carried out at different spray conditions to measure the particle velocity and temperature. The measurement is based on the two-colour pyrometry and a fast CCD camera [9]. *Coatings* were sprayed onto the steel plates having a size of 25×50×2 mm for microstructural and property characterization. The microstructural development was controlled by controlling the traverse rate of the gun and the powder feed rate resulting to a certain thickness per pass.

2.3. Characterization

Powder agglomerate size was determined by using Lecotrac – LT100 particle size analyzer. The crystal structures of the powders and the coatings were characterized by X-ray diffraction (XRD) using Cu-K α and Mo-K α radiation. Electron microscopy using JEOL JSM-6400 (SEM) combined with PGT PRISM 2000 X-ray analyzer, LEO982 Gemini (FEG-SEM), and Philips CM 200 (FEG-STEM) combined with Noran Voyager X-ray analyzer were used to study the coating microstructures.

Hardness of the coatings was determined by Vickers micro hardness method using a weight of 300 grams. Instrumented nanoindentation with a Nanotest 550 instrument equipped with a 0.79 mm ball indenter was used to characterize the elasto-plastic properties of the coating. Calculation of elastic modulus was made by using the method developed by Field and Swain [10,11]. Wear resistance of the coatings was evaluated by rubber wheel abrasion test according to standard ASTM G 65-91.

3. Results and Discussion

3.1 Powder Microstructure

Powders were analyzed before HVOF spray tests to confirm the phase structure of the particles. Powders consisted of α -alumina and appearance of each alloying element was approved for each powder type. Size distribution of the powder fraction was measured to be between 2 and 29 μm . Detailed information of the produced powders and the reference powder are presented in Table 1. Typical morphology for the powders is presented in Fig. 2.

Table 1. Spray powders for HVOF experiments.

Powder	Material code	Manufacturer and method	Agglomerate size	Crystal size for alumina
Al-1110	ref- Al_2O_3	Praxair, fused and crushed	5-22 μm	Conventional
Boehmite	n- Al_2O_3	VTT, agglomerated and sintered	2-25 μm	nano
Boehmite	n- Al_2O_3 -5% Ni	VTT, agglomerated and sintered	2-26 μm	nano
Boehmite	n- Al_2O_3 -5% NiO	VTT, agglomerated and sintered	2-21 μm	nano
Boehmite	n- Al_2O_3 -5% ZrO_2	VTT, agglomerated and sintered	2-29 μm	nano
Boehmite	n- Al_2O_3 -5% SiC	VTT, agglomerated and sintered	2-29 μm	nano

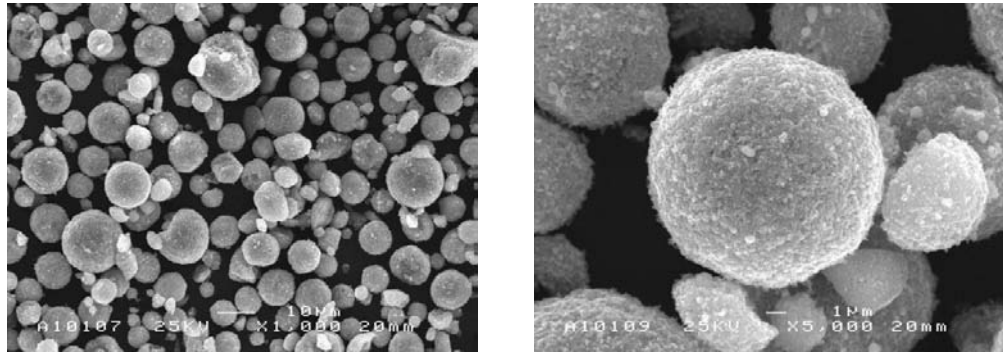


Fig. 2. SEM micrographs of the spray dried Al_2O_3 – 5%Ni particles at the magnification of 600 \times and 3000 \times .

3.2 Spray Process Optimisation

Spray parameters were optimised in order to produce coating with a dense structure combined with a desired phase structure. Large amount of different spray conditions were studied varying the gas ration of hydrogen and oxygen to produce different melting stages for the particles. Particle velocities and temperatures were measured with the on-line diagnostic. Selection and optimization of spraying parameters is described in detail elsewhere [12].

Two spraying conditions were selected for more detailed studies: condition 1 with gas parameters of H_2 :775 l/min; O_2 270 l/min; N_2 : 20 l/min, and condition 2 with gas parameters of H_2 :700 l/min; O_2 350 l/min; N_2 : 20 l/min. Spray distance in both cases was 150 mm. Both the conditions produced high particle velocities with slightly different particle temperatures.

3.3 Coating Microstructure

In this paper the results for the coatings produced by spray condition 1 are presented. The microstructure of the coatings was studied from the polished cross sections as well as from the fracture surfaces of the coatings. Polished cross sections were analyzed by SEM in BEI mode, which ensures good contrast for studying flattening rate of the particles and adhesion of the lamellae. All coatings had a dense structure with good lamellar bonding as shown in Fig. 3.

The distribution of nickel in the cross section of the sample produced using n-Al₂O₃-5%Ni powder is shown in Figure 3c. The light areas indicate the presence of nickel in the lamella boundaries of the coating. In the coating produced from the powder n-Al₂O₃-5%NiO also some light areas in the cross section can be observed (Fig 3d). These were analyzed by XRD and EDS to be also metallic nickel. Both micrographs indicate that some amount of nickel is deposited into the splat boundaries, i.e. interlamellarly. Amount of nickel in the lamella boundaries of the coating produced from the powder n-Al₂O₃-5%NiO is however much lower compared to the coating n-Al₂O₃-5%Ni using metallic nickel as alloying material in the spray powder.

More detailed analysis for the n-Al₂O₃-5%Ni coating showed that some amount of nickel still exists inside the matrix as nano sized particles, while some of the nickel is transferred to the lamella boundaries, and some nickel is apparently lost during the HVOF spray process [13,14].

Coatings made of a mixture of Al₂O₃ and ZrO₂ (Fig. 3 e) or Al₂O₃ and SiC (Fig. 3f) particles are homogenous, and no clear two phase structure is observed. This suggests that ZrO₂ and SiC may be located inside lamellas as small precipitations. However some limitations to separate these two phases in BEI mode exist and further TEM analysis to confirm this is under way.

Different melting temperatures of the alloying elements produced different coating microstructures. Despite the fact that particles in the HVOF process are in the molten stage only for a few milliseconds, the time is long enough for nickel partly to transfer into the lamella boundaries. Original nanosized nickel structure has remained only partly in the alumina matrix. While introducing alloying elements with higher melting temperature, the lower amount of alloying element is transferred to the lamella boundaries. In the case of powder n-Al₂O₃-5%NiO, nickel oxide seems to be reduced to the metallic nickel during HVOF spray process. Despite this reaction the amount of nickel observed in the lamella boundaries is not as high as it is in the case of coating produced from the powder n-Al₂O₃-5%Ni.

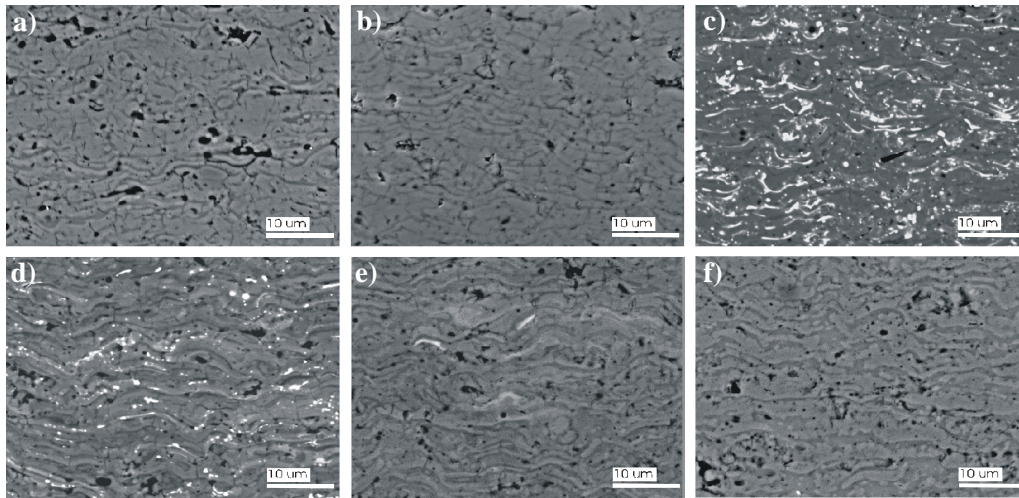


Fig 3. SEM-BEI micrograph of the polished cross sections for the coatings a) ref- Al_2O_3 , b) n- Al_2O_3 , c) n- Al_2O_3 -5% Ni, d) n- Al_2O_3 -5% NiO, e) n- Al_2O_3 -5% ZrO_2 , and f) n- Al_2O_3 -5% SiC.

3.3 Coating Properties

Micro hardness and abrasive wear loss were determined for all coatings. Results are presented in Fig. 4. As compared to the reference coating, which is sprayed by using a commercially available powder, the hardness is clearly improved, when the nanocrystalline coating structure is introduced. Introducing alloying elements such as NiO, ZrO_2 and SiC slightly reduces the hardness, but it still remains higher than for the reference coating. Introduction of the metallic nickel to the structure decreases the hardness below the reference sample. A large amount of metal located in the lamella boundaries is assumed to cause such a decrease.

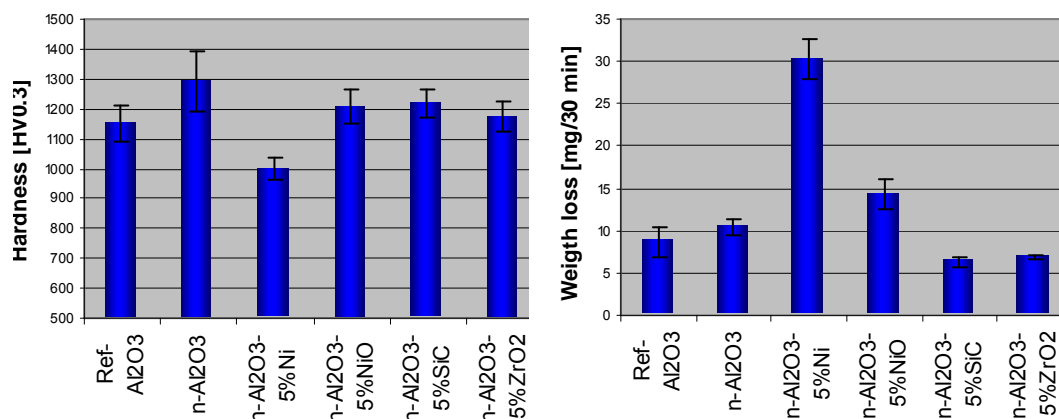


Fig 4. a) Vickers hardness (HV0.3) number and b) the weight loss in rubber wheel abrasion test.

Wear resistance of the coatings seems to correlate with the coating hardness as presented in Fig. 5b. The nickel alloyed coating having the lowest hardness has the highest wear rate obviously due to the appearance of metallic nickel in the lamellar boundaries. In the same way the coating produced from NiO-alloyed powder, having also some metallic nickel in the lamellae boundaries has higher wear rate as compared to the other coatings. Introduction of nanocomposite structure seems to decrease the wear rate of the coatings. The lowest wear rates were observed for the coatings n-Al₂O₃ -5% ZrO₂ and n-Al₂O₃ -5% SiC, as shown in Fig 5b. It can be concluded that introduction of alloying that remains through the HVOF spray process improves the coating wear resistance. This may be partly explained by the higher fracture toughness, which is still under investigation by the authors. Good fracture toughness for the Al₂O₃-Ni-type of coatings has been demonstrated earlier [13].

The elastic modulus was determined for the coatings ref-Al₂O₃, n-Al₂O₃ and n-Al₂O₃ -5%Ni. Measured values were 95 MPa for ref-Al₂O₃, 114 MPa for n-Al₂O₃ and 118 MPa for n-Al₂O₃ -5%Ni, respectively. According to the instrumented indentation measurements, the elastic modulus remains in nanostructured coatings approximately at the same level independent of nickel content. The values obtained, however, are clearly higher than those of the reference coating and those published for plasma sprayed alumina coatings [1].

4. Conclusions

In this paper raw material development and HVOF process to produce nanocomposite alumina coatings have been described). It was found out that by introducing nanocomposite structure in to the dense ceramic coating the wear resistance and hardness of the coating can be improved. By varying alloying material, the microstructure and properties of the produced coating can be varied. Depending on the application each of produced coatings can offer potential protective capacity.

Produced types of coatings are considered to be a potential candidate for a protective coating in the harsh environments, where excellent chemical and corrosion resistance is needed.

Acknowledgement

This work was sponsored by TEKES (The National Technology Agency of Finland), VTT (Technical Research Centre of Finland), and Finnish industries (Kemira Pigments Oy, Fortum Oil Oy, Rautaruukki Oyj, OMG Kokkola Chemicals Oy, Outokumpu Research Oy, ABR Innova Oy, Pikoteknik Oy, Ionhawk Oy, and Stratum Oy).

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