Manufacture and Properties of Composite Coatings: An Introduction

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Composite layers are capable of varying surface properties of parts over wide ranges. The galvanic route and thermal spraying are predestined to create composite layers. Wear resistance can be realized by a metallic matrix and nonmetallic reinforcing component that serves as a disperse phase. The goal of this article is to report on experimental results gained from samples produced galvanically. Improved wear resistance and hardness of the composite layers are main topics.

The thermal spray process requires more sophisticated processing techniques if the desired components cannot be supplied by individual injectors or mechanically premixed. In cases where pneumatic material feed (e.g., carbon short fibers) is not possible, the material supply must be achieved by agglomerated powders containing the second phase as a constituent. Suitable agglomerated powders allow a control of thermal decomposition of the sprayed materials by using additives as admixture to the agglomerate. Practical examples are outlined in the article.

Keywords	composite coatings, galvanically produced coatings, manufacturing processes, wear resistance

1. Introduction

Engineering progress continuously modifies the requirements for construction materials. From economical and technical points of view, surface coated parts are very promising. Durability and performance can be controlled widely by suitable coatings. Examples are wear and corrosion resistant coatings.

Recently composite layers have attracted much attention due to their outstanding properties. In general, composite layers consist of, at minimum, two simultaneously existing phases, which modify material properties in wide ranges (Fig. 1).

These phases usually belong to different material categories, such as metallic, inorganic-nonmetallic, or organic materials. One of these forms is intended to form the matrix, whereas the second disperse phase serves as a reinforcement component. The adhesion between the composite phases as well as between substrate and each single phase are the parameters that control the final performance.

Depending on the morphology of the selected reinforcement component (particle or fiber) the composite layer is termed particle or fiber reinforced. Multilayer and nanolayer reinforcement systems are regarded as two-dimensional reinforced composites.

Analogous to composite materials, the properties of composite layers are based on elemental (chemical) and structural interaction of the (a) matrix phase (including internal consistency, internal strains, etc.) with (b) disperse phases (composition, appearance, volume content, etc.) by (c) interfacial zones between reinforcement components and matrix created during the coating process or induced by thermal posttreatments.

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Composite layers additionally have to secure interface stability and strength between the substrate and composite layer. The importance of substrate surface treatment results from this fact.

Composite coatings are applied mainly if the demands are high and complex. They are used either as the primary coating or for coating repair. They bring about:

- An increase in strength and a binding effect (e.g., high strength phases in an unhardened, tough matrix)

- The creation of different compositional and phase ranges, which can absorb or scatter energy, relax stress, and divert, catch, or bridge cracks

- An improvement of tribological properties (wear reduction, friction modification)

- An improvement of corrosion resistance

- An improvement of thermal resistance

- An enhancement of catalytic properties

- An increase in porosity and roughness

- An improvement of decorative effect

- Production of barrier effects (e.g., thermal insulation)

Examples for matrix and dispersal materials are shown in Table 1.

The incorporated particles influence coating properties in various ways. It is possible that they influence the material coating structure during its growth, and conversely, their existence in the coating influences the properties. The properties of the metal matrix and the particle properties frequently complement each other. The content, distribution, shape, size, and hardness of hard particles and properties of the matrix cause the improved strength and wear behavior of coatings.

It can be seen from the theory of dispersion hardening that to achieve a hardness as high as possible, small, hard, and evenly formed particles in fine distribution must be incorporated in the coating. The most favorable particle size (the critical diameter) should be between 10 and 20 nm (Ref 2). The optimal work

hardening can be achieved if the real particle diameter is similar to the critical diameter for a high strength, and the particle diameter is slightly above the critical diameter to gain a sufficient toughness. The interaction components between particles and dislocations will decrease, and, therefore, the dispersion hardening effect will decrease as well, if the diameter of particles is higher than the critical diameter. If the particles are thermodynamically stable, their distribution degree will also be preserved at higher temperatures. In this case the particles impede recrystallization and grain growth and raise the high temperature strength.

The increase in strength, particularly, is based on interactions between the particles and the dislocations. A cutting of particles by dislocation lines is dominant at coherently incorporated particles in the matrix material. If the coherence decreases, the particles are surrounded by a coherence field that hinders dislocation motion. The greatest work hardening effect will occur if the particles are incorporated incoherently and are harder
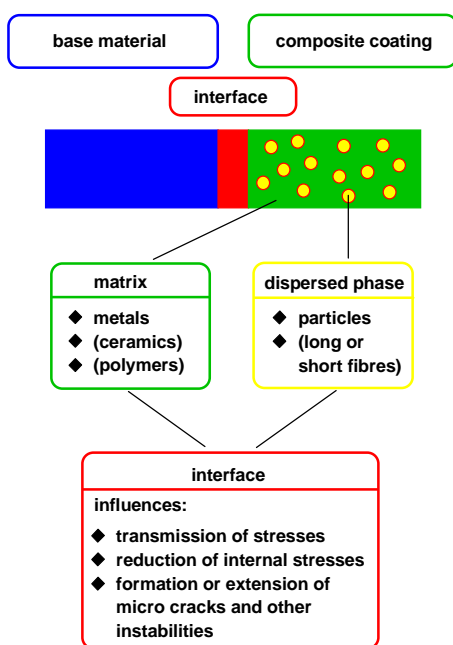
than the matrix. Then the particles cannot be cut and must be encircled by forming dislocation rings. The Orowan mechanism is valid in the range of microelongation; the obstacles are encircled at higher elongations by cross slide (Ref 2).

Options of incorporation or in situ forming of a disperse phase within a matrix (one or more processing steps) are outlined by the example of nonmetallic phases within a metallic matrix used for the coating (Fig. 2). Figure 3 shows various processes suitable to fabricate composite layers and posttreatments.

Electrochemical plating of dispersal coatings and the thermal spraying of composite coatings are presently among the most important manufacturing techniques for composite coatings. Recent developments are introduced in the following section.

2. Electrochemical Plating of Composite Coatings (Dispersal Coatings)

Technological fabrication can occur according to two basic principles:

The first method involves small particles that are dispersed in the electrolyte. They arrive at the phase boundary electrolyte/cathode surface as a result of external, forced convection, and, probably due to small electrophoresis effects. As a consequence of migration and electrostatic effects, the particles move

Fig. 1 Schematic of a composite coating (Ref 1)
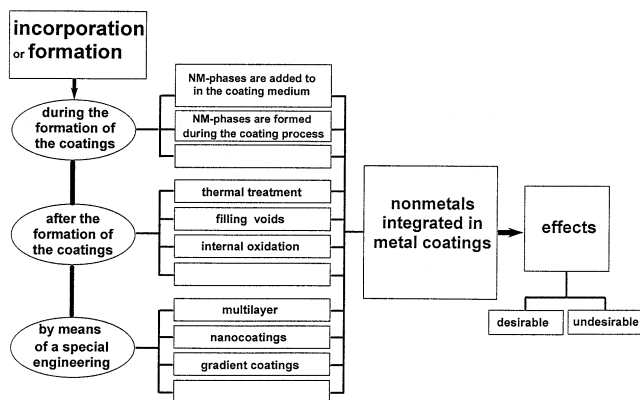
Fig. 2 Nonmetals or nonmetallic phases in metal coating. (NM, nonmetallic)

Table 1   Materials used within composites

Matrix materials

Metals (e.g., Ni, Cu, Fe, Cr, Co, Ag, Au, Zn, Sn, Cd, Pb, Pd, Al)
Metal alloys (e.g. , NiCr, NiAg, CuNi, CuAg, NiCrBSi, steel alloys)
Polymers (e.g., PA)
Ceramics (e.g. , Al_2O_3, $MgO \times ZrO_2$, SiC, BN, S_4, Ti-Si-C, Ti-Ge-C)
Carbon

Dispersal materials

Carbides (e.g., SiC, TiC, Cr_3C_2, WC, B_4C, ZrC, HfC)
Oxides (e.g. , Al_2O_3, SiO_2, TiO_2, Cr_2O_3, ZrO_2, UO_2, BeO)
Borides and nitrides (e.g., Cr_3B_2, TiB_2, ZrB_2, HfB_2, BN, B_4N, TiN, AlN)
Diamond
Graphite, MoS_2
Polymers (e.g., polytetrafluoroethylene, polyethylene, polyvinyl chloride, acrylonitride-butadiene-styrene)
Metals (e.g., Cr, W)
Others (e.g., glass, CaF_2, $BaSO_4$)

Fig. 3 Possibilities of manufacture and additional treatment of composite coatings

to a location near the surface where they can be deposited. They must remain in this vicinity for a sufficiently long time until they become incorporated in the matrix. The second method uses bigger particles that must be able to sink to the cathode surface by suitable technical methods, or they are in a fixed bed and become incorporated in the growing layer. Use of one method or another depends on particle size and technical equipment. The dispersal method can be applied up to particle diameters of 10 μm (perhaps more than 10 μm). It is possible to produce coatings with very fine and coarse particles (Fig. 4 and 5).

The existence of particles in the electrolyte, especially in the region of the phase boundary, influences the electrochemical system and therefore, the material structure of the coating matrix. For instance the crystal size can be reduced. This causes an improvement of mechanical properties. The existence of particles in the coating induces matrix work hardening, reduces the internal tensile stresses, and improves the tribological surface properties (e.g., decrease of adhesion and friction).

Although particles of less than 100 nm diameter are available, many problems must be solved. However, with regard to electroplating, research in the field of nanoparticles for the application in dispersal coatings is necessary for the creation of a stable suspension or a system that permits migration of nanopar-
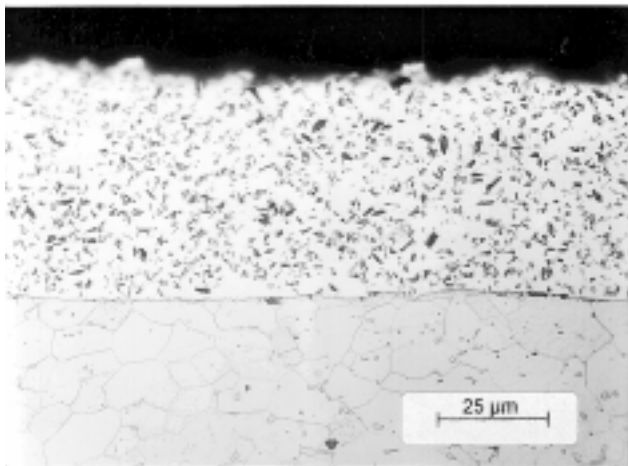
ticles to the cathode. The agglomeration of powder particles in the electrolytic bath must also be prevented. It should be noted that all properties of particles (e.g., hardness) are optimized.

The experimental investigations were carried out with an electrolytic bath of nickel sulphate with SiO_2 nanoparticles (Monospher, Merck Company, Darmstadt, Germany) rather than with Al_2O_3 and SiC particles (Fig. 6).

The hardness and the tribological behavior have been improved. The portion of hard particles in the electrolytic bath and the portion of particles in the coating are different. Usually the concentration of particles in the electrolyte is higher than in the coating. The solid incorporation in the coating should be evaluated only qualitatively. It was also clear that the solid content of the coating increases with the content in the electrolytic bath. The microhardness and scratch energy density (the resistance against abrasive wear) also increased (Fig. 7) (Ref 4, 5). The sliding wear and oscillation wear behavior could be improved (Fig. 8 and 9).

The results of oscillation wear behavior show that the behavior of coatings with monospheres is better than the behavior of coatings with alumina. It is most likely that the reason is found in the particle form. The monospheres are spherical in form, but the alumina particles have a sharp-edged morphology and, therefore, promote abrasive wear. It has been proven that the spherical nanoparticles can open new and favorable possibilities in the electrochemical plating of dispersal coatings.

Fig. 4 Micrograph of a Ni-SiC composite coating

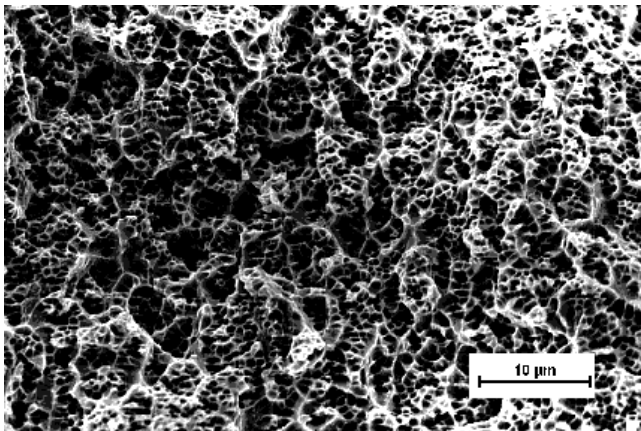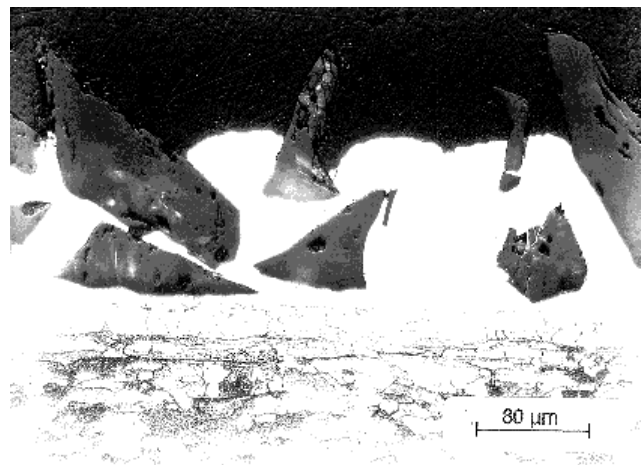**Fig. 5** Micrograph of a Ni-SiC composite coating for grinding

Fig. 6 Scanning electron micrograph showing the grain structure of an Ni-SiO$_2$ coating. Nano-SiO$_2$ particles were in the cavities.
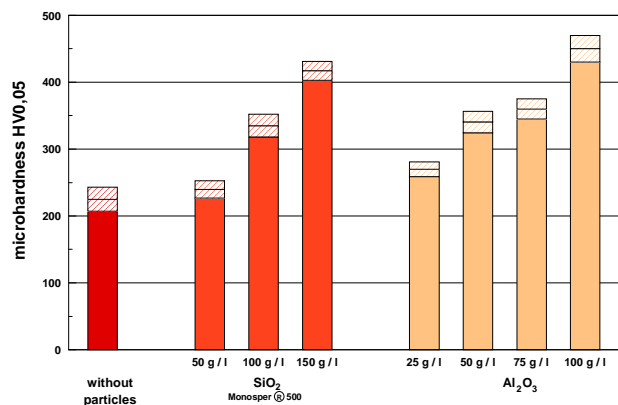

Fig. 7 Microhardness of nickel dispersal coatings (Ref 3)

3. Thermal Spraying of Composite Coatings

Various composite coatings can be produced with thermal spraying (e.g., vacuum plasma spraying) (Ref 6). Different routes are possible. Particles are mixed or agglomerated with the other components of spray powder before or during the spray process. Problems in this case may be, for example, the portion of particles in the powder and in the coating are very different, or the distribution of particles in the coating may be uneven. It is not possible to use small particles (less than 1 μm), and, therefore, the dispersion hardening cannot be reached.

An alternative method is to form spray powder particles that consist of the dispersion hardened material. The problems with this method are at powder production and processibility at the thermal spray process (Ref 4).

The third method is the application of reactive plasma spraying, for example, for the manufacture of TiC and TiN reinforced titanium coatings (Ref 6).

A strong focus in research now is on aluminum or aluminum-alloys composite coatings and Si_3N_4 coatings.

Light metals such as aluminum or aluminum alloys are very important for the reduction of construction weight. But their ap-plication frequently is limited by their low corrosion and wear resistance and their poor sliding properties. Aluminum composite coatings gained much interest as elements of lightweight construction. This article investigates aluminum and aluminum-silicon coatings with hard particles of Al_2O_3, SiC, and TiC (Ref 7, 8). The components were mixed mechanically before commencing the thermal spraying process. As a result, the content of hard particles in the coating depends on the amount of particles in the spray powder and on spray conditions. The fraction of hard particles that can be incorporated by this show a saturation limit.

The thermal sprayed composite coatings indicated that the coating properties are improved as a consequence of the amount of hard, solid particles, for example, a rise in hardness or wear resistance. It is interesting that spray conditions can be the same as conditions for aluminum spraying, and it is not necessary to use the energy intensive Al_2O_3 spray conditions (Fig. 10).

It was found that increased plasma energy caused melting of α-alumina particles and improved adhesion between lamellar particles and the matrix but also a partial conversion of α-alumina into less abrasion resistant γ-alumina.

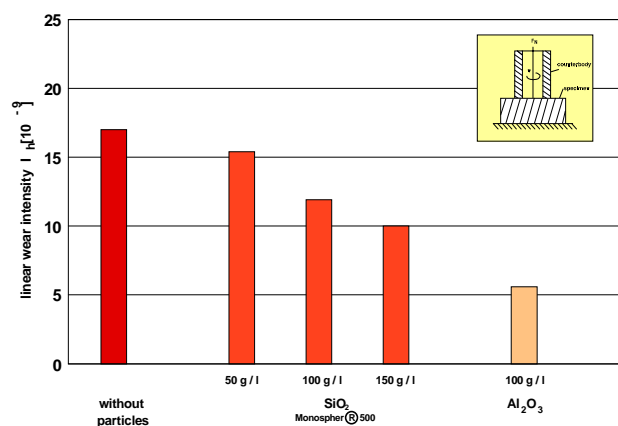Fabrication of carbon short fiber reinforced aluminum coatings by thermal spraying is successful as long as fibers

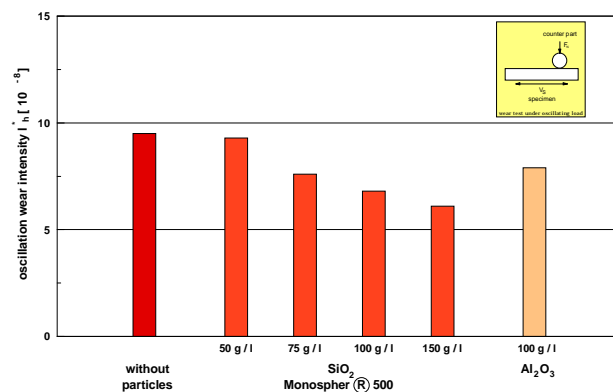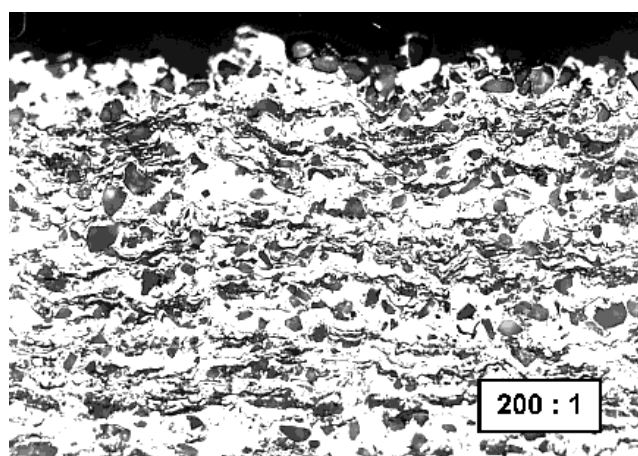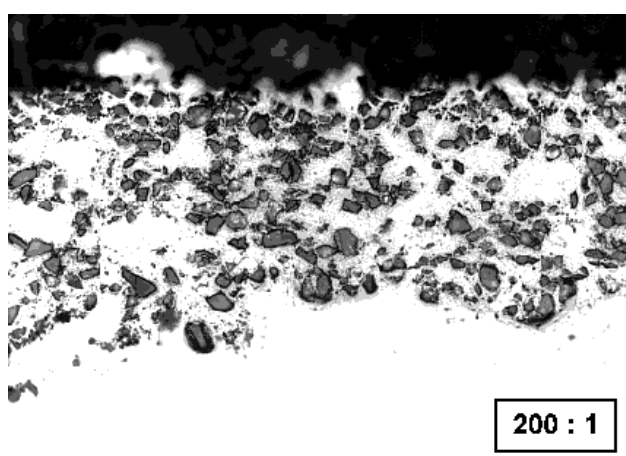**Fig. 8** Sliding wear behavior of nickel dispersal coatings (Ref 3)

Fig. 9 Oscillation wear behavior of nickel dispersal coatings (Ref 3)

(a)

(b)

Fig. 10 Micrographs showing the structure of different thermal sprayed Al-Al_2O_3 composite coatings (Ref 7) spray conditions of (a) Al_2O_3 and (b) aluminum
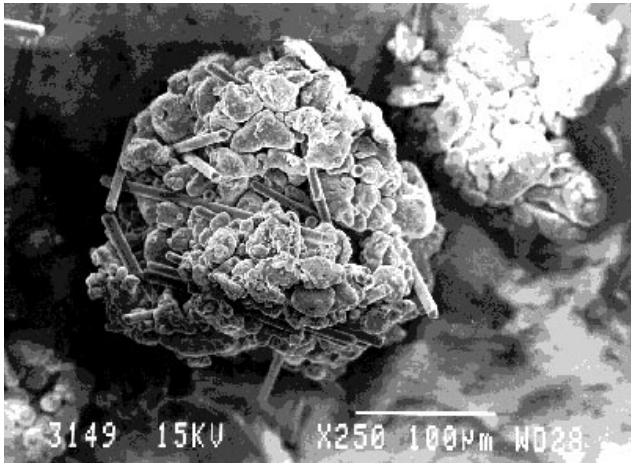
Fig. 11 Micrograph (Ref 9) showing an agglomerated spray powder particle consisting of aluminum with carbon short fibers

Fig. 12 Micrograph showing a Si_3N_4 containing spray powder particle (Fraunhofer Institute for Ceramic Technologies and Sintering Materials)

and aluminum powder form agglomerates that feed and permit efficient spraying (Fig. 11). Mechanical mixing alone is not sufficient. Optimized spraying conditions create coatings of low porosity and fiber contents of approximately 8 wt%.

The thermal spraying of silicon nitride containing coatings requires special powders securing intimate adhesion of silicon nitride particles with one of the matrix components (Fig. 12).

4. Conclusions

The following conclusions can be drawn:

Electrochemical plating and thermal spraying are very suitable techniques for creating composite coatings. Their main advantages are superior tribological properties of materials, and thus they open a wide field of technological applications.

Acknowledgments

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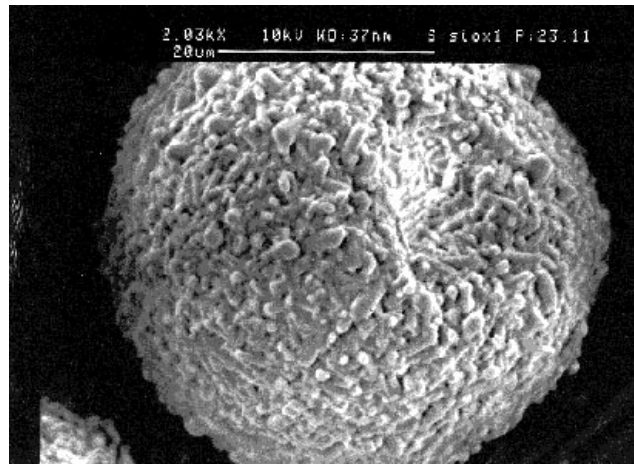1. S. Steinhäuser, Dispersed Nonmetallic Phases in Coatings (Composite Coatings), *Proceedings of Nonmetallics in Metals '94,* D. Hirschfeld, Ed., DGM Informationsgesellschaft mbH Oberursel, Germany, 1995, p 11-22, and *Mater. wiss. Werkst. tech.,* Vol 26, 1995, p 608- 614

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