

# COMPOSITE COATINGS: MANUFACTURE, PROPERTIES, AND APPLICATIONS

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*The surface properties of structural components have a strong influence on their behaviour. In many cases such components are stressed in the surface region by a combination of mechanical, tribological, corrosive, and thermal factors. Under these circumstances, deposition of composite coatings can provide effective surface protection. Deposits can be coated on steel, light metals, ceramics, plastics, and other materials. Composite coatings consist of a metal matrix with, in general, non-metal solid particles or short fibres. The most important coating processes are electrochemical or electroless plating and thermal spraying. This paper reviews the manufacture, properties, and applications of composite coatings and summarises new developments*

*in this field. Fine particles with diameters less than 100 nm are available and are investigated in connection with electroplating experiments. Thermal sprayed aluminium composite coatings on light metals have been manufactured and evaluated. Finally, thermal sprayed composite coatings with short fibres are described.*

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## INTRODUCTION

### Survey of composite coatings

The composition, structure, and surface characteristics determine the properties of materials. Applied stress can cause degradation of properties or even damage to the material. Coating can reduce the effects of stress in many cases (Fig. 1). Dispersal of solid phases in the coatings (Fig. 2)<sup>1</sup> can influence the coating properties and as a rule improves them. The combination of matrix (base material) and dispersal phases determines the properties and so careful selection of this combination is very important. Mainly non-metal components in the form of particles or, in small amounts, short fibres, are used as the dispersal phase. These second phases are incorporated during growth of the coating or created later within the coating (Fig. 3).

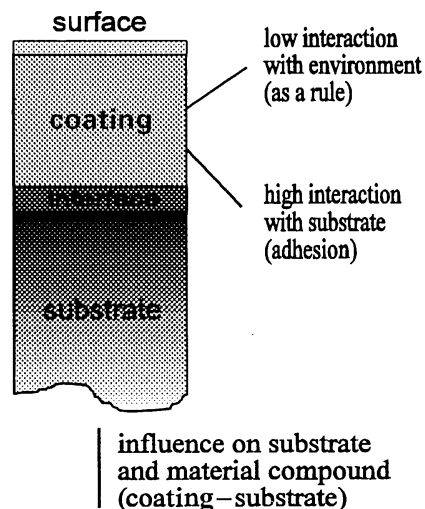
As an example, up to 14 wt-% of phosphorus or boron can be incorporated into a nickel coating during electroless nickel plating. An amorphous coating structure with around 8 wt-% (or more) phosphorus or boron will be created. Phosphorus can also be incorporated during electroplating. Oxidation can increase the amount of oxide in coatings during thermal spraying, and can be achieved if, for instance, thermal spray powder or wire is oxidised during manufacture or during the thermal spray process. As a result, coating hardness can be raised, but if the oxide content is increased, the other coating properties generally suffer.<sup>2,3</sup>

A reactive metal in a more precious metal can be oxidised in an oxygen atmosphere. Fine dispersed oxides increase the hardness (internal oxidation). Thermal treatment of coatings with phosphorus or boron causes precipitation hardening and therefore an improvement in coating properties. Dispersed phases can also be incorporated into cavities within the coatings (e.g. in pores or microcracks). In this way the coating properties can be improved (e.g. infiltration of MoS<sub>2</sub> or polymers, production of phosphates or nitrides, incorporation of dispersed phases in microcracks of chromium deposits).<sup>4,5</sup> Molten metal (e.g. steel) in a process called compound

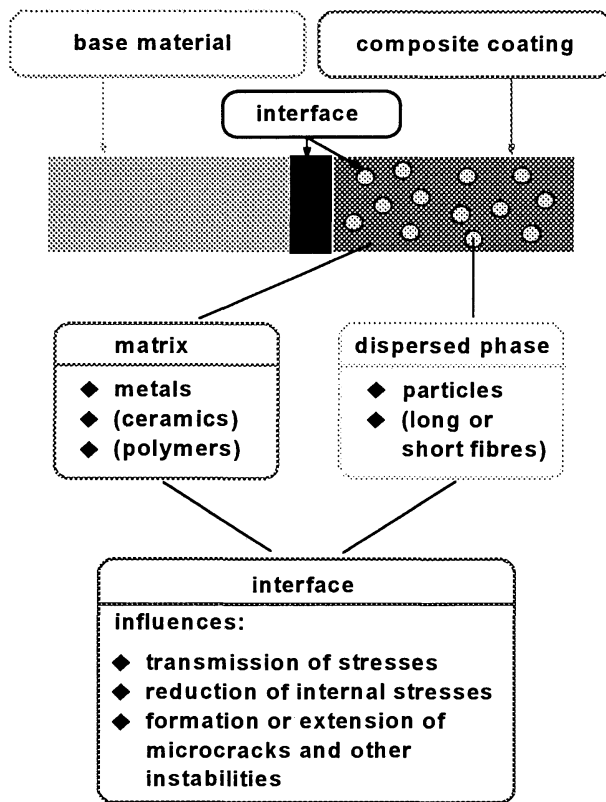
casting can contain dispersed carbides (e.g. VC, WC, MoC) and is then cast on the surface of highly stressed tools such as a drop forging die; methods including laser or electron beam remelting, plasma welding, and deposit welding can be used. In this way hard alloys on iron, nickel, or cobalt bases with carbides, borides, and other dispersal phases have been produced.<sup>6-9</sup>

Multilayers and nanocoatings also fall into the category of composite coatings. Such systems are useful as deposits on tools, particularly by CVD. Similar layers are produced by PVD.<sup>10,11</sup> Gradient coatings can be produced by, for instance, thermal spraying.<sup>12</sup> In addition, combinations of coating processes are possible, e.g. a combination of electrochemical with PVD or thermochemical processes. Of the large number of methods for incorporating solid particles into coatings, most involve the dispersal phase already being contained within the coating material or coating medium.

A great variety of coatings and treatment processes now exists. Most published articles have discussed



1 Functions of coatings



2 Schematic depiction of composite coating

electrochemical plating of composite coatings but recently much work has been done on thermal sprayed composite coatings. Some examples are the electroplating of Ni, Fe, and Al dispersion coatings. Important applications are found in motor production (especially motors for tools, such as power saws, but also for motorcycles and cars) and in the prevention or reduction of tool wear. Nickel and cBN dispersal coatings are used for abrasive tools. Electrochemical composite deposits find application in the textile industry (e.g. to rough up fibres) and for the improvement of unclosed pair elements. Thermal sprayed composite coatings can be applied at high tribological and corrosive loads, e.g. for

energy generation, steel manufacture, and metal forming.<sup>13-21</sup>

**Structure–property relations of composite coatings**

Composite coatings consist of matrix and dispersal phases (see Fig. 2). The interactions of different constituent phases induce modified composite properties. The dispersal phase can change the coating structure and properties as well as the surface and adhesive properties.

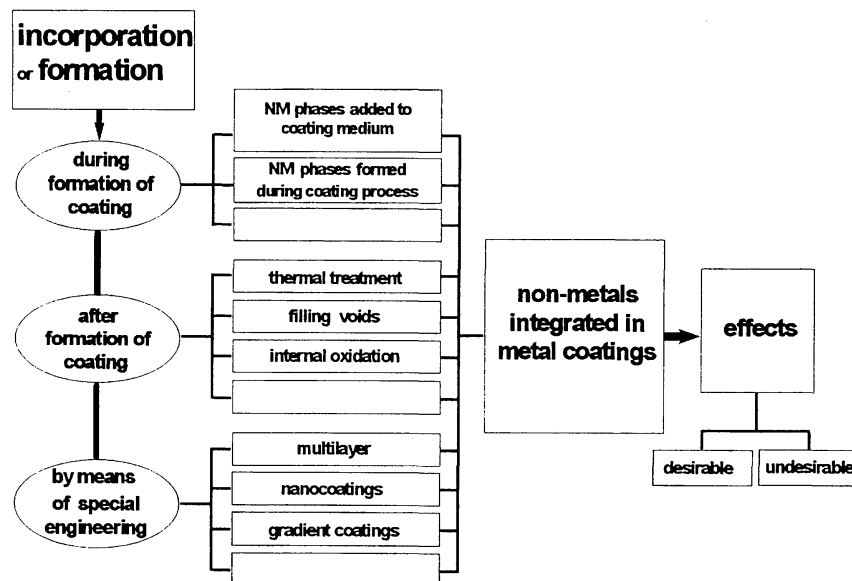
Composite coatings are used for both primary and repair coating. They can produce a variety of effects, including:

- increasing strength and providing a support effect (high strength phases in an unhardened, tough matrix)
- formation of zones able to absorb or scatter energy, relax stress, and divert, catch, or bridge cracks
- improvement of tribological properties (wear reduction, friction modification)
- improvement of corrosion resistance
- improvement of thermal resistance
- increasing porosity and roughness
- promotion of catalysis
- decorative enhancement
- production of barrier effects (e.g. thermal insulation).

Examples of matrix and dispersal materials are given in Table 1.

The incorporated particles modify coating properties in various ways, including influencing coating structure during coating growth and modification of coating properties by the simple physical existence of the particles in the coating. Properties of the metal matrix and particles frequently complement each other synergistically. The content, distribution, shape, size, and hardness of hard particles and the properties of the matrix influence the strength and wear behaviour of coatings.

It can be seen from the theory of dispersion hardening that to realise maximum hardness small and hard particles of uniform shape have to be finely dispersed in the coating. The most favourable particle



3 Non-metals or non-metallic (NM) phases in composite coatings

size (the critical diameter) is between 10 and 20 nm. Optimal work hardening will be realised if the particle diameter is near the critical diameter for high strength and also somewhat over the critical diameter for sufficient toughness. The interactions between particles and dislocations and therefore the dispersion hardening effect will decrease if the diameter of particles is higher than the critical diameter. For thermodynamically stable particles their spatial distribution will be preserved at higher temperatures; in this case the particles prevent recrystallisation and grain growth and raise the high temperature strength.

In particular the rise in strength is caused by the interactions between the particles and dislocations. Cutting of the particles by dislocation lines is dominant in the case of coherent particles. If coherence decreases, the particles are surrounded with a coherence field which hinders the motion of dislocations. The greatest work hardening effect will occur if the particles are incorporated incoherently and are harder than the matrix. Then the particles can not be cut and must be encircled by dislocation rings. The Orowan mechanism is valid in the range of microelongation; at higher elongations the obstacles are encircled by cross-slide.<sup>22</sup>

Electrochemical plating of dispersal coatings and thermal spraying of composite coatings are currently two of the most important techniques for fabrication of composite coatings. Some further developments in these processes will now be outlined.

## RESULTS AND DISCUSSION

### Electrochemical plating of composite coatings

The technology of electrochemical plating of composite coatings is based on two principles. First, small particles can be dispersed in the electrolyte. They reach the phase boundary between electrolyte and cathode surface as a result of external, forced convection and, probably, small electrophoresis effects. As a consequence of migration and electrostatic effects the particles gather in the region of the deposit, where they have to be fixed until they are buried by the electrocrystallising matrix. Second, bigger particles are forced to sink to the cathode



4 Cross-sectional micrographs of Ni-SiC coatings: lower coating is for grinding

surface by suitable methods or they are already in a 'fixed bed' from which they become incorporated into the growing layer.

The choice of fabrication method depends on particle size. The dispersal method can be applied up to particle diameters of approximately 10 µm. Examples of coatings with very fine and also with coarse particles are shown in Fig. 4.

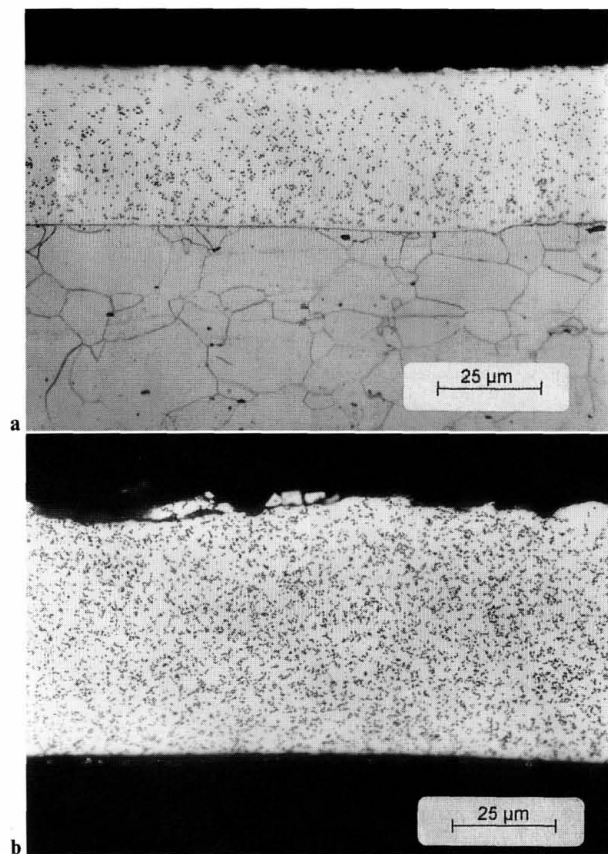
The existence of particles in the electrolyte, especially in the region of the phase boundary, influences the electrochemical system and therefore the matrix structure. For instance, the crystal size can be reduced which may result in improved mechanical properties. The existence of particles in the coating results in matrix work hardening, reduces internal tensile stresses, and improves the tribological surface properties (e.g. decreases adhesion and friction).

Until recently particles sufficiently fine for dispersion hardening have not been available, but now some sources are offering powders with diameters of less than 100 nm. Several problems in electroplating remain to be solved. Research in nanoparticles for the manufacture of dispersal coatings is still developing; as an example, work is necessary on the creation of stable suspensions and the motion of nanoparticles to the cathode. The agglomeration of powder particles in the electrolytic bath must be prevented. Also particle properties such as hardness need improvement.

Recent experimental investigations have made use of nanoparticles for the first time. They used a special electrolytic bath based on nickel sulphate with SiO<sub>2</sub>

Table 1 Examples of materials used in matrix and dispersal phases of composite coatings

Class of material	Matrix phase	Dispersal phase
Metals	Ni, Cu, Fe, Cr, Co, Ag, Au, Zn, Sn, Cd, Pb, Pd, Al	Cr, W
Metal alloys	NiCr, NiAg, CuNi, CuAg, NiCrBSi, steels	...
Carbides	...	SiC, TiC, Cr <sub>3</sub> C <sub>2</sub> , WC, B <sub>4</sub> C, ZrC, HfC
Oxides	...	Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> , TiO <sub>2</sub> , Cr <sub>2</sub> O <sub>3</sub> , ZrO <sub>2</sub> , UO <sub>2</sub> , BeO
Borides/nitrides	...	Cr <sub>3</sub> B <sub>2</sub> , TiB <sub>2</sub> , ZrB <sub>2</sub> , HfB <sub>2</sub> , BN, B <sub>4</sub> N, TiN, AlN
Polymers	PA	PTFE, PE, PVC, ABS
Ceramics	Al <sub>2</sub> O <sub>3</sub> , MgO-ZrO <sub>2</sub> , SiC, BN, Ti-Si-C, Ti-Ge-C	...
Other	C	Graphite, diamond, glass, CaF <sub>2</sub> , BaSO <sub>4</sub>



a  $50 \text{ g L}^{-1} \text{ SiO}_2$ ; b  $150 \text{ g L}^{-1} \text{ SiO}_2$

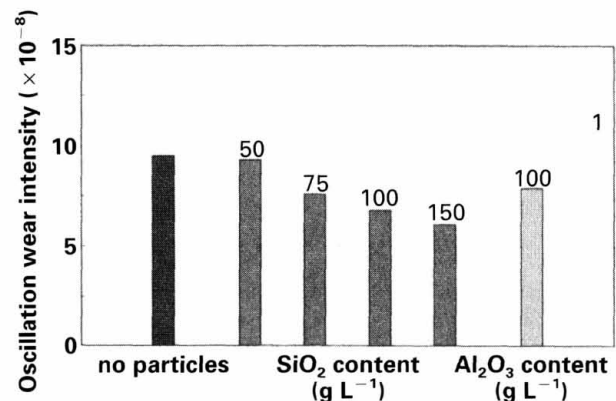
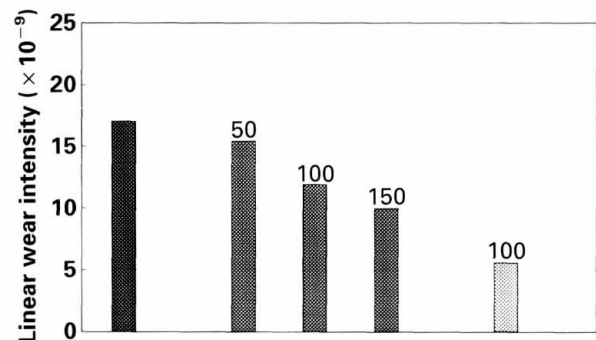
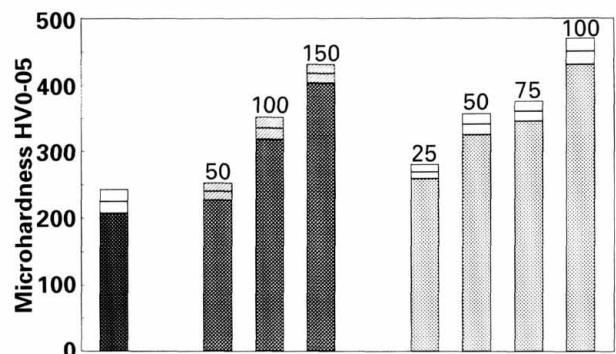
5 Micrographs showing structure of Ni-SiO<sub>2</sub> coatings after immersion in electrolytic bath

nanoparticles of fixed diameters (100 or 500 nm; Monospher, Merck, Darmstadt, Germany) in different concentrations. Comparisons with Al<sub>2</sub>O<sub>3</sub> and SiC particles of diameters 5 to 10 μm were performed by separate experiments. The incorporation of solid particles in the coating was evaluated qualitatively by image analysis. It was clear that the solid content of the coating increased with the particle concentration in the electrolytic bath (Fig. 5). Hardness and tribological behaviour (e.g. sliding and oscillation wear) of coatings have been improved (Fig. 6).<sup>23-25</sup>

The results of oscillation wear tests are interesting because coatings containing monospheres show less wear than those with alumina. It is most likely that the reason for this is the particle form: monospheres are spherical whereas alumina particles are sharp edged and therefore promote abrasive wear. It is expected that the use of spherical nanoparticles will lead to new and improved routes for electrochemical plating of dispersal coatings.

#### Thermal spraying of composite coatings

With thermal spraying, various composite coatings can be produced.<sup>26</sup> Several different methods are available. In one technique, particles are mixed or agglomerated with the other components of the spray powder before or during the spray process. Shortcomings of this process include the following: the portions of particles in powder and coating can be very different; the distribution of particles in the coating may not be homogeneous; and the method is limited to particles larger than 1 μm in diameter

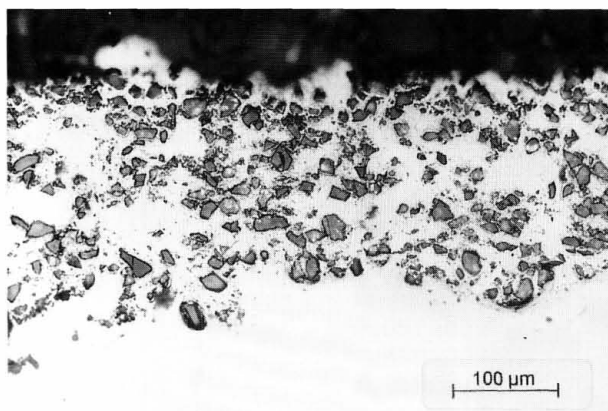


6 Graphs showing properties of nickel dispersal coatings: contents of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in electrolytic bath are given

and therefore dispersion hardening can not be achieved. Alternatively, the spray powder particles consist of dispersion hardened material. Powder production and application of the thermal spray process are problematic in this case.<sup>24</sup> Another method involves the application of reactive plasma spraying, e.g. for the manufacture of TiC and TiN reinforced Ti coatings,<sup>27</sup> which is unfortunately restricted to few applications. The following remarks apply to the first method, especially to aluminium or aluminium alloy composite coatings. The coatings were sprayed by different processes.

Light metals such as aluminium or aluminium alloys are very important for reducing construction weights but their application is frequently limited by their low corrosion and wear resistance and their poor tribological properties. It is therefore necessary to apply coatings. Aluminium composite coatings for light metals have therefore recently generated interest. Aluminium and AlSi coatings containing hard particles of Al<sub>2</sub>O<sub>3</sub>, SiC, and TiC have been investigated (Fig. 7).<sup>20,26</sup> The content of hard particles in



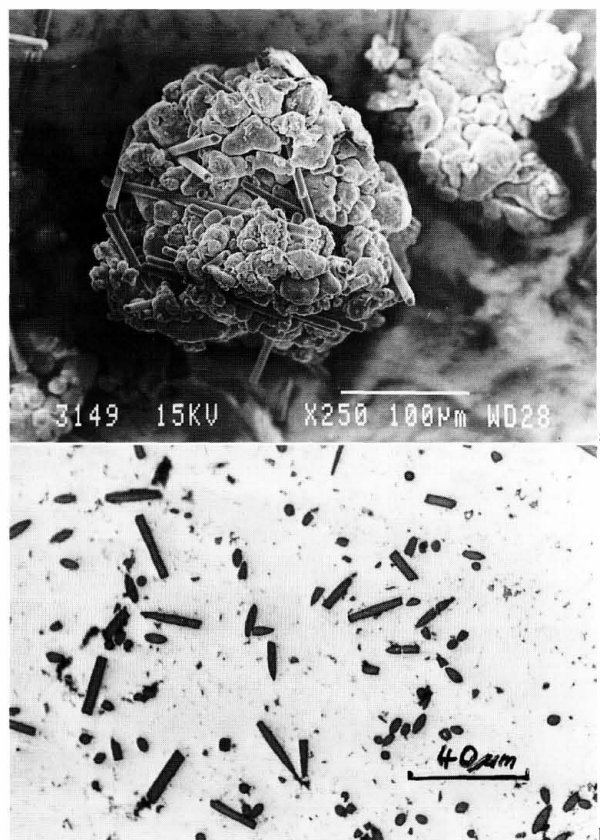


7 Micrograph showing structure of thermal sprayed composite coating

the coatings was shown to be dependent on the particle content in the spray powder and on spray conditions; it increased up to a limit depending on the content in the powder.

For thermal sprayed composite coatings, it can be shown that coating properties are improved as a consequence of increasing the number of hard, solid particles (Fig. 8). It is interesting that the spray conditions can be the same as the conditions for usual aluminium spraying; it is not necessary to use the energy consuming  $Al_2O_3$  spray conditions.

In different electrochemical and thermal spray experiments the feasibility of codeposition of short fibres instead of particles has also been investigated. The results gained from aluminium coatings containing short carbon fibres produced by thermal spraying



9 a micrograph showing agglomerated spray powder; b micrograph showing structure of thermal sprayed composite coating with carbon short fibres

(VPS) are shown in Fig. 9. The spray powder was composed of aluminium carbon fibre agglomerates. About 8 vol.-%C was incorporated into the coatings (Fig. 9). The wear characteristics have already been improved (oscillation wear reduced from 0.24 to 0.21  $\mu m$  with 4 vol.-%C fibre content and to 0.17  $\mu m$  with 8 vol.-%C) and further investigations are in progress.<sup>28</sup>

## CONCLUSIONS

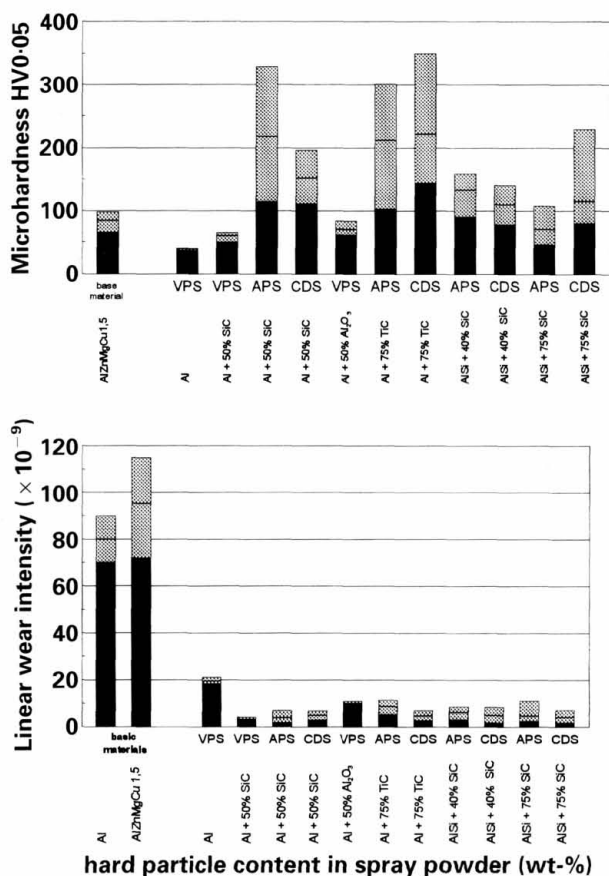
It can be stated that composite coatings offer favourable options for the improvement of the tribological properties of materials and thus make broad application on significant scales possible. Electrochemical plating and thermal spraying have been shown to be important techniques for the manufacture of composite coatings.

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## REFERENCES

1. S. STEINHÄUSER: *Mater.wiss. Werkst.tech.*, 1995, **26**, 608–614.
2. J. DROZAK, H.-T. WEICHERT, and H.-D. STEFFENS: in 'Verbundwerkstoffe und Werkstoffverbunde', (ed. G. Leonhardt



8 Graphs showing properties of thermal sprayed coatings

- et al.*), 627–634; 1993, Oberursel, Germany, DGM Informationsgesellschaft mbH.
3. W. MILEWSKI: in 'Verbundwerkstoffe und Werkstoffverbunde', (ed. G. Leonhardt *et al.*), 651–658; 1993, Oberursel, Germany, DGM Informationsgesellschaft mbH.
  4. U. BURAN: in 'Verbundwerkstoffe und Werkstoffverbunde', (ed. G. Leonhardt *et al.*), 741–748; 1993, Oberursel, Germany, DGM Informationsgesellschaft mbH.
  5. G. SCHMIDT: Dissertation, TU Chemnitz, Germany, 1986.
  6. H. HAFERKAMP, F. W. BACH, and R. SIEGERT: in 'Verbundwerkstoffe und Werkstoffverbunde', (ed. G. Leonhardt *et al.*), 393–400; 1993, Oberursel, Germany, DGM Informationsgesellschaft mbH.
  7. U. DRAUGELATES, B. BOUAIFI, and T. PLEGGE: in 'Verbundwerkstoffe und Werkstoffverbunde', (ed. G. Leonhardt *et al.*), 329–344; 1993, Oberursel, Germany, DGM Informationsgesellschaft mbH.
  8. U. DRAUGELATES and B. BOUAIFI: in 'Werkstofftechnologie im Wandel', 197–204; 1991, Universität Dortmund, Germany, Innomat Sonderausgabe.
  9. S. THIEMER: Diplomarbeit, TU Chemnitz, Germany, 1996.
  10. H. HOLLECK: *Metall.*, 1989, **43**, 614.
  11. K. KELLER and A. SZABO: in 'Verbundwerkstoffe und Werkstoffverbunde', (ed. G. Leonhardt *et al.*), 763–772; 1993, Oberursel, Germany, DGM Informationsgesellschaft mbH.
  12. J. PETERSCHEIM: in 'Verbundwerkstoffe und Werkstoffverbunde', (ed. G. Leonhardt *et al.*), 773–780; 1993, Oberursel, Germany, DGM Informationsgesellschaft mbH.
  13. G. PURSCHE, A. HENKER, and G. SCHMIDT: *Schmierungstechnik*, 1991, **22**, (6), 185–189.
  14. E. LUGSCHEIDER, P. JOKIEL, P. REMER, K. YUSHCHENKO, Y. BORISOV, P. VITIAZ, and S. STEINHÄUSER: in 'Thermal spray industrial applications', (ed. C. Berndt *et al.*), 79–83; 1994, Materials Park, OH, USA, ASM International.
  15. L. BULA: in 'Verbundwerkstoffe und Werkstoffverbunde', (ed. G. Leonhardt *et al.*), 723–731; 1993, Oberursel, Germany, DGM Informationsgesellschaft mbH.
  16. H. DOSTAL: Dissertation, TU Chemnitz, Germany, 1988.
  17. S. STEINHÄUSER *et al.*: in 'Verbundwerkstoffe und Werkstoffverbunde', (ed. G. Leonhardt *et al.*), 353–360; 1993, Oberursel, Germany, DGM Informationsgesellschaft mbH.
  18. K. MAIER: in 'Verbundwerkstoffe und Werkstoffverbunde', (ed. G. Leonhardt *et al.*), 683–690; 1993, Oberursel, Germany, DGM Informationsgesellschaft mbH.
  19. J. LUKSCHANDEL: in 'Verbundwerkstoffe und Werkstoffverbunde', (ed. G. Leonhardt *et al.*), 691–697; 1993, Oberursel, Germany, DGM Informationsgesellschaft mbH.
  20. B. WIELAGE, M. ZSCHUNKE, A. HENKER, and S. STEINHÄUSER: Proc. Conf. INNOMATA '96, Dresden, 1996, Frankfurt am Main, Germany, DECHEMA eV, 1996, 51–52.
  21. S. STEINHÄUSER and B. WIELAGE: in 'Verbundwerkstoffe und Werkstoffverbunde', (ed. G. Leonhardt *et al.*), 315–318; 1993, Oberursel, Germany, DGM Informationsgesellschaft mbH.
  22. W. SCHATT: 'Einführung in die Werkstoffwissenschaft', 346–347, 391; 1984, Germany, Verlag für Grundstoffindustrie Leipzig.
  23. C. WEBER: Diplomarbeit, TU Chemnitz, Germany, 1993.
  24. S. STEINHÄUSER and B. WIELAGE: in 'Thermal spraying – current status and future trends', (ed. A. Ohmori), 693–697; 1995, Materials Park, OH, USA, ASM International.
  25. G. SCHMIDT and S. STEINHÄUSER: *Tribol. Int.*, 1996, **29**, 207–213.
  26. E. LUGSCHEIDER, P. REMER, S. STEINHÄUSER, *et al.*: Technical report of EWISCO (East West Institute Surfacing Co-operation) 1991–1994; Aachen, Germany, RWTH Aachen, Werkstoffwissenschaften.
  27. E. LUGSCHEIDER, U. MÜLLER, and P. JOKIEL: in 'Verbundwerkstoffe und Werkstoffverbunde', (ed. G. Leonhardt *et al.*), 699–706; 1993, Oberursel, Germany, DGM Informationsgesellschaft mbH.
  28. B. WIELAGE, K. FLEISCHER, and A. HENKER: in 'Verbundwerkstoffe und Werkstoffverbunde', (ed. G. Ziegler), 65–66; 1996, Oberursel, Germany, DGM Informationsgesellschaft mbH.

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