METHODS OF COMPOSITE COATING: A REVIEW

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The surfaces of tools exposed to high wear stresses need coatings with high hardness and wear characteristics, e.g. diamond coating or coating with composites. Wear resistant, high hardness coatings can be prepared by laser technology, by brazing, or by electrochemical or electroless methods in aqueous solution. The results of research on preparations of surface composites are collected in this review.

Keywords: composite materials, laser cladding, laser melt injection, electroless plating, electrochemical coating

Introduction

A lot of engineering components are exposed to high wear stresses, for example drill bits for oil drilling. The failure of these engineering components is initialized from the surface in processes such as wear, corrosion, fatigue or fracture. A coating on the surface can improve the surface properties and decrease the failure rate. Several techniques have been applied to protect the surface of components, such as chemical vapour deposition [1], physical vapour deposition methods [2, 3], laser cladding [4], laser melt injection [5], electroplating composite [6] or electroless plating [7]. Composite coating with refractory ceramic particles can result in good wear resistant properties, similar to CVD or PVD coatings. In the following sections we will focus on the laser methods, brazing and aqueous chemistry methods for producing composite coatings.

1. Composite coating by Laser cladding

Surface composite coating can be produced by the laser cladding method, which is reminiscent of the traditional hardfacing welding. In this process, a laser beam is used as the heat source to melt the hardfacing alloy onto the substrate and the reinforcing particles. Laser cladding provides good metallurgical bonds and minimal dilution, which are hard to achieve by other hardfacing techniques [8].

Laser cladding of composite coating has been developed for its capability of introducing hard particles such as WC [4], TiC [9], SiC [10] and Cr3C2 [11] as reinforcements, each of which have very high hardness and good wear resistance. Among the hardfacing alloys, nickel-based alloys are most frequently investigated in recent years owing to their added characteristics of excellent resistance against abrasion and corrosion at higher temperatures [8].

A Cr3C2-Ni(Ni + Cr) composite coating can be produced by the laser cladding method [11, 12]. The hardness of the Ni or N-B coating is improved by adding Cr3C2 phase into the Ni or Ni-B, owing to the complete dissolution of the Cr3C2 particles in the Ni matrix alloy. The dissolution of the Cr3C2 can increase the Cr and C concentration in the melted Ni-alloy.

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and during the rapid cooling process Cr$_2$C$_3$, Fe$_{23}$(C, B)$_6$ phases can be formed, causing an improvement in the hardness of the coating [11]. The hardness and wear resistance increase as the amount of Cr$_2$C$_3$ phase in the coating is increased [13].

Partial dissolution of the reinforcing particles can be observed in the case of a WC$_p$/Ni–Cr–B–Si–C composite [4]. Metastable phases, i.e. α-W$_2$C, W$_2$C and η–β–M$_6$C compound, can be formed on the interface of the WC particles. These phases deteriorate the mechanical properties of the composite [4].

The partial dissolution of reinforcing particles has also been observed in a TiC/Ni–Cr–B–Si–C composite on steel. During cooling the dissolved TiC can crystallise on the surface of the undissolved TiC [14]. When using TiC in an Ni-based alloy, an intermetallic phase with Ti cannot be observed [15, 4].

2. Composite coating by laser melt injection

Composite coating can be prepared by Laser Melt Injection (LMI) technology. In this case the surface of the substrate can be melted by laser beam (the depth of the pool is approximately 1 mm), and the solid particles (particle size 10 to 100 μm) can be delivered into this pool by inert gas.

There are disadvantages to this method: the first is that the solid particles are not wetted sufficiently by the melted alloy. Good wettability is needed for pushing the particles into the melted alloy with low energy, and perfect wettability is required for spontaneous immersion [16, 17]. The other difficulties of the preparation of a composite coating with this method are the large differences in density between the melted metal and the reinforcing particles and the chemical reaction on the surface of the particles/metal matrix. These difficulties can be solved when the particles are formed in-situ during the cooling of the melted metal. In-situ composite coating has been prepared for an Al$_2$O$_3$ particle-reinforced carbon steel surface composite coating [18] or the in-situ production of bulk Fe/TiCp [19].

Of course, not only in-situ but also ex-situ composite layers can be formed by the LMI method. Ex-situ means the reinforcing particles are prepared independently from the LMI process. Various ex-situ composite layers have been prepared by LMI method in the last two decades: i.e., a SiC particle-reinforced composite coating [20, 21], WC particle-reinforced coating on titanium alloys [5, 22], a WC particle composite with Fe matrix [23, 24], or a TiB$_2$ particle-reinforced surface composite on steel substrate [25].

In the case of the preparation of an ex-situ WC particle-reinforced Fe surface composite, it was observed that the WC particles can be dissolved or can be melted during the LMI process. From the melted or dissolved WC a Fe$_5$W$_4$C compound layer can be formed on the top of the surface composite. The same compound layer can be observed on the surface of the undissolved WC particles [23]. It was found that 10 w% WC (particle size 80 μm) is sufficient in the WC$_p$/Duplex Stainless Steel system for a significant (approximately 50%) improvement in the wear properties [24].

3. Composite coating by brazing

When using laser technologies the sample can become deformed due to mechanical stresses, because of the rapid cooling of the melted part and the non-uniform temperature. In order to avoid such high mechanical stresses in the sample, there is growing interest among researchers in composite coating preparation by brazing. High vacuum or an inert gas atmosphere is used in the brazing process, and the whole sample is heated up. In this method the mechanical stresses in the sample can be avoided or reduced.
WC, or diamond particles or other particles with high hardness and wear resistance are used as reinforcing materials in the composite coating. The following reinforcing/matrix material pairs can be used for composite coating: i.e. WC/NiCrBSi (Co) composite [26, 27], WC/Co/CuZnNi [28], WC-8TiC-3TaC-8Co/Cu-Zn-Ni [29], diamond/Ni-Cr [30], and diamond/Cu composite [31].

A Co-coated WC particle-reinforced (particle size range 40–70 μm) Ni-based brazing alloy composite coating was made by Lu et al. [27]. In this case the Co-coated WC powder and Ni-Cr-B-Si brazing alloy powder were mixed separately with an organic binder. The surface of the WC particles was covered by Co in various amounts. The mixture of the powders and the binder was used to prepare belts by rolling. These belts were applied for the brazing. The WC-Co-binder belt was placed on the surface of mild steel, and this was covered by the Ni-based belt. The brazing was carried out in a vacuum furnace. The brazing temperature was 1060 °C and the holding time was 10 min. The Co coating on the WC particles improved the wettability of the particles in the brazing alloy, but during the brazing Co dissolved in the matrix. The dissolved Co can decrease the hardness and wear resistance of the coating. Not only brazing belts but also brazing paste can be made from a powder of the brazing alloy and the reinforcing material using a larger volume of organic binder. The brazing pastes are more suitable for preparing composite brazing coating on the complex surface of engineering components.

Alloys with a lower melting point, such as Ag-Cu-Ti alloy, can produce composite coating between 820 and 940 °C. A good example of this is the work of Wu et al. [31], in which the development of a diamond particle-reinforced Ag-Cu-Ti matrix composite on Al₂O₃ substrate was studied. They found that a reaction takes place between the diamond particles and the brazing alloy (matrix), as well between the Al₂O₃ substrate and brazing alloy; as a result TiC (on the interface of diamond/brazing) and Ti₃(Cu, Al)₂O compounds form (on the interface of Al₂O₃/brazing), ensuring the good bonding strength of the brazing joint. It was found furthermore that these reaction-product coatings on the surface of the reinforcing particles can improve the mechanical properties when these form a thin coating with thickness of around 2 μm, but thicker coatings on the particles decrease the mechanical properties. In this case the aim is to achieve thin coating. The film thickness can be reduced by reducing the brazing time.

The reaction between the diamond particles and the matrix alloy can also be observed in the case of another matrix alloy, such as a diamond/Ni-Cr based alloy composite system [30]. In this system the diamond/matrix Cr₃C₂ and CrC₃ compounds appearing on the interface can decrease the mechanical properties of the composite. In this case we have another problem, namely the diamond graphitisation promoted by Ni, which can catalyse the activation energy reduction in graphitisation. The hardness of the composite is reduced by the graphitisation of the diamond.

### 4. Composite coating from aqueous solutions by electrochemical and electroless methods

Not only nanoparticle-reinforced composites but also Ni or Co coatings are appropriate for improving the wear resistance of the cutting tool. One of the production methods of composite and alloy coating is from aqueous solution by electrochemistry i.e. Ni/TiO₂ [6], Ni/SiC [32, 33], alloyed matrix composites, i.e. Ni-W/SiC [34], Ni-Co/SiC [35], Ni–B/CeO₂ [36] and Co/SiC [33, 37].

Ni/SiC and Co/SiC [33, 37], Ni-W-P/Al₂O₃ [7], and Ni–P/Si₃N₄ [38] composite coatings can be prepared by the electroless method. Electroless plating is good for preparing a metallic
coating on the surface of tools, i.e. Ni-P [39], Co-P [40], Co-B [41]. Both electrochemical and electroless plating are easy methods which are applicable for preparing coatings on tools with complex surfaces.

Comparing the features of electrochemically deposited Ni and Ni/SiC composite coatings, we find that the Ni/SiC composite hardness and wear characteristics are better than those of Ni coatings which are produced in the same manner. The Ni-5% SiC nanoparticle-reinforced composite coating has a maximum microhardness and wear rate of 730 Hv and $2.5 \times 10^6$ mm$^3$/J, respectively (The microhardness and the wear rate of the Ni coating were 550 Hv and $5.5 \times 10^6$ mm$^3$/J, respectively). The reason for this is that the SiC nanoparticles deposited in the nickel matrix restrain the growth of the nickel grains and the plastic deformation of the matrix under loading, due to grain fining and dispersive strengthening effects [42].

Similar results were obtained also in the case of electroless Ni-W-P coating and Ni-W-P/Al$_2$O$_3$ composite coating [7]. Table 1 shows that the hardness of the composite is only slightly improved against the Ni-W-P coating. However, the value of hardness can be doubled by annealing at 400–500 °C.

**Table 1**

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<tr>
<th>Type of coating</th>
<th>Microhardness (VHN$_{500g}$)</th>
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<tr>
<td></td>
<td>As-plated 200 °C 400 °C 500 °C 600 °C</td>
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<tr>
<td>Ni-W-P coating</td>
<td>578±29 612±16 1052±23 992±10 797±14</td>
</tr>
<tr>
<td>Ni-W-P/Al$_2$O$_3$ composite coating</td>
<td>581±18 836±47 1178±48 1227±72 939±42</td>
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Reduction of hardness with respect to higher annealing temperature is a consequence of Ni$_3$P grain coarsening, Ni recrystallisation and the elimination of point defects. The decrease in hardness at 600 °C can be attributed to the precipitation of a major amount of Ni crystallites compared to the Ni$_3$P phase [7].

In the case of electroless Ni-B coating we can achieve a significant increase in the value of hardness by heat treatment. The reason for the increase in hardness is the phase transformation from as-deposited coatings (rather soft supersaturated fcc nickel) to crystallised Ni$_3$B nickel-boride (orthorhombic system) during heat treatment [43].

The properties of the composite coatings show significant differences according to whether the electroless or electrolytic method was used. Co/SiC composite coatings were investigated by Rudnik et al. [37]. A multilayer composite coating was formed, and they found that the hardness of samples made using the electrolytic method was 17 times higher than that of the base metal (aluminium), while the hardness of the electrodeposited composite coating was 9 times higher than that of the base metal [37].

**Summary**

In this review we have collected the results of research on preparations of surface composites and coatings, and here we summarize the findings.

Using the laser technologies there are some difficulties in the preparing of the composite coating. On is the poor wettability between the melted metal and the reinforcing particles and another is the chemical reaction between the two phases. Both the poor wettability and the
chemical reaction can decrease the mechanical properties of the composite coatings. These difficulties can be solved when the reinforcing particles are formed in-situ during the cooling of the melted metal. For example by adding Cr$_7$C$_3$ particles into the melted Ni or Ni-B matrix during the heat process, the Cr$_7$C$_3$ particles can completely dissolve in the Ni matrix alloy. During the rapid cooling process Cr$_2$3 and Fe$_{23}$(C, B)$_6$ phases can be well dispersed in the matrix, causing an improvement in the hardness of the coating.

Mechanical stresses may occur in the sample using the laser methods because of rapid cooling of the melted part and the non-uniform temperature. In order to avoid such high mechanical stresses in the sample, there is growing interest in composite coating preparation by brazing under high vacuum or an inert gas atmosphere, where the whole sample is heated up during the brazing process. A brazing belt or brazing paste can be made from the powder of the brazing alloy and the reinforcing material using a large volume of organic binder. The brazing pastes are especially applicable for preparing a composite brazing coating on the complex surface of engineering components.

The electrochemical and electroless methods are also suitable for preparing wear-resistant compounds or composite coatings on complex surfaces, but provide weaker bonding between substrate and coating than brazing. Electroless plating may yield higher hardness than electrochemical plating.

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References
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