Strength Characteristics of Plasma-Sprayed Coatings from Mixed Nickel-Aluminum Powders

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One of the basic conditions of reliable operation and long useful life of coatings produced by spraying is stability and a sufficiently high level of mechanical properties at normal and elevated temperatures. If a coating is to meet this requirement, chemical reaction processes must occur between its particles and the substrate and also among the particles themselves. With sand-blasted substrates, the forces with which coatings interlock with their surface irregularities are generally small (~ 30-50 kg/cm²) and comparatively unstable.

For any pair of metals coming into contact with each other during spraying, the strength of adhesion is

$$\sigma = f(T_c, \tau, P),$$

where $T_c$ is the particle/substrate contact temperature, $\tau$ the time of the impact and solidification of a particle, and $P$ the pressure generated during the impact of the particle. The extent to which the reaction between particles being deposited and a substrate can be regulated by varying the time $\tau$ and the pressure $P$ is very limited, and depends on the physics of the process [1, 2]. Therefore, raising the particle/substrate contact temperature $T_c$ is the principal means of increasing the adhesion of spray-deposited coatings. In a general case, the contact temperature $T_c$ is determined by the substrate temperature at the instant of spraying, the temperature of the particles being deposited, and the thermophysical properties of the substrate and coating materials.

With metallic substrates, the possibilities of preheating are generally restricted by the rapid growth of oxide films on their surfaces. For such materials as copper and its alloys, preheating temperatures must not exceed 100-200°C, and only some chromium-nickel alloys can be heated up to 200-400°C. It follows, therefore, that to improve the mechanical characteristics of coatings, it is necessary to raise the particle temperature.

From experimental investigations of the spraying process it is known that, in spite of the high temperature of plasma, the temperature of metal particles at the instant of deposition on a substrate in practice does not greatly exceed their $T_m$. Now the particle temperature cannot be raised effectively by employing high-enthalpy diatomic gases in order to increase the thermal efficiency and length of plasma jets. Apart from this, this method leads to overheating and oxidation of the substrate, particularly with short spraying ranges.

Another way of increasing the thermal activity of particles being sprayed is to use thermally reactive materials. An example of such materials is a powder consisting of aluminum particles coated with nickel [3, 4]. The particles of this powder are first heated up by the plasma and then by the exothermic reaction of the aluminum with the nickel. The reaction leads to the formation of new, intermetallic compounds characterized by high hardness, good thermal-fatigue resistance, and excellent atmospheric-oxidation resistance [5].

The energetic state of particles is generally judged, to a first approximation, by their temperature. However, this is a very incomplete characteristic, since it does not take into account the possibility of the
**TABLE 1. Energetic Characteristics of Some Materials Used for Spray Deposition**

<table>
<thead>
<tr>
<th>Material of particles</th>
<th>( T_m ) °K</th>
<th>( C_p T_m ) kcal/g-atom</th>
<th>( q ), kcal/g-atom</th>
<th>( Q ) at ( T_m ) kcal/g-atom</th>
<th>( H ) at ( T_m ) kcal/g-atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>3653</td>
<td>29.4</td>
<td>8.4</td>
<td>--</td>
<td>37.8</td>
</tr>
<tr>
<td>Mo</td>
<td>2993</td>
<td>21.0</td>
<td>6.6</td>
<td>--</td>
<td>27.6</td>
</tr>
<tr>
<td>Ni</td>
<td>1726</td>
<td>11.29</td>
<td>4.2</td>
<td>--</td>
<td>15.49</td>
</tr>
<tr>
<td>Al</td>
<td>933</td>
<td>4.3</td>
<td>2.6</td>
<td>--</td>
<td>6.9</td>
</tr>
<tr>
<td>Ni–Al (50 at. % Ni)</td>
<td>1910</td>
<td>12.08</td>
<td>3.4</td>
<td>11.95</td>
<td>27.41</td>
</tr>
<tr>
<td>Ni–Al (75 at. % Ni)</td>
<td>1658</td>
<td>10.4</td>
<td>3.8</td>
<td>8.34</td>
<td>22.57</td>
</tr>
</tbody>
</table>

*Note. \( T_m \) = melting point, \( C_p T_m \) = heat content at the melting point, \( q \) = melting heat, \( Q \) at \( T_m \) = reaction heat, \( H \) at \( T_m \) = enthalpy at the melting point.*

energy of particles growing as a result of internal processes such as melting, phase transformations, and chemical reactions. Because of this, it is preferable to describe the energetic state of particles in terms of their enthalpy,

\[ H = C_p T_p + q + Q, \]

where \( C_p \) is the heat capacity of the solid material of the particles (kcal/mole-deg K), \( T_p \) the particle temperature (°K), \( q \) the melting heat (kcal/mole), and \( Q \) the reaction heat (kcal/mole).

The molar heat capacity of any solid metal at high temperatures (well above its Debye temperature) is almost constant, and amounts to 6-8 kcal/mole-deg K. Values of \( C_p \) above this level (6 kcal/mole-deg K) are usually linked with the formation of defects of solid state structure (vacancies) and are characteristic mainly of the refractory metals tungsten and molybdenum [6].

The strongest adhesion (up to 250-270 kg/cm²) to the majority of metals is exhibited by coatings of tungsten and molybdenum, which are characterized by large values of entropy \( H \) at their melting temperatures (Table 1). In tear-away tests, rupture frequently occurs within the tungsten or molybdenum coating itself, and in practice it is therefore impossible to determine the strength of adhesion of these metals to substrates. The strong adhesion of these coatings to substrates is due to the fact that the surface activation energy is less for the majority of metals (1.5-2.5 eV/atom) than for tungsten and molybdenum (3.4-4.3 eV/atom).

Because of the high enthalpy of their particles, refractory metals adhere firmly to substrates without any special preparation of the latter's surfaces. To obtain similar results in the spraying of less refractory metals, the surfaces of components must be sandblasted.

In spite of their good mechanical characteristics, however, tungsten and molybdenum cannot be recommended as coating or undercoat materials for operation at elevated temperatures in oxidizing atmospheres. Both metals rapidly oxidize at temperatures above 300-400°C, and the resultant volatile oxides "burst" the main protective layer covering the undercoat.

A material showing great potential for the deposition of coatings is nickel–aluminum powder composed of nickel-coated aluminum particles [4]. The exothermic reaction occurring between the nickel and aluminum components enables the enthalpy of particles of this powder to attain values close to those of the enthalpies of tungsten and molybdenum (Table 1) providing the spraying process employed ensures that the reaction can proceed to virtual completion. According to the nickel–aluminum constitution diagram, four intermetallic compounds can form in this system, namely, \( \text{NiAl}_3 \) and \( \text{Ni}_2\text{Al}_3 \) (dissociation temperatures of 854 and 1133°C, respectively) and \( \text{NiAl} \) and \( \text{Ni}_2\text{Al} \) (melting points of 1638 and 1385°C, respectively) [5]. Decreasing the nickel content below 50 at.% sharply lowers the solidification temperature and results in the formation of the less thermal-fatigue-resistant phases \( \text{Ni}_2\text{Al}_3 \) and \( \text{NiAl}_2 \). Because of this, it is desirable that powders used for spray-deposition should have nickel contents ranging from 50 to 75 at.%.

Under real plasma-spraying conditions, the flight time of particles from the nozzle to the substrate is very short, and the resulting coating may contain various nickel aluminides together with some unreacted nickel and aluminum. At an excess of nickel (more than 50 at.%), the coating is likely to contain the more thermal-fatigue-resistant aluminides.