Plasma Spraying of Metallic and Ceramic Materials

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PREFACE

Protective coatings and their formation have become the subject of many research works and patents, since they have found extensive application with considerable economic merits in the national economy. A large number of works dealing with research on materials and methods of coating formation is published in the world every year. The coatings and the methods of their fabrication are very diverse nowadays. Available technical sources present several classifications of methods of coating formation as well as the coatings proper. One of them classifies the coatings according to their purpose and application and the physical or chemical nature of the coatings; others classify coatings according to the alloying elements, or the nature of the phases formed in the surface layer, or according to technology used.

One group of coating formation follows the methods of thermal spraying where flame, electric arc, plasma and explosion techniques belong. Filler material can be either in the form of wire, stick or powder. In general, metals, ceramics, cermets and plastics can be coated by spraying.

This monograph is devoted to only one of the many methods of thermal spraying — namely plasma spraying of metallic and ceramic materials. Since, for the time being, there is a lack of literature from this field, we hope that this work will be valuable for the technical public and of consequence also for the national economy.

The authors

1 INTRODUCTION

Plasma spraying technology is an improved development of flame metallizing. The metallization process was invented and patented in Switzerland by Dr. Ing. Max Ulrich Schoop in 1910. In its early stage, due to insufficient heat source — oxyacethylene flame — the method was used mainly for the flame spraying of zinc. M. U. Schoop at the same time invented the arc spraying technique which was, however, far from perfection because of the primitive electric equipment, mainly the D. C. sources. For this reason arc spraying was considerably surpassed by flame metallization, which started to develop in the U. S. A. in the early thirties; and its application was extended by the spraying of anticorrosion zinc and aluminium coatings and the renovation of machine parts by spraying steel and bronze. At that time, the method of spraying powder materials was employed, rather than the initial spraying of wire. In Europe, mainly in Germany, M. U. Schoop and his followers tried to employ powder metallization, however with less success. Rapid development and improvement of this technology was observed in fifties, connected with the fast development in the powder materials, thus opening new fields for the application of metallization. At that time, besides some hardfacing materials, alumina and zirconium also became interesting.

After World War II a rapid development in arc spraying was achieved. After 1945 considerable attention to arc spraying was paid in the USSR, Czechoslovakia and Poland. In the USSR 10 different prototypes of spraying equipment were developed and about 2 000 spraying machines were produced annually: 10 % of them were determined for flame spraying and 90 % for arc spraying. In 1967 about 200 machines for arc spraying were in service in the Federal Republic of Germany.

Flame and arc metallizing were from the time of their origins restricted by the low temperature of the oxyacethylene flame and/or the electric arc. This meant that the materials with a melting point of, say 2 700 °C could not be sprayed. The attempts to extend the temperature range of the heat source resulted in the development of plasma spraying technology, which brought about another advantage — spraying in the environment of inert plasma gases which considerably reduced the oxidation of molten particles during their flight through the air and at their incidence on the substrate. Temperatures over 17 000 °C, attainable by commercial plasma torches, are considerably higher than the melting and even the evaporation points of all known materials. The 6 500 °C to 11 000 °C temperature range can be considered as optimum in most spraying applications.

In order to understand plasma spraying the term "*plasma*" must be elucidated first of all. American physist Langmuir in 1928 called plasma a state of a gas which, besides the neutral atoms and molecules, contains also positively and negatively charged particles — ions and electrons. Common gases during their heating obey the classical physical and thermodynamical laws. However, plasma does not obey those laws and therefore many scientists considered it as the fourth state of mass, differing from solid, liquid and gaseous states.

Nevertheless, the plasma state can be often observed in nature. Let us mention for example the plasma clouds consisting of nuclei of hydrogen atoms and electrons expelled during eruptions on the Sun. These plasma clouds, approacing our Earth at 1 500 km . s^{-1} velocity, cause the familiar Polar glare, magnetic storms and ionospheric disturbances. The basic data about similar plasmas in nature, as e. g. solar corona, ionosphere etc., and also about some laboratory plasmas, are given in Tab. 1.

Table 1

Characteristics of some natural and laboratory plasmas

Plasma type	Interstellar mass	Ionosphere	Solar corona	Electric arc	Electromagnetic impacts	Thermonuclear discharges	Mass inside the Sun
Number of electrons in 1 cm^3	1—10^3	10^3—10^5	10^8	10^{16}—10^{18}	10^{15}—10^{18}	10^{16}	10^{22}—10^{25}
Temperature of electrons (K)	10^4	$2 . 10^3$	10^6	10^4	$5 . 10^4$	10^6—10^8	10^7
Induction of magn. field (T)	10^{-9}	$5 . 10^{-5}$	10^{-4}—10^{-6}	10^{-4}—10^{-7}	10^{-9}	10^{-7}—10^{-9}	—
Mean thermic velocity (cm . s^{-1})	$7 . 10^7$	$3 . 10^7$	$7 . 10^8$	$7 . 10^7$	10^8	$7 . 10^8$— $6 . 10^9$	$2 . 10^9$
Plasma frequency (Hz)	$9 . 10^3$— $3 . 10^5$	$3 . 10^5$— $9 . 10^6$	$9 . 10^7$	$9 . 10^{11}$— $9 . 10^{12}$	$9 . 10^{11}$— $9 . 10^{12}$	$9 . 10^{11}$	$9 . 10^{14}$— $3 . 10^{16}$

Technical exploitation of plasma — plasma arc — in the so-called plasma torch began about 1958. Depending on the arrangement of the electrodes between which the electric plasma arc burns, two basic types of plasma torches can be distinguished. When the arc burns between the negative cathode and positive anode, realized in the form of a nozzle inside the torch, we speak about a torch with *a non-transferred arc* (Fig. 1). When the positive pole from the

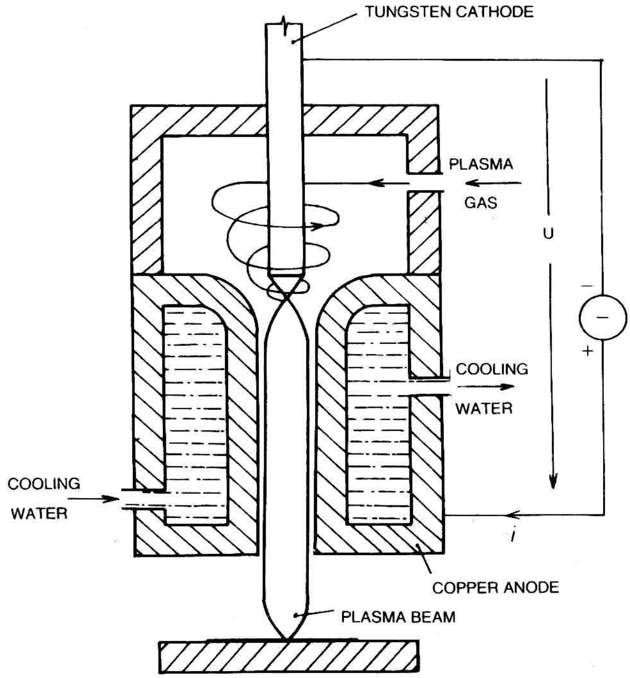

Fig. 1 Scheme of a plasma torch with non-transferred arc

nozzle is transferred to an external conductive material located in front of the nozzle, the arc will burn between the cathode inside the torch and the external conductor. In such a case we speak about a torch with *a transferred plasma arc* (Fig. 2). Corresponding to these basic arrangements of electrodes, different fields of application and special torch types with individual plasma technologies were developed. The torch with non-transferred arc provides a plasma beam used as a heat source for melting different materials in the technologies of plasma spraying, melting down and in the plasma furnaces. The torch with transferred arc is generally used for a constricted beam, usually employed in the technologies of plasma welding, surfacing and metal cutting.

According to the type of material sprayed the torches can be designed either for *the spraying of wire* or *spraying of powder*. One advantage of the first technique is a higher purity of material produced in the form of wire, resulting in higher purity of the sprayed layer, the second technology, however, offers the advantages of a wider assortment of powders, even from the materials which cannot be produced in form of wire, such as hard-to-melt materials, oxides, carbides etc. Powder spraying systems are widely used in the U. S. A. and in Western Europe. In the USSR, on the other hand, wire spraying technology is wide-spread.

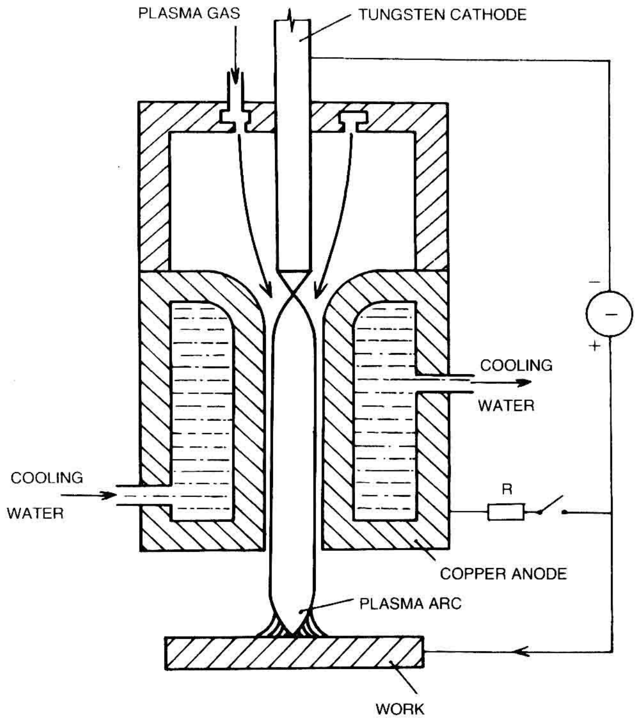

Fig. 2 Scheme of a plasma torch with transferred arc

The present work will be next dealing with *the plasma torch with non-transferred arc*, namely with the technology of plasma spraying of powdered metallic and ceramic materials. This technology, from its invention up to its present state, has passed through many stages. In industrially advanced countries — mainly the U. S. A., Switzerland, France, the FRG and the USSR — plasma spraying technology is widely utilized in various industrial branches. Recent developments by some producers of plasma equipment, mainly in the U. S. A. and in Switzerland, has ensured a sufficient number of automatic plasma spraying mechanisms and programmable robots on the world market, performing diverse operations in series production.

2 PHYSICAL PRINCIPLES OF PLASMA SPRAYING PROCESS

2.1 PLASMA BEAM

2.1.1 Characteristics of plasma beam

According to the definition of H. Langmuir, *plasma* is the highly ionized state of mass, consisting of molecules, atoms, ions, electrons and light quantums. One cm^3 contains about 19^9 to 10^{10} charged particles.

For better understanding of the term "plasma beam" some explanation of principles from the theory of gas mechanics would be valuable. Let us suppose principially that the properties of a gas are primarily dependent upon the movement of its individual molecules. During this movement the molecules mutually exchange the energy and pulse due to collisions of their elementary particles. If a certain amount of energy is supplied to a gas, the velocity of the molecules increases. The higher this velocity, the more frequent also are the mutual collisions of particles. A temperature increase of the affected gas is thus a natural consequence of this energy process. The velocity of the particles may attain such a high level that, in the case of a two-atom gas, the molecules disintegrate into atoms due to mutual collisions. This process, taking place in the plasma arc, is called *dissociation*. In the case of hydrogen molecules, the dissociation process takes place within the 2 500—6 000 K temperature range. When higher levels of energy are supplied, the velocity can achieve such a high level that not only molecules are dissociated, but also electrons can be forced out from the electron envelope of atoms. The energy needed for forcing an electron from its path is higher than the energy needed for the dissociation process. It is called *the ionization energy*, and the whole process, taking place also in the plasma arc, is called *ionization*.

The ionization process can be explained in more detail with the example of an atom with two electrons (Fig. 3). Around the atom nucleus with two + charges, two electrons e_1 and e_2 rotate in two paths close to the nucleus. Each electron has its own energy, E_1, E_2. The normal condition of this atom is neutral, since both + charges of the nucleus are balanced with the two — charges of electrons which rotate around the nucleus. When sufficient energy is supplied from outside at least one electron e_2, the one with the highest energy E_2 will jump over to the more distant path, characterized by a higher energy E_2'. The atom is now in the ionized, excited state. The amount of energy necessary for forcing the electron from its original position, to ionize the atom, is called the ionization energy of that atom. At this stage, two particles can already be distinguished. The first one is *the ionized atom* — the original atom without one electron — and the other is *the free electron*. The ionized atom is called *an ion*, while its electric charge without one electron is + 1. The free electron has a — 1 charge. Since the free electron e'_2 tries to attain the state with the lowest energy as soon as possible, it will soon return to its previous path where it will attain its original energy state. During this process the released energy, given by the difference $E' = E'_2 - E_2$ will be delivered either in the form of kinetic energy or electromagnetic radiation. This procedure can be applied to two or more neutral atoms creating a molecule which can be again considered as an independent particle.

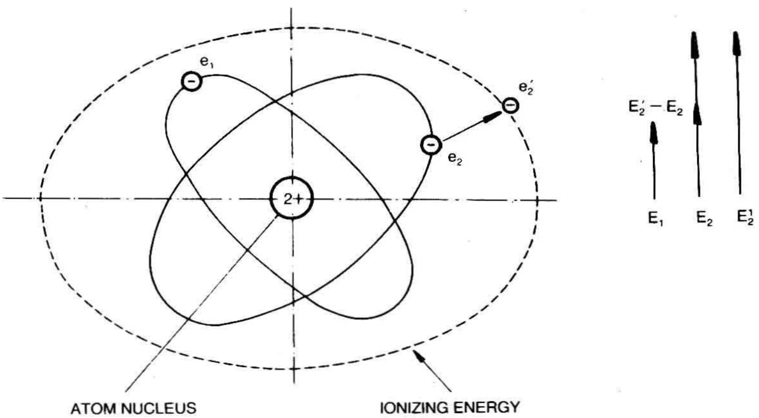

Fig. 3 Excitation of neutral atom

The final consequence of the whole dissociation and ionization processes is *plasma* as a state of mass, containing the electrically charged particles. However, it must be noted that the plasma is outwardly neutral, since in it the same number of electrically positive and negative charges must be distributed. The processes of dissociation and ionization are thermally balanced. This means that in dependence on temperature, an equilibrium state between dissociation and ionization on the one hand, and the appropriate reciprocal processes on the other hand, is attained.

The dissociated and ionized gas in thermal equilibrium obeys the Saha's equation [1]. This equation, expressing the ionization degree, follows from statistical thermodynamics and expresses *the equilibrium of reaction*

$A^{i+} \rightleftharpoons A^{(i+1)+} + e$ for the one-atom gases, or reaction

$N_2 \rightleftharpoons 2N$ for the two-atom gases.

The adapted Saha's equation [2] is