PLASMA SPRAYING

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Abstract—Plasma heating and spraying of different materials are considered. Data are given on the energy balance of plasma jets. It is shown that, using plasma spraying, one can produce coatings and composite materials. Physicochemical processes causing formation of strong bonds between coating and substrate are considered. Experimental investigations of the rate of increase of bond strength for melted particles which are being sprayed on the polished surface of specimens have shown that the main stage in this process is chemical interaction of a particle and the substrate. Data on interaction of 80 pairs of materials are given. These are activated processes, and the activation may be due to heating of the substrate and overheating of the sprayed particles. The effects of different parameters both on the type of reactions and their kinetics are analysed. The activation energy for the formation of a strong bond between metals by spraying is approximately half the bond energy of atoms in the metal lattice of a substrate.

INTRODUCTION

The development of engineering is essentially determined by the possibility of creating and of producing, in sufficient quantities, structural materials meeting the requirements of modern technology. A trend to use high and low temperatures, low and high pressures, high rates of gas flow and concentrated energy fluxes in all modern fields of engineering—power and transport, missile, astronautics, aeronautics and atomic power engineering is rapidly developing. In these extreme conditions, engineering material problems are in some cases solved by appropriate choice of coatings, which may sharply increase the service life of equipment.

The development of thermal plasma generation, at the end of the fifties, has put an effective and convenient means for materials production and treatment at the disposal of technologists. Plasma spraying for the building up of coatings has taken a prominent place among methods of coating production. Plasma coatings are used for protection against overheating, corrosion, erosion effect of hot gas fluxes, for electric insulation, for increasing wear and heat resistance etc. Recently plasma spraying technology has been used to produce high strength high-modulus composite materials.

In this lecture heat transfer and gas dynamic charac-teristics of thermal plasma jets, used for materials spraying, will be considered. Two-phase plasma jets, carrying disperse condensed phase material which is accelerated, heated up, melted and evaporated by plasma arc, are being analysed. Special attention is paid to the physico-chemical processes leading to formation of strong bonding of coatings with a substrate material. Technological possibilities for producing various coatings by plasma spraying and for forming metallic matrices for fibre reinforced composite materials are shown.

1. PLASMA HEATING OF RODS AND POWDERS

Rod and wire melting

In plasma spraying the coating is formed by molten particles being brought onto the substrate by the plasma jet. Both plasma spraying of rods and wires and complete melting of the sputtered material is achieved when wires or rods are melted by plasma jet (Fig. 1). The sputtered particles get somewhat cooled on their way to the substrate. However, direct calorimeter measurements have shown that the temperature of particles even of the most refractory metals (tungsten, molybdenum), at a distance of 100–150 mm from the nozzle is close to the melting temperature.[1]
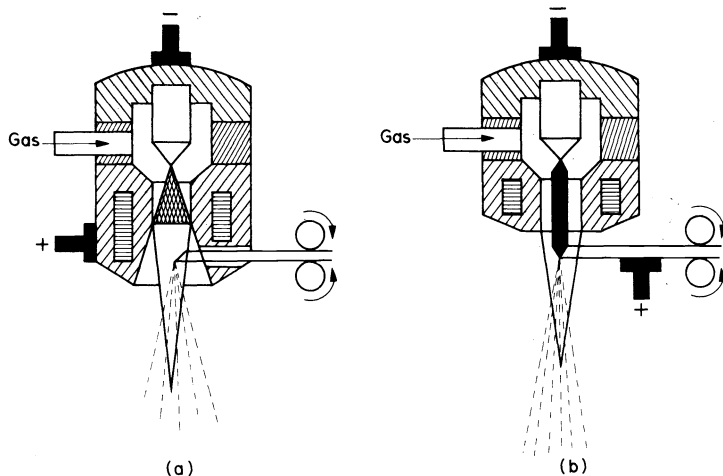

Fig. 1. Spraying of neutral (a) and current-conducting (b) wire (open anode) by arc plasma.

When spraying neutral wire by plasma jet, heating and melting is due to the heat transmitted from plasma by convection, thermal conductivity and plasma radiation. The heating efficiency η_u does not exceed a few per cent, e.g. for tungsten and molybdenum 1 mm wire η_u 2–3%.[5]

When sprayed wire is connected electrically to the plasma arc anode, wire heating and melting is enhanced appreciably by the current electrons giving rise to 80–90% of the entire energy absorbed by the wire. About 90% of the energy is consumed by wire melting and about 10%—by evaporation. At an average mass temperature of the argon plasma jet of 8000°K, the heating and melting of a neutral tungsten wire fed to the edge of the plasmatron nozzle absorbs about 2% of the arc energy and the molybdenum wire—about 3%. The coefficient of the heat transfer coefficient from plasma to the wire amounts to 4200 W/m² deg for tungsten wire and 6300 W/m² deg for molybdenum wire. The efficiency is abruptly increased from 2 to 3% for simple heat exchange with the plasma jet, and to 10% for energy transfer by charged particles in the electric field when the wire is connected to the anode.

Plasma powder heating up

Despite the high temperature of the plasma jet it is rather difficult to melt particles uniformly and completely: there are several reasons for this. Only a few of the plasma-forming gases are capable of effectively transmitting heat to the powder; non-metallic powders having low conductivity are rather slowly heated; the time that the particles stay in the plasma jet is rather short and not all the powder passes through the jet high-temperature zone. According to simple evaluations, the residence time in the plasma jet is of the order of 10^{-3} s. Powders supplied to the column of the constrained arc discharge are the most effectively heated (Fig. 2a). However, it is difficult to find a rather reliable design arrangement of such a plasma generator.[2,3] Therefore, in most cases the powder is introduced beyond the arc anode, directly into the plasma wake (Fig. 2b). In order to fix the length of the arc and thereby to stabilize the discharge the anode nozzle is usually provided with a step or with widening of the outlet.

Powder suspended in the transporting gas jet is blown into the nozzle or directly into the plasma jet formed at the edge of the nozzle. Under the effect of gas dynamic and inertia forces the powder penetrates into the plasma

jet and is heated up and accelerated therein. Two interrelated problems connected with the interaction of plasma jet and powder particles must be examined: 1) the dynamics of particle motion in a plasma jet which incorporates the analysis of velocities and trajectories of particle motion taking into account their drag resistance; 2) the heat exchange and the heating up of powder particles in a plasma jet.

At present no single approach to the solution of these problems exists, because of the complexity and variety of physical and chemical phenomena responsible for the processes in the thermal plasma.[6] As a matter of fact, the heat exchange in plasma comprises the following phenomena: 1) gas dissociation and ionisation as well as the reverse processes of recombination and association which may have non-equilibrium character; 2) the effect on energy transfer of the diffusion of atoms, ions and electrons with a subsequent recombination or association in the boundary layer or on the body surface; 3) plasma radiation.

Evaluating particle motion and heating up

Despite the wide scope and variety of theoretical plasma physics investigations, for practical purposes it is necessary to use a semi-empiric approach which combines the physical concepts, involved in the interaction between plasma and solid body, with the direct experimental data. From a simple model developed by A. V. Nikolaev,[4,7] equations can be derived for the motion of individual particles of the condensed phase, for the Reynolds numbers Re < 1 in the isothermal jet (without taking into account particles collisions)

$$v_r = v_n\left[1 - \exp\left(-\frac{t}{t'}\right)\right]; \ x = v_n t - v_n t'\left[1 - \exp\left(-\frac{t}{t'}\right)\right] \tag{1}$$

and for Re > 2.

$$v_r = \frac{v_n t}{t'' + t}; \ x = v_n\left[t - t'' \ln\left(1 + \frac{t}{t''}\right)\right] \tag{2}$$

where v_r and v_n are the respective particle and plasma jet velocities in cms⁻¹, t is time in seconds and t' and t'' are the acceleration period time constants, i.e. the time required for the particles to reach the velocity of the jet
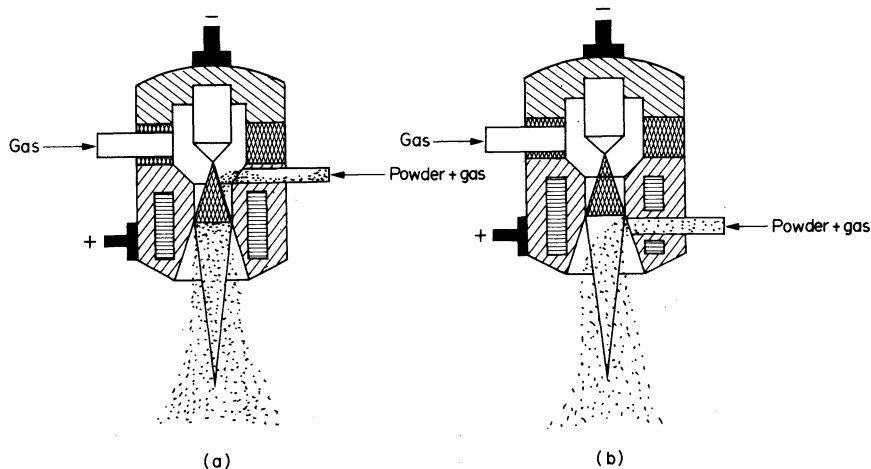

Fig. 2. Introducing powder into the plasma arc column (a) and into plasma jet (b).

provided the particles move all the time at an initial acceleration

$$t' = \frac{d_r^2\gamma}{18\nu\rho}; \quad t'' = \frac{4d_r\nu}{3\psi v_n\rho}, \tag{3}$$

where d_r—particle diameter, cm; γ—density of its material, $g.cm^{-3}$; ν—kinematic viscosity of plasma, $cm^2.s^{-1}$; ρ—density of plasma, $g.cm^{-3}$; ψ—coefficient of particle resistance. Formulas (1) and (3) make it possible to evaluate the effect of plasma parameters and powder properties on powder particle movement in the jet.

Table 1. Biot number for plasma heating of powder[4]

Powder material	Thermal conductivity coefficient of powder material (W/m °K)	Ar	N₂	NH₃	H₂
ZrO₂	2·39	0·18	0·63	3·5	5·5
Al₂O₃	5·86	0·07	0·26	1·4	2·2
MgO	5·86	0·07	0·26	1·4	2·2
BN	9·2	0·05	0·16	0·9	1·4
SiC	41·90	0·01	0·04	0·2	0·3
Ti	18·00	0·02	0·08	0·5	0·7
Fe	40·00	0·01	0·04	0·2	0·3
W	100·00	0·004	0·015	0·08	0·1

Comment: The number $N_u = 2$; the mean mass plasma temperatures are: argon 10,000°K, nitrogen 5000°K, hydrogen and ammonia 3500°K. The thermal conductivity coefficient of powder is taken for $0.5\,T_{melt}$.

The heating of powder is governed by the Biot criterion, i.e. the ratio of the plasma and the particle material conductivities, $Bi = \lambda_n/\lambda_r$. For a low conductive plasma, as a rule $Bi < 1$, which means that the particle heating process in argon, helium, nitrogen is governed by the jet phenomena. With a high conductive plasma heating oxides and other materials with low conductivity $Bi > 1$ (Table 1) in hydrogen, ammonia, etc. the limiting link is heat transmission into the particle mass.

The particle temperature rise at $Bi \leqslant 1$ can be expressed by

$$T_r = T_n - (T_n - T_{r0})\exp\left(-\frac{t}{t'''}\right) \tag{4}$$

where T_n and T_{r0} are the plasma temperature and initial temperature of the particle respectively, and t''' is the heating up time constant

$$t''' = \frac{c\gamma d_r}{6\alpha}, \tag{5}$$

c is the heat capacity of the particle, $cal.g^{-1}\,grad^{-1}$; α is the coefficient of heat transfer from plasma to particle, $cal\,cm^{-1}\,s^{-1}\,grad^{-1}$.

The time constant for heating particles is one or two decimal orders lower than the time constant for their acceleration, which is favourable for the efficiency of plasma powder heating up.

In plasma spraying and spheroidisation processes, the ratio of mass throughput of powder G_n to the rate of plasma gas mass flow G usually does not exceed 5. Under these conditions, the jet temperature and its flow-rate are decreased by 20–30%.[8] The effective heat power q when heating powder in the jet, i.e. the energy transferred to the powder per unit time is proportional to the plasma temperature T, to the length of the thermal active zone l, to the coefficient of heat transfer α and inversely proportional to the velocity.

$$q \approx \frac{lT}{v_r}. \tag{6}$$

Plasma generators

Three types of arc stabilisation are used in the plasmatrons designed for powder spraying (Fig. 3): by axial or by tangential flow of gas and by magnetic twisting of the arc column. The tangential gas injection and the magnetic rotation cause turbulence in the plasma jet and thus provides better conditions for heat exchange and powder heating up.[4]

At present, improved plasma equipment for high productivity spraying is being developed. Use is made of magnetic stabilisation, employing high-enthalpy gases, pulse plasma sources, sources with the modulation of plasma jet parameters, etc. The magnetic rotation of the arc makes it possible to utilise the high-enthalpy gases (hydrogen, ammonia) with a long jet, as well as to intensify the heat transfer to the particles by increasing their relative velocity, the jet turbulization and the uniformity of power distribution.[4]

Pulse arc

For plasma spraying use is also made of wire electrode 1 melting by a pulse arc burning in the outer cylindrical electrode 3 (Fig. 4). The pulse supply source 2 consists of an energy capacitance storage device (~250 J), a charge rectifier (500 V) and a pulse initiating generator. The plasmatron is placed in a controlled atmospheric chamber where the spraying process takes place.[9] Discharge lasts for a period of 100–600 ms.[9,10] The maximum current in the first half-period, when the capacitance of the battery ranged from 200 to 3000 mF, amounted to 7–13 kA. The arc voltage at maximum current intensity was 100 V. The battery was fully discharged during one pulse. The losses of energy in the discharge circuit did not exceed 30%. The main part (70%) of the discharge energy was released in the first half-period. The plasma-jet was formed due to the
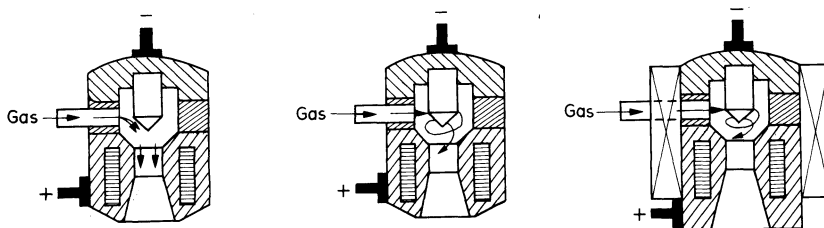

Fig. 3. Arc stabilising in powder spraying plasmatrons: by the axial gas flow (a), by tangential gas flow (b), by gas flow and magnetic arc rotation (c).
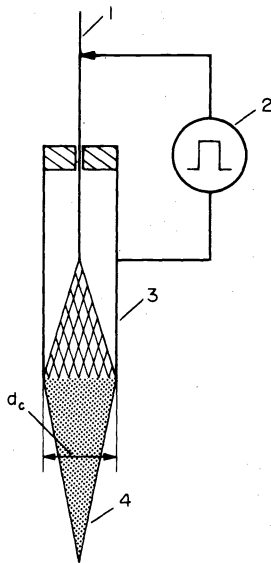
Fig. 4. Plasma pulse generator for spraying with an eroding electrode[10]: (1) rod electrode; (2) pulse power source; (3) tubular electrode; (4) plasma jet carrying the products of rod electrode erosion.

evaporation of the wire electrode, as well as to the heating and outburst of gas from the plasmatron channel. The length of the plasma jet was 150 mm. The rate of the jet flow movement was about $(1-3)10^3 \, \text{m.s}^{-1}$.

With single pulses, the spraying takes place mainly in the vapour phase; with a series of pulses, a finely dispersed liquid phase emerges in the erosion products. The effective efficiency of the wire heating up amounts to 20-30% for the pulse erosion plasmatron. This substantially exceeds the efficiency of wire heating by d.c. plasma arc (~10%).

The efficiency of heating up wires and powders

The thermal efficiency of plasma powder spraying is determined by the design of the plasmatron. With wire spraying the design peculiarities of the plasma sprayer do not appreciably affect the thermo-physics of the process. The wire spraying process has a higher productivity and energy utilisation, as well as spraying stability, since the wire is fully melted in the plasma jet. The efficiency of heating powder in a conventional spraying plasma jet amounts to 2%. The powder heating efficiency, at $Bi < 1$, should be increased by prolonged particles residence time in the heating zone, $t = 1/v_r$, and by intensifying the heat transfer, by raising the jet temperature and the heat transfer coefficient. In case of $Bi > 1$, the rise in heating time is the main factor of efficiency improvement.

The energy balance of the plasma wire spraying (Fig. 5) shows that the fraction of energy heating the substrate by plasma and sprayed material amount to several per cent (up to ~10%) of the arc energy. Up to 60-80% of the energy balance is consumed by heating up the plasma forming gas. A part of this energy is spent in spraying, accelerating and heating the particles.

Efficiency of heating powders for spraying has been raised by improved plasmatron designs and stands close to, or somewhat higher than, the thermal efficiency of the wire spraying process.

It is not so easy to evaluate the role of the technological parameters involved in the powder heating and to determine ways of improving the efficiency of the spraying process. However, the analysis of the spraying process parameters and of the plasmatron design characteristics leads to some useful conclusions.

The temperature and plasma enthalpy space distributions near the arc discharge may differ significantly. In the argon plasma the energy flux is very non-uniformly distributed across the flow cross-section, and maximal energy flux rate does not coincide with the axis of the flow (Fig. 6) where temperature 1 attains a maximum. Heat transfer from plasma to powder is increased significantly by injecting the particles into the high enthalpy portion of the plasma jet cross-section. Since the highest energy content is being carried in this flow portion, powder heating will not drop the mean gas temperature considerably. This is particularly essential for the low power plasma jets. With one-sided introduction of powder into the plasma jet, it occupies just a portion of the high-enthalpy zone (position 3 in Fig. 6) of the jet. Evidently, it is necessary to fill the cross-section of the jet uniformly with
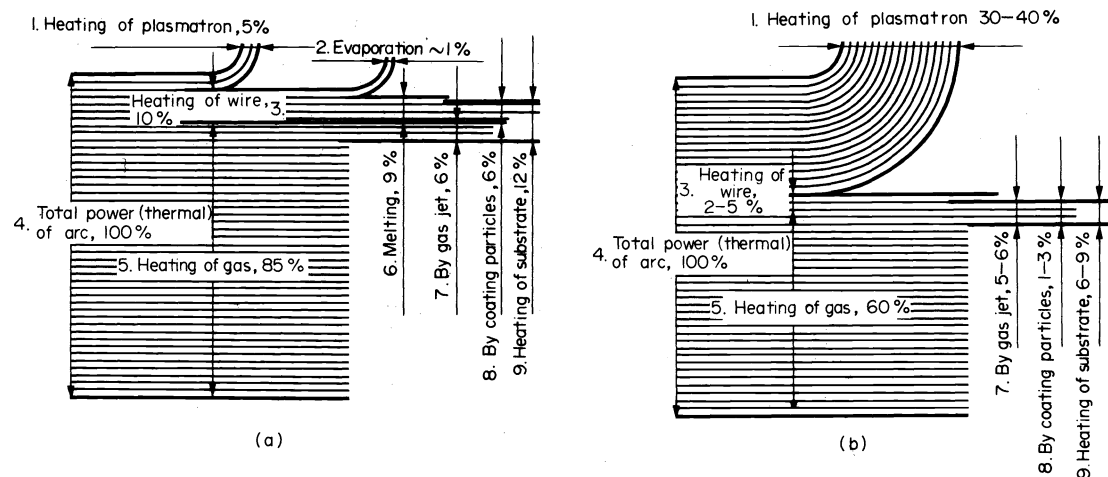

Fig. 5. Energy balance of plasma spraying anode-wire (a) and neutral wire (b): arc power—10–12 kW; argon plasma; spraying distance 100 mm. Key: (1) heating of plasmatron, (2) evaporation ~1%, (3) heating of wire, (4) total power (thermal) of arc 100%, (5) heating of gas, (6) melting, heating of substrate: (7) by gas jet, (8) by coating particles.
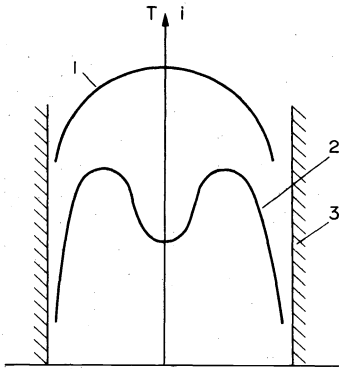
Fig. 6. Schematic distribution of temperature (1) and enthalpy (2) across the plasma jet section; (3) nozzle walls.

powder. This will improve the thermal efficiency when utilising the jet energy.

The efficiencies for plasma heating and spraying processes are given in Table 2.

The approximate energy balance for plasma spraying (Fig. 7) shows that when injecting powder into the arc, efficiency rises from 5 to 30%. The energy of the plasma jet consumed for heating the substrate by spraying is shown approximately.

Table 2

Type of plasma heating	Efficiency (%)
Gas heating	
argon	10–70
hydrogen	30–80
Massive body heating by:	
plasma jet	10–50
plasma arc	30–75
Wire spraying:	
by plasma jet	2–5
by plasma arc	10
Powder heating introduced into:	
plasma jet	4–5
arc column	20–30

2. THERMAL AND CHEMICAL EFFECTS OF THE SPRAYING PLASMA JET

Chemical transformations in sprayed particles

The coating formed of sprayed particles differs by its physical–chemical composition and mechanical properties from the initial material. Under the effect of plasma, the sprayed material is melted and absorbs oxides and gases. Very often some components are selectively evaporated and new compounds are formed. The transformations in the sprayed material are due to the high temperature and chemical activity of the plasma jet as well as to the large relative surface of the molten material dispersed into fine particles.

When spraying in a free atmosphere, jets of inert plasma-forming gas do not prevent these processes. In a turbulent argon plasma jet, the oxygen concentration rapidly increases with the distance from the nozzle (Fig. 8). Oxygen content in the aluminium AMG5 alloy coating has risen from 0·02% with spraying distance 50 mm to 0·4% with 150 mm distance and the content of aluminium oxide risen from 0·09 to 0·8%. These values of oxygen content in the coating are one or two orders higher than the equilibrium oxygen content in the aluminium solid solution. When spraying steel, the oxygen content in the coating amounts to 2·5–5·7% which greatly exceeds the

Fig. 8. Oxygen and argon content in plasma jet and aluminium oxide content in the coating depending on the distance from the nozzle L.
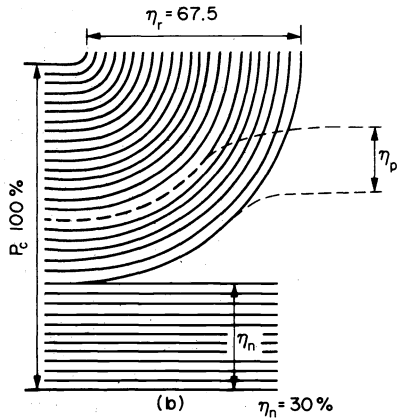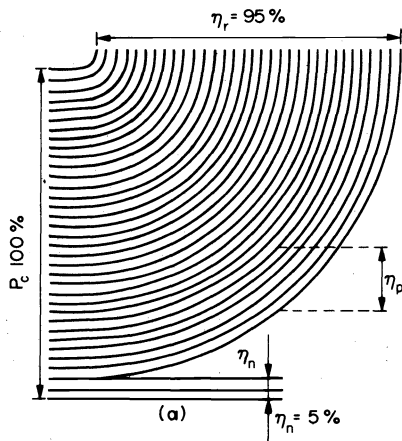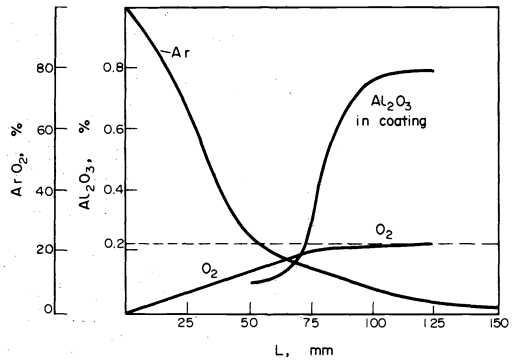

Fig. 7. Energy balance of plasma powder spraying: injecting the powder into plasma jet (at the edge of the nozzle) (a), to the arc column (b) near the cathode: P_c–plasma energy; η_r, η_p and η_n–efficiencies of heating the plasma forming gas, sprayed substrate surface and particles (up to melting temperature).

solubility of oxygen in liquid steel at the melting temperature (0·21%) and even in liquid steel overheated to 2000°C (0·87%). Similar phenomena are observed with the solubility of nitrogen and the formation of nitrides.

The spraying of wire or bars is a result of the dynamic gas effect of the plasma jet tearing off and dispersing the molten metal and of the counteracting surface tension. To obtain high quality coatings and to regulate their density, it is necessary to control the spraying dispersity. An analysis of the forces acting on the molten drop located at the end of the wire has shown[11] that the diameter of particles, separated from the wire can be expressed by

$$d_r = \frac{3 \cdot 35 d_c^2}{Q(1 + 3 \cdot 67 \cdot 10^{-3} T)} \sqrt{\frac{d_w \sigma}{\rho}},$$

where d_c—diameter of the plasmatron nozzle, m; Q—rate of gas flow, $m^3 s^{-1}$; d_w—wire diameter, m; σ—surface tension, $j.m^{-2}$; ρ—plasma density, $kg.m^{-3}$; T—temperature, °C.

This relationship enables one to evaluate the effect of the process parameters on the spraying dispersity. The arc current determining the plasma temperature affects essentially the dispersity. The increase of the arc current from 200 to 450 A changes appreciably the fractional composition (Fig. 9), augmenting the fraction of fine particles and improving their uniformity.

By controlling the chemical composition of plasma gas it is possible to affect the properties of the sprayed material by oxidation and gas saturation. By spraying the material in a controlled atmosphere it is possible to refine or to alloy the coating. The plasma atmosphere enables the decomposition of unstable compounds that tend to be dissociated to be delayed, e.g. such as carbides.

Influence of spraying on thin elements

Thermal and chemical effects that plasma and heated gas jet exert on a massive substrate plate are, as a rule, negligibly small. However by spraying on thin objects—wires, non-organic fibres, foils, the plasma jet can drastically change their properties. Fibres and wires are now used for the production of reinforced coatings and composite materials. These coatings offer high strength and high stability of properties over a wide temperature range.

The following experimental results illustrate the influ-

ence of plasma spraying on fibre properties. A very pronounced effect is produced by an argon plasma jet (Fig. 10)[1,14] on boron fibre and on boron fibre with B_4C coating (curves 1 and 2). The reduction of boron fibre strength reaches 25% at a distance of $L = 50$ mm from the edge of the plasmatron nozzle. The fibre has been heated by plasma jet for 8–10 s which corresponds to the period of fibre plasma spraying. The diameter of the fibres was approximately 100 μm, the thickness of the coating layer—2–3 μm. The reduction in strength of the boron fibre and the fibre with B_4C coating is attributed to the absorption and chemical effects of the plasma jet on the defective fibre surface. Boron fibres under the oxidising heating are subjected to local surface corrosion.[12]

The same plasma effect on the SiC fibres, or fibres of boron with the SiC coating (curves 3 and 4), does not appreciably change the strength of these fibres, since silicon carbide is rather resistive to air oxidation. The plasma jet may influence the fibre properties by a purely thermal effect or by a thermal effect involving gas surface corrosion. If the corrosion effect is neutralised by a protective fibre coating, or the fibre itself is rather stable to the gas chemical effect, then the plasma jet exerts
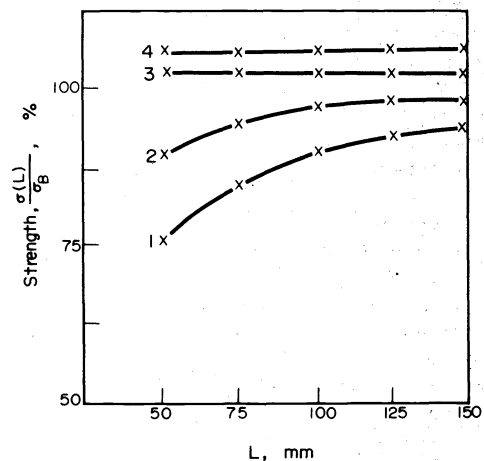

Fig. 10. Fibre relative strength $\sigma(L)/\sigma_b$ affected by argon plasma jet action for 8–10 s: (L) the fibre distance from plasma torch nozzle; (1) boron fibre B; (2) boron fibre with B_4C coating; (3) boron fibre with SiC coatings; (4) SiC fibre.
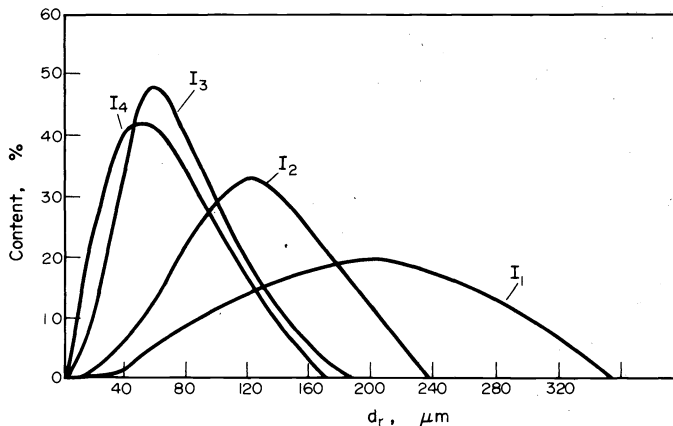

Fig. 9.

primarily, a thermal effect. When heated in the argon plasma torch, both boron fibres with SiC coating, and the SiC fibres, get somewhat stronger (up to 10% of the initial strength). This is associated with a favourable redistribution and a partial removal of internal stresses in the heated fibres.

To evaluate the kinetic effect of plasma jet on the boron fibres under consideration, experiments have been conducted.[13] Their strength, depending on the time period of plasma action (Fig. 11), has been measured. With the fibre at fixed distances from the plasma torch nozzle ($L = 50$ and 100 mm) a simultaneous evaluation of fibre temperature $T_f(t)$ as a function of time was made. At a distance 50 mm the maximum fibre temperature of 520°C is reached in 10–12 s (and subsequently it did not go up) (Fig. 11a). Due to heating, the strength of boron fibres and boron with coating B_4C has been reduced by 20–30%, but is little affected (within 5%) by SiC fibres and boron with SiC coating. During the temperature rise the strength drops rapidly, but when the maximum temperature is attained, the rate of decrease of fibre strength is slowed down. Such a pattern of kinetic curves allows one to assume that the strength decrease may be attributed to the absorption strength reduction of boron fibre both bare and with B_4C coating under the effect of the chemically active gases of the plasma torch.

A similar strength reduction effect can be observed when the fibre distance from torch nozzle is $L = 100$ mm (Fig. 11b).[13,14] However, due to lower jet efficiency, the maximum temperature of fibre heating does not exceed 330°C, while its strength is decreased by not more than 5–12%.

By controlling both the plasma jet effect, and using protective coatings it is possible to regulate the properties of fibres. Silicon carbide fibres and protective coatings are resistant to the oxidising plasma jet.

Particle spraying exerts a still more complicated effect on the fibre strength. The fibre strength can be reduced considerably in the particle impaction and deformation spots by: local overheating of fibre, chemical effect of the jet and the particle material in the local heating spot complicated by absorption, high level of local residual stresses.

For an approximate qualitative estimation of the thermal effect of the particles, the temperature and the time of contact must be calculated.

3. FORMATION OF COATINGS

The plasma sprayed coating is a kind of sandwich material (Fig. 12) built up of strongly deformed fine particles, crystallised at a very high rate of cooling. However, the methods previously used for analysing the properties of coatings did not take into account the peculiarities of the deformation conditions and the texture structure of plasma sprayed coatings. As a rule, the properties of a coating, as a whole, have been studied and some operating characteristics have been determined. It became necessary to clear up the kinetics of the physico-chemical phenomena determining the formation of the coating and to establish the influence of the parameters of plasma spraying on the coating's properties.

We've investigated both the development of thermal and dynamic processes which follow the impact, and the flow and solidification of the sprayed particles during the coating formation. Even with the maximum rate of plasma spraying, the particles are deposited on the already crystallised and cooled preceding layer. Therefore, the properties of the whole coating can be regarded as the result of deformation and solidification processes of individual particles and their contact interaction.[15,16]

A precision procedure using special instruments have been developed for analysing the adhesion strength of the particles deposited on the substrate (Fig. 13). A correlation between the properties of individual particles and the
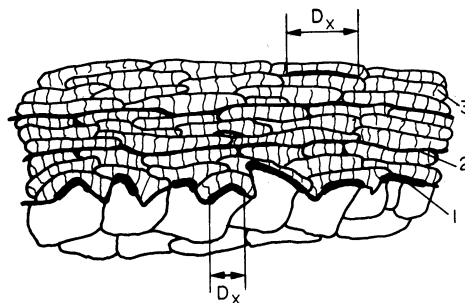

Fig. 12. Texture of plasma sprayed coating: (1) contact surface between the coating and substrate; (2) contact surface between layers ; (3) contact surface between particles. (D_x) diameter of the fused contact surface portion.
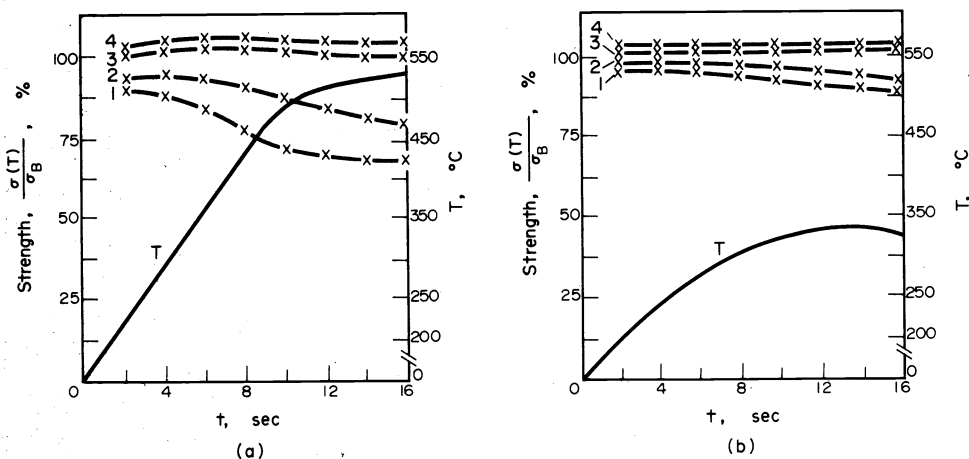

Fig. 11. Fibre relative strength $\sigma(T)/\sigma_b$ and fibre temperature (T) depending on the time period t of argon plasma jet heating; fibre distance from the torch nozzle: (a) $L = 50$ mm; (b) $L = 100$ mm. 1, 2, 3, 4—same as in Fig. 10.
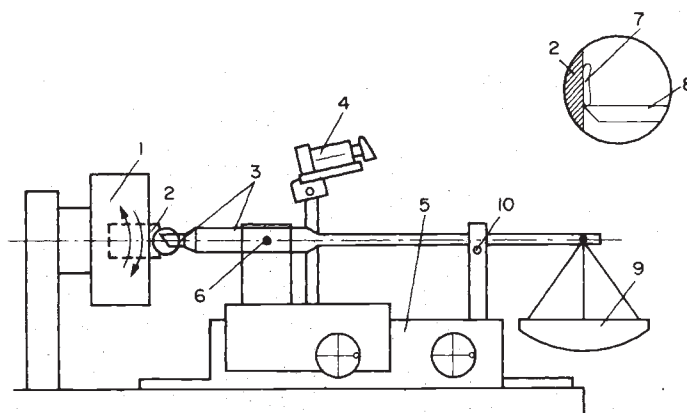
Fig. 13. The instrument for measuring the adhesion strength of the particles: (1) rotating sample holder; (2) sample; (3) lever with a hard fine-sharpened end (micro-knife); (4) two binocular magnifying glasses (the second one is not shown to control the knife position and the shearing process; (5) stage allowing for longituditudal and transverse motion of level 3; (6) two taper screws to control lever 3; (7) the particle; (b) shearing knife; (9) load dish; (10) lever lock.[15]

coating as a whole was established. Properties of the following deposits: oxides on metals; metals on oxides; oxides on oxides; metals on metals; oxides on graphite; and metals on graphite were investigated, as well as a particular case of interaction, occurring by deposition of metal matrices on reinforcing fibre nets in a composite material.

The scanning electron microscope investigation on the fracture surfaces in the contact area under the particles (Fig. 14) showed the discreteness of the particle interaction and allowed the kinetics of its development to be traced. In the initial stages of the deposition process only single particles are firmly joined to the base material. As the number of such particles increases the adhesion strength of the deposit rises. At the maximum adhesion strength, the spots of particles sticking to the substrate actually fill up the entire contact surface.

Several problems of thermal and dynamic impact, and spreading and solidification of particles on the substrate have been solved by methods of thermal physics and hydrodynamics used in analysing the materials interaction by a depositing process. Calculations have shown that the time period of particle solidification on a massive body surface, for the majority of materials, amounts to micro-seconds, complete cooling—to $10^2\,\mu$s. In the thermal effect area zone under the particle which does not exceed 20–30 μm, the temperature gradients reach $10^5\,\text{K cm}^{-1}$.

The adhesion strength of the sprayed particles is determined by the reaction in the contact zone under the particles.[15,16] The rate of this reaction can be described by an exponential equation. Denoting by $N(t)$ the number of atoms that would react during time t, the time period of interaction will be expressed by

$$t = -\frac{1}{\nu}\ln\left(1 - \frac{N(t)}{N_0}\right)\exp\left(\frac{E_a}{kT_k}\right), \qquad (7)$$

where ν—frequency of natural oscillations of atoms, s^{-1}; N_0—number of atoms in the particle and the substrate surface entering into the physical contact; E_a—activation energy, kcal mol^{-1}; k—Bolzmann's constant; T_k—contact temperature between particle and body surface, °K.

The relationship $N(t)/N_0$ can be approximately determined by the relative strength of the coating formed

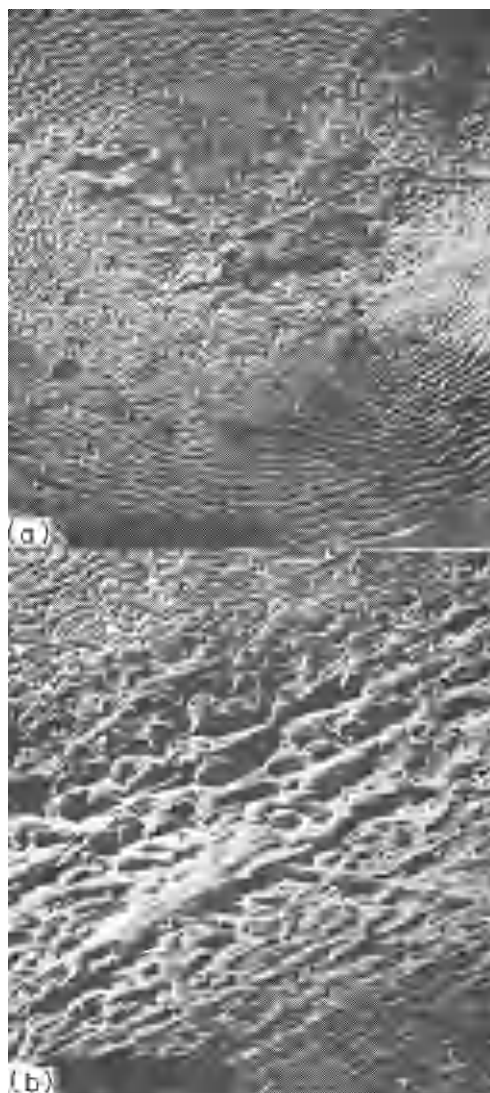Fig. 14. Fracture surface of silver substrate under the torn off particle. Magnification: (a) ×300 (b) ×3000.
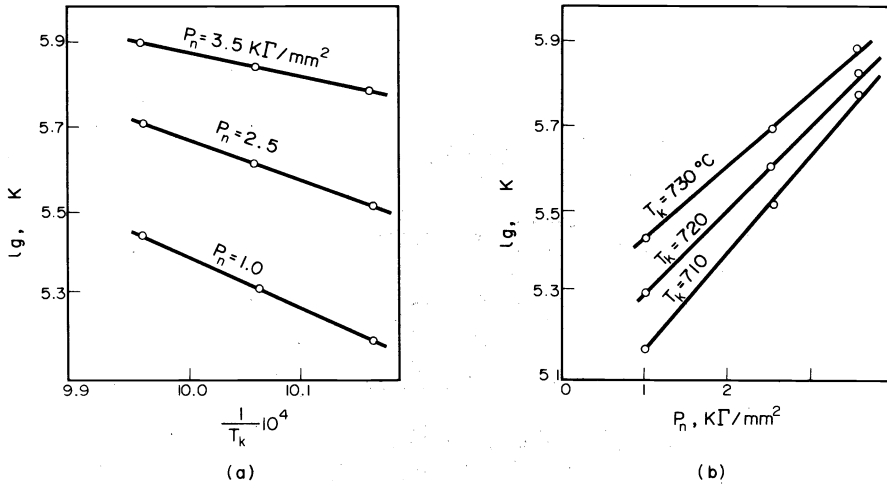
Fig. 15. Constant K of strength growth rate of silver particles adhesion to silver substrate: (a) depending on the inverse temperature $1/T_k$; (b) depending on pressure P in the contact area.[16]

$N(t)/N_0 \approx \sigma(t)/\sigma_m$, where $\sigma(t)$ = strength developed at time t; σ_m—maximum strength at the end of the process.

The strength growth rate constant for particle cohesion is expressed by

$$K = -\frac{1}{t}\ln\left[1 - \frac{N(t)}{N_0}\right]. \tag{8}$$

The logarithm of the constant is linearly dependent on the inverse temperature in the contact zone (Fig. 15a). By increasing pressure the process becomes less dependent on the temperature. The dependence of the $\ln k$ on pressure is also linear in the pressure range under consideration (Fig. 15b).

The pressure rise diminishes the effective value of the activation energy of bond formation, thereby expediting the process (Fig. 16). The impact pressure, determined by the velocity of particles, is an activating factor and, just as the temperature, helps to form high strength bonding of particles.

The activation energy was determined for plasma spraying of metals on metals, metals on oxides, oxides on oxides, metals on graphite, and oxides on graphite. When depositing metallic coatings on metals, the activation energy depends on the bond energy value in the substrate metallic lattice. The activation energy when depositing oxide coatings on oxides is close to the energy of single metal–oxygen bonds in the substrate. Oxides with a low
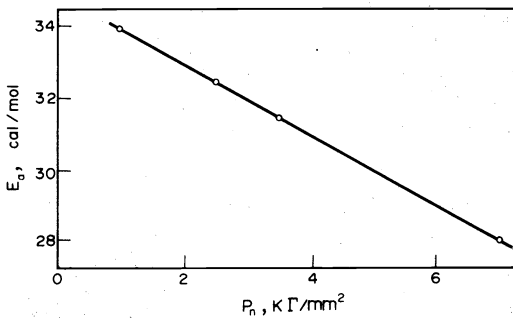

Fig. 16. Activation energy E_a of the process of bond formation depending on pressure P_n developed in the contact area of silver substrate at silver particle impact.[16]

bond energy may form solid coatings at a lower temperature. This phenomenon gives foundation to the development of sublayers that ensure a strong adhesion between the oxides and the base metal, e.g. silicate and boronsilicate sublayers for plasma sprayed coatings of aluminium oxide and zirconium dioxide.

One of the most important practical characteristics of plasma sprayed coatings is a low depth material interaction on the boundary of the coating and base material which is due to the comparatively short time of dynamic and thermal action. When developing plasma technology, for the production of composite materials this property of plasma spraying becomes useful in the manufacture of prefabricates.

4. PRODUCTION OF COMPOSITE MATERIALS

Plasma technology helps to produce quite new types of materials with properties considerably exceeding the properties of known and widely used materials.[16] The need for materials having unusual characteristics constantly grows in connection with the development of new industries, which are characterised by rapid increase in operating loads, temperatures, aggressiveness of acting media, etc. Accordingly, more stringent requirements arise in terms of high temperature strength, heat resistance, specific strength and rigidity of construction materials. The conventional methods of metallurgy and materials processing are sometimes incapable of improving further the technical characteristics of the materials, so that fundamentally, a new technological approach is required.

Rather special properties result if two or more components in a composite material combined. Their prototypes are found in reinforcing coatings. The matrix material is deposited by plasma spraying on the reinforcing fibre and produces the prefabricated material in the form of semi-finished sheets (Fig. 17a) or finished products (Fig. 17b,c). Depending on the type of initial raw material, the continuous or discrete fibres laid in a linear or net-type forms may be sprayed on. The one-layer sheets are then assembled in a batch of an appropriate thickness to be pressed and joined together.

Plasma technology provide wide possibilities for producing composite prefabricates which are subse-
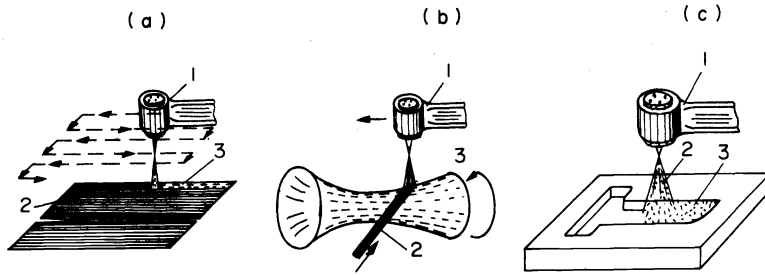
Fig. 17. Production of reinforced composite materials by plasma spraying: (a) spraying on nets or fibres; (b) spraying
with a simultaneous fibre deposition; (c) spraying on discrete fibres or whiskers placed in the mould.[16]

quently treated by explosion impact, hot stamping at high pressures, rolling, sintering, etc. Complicated shape products may be produced by the laying or cooling the reinforcing fibre with simultaneous spraying on the matrix material which fixes the fibre in its proper place (Fig. 17b).

At present threads, fibres, whiskers and thin wires are used for reinforcing, having a strength that approaches the theoretical which is determined by the bond energy of the lattice. Many of these materials have a low specific gravity and are abundantly available and inexpensive, e.g. carbon, aluminium oxide, silicon carbide, silicon dioxide, silicon nitride, etc. (Table 3). Particularly promising are lightweight high-strength fibres, such as carbon fibre.

For large scale utilisation of these high strength materials it is very important to develop an effective technology for producing composite materials.

In accordance with the theory of strength of materials the reinforced material must contain a rather high volume of fibre, e.g. not less than 20%. In this case only, it is possible to provide such a distribution of fibre in the matrix that would ensure the overlapping of the stress fields around fibres. The elastic matrix is uniformly distributed and transmits the load among the high strength fragile fibre. The strong adhesion of the fibre to the matrix should be based on the development of chemical bonds. Such a composite material combines high strength with good resistance to crack propagation. Working strength of composite materials depends on the elasticity modulus E, since large deformations are not allowed in constructions (e.g. in aviation not more than 1%). The high elasticity modulus of the reinforcing fibres meets the rigidity requirements imposed on the composite material. For some fibres (Table 3) ratio E/γ is higher by one decimal order over the conventional construction materials, thereby promising a substantial weight reduction in engineering structures.

Let us consider the physico-chemical principles form-

ing the basis for the technological processes involved in plasma spraying production of composite material. The fibre strength is considerably higher than the strength of the matrix material, so the energy of their lattice bonds will also differ considerably (Table 4). Therefore, the process of joining fibre with the matrix will be limited by the activation energy of the fibre surface. Fibre activation will require a higher energy input than is necessary for the compacting and strengthening of a soft and plastic matrix material.

The short thermal and mechanical interaction period between the fibre and particles of matrix materials (10^{-2}–10^{-4} s) is a very important advantage in the plasma spraying process.

Due to the intensive effect of the particle interaction processes with the fibre surface, strong chemical bonds are built up on their boundary. Short time interaction limits the development of recrystallisation and diffusion processes and the formation of new phase nuclei. Therefore, it is possible, for example, to spray nickel particles on steel wires, providing a solid bond without annealing the wire. The emergence of brittle phases on the fibre matrix contact surface may weaken the composite material and may lead to its crushing under load.

Table 4. Energy of lattice chemical bonds in fibre and matrix materials (sublimation heat for metals and atomisation energy for oxides; in brackets the energy of single bonds Me–O)

Fibre material	Energy (kcal/mol)	Matrix material	Energy (kcal/mol)
W	200	Zn	31
Mo	157	Mg	35
B	130	Li	38
Fe	96	Ag	67
Al_2O_3	370 (61)	Cu	80
SiO_2	400 (104)	Ni	101

Table 3. Properties of certain reinforcing elements used in producing composite materials

Material	γ, (g/cm^3)	$E \cdot 10^{-3}$, (kg/mm^2)	σ_b, (kg/mm^2)	$\dfrac{E}{\gamma} \cdot 10^{-6}$, (m)	$\dfrac{\sigma_b}{\gamma}$, (km)	Melting temperature (°C)
Carbon (whiskers)	2·3	100	2400	43·5	1000	3500
Carbon fibre	2·0	60	800	30·0	400	
Aluminium oxide (Whiskers)	4·0	54	1500	13·5	380	2050
Iron (whiskers)	7·8	30	1300	3·84	170	1530
High carbon steel wire	7·8	21	420	2·74	54	1530
Tungsten wire	19·3	42	380	2·69	20	3400
Fibreglass	2·5	10	360	4·0	140	

The process of chemical interaction between the particles of the sprayed matrix and the fibre, and the building up of the strong cohesion between them can be described, for isothermal conditions, by the expression derived from eqn (7)

$$\frac{N(t)}{N_0} = 1 - \exp\left[-\frac{vt}{\exp\left(\frac{E_a}{kT_k}\right)} \right]. \qquad (9)$$

This expression allows the interaction between materials in the course of spraying with particle velocities of up to 50–100 m/s to be evaluated. The ratio $N(t)/N_0$ is approximately taken equal to the instantaneous relative strength $\tau(t)/\tau_{max}$ of the fusion bonding of the fibre and the matrix. The calculated and experimental results are in good agreement (Fig. 18).

Thus, matrix plasma spraying solves the technological problems involved in the production of composite materials based on metal matrices. Plasma spraying offers essential technological advantages:

1. The high plasma temperature enables any materials, even the most refractory metals or oxides to be sprayed.

2. By choosing an appropriate plasma gas composition, it is possible to affect the properties of the matrix material by carrying out refining, alloying, gas saturating, oxidising, etc. The plasma atmosphere can delay the decomposition of the unstable compounds which are susceptible to thermal dissociation, e.g. carbides.
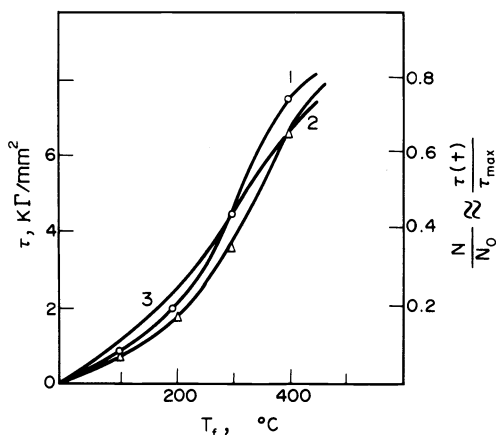
3. The plasma spraying process can also be used for depositing protective coatings on composite material products.

CONCLUDING REMARKS

The plasma spraying process offers diverse possibilities of depositing coatings and of producing composite materials with high strength and rigidity. An important advantage of plasma process technology consists in the possibility to control accurately the physico-chemical interaction between materials, and at the same time to generate strong bonds between the sprayed particles and the base fibre surface. It might be expected that plasma spraying will help to produce construction materials with the theoretical strength of individual elements.

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Fig. 18. Experimental curves 1 and 2 of shearing adhesion strength τ of the aluminium matrix sprayed on the reinforcing steel wire EP-322 with diameters of 150 μm (1) and 300 μm (2); curve 3 calculated according to expression (9) at $v = 10^{13}$ s^{-1}. $E_a = 1.8$ eV, $t = 10^{-3}$ s.