FUNDAMENTALS OF COMBUSTION PRODUCTS PLASMA - SURFACE AND PARTICLE INTERACTION

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Abstract

Multicomponent reactive plasma of the products of combustion of hydrocarbon gas with air is characterized by a combination of unique transporting and thermal-physical properties. These properties were the key for the development of a new scientific-and-technical area and made attractive the use of such a plasma in the technology for plasma and electric-arc spraying and treatment of materials.

1. Introduction

Processes developed by the authors, which involve the use of plasma of the products of combustion of air with a fuel hydrocarbon gas, take a special place among other plasma processes for materials treatment. Owing to a number of unique properties of this plasma, such as high heat capacity and thermal conductivity, high controllability of oxidation-reduction potential, availability and relatively low cost, the processes on its base are of an increasing interest for research and industry.

Cost effectiveness and technical expediency of using air-gas mixtures become particularly appreciable with an increase in the power of a plasmatron and transition to supersonic velocities, where the optimal conditions shift towards the range of the high plasma gas flow rates and where the time of contact of particles with an ambient atmosphere is reduced.

Comprehensive investigations (both experimental and those based on mathematical models) yielded the relationships between principles of building the electric-arc equipment, peculiarities of the processes of generating the combustion products plasma, its interaction with materials and the final technological result.

2. Combustion products plasma and its properties

To provide the required parameters of the atmospheres is an indispensable condition for making the plasma treatment processes as effective as possible. Oxidation-reduction and transporting properties of the combustion products plasma are determined by its composition.

Analysis of variations in a composition of the air-gas plasma [1] depending upon the temperature shows that a CO_2 molecule has the lowest stability. It is characterized by the earliest and most complete dissociation occurring during heating. The next to dissociate is H_2O. At a temperature above 4000 K both CO_2 and H_2O are almost absent.

Molecular hydrogen H_2 is present in a large amount (15 vol.% at a α = 0.6) in a rich mixture also at a $\alpha \cong 1$ at a temperature of up to 5000 K as a result of dissociation of water. Variation in the concentrations of the combustion products with temperature is most intensive at 3500 K. The CO molecule is stable, and it is present in the plasma at a temperature of up to 8500 K. Atomic hydrogen and oxygen are formed in heating to a temperature above 2500 K, while nitrogen is formed at a temperature of more than 4500 K. Equilibrium carbon (in the gas phase) is formed at a temperature of more than 5500 K due to dissociation of CO, reaching a maximum content of 4-5 % at 8500 K. An increase in temperature over 7000 K is accompanied by a substantial increase in the concentration of an electron gas. For example, at 9000 K it is 1 vol.% and at 12000 K it amounts to 12 vol.%.

At the same time, the concentration of positive singly charged ions N^+, C^+, H^+ and O^+ grows as well.

Negative singly charged ions O^-, N^-, H^- and C^- are also formed in the combustion products plasma. Their highest content equal to 10^{-3} vol.% is found in a temperature range of $(10\text{-}14)\cdot 10^3$ K. In a temperature range of up to 20,000 K the second-order ionization is still insignificant. Thus, at 20,000 K the content of O^{2+} is no more than $1.5\cdot 10^{-3}$ vol.%.

We should note a peculiarity of the ion state of the combustion products plasma in a temperature range of $(9\text{-}13)\cdot 10^3$ K, where carbon makes a substantial contribution to the ionic current transfer.

At $T = (4\text{-}7)\cdot 10^3$ K the plasma contains mostly nitrogen and carbon monoxide in a molecular form, the oscillation temperature of which can be easily "frozen" during expansion of the plasma. Oxygen and hydrogen are in the atomic state. Therefore, they can actively interact with a material treated. For example, at T = 4000 K and a $\alpha = 0.6$ the content of atomic oxygen is approximately 9 %. At a $\alpha = 1$ the content of atomic hydrogen is approximately 20 %, that of carbon monoxide is 7 % and that of oxygen is 15 %.

Values of the specific energy inputs during plasma spraying and hardening of the majority of materials amount to 5-10 kW h/m^3. According to the upper limit of the specific energy (10 kW h/m^3), the mean mass temperature of the plasma jet is approximately 6500 K and that of the constricted arc is approximately 12,000 K.

Plasma of the products of combustion of CH_4 has a sufficiently high heat content. At a power take-off of 1 kW h/m^3, its temperature decreases only by 200 K within a range of both relatively high temperatures, i.e. 8000-6000 K, and relatively low temperatures, i.e. 4000-3000 K. Owing to chemical reactions, thermal conductivity of the combustion products plasma is much higher than thermal conductivity of the "frozen" mixture.

The characteristic feature of generation of the electric-arc plasma is that the discharge burns in a channel of the plasmatron in strong radiation and sound fields. The level of the sound pressure in the plasmatron is rather high and amounts to 140 db. The sound is excited by turbulent pulsations of the plasma flow.

The zone of disturbance of the local thermal equilibrium (LTE) is formed in a region where a cold multiatomic gas is introduced into the ionized columns of the arc plasma. In the case of using molecular gases, the difference between the electron and oscillation temperatures and the translation and rotation temperatures can be several thousands of degrees.

In such a case, in a local region of the plasma flow the possibility exists of reversing the effect of the second (volumetric) viscosity, i.e. it can lead to amplification of the sound, rather than to its attenuation [2]. The oscillation-translation non-equilibrium of $T_K > T$ with propagation of the sound waves becomes a source of the energy which is transferred to the wave during the thermal deactivation process.

At a sufficient difference between the oscillation T_K and translation T temperatures, the second viscosity can become negative and cause an increase in the acoustic disturbances. The relaxation viscosity ξ can significantly exceed (e.g. by two orders of magnitude at a temperature of several thousands of degrees) the shear viscosity η.

Formation of the negative (reversed) viscosity in an oscillating non-equilibrium gas leads to instability and other effects that have no analogues in an equilibrium gas.

In the molecular oscillating non-equilibrium gas, the intensity of the acoustic field can exceed the intensity of this field induced by a natural turbulence. The effective amplification of sound due to reversal of the effect of the relaxation viscosity occurs at frequencies of 10^4 -10^5 Hz.

It can be suggested that an increase in the intensity of the acoustic field in a non-equilibrium environment (as compared with the equilibrium one) is equivalent to the effect of an external sound source. Therefore, an amplified sound in the non-equilibrium region of the environment can affect the natural turbulence. In addition, downstream in the region where gas can be regarded as the equilibrium one and where the relaxation viscosity is positive and high, there should be an intensive absorption of the energy of an "excessive" acoustic field. These effects can have a marked influence on parameters of the plasma flow, providing that the non-equilibrium energy of molecular oscillations, which is transformed into the energy of the amplified acoustic wave followed by its dissipation, is comparable with the total energy of the plasma.

3. Movement and heating of a dispersed material in the plasma flow

Behaviour of particles of the dispersed phase in the plasma during their acceleration and melting is characterized by the processes of fragmentation and coagulation.

Velocity and temperature of the plasma and particles of the powder, as well as its granulometric composition play a decisive role in the plasma-jet processes associated with treatment of the dispersed materials. Under real conditions, the dispersed phase transported by the plasma can substantially differ in its granulometric composition from the initial powder [1]. This difference is primarily a result of aerodynamic fragmentation of the molten particles. Fragmentation can have a fundamental effect on the final result of the process. For example, in some cases of plasma spraying of protective coatings this fragmentation can be helpful, while in other cases it can be undesirable. Intensification of fragmentation of the dispersed raw materials in the plasma jet is indicated for the technologies of the manufacture of metals and their compounds (carbides, nitrides, etc.). This is associated with the fact that completeness of transformation of the dispersed raw materials into an end product depends upon the degree of their evaporation, while fragmentation of droplets of the melt speeds up boiling and dissociation of oxides treated in the plasma.

Changes in the granulometric composition of the dispersed phase can be regarded as a result of complete or partial melting of particles and their subsequent fragmentation under the aerodynamic effect of the jet, as well as fragmentation and coagulation in collision of particles against each other.

Stability and destruction of the droplets under the effect of the aerodynamic forces are characterized by such dimensionless parameters as Weber (We), Laplace (Lp), Mach (M), Bond (Bo), Reynolds (Re) numbers and others. The most important among them is the Weber number , $We = | \vec{V}_g - \vec{V}_S | \rho_g d_S / \sigma_{s.t.}$, where $\vec{V}_g$ and $\vec{V}_S$ are the gas and droplet velocities, d_S and $\sigma_{s.t.}$ are the diameter and surface tension of the droplet and ρ_g is the gas density. Fragmentation of the droplet can be different in character, depending upon the intensity and time alterations of the load. The droplet is destructed if the condition of We = We* is met, where We* is the critical Weber number equal to the minimum Weber number, above which the droplet is sure to destruct with a certain delay τ_{ind} called the induction time.

The primary conclusion which can be made on the basis of analysis of the theoretical and experimental investigations is that the plasma-jet processes associated with treatment of powders can give rise to conditions favourable for fragmentation of particles of different materials, and the time needed to destroy a particle upon reaching critical parameters is by several orders of magnitude shorter than the time of acceleration of the particle and its heating up to a melting point.

The fragmentation process results in redistribution of the granulometric composition of the powder along the plasma jet and associated changes in dynamics and heating of the particles. It should be noted that coagulation of the droplets in the flow also takes place. However, the experience indicates that under conditions of thermal spraying (plasma powder and wire spraying, electric-arc metallizing) it is fragmentation that is dominant. Within the investigated ranges of relative velocities (<4000 m/s), for small fractions, $\overline{d}_S$ = 12.5 microns, the Weber number can grow after melting of a particle due to a decrease in surface tension caused by heating. However, it never reaches the critical value of We*. Fine particles quickly start boiling in the plasma flow. Fragmentation of the moving particles in the plasma flow starts from coarser fractions. As the relative velocity V_g-V_{SO} increases, more and more fine fractions are involved in the fragmentation process. Coordinate of the fragmentation point, x_{ifr}, determined by the induction time τ_{ind}, depends upon the V_g, V_{SO}, i and T_g parameters. Despite a strong dependence of x_{ifr} - x_{imelt} upon the above parameters, its absolute value is small. The effect of a gradient nature of the plasma flows on the fragmentation process should be taken into account at low relative velocities of V_g - V_{SO} for particles with small values of $\overline{d}_S$ and at high temperatures of the plasma.

The induction time τ_{ind} and the character of fragmentation of a droplet greatly depend upon whether the We number increases or not upon reaching a critical moment, τ_{cr} (where We = We*). If We = We* = const at $\tau > \tau_{cr}$, normally there occurs vibrational fragmentation resulting in the formation of a few approximately equal fragments. If at $\tau > \tau_{cr}$ the We number increases (due to a decrease in surface tension during heating of a particle), destruction occurs without preceding vibration of a droplet to form many polydispersed fragments. Fixed at 1, the mass differential function of distribution of diameters d_{SJ} of fragments of a droplet d_{SI} is approximated by the normal logarithmic law.

Pulsations of the transporting plasma flow can intensify fragmentation of the molten powder particles. Fragmentation of droplets is enhanced by resonance oscillations of the environment and the droplet itself. At a high subsonic velocity, pulsations of the flow have no effect on the process of fragmentation of the droplet in the flow. In addition, at $M \to 1$ the amplitude of pulsations of the hydrodynamic parameters decreases. To eliminate pulsation fragmentation of the droplets, spraying should be carried out using the high-rate gas flows.

Calculations shows that under conditions of spraying realized in the commercial plasmatrons with a self-stabilized arc, pulsations of parameters cause fragmentation of droplets to occur at a lower value of the critical Weber number, as compared with the stationary flow. In processes of plasma treatment of the dispersed phase, fragmentation is complicated by the presence of a solid core in the particles.

However, despite this fact, there are some moments in common. Fine particles up to 50 microns in size do not decompose, while crushed irregular particles become spherical. For particles more than 60 microns in size of materials with a low thermal conductivity (AL_2O_3, ZrO_2, Cr_3C_2), fragmentation occurs because of separation of a boundary layer of the melt by a high-rate plasma flow. Removal of a mass of liquid from the peripheral boundary layer is determined by a slip speed, temperature of the melt and size of a particle. Decomposition of particles with a high thermal conductivity occurs due to their deformation and splitting into two or more particles, as well as due to separation of the boundary layer.

Along with fragmentation of particles, their coagulation also takes place in flight. Fine particles (1-5 microns) most often collide against coarse particles (~ 100 microns): fine particles join the coarse ones, as a rule, without any deformation, despite the fact that they are always in a molten state. Their trajectories hardly differ from the lines of current of the transporting medium. As the colliding particles increase in sizes, changes in their shapes become more and more substantial.

Under conditions characteristic of plasma spraying, the Re_S criterion amounts to 10-15, while heat exchange taking place through a conducting component amounts to 60-70 %, that through a convective component is 20-30 %, radiation losses are 1-3 % and evaporation losses are 1-10 %. The fragmentation process prevails over the coagulation one and is determined by the plasma composition. With an increase in the fuel gas content of the mixture, the content of fine particles (0-50 microns) increases and that of coarse particles (100-160 microns) decreases. The function of size distribution of particles shifts towards particles of a smaller size.

Recent advances in the development of thermal spraying equipment and processes are associated with increased velocities of particles sprayed.

Acceleration and heating of particles in the supersonic flow have certain specific features.

The supersonic flow is an efficient means for acceleration of particles. However, efficiency of the thermal effect decreases with an increase in the M number. Calculations show that under conditions of the supersonic flow along the particle at sufficiently high values of the M number, a change in its temperature is insignificant. So, at an initial temperature of the particle equal to $T_{SO}/T_\infty = 1$, the supersonic flow temperature is $T_{pl}/T_\infty = 10$, $Re = 10$ and $M = 5$, the maximum increase in the particle temperature is 24 %, while at $T_{SO}/T_\infty = 1$ a decrease in the particle temperature is 6 % at the same Re and M. Therefore, in plasma spraying it is advisable to use elongated slightly underexpanded supersonic jets with a large number of "rolls".

Because of the developed surface of the sprayed particles, their overheating ($T_S > T_{melt}$) and high temperatures of the plasma in the initial region of the jet, they intensively interact with the environment. Using a mixture of air with methane or propane-butane in the processes of plasma deposition of coatings allows the controllable atmospheres to be produced within a zone of heating and movement of the powder particles. The degree of development of oxidation-reduction and dissociation processes in a material sprayed as a result of the thermochemical effect of the plasma on dispersed particles decreases with an increase in the velocity of the powder particles, i.e. with reduction in the time of interaction. The practically tangible effects are achieved in using the supersonic flows. Comparison of properties of the coatings produced using sub- and supersonic flame and plasma spraying machines definitely indicates to a fundamental advantage of the supersonic flows. The appreciable contribution to improvement in all properties of the coatings is achieved owing to a minimum variation in chemical composition of the material sprayed.

The process of plasma spraying combined with purposeful chemical transformations is one of the methods which can be used to synthesize new materials [3]. In this case we can produce a new class of coatings containing nitrides, carbides or oxides synthesized in the plasma.

The first stage of the process, where the powder particles are in contact with a fuel gas, is their heating, which can be accompanied by chemical reactions occurring in the surface layer of a particle. However, low rates of diffusion in the condensed phase fail to provide a high yield of the desired product (nitride, carbide) in a short time of 10^{-3}-10^{-5} s for which the material dwells within the zone of high temperatures, even at the absence of thermodynamic restrictions. The degree of transformation of the dispersed material into the end product can be greatly increased if chemical reactions take place in the gas phase with its condensation from vapour at the stage of hardening.

The supersonic plasmatron with a plasma-chemical reactor was used for spraying. The temperature parameters were selected so that approximately 20 % of the material evaporated. In a region of the supersonic flow in the plasma reactor, prior to hardening, the vapour cloud coincides with the dispersed phase. The supersonic two-phase flow is characterized by a high density of the dispersed material due to low dissipation and a high slip of the phases. These circumstances lead to the fact that a larger part of the condensate in the form of ultra-dispersed particles (10-1000 A) coagulate in flight with particles of the sprayed material.

Analysis proves that the synthesized highly dispersed titanium nitride condensed on a particle has a developed specific surface and an increased number of defects of the crystalline lattice.

In a general case, size of particles formed in the flow is a function of rate of chemical reactions, oversaturation of the system, temperature of the process, mass transfer coefficient, solidification time and other factors associated with the nature of the solidifying material.

4.Interaction between plasma and surface

It can be suggested on the basis of analysis that the combustion products plasma is more power-intensive than plasma of any biatomic gases. Heat transfer from the combustion products plasma to a workpiece heated increases both owing to a high temperature level and owing to a change in transporting properties of the dissociated combustion products (due to their subsequent recombination). Therefore, the arc plasmatrons operating with an air-gas mixture are indicated for intensive local heating and melting of small surfaces, as are the cases of high-speed hardening, cutting or alloying of steels, glazing of building materials, spheroidization of powders, heating of metal edges, etc. Parameters of surface heating were determined through solving the equation of non-stationary thermal conductivity with the appropriate boundary conditions. Dependence of the depth of heating to T = 850 C upon the heat transfer coefficient can be approximated by the following relationship:

$$\delta_h = 1{,}73\cdot 10^5\, [(T_{ef} - T_{av})^{-1{,}44}/\alpha],\ \text{mm}$$

where T_{ef} is the averaged temperature of the heating medium, K; T_{av} is the averaged temperature of the workpiece heated, K, in the layer with a thickness of δ_h, mm; and α is the heat transfer coefficient, W/m deg.

The relative travel speed can be approximated by the following expression:

$$W = 4{,}28\cdot 10^{-9}\, l_h\, (T_{ef} - T_{av})^{0{,}46}\cdot \alpha^2,\ \text{m/s}$$

where l_h is the length of the heating zone, m. Accuracy of the formulae given is ± 10 %.

Optimization of the process of surface plasma hardening was done using the modern computer facilities. Solution of this problem is associated with the possibility of reliably predicting the material structure through selecting the thermal effect parameters. Optimization of the technology is reduced to making special arrangements in order to produce the preset configuration of the plasma flow and to choosing the required conditions of the hardening process, predicting the structures formed and residual stresses induced. The entire work on the development of software was broken into three interrelated and, at the same time, sufficiently independent stages. The problem of calculation of thermal cycles for an arbitrary microvolume within the region treated for the preset type of a material was solved at the first stage. The second stage of the work was associated with the development of software for modelling the processes of structural transformations, as well as physical and chemical transformation taking place in a material investigated under substantially non-equilibrium conditions of rapid heating and cooling, based on the currently available fundamental concepts of the processes under consideration. The tasks of the third stage of the software development involve construction of the correlation models of the "material structure - physical-mechanical properties" type.

5.New plasma equipment and technologies

Based on the above-described ideology R & D Center PLAZER has developed and mastered the manufacture of a number of new types of plasma equipment to realize its new technologies [4]. The PLAZER supersonic plasma spraying process [5] can be employed for all typical cases of high-productivity plasma spraying of high-quality coatings.

The new catalytic neutralizer has been developed for comprehensive purification of automotive exhaust gases using the PLAZER plasma spraying technology. It is characterized by a decreased (10-20 times) content of precious metals and a high level of purification of harmful materials, i.e. CO - 80-90 %, NO_x - 60-65 %, C_mH_n - 50-55 %.

The new equipment and technology for electric-arc metallizing in the supersonic flow of the combustion products allow the heavy-loaded necks of locomotive crankshafts to be effectively repaired.

The PLAZER surface plasma hardening technology is characterized by new capabilities for increasing contact-fatigue strength of metal and, as a result, improving reliability of the wheelsets of the rolling and traction stock. Intensity of wear of ridges of the wheelsets after plasma hardening is much lower (2.5-3 times) than that of the mass-produced wheetsets.

References

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