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Review of solution precursor spray techniques applied to obtain ceramic films and coatings

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Abstract

The review describes the techniques of film and coatings deposition using solution as a feedstock. After a short description of the processes of: (i) spray pyrolysis; (ii) solution precursor plasma spray (SPPS); and, (iii) solution precursor high velocity oxy-fuel, some properties of solution feedstock are discussed. The properties include the chemical composition of solutions used to synthesize typical coatings, which determine the flow of solution in a pipeline and its injection to plasma or flame. The chemical and physical phenomena occurring at spraying are described including atomization in gas, heating and vaporization of solution, precipitation of solution and formation of solid and heating of this solid. The molten solid is then splashed onto substrate. Typical coatings formed using solution precursor spraying and the applications of solution precursor thermally sprayed coatings are reviewed.

1 Introduction

The spray pyrolysis started to be used as early as in the 60-ties of the last century [1]. The method was used to synthesize films of metal oxides, sulfides and selenides. The use of the torches generating combustion flames and plasma jets to process liquid solutions was first applied at the end of the 20th century [2]. The authors were inspired by the spray pyrolysis process. The torches generating high velocity flames have started to be used more recently [3]. The use of liquid feedstock in thermal spraying instead of usual solid powders was inspired by an interest in obtaining coatings having fine microstructure. Such coatings were easier to be sprayed with liquid feedstock (solution or suspensions) than with fine solid powders. In addition, thermal spraying is a well-established technology. The use of this technology for producing such coatings is industrially advantageous because of a dense network of job shops having expertise in coatings deposition, high productivity of coatings manufacturing and also a dynamic and well organized community of involved professionals.

2 Solution spray techniques

2.1 Spray pyrolysis

The technique of spray pyrolysis consists of atomizing the solution directed towards a hot substrate. The solutions of metal salts dissolved in organic or water are used generally to obtain coating of metal oxides. The atomized droplets impact the heated substrate to form lamellas and undergo a thermal decomposition. The substrate temperature is the main parameter, which influences the morphology and properties of coatings [4]. The final coating is a superposition of overlapping lamellas.

2.2 Solution precursor plasma spraying

The d.c. torches generate arc which heats working gases to form plasma jets. The jet's temperature, in a conventional plasma torch, reaches 14 000 K and its velocity on the nozzle exit reaches 800 m/s. The torches used in SPPS process [5]: (i) conventional, one cathode one having radial introduction of solution, (ii) three-cathode torch having axial introduction of solution; and (iii) segmented anode torches. The injection of solution can be made by an atomizer or by a nozzle. The working gases used to generate the plasma is usually argon with a molecular gas such as hydrogen or nitrogen. The molecular gases are

added in order to increase the thermal conductivity of the plasma. The conventional one-cathode torches have important fluctuations and instabilities depending on kind of working gas [6]. The molecular gases contribute considerably the voltage arc fluctuations in the kilohertz frequency range. The use of three-cathode torches without the use of molecular gases maybe a solution of the fluctuation problem [7].

2.3 High velocity oxy-fuel spraying

The high velocity oxy-fuel torch is fuelled by a combustion hydrocarbon gases as ethylene, propylene and many others or hydrocarbon liquids as kerosene which is atomized prior to combustion. The combustion takes place in a chamber under high pressure, which varies from 0.3 to 4 MPa. The resulting jet issuing from a nozzle may reach temperature of about 3000 K and supersonic velocity by 2000 m/s. The solution can be injected radially, externally to the gun, directly into the HVOF flame or axially, directly into the combustion chamber [3].

3 Preparation of solutions

The precursors used for solution spraying of metal oxides films and coatings are generally the salts of metals and very frequently nitrates and acetates. In this way it is possible to obtain coatings of multi-oxide compound such as e.g. YBCO or YIG. Some authors, like [8], used the nitrates as the initial products to start sol-gel procedure to obtain fine particles. Such additives as acetic acid modify the chemistry of solution and influence the morphology of coatings. For example the structure of TiO₂ was changing from cracked to crack-free after the introduction of acetic acid into the solution [4]. The salts are used as solutions in water or in ethanol.

4 Phenomena occurring at spraying

The phenomena occurring during spray pyrolysis can be summarized by taking an example of spraying of metal salt solution onto a heated substrate. The most important of them is the deformation of the liquid into droplet and its thermal decomposition leading to the formation of the desired compound on the substrate [4]. The phenomena in-flight include mainly aerodynamic breakdown accompanied by the chemical reaction that occurs on the substrate.

The solution precursor thermal spraying includes more phenomena occurring in-flight occurring before the impact with the substrate (see Fig. 1):

- aerodynamic break up;
- heating, vaporization and internal precipitation;
- internal pressurization and droplet breaking-up;
- solid particle sintering, heating;
- melting and evaporation from the melt.

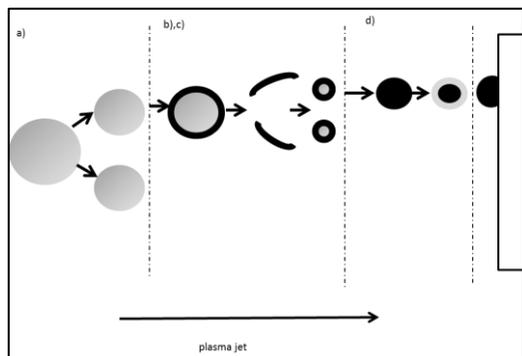


Fig. 1. Phenomena which occur during a flight of a solution droplet in a high temperature gas jet [9].

4.1 Injection

The solution may be transported to the injector with the use of a peristaltic pump or by a pneumatic transport. Its flow rate is controlled by the rotation of motor rollers or by the pressure acting on the fluid, respectively. The solution may be atomized as in spray pyrolysis process or injected as a liquid stream to the jet or flame. The atomization is a process of which the external energy phase is needed to break up the liquid bulk.

The liquid stream undergoes an aerodynamic break up and the ligaments and large droplets are formed. Then, depending on the drag force acting on the droplet and their surface tension the large droplet may disintegrate into smaller ones. The process is called secondary break up [10]. This process leads to the formation of finer microstructure.

4.2 Physico-chemical phenomena

The droplets formed by successive break ups undergo rapid vaporization of solvent in hot temperature flame or jet. Consequently, the concentration of solute at the droplets surface increases, what may lead to precipitation in this region (because the concentration of solute reaches the super-saturation limit). The process is known as homogeneous precipitation [9] and was investigated for different thermal spray processes by e.g. [9, 11] and many others. The formation of solid crust outside of heated liquid leads to an increase in internal pressure inside a shell. Under the action of the pressure the shell may get fractured and smaller droplets of liquid get free and the process of precipitation and shell formation may be repeated. The processes may lead finally to the formation of solid particle as shows it Fig. 1.

The chemical phenomena occurring in flight of liquid droplet depend on the used metal salt precursor and on temperature. Generally, the sequence of chemical reactions includes evaporation of solvent, precursor pyrolysis and crystallization [12]

5 Possible applications of coatings

The solution precursor spray techniques including spray pyrolysis and thermal spray techniques are at present intensively explored. The potential advantage of these technologies can be related to the purity of the initial liquid precursors, which enable chemically pure coatings to be synthesized. The particularity of processing of small nanoparticles renders it possible to obtain such phases as α - Al_2O_3 , or TiO_2 crystallized as anatase obtained which are difficult to obtain using conventional thermal spray technique. Finely grained microstructure has another advantage, which is small thermal conductivity useful while synthesizing thermally insulating coating for TBCs. The capacity to coat large surfaces must be also underlined. Not but not least, the possibility of obtaining columnar microstructure, is useful for enhancing the thermal shock resistance of coatings. The properties of solution precursor sprayed coatings have been tested by now for the following applications:

- SOFC as electrodes, i.e. Ni-YSZ as anode, V_2O_5 as cathode and YSZ as solid electrolyte;
- TBC made of YSZ and of $\text{ZrO}_2\text{-La}_2\text{O}_3$;
- optoelectronic applications of $\text{Eu:Y}_2\text{O}_3$ or CZST coatings;
- dielectric coatings in electronics made of α - Al_2O_3 ;
- photocatalysis of TiO_2 coatings;
- magnetic applications of YIG coatings;
- biomedical coating of TiO_2 – rutile coatings.

The further perspectives of application these coatings in industry are related to the better control of the deposition process.

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