

## Toward a new era of plasma spray processing\*

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*Abstract:* The recent global trend of materials R&D is shifting from “monolithic” to “materials system” and from “bulk” to “thin film and coating”. It is thus a natural consequence that plasma spray processing, as an affordable and effective thin film and coating technology, is attracting global attention in materials engineering. Unfortunately, however, the current plasma spray technology for thin film and coating seems to not yet reach the sufficient technological level to meet the requirements from the fields where this technique was not applicable in the past. In this context, this paper will point out the disregarded but important issues involved in conventional plasma powder spraying to fit for high technologies and infer the future potential of novel plasma spray processing with the use of extended feedstock like gases, liquids, and various-sized powders. In particular, special attention will be given to recent challenges aiming at a development of a co-deposition process of droplets and vapors, namely, comprehensive plasma spraying.

*Keywords:* plasma powder spraying; plasma vapor spraying; comprehensive plasma spraying; mesoplasma; thermal barrier coating.

### INTRODUCTION

In recent years, the global trend in the field of materials R&D is shifting from “bulk” to “coating” technologies. It also goes without saying that the primary factor in materials development is “affordability”, without which, efforts are only the research of materials for the sake of research. Even for the process development, affordability must be considered unexceptionally. In this regard, it is a natural consequence that plasma spraying is attracting attention globally. However, considering the future advancement of materials processing, the current level of plasma spraying technology is not sufficient to respond to the demands in the fields where plasma spraying has not been applied in the past. In fact, judging the current situation on the basis of the development of this field over the last 30 years, it can be said that the level of rapid advancement desired in fields such as electronic, automotive, aerospace, biomedical, and the next-generation nanocoatings cannot be met if only the currently available technologies are used. I wonder if I am the only one who believes that new viewpoints and principles regarding the fundamental research concept should be introduced. In reality, compared to the number of reports on application research, the number of reports on basic research carried out to derive universal principles is extremely small. This is one of the characteristics of research trends in this field. Regarding the lack of basic research, I occasionally read review papers that describe the difficulty of performing basic research in the plasma spraying process because of 500 or more combinations of parameters in-

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volved in the process. Even if this is the case, research performed in universities and institutes should not adopt the same methodologies as those applied in private industries.

In the first half of this article, therefore, I will point out the disregarded but important issues involved in the advancement of plasma spraying technology. The future potential of novel plasma spray processing will be reviewed in the second half, by referring our recent projects aiming at a development of novel deposition processes for silicon films by maso-plasma chemical vapor deposition (CVD), and of thermal barrier coatings (TBCs) by novel comprehensive plasma spraying.

## PLASMA SPRAYING IN A BROAD SENSE

The term “plasma spraying” is somewhat ambiguous. The primary meaning of this term may be “injection plasma processing”, in which raw materials are injected either in the liquid, vapor, or powder form and subjected to physical, chemical, or both reactions in the plasma. According to the different interactions of injected materials with plasma and/or environment, this technique can be classified into three elemental processes as summarized in Fig. 1: (i) plasma spray synthesis in which various vapor mixtures are created via decomposition and/or chemical reactions of gas or liquid raw materials, (ii) plasma flash evaporation in which fine powders are injected and decomposed completely to form high-temperature vapor mixture, and (iii) plasma spray melting in which rather coarse powders are injected in the plasma and melted completely to form droplets. When one introduces effective quenching or cooling process to each case, i, ii, and iii can be applied for the production of nanoparticles and for spheroidization of powders. In practice, these processes have been used in industry. In any elemental processing, the fundamental role of the plasma is to provide reactive or inert “extreme high-temperature” environment and its “flow”. The thrust of “plasma spray processing” is therefore an effective use of “high-temperature gas flow” that is not achievable by combustion flame. In some cases, the power input part itself is utilized. However, the “flow” should be controlled if the unique characteristics of the thermal plasma are to be used effectively. Further potential of thermal plasma will be exerted not simply from the role as a heating medium but from the use of the physical and chemical phenomena during heating/cooling in the plasma or plasma/ambient boundary. In this respect, the fundamental approach to the plasma spray processing is essentially different from that generally considered in low-pressure plasma processing. It is, however, difficult to control the plasma flow magnetically except the electrically conducting path in the plasma. Alternatively, the plasma should be controlled based on fluid dynamics. In addition, power units, plasma torch, and plasma flame all have to be taken as important “cogs” in the “plasma system” as they are cooperatively interacting with each other from the plasma control point of view. In other words, individual components of the plasma system have to be developed considering the overall performance as a whole system, which is particularly critical when scaling-up the plasma facilities. In the application of thermal plasma to industry, additional attention has to be paid to the material amounts requested by industry, with respect to the capacity that specific plasma technology can accommodate. Therefore, a treatment of volatile organic compounds (VOCs) at a rate as fast as 100 kg/h is regarded as an innovative progress of this technology [1]. This in turn indicates that a 100-kW-class thermal plasma system can treat the powder, liquid, or vapor at 1, 10, and 100 kg/h, respectively, if it is of economical worth.

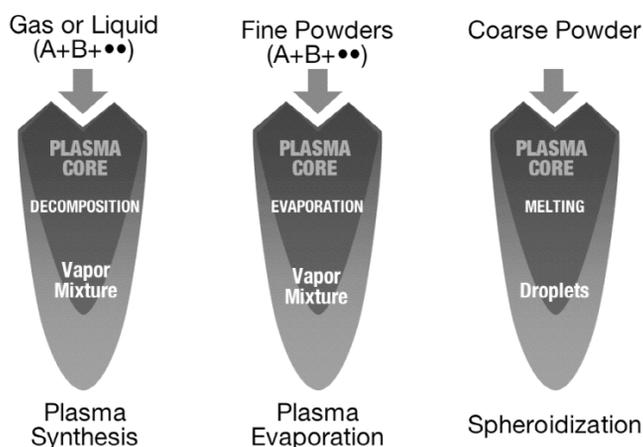


Fig. 1 Various elemental processes in plasma spraying with different feedstocks.

### PLASMA SPRAYING FOR COATING TECHNOLOGY

The incorporation of additional functions with coatings to bulk base materials is becoming more important in view of the current technological trends described by “nanotechnology”. Figure 2 summarizes typical thin film technologies as a function of production speed and values achieved. Plasma powder spraying can be classified as a leading coating technique due to its extreme fast production rate and affordability. In contrast, the CVD and evaporation attain films with added functions despite slow deposition rates. The future technology, therefore, may be the one that possesses both high rate deposition capability and high functional values, with “viable”, “sustainable”, and “affordable” aspects. Taking these values into account, the arrows shown in the figure will be the directions in which the current techniques should evolve as the next generation of film/coating technologies. It is plasma spraying that realizes such technological directions by adopting substrate in the plasma tail flame. In this context, the above-mentioned elemental steps i–iii in the plasma spraying can be redefined as (i) plasma spray CVD (PS-CVD), (ii) plasma spray physical vapor deposition (PS-PVD), and (iii) plasma powder spraying, respectively, as shown in Fig. 3. Note that the key role of plasma is to change the deposition principle of the conventional CVD and PVD by alternating the precursors to be deposited in the extremely non-equilibrium boundary layer originated from the plasma–surface interaction.

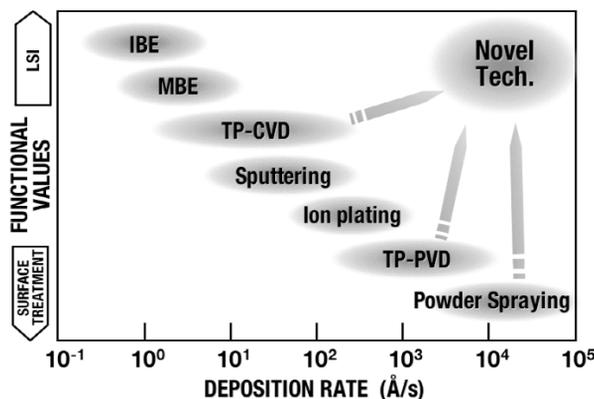


Fig. 2 Classification of coating technologies with their functional values and processing rates.

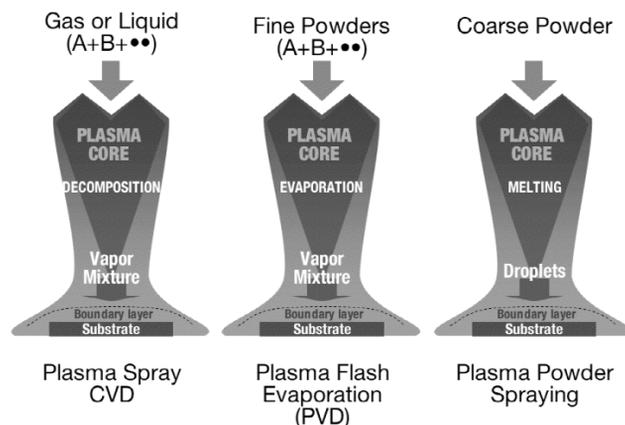


Fig. 3 Elemental processes in various plasma spraying for deposition on substrates.

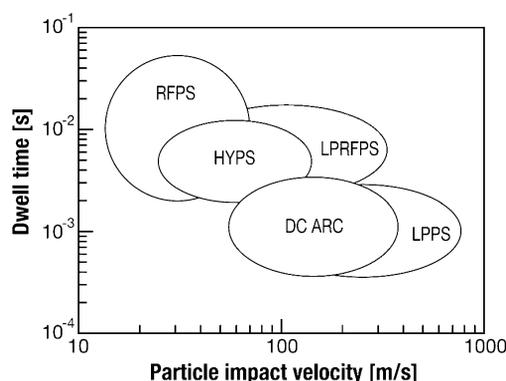
## PLASMA POWDER SPRAYING

### Reexamination of research related to plasma powder spraying

A plasma powder spraying system can be classified into the following three regions: (1) plasma torch region; (2) heating, melting, and acceleration region of powder particles; and (3) deposition region. Plasma-sprayed layers are typically comprised of splats with variable levels of flatness, spherical particles, unmelted particles, and various forms of pores, as a result of the combination of the above three regions (1–3). In other words, the plasma-sprayed layer is a coating consisting of an aggregate of particles each having different trajectories and thermal histories. The approach to plasma spraying research greatly depends on whether we accept these coatings as they are. In my opinion, many application-oriented researchers have accepted the coating technologies as they are without considering the strengths and weaknesses of the two approaches. However, it is very natural to believe that if we were able to have an ideal spraying technology with which the trajectory and thermal history could be completely and homogeneously controlled, we would obtain a coating completely different from such an inhomogeneous structured coating. I think we cannot expect to realize new development in plasma spraying technology without introducing this approach. For this reason, from the standpoint of the people who did not accept the spray coatings as they were, I briefly describe the origin of the above distributions for each region (1–3).

The distribution in region 1 is caused mainly by the method of powder supply to the plasma and the sharp gradients in the radial direction of temperature and velocity fields present in plasma. Generally, the powder is supplied perpendicular to the plasma flow direction. Thus, even if the injected particles are of the same size, a velocity distribution of particles develops owing to the carrier gas velocity distribution and in-homogeneity of plasma. As a result, different trajectories and thermal histories are generated. The most effective means for controlling the distribution is axial injection of the powders. In practice, there have been several attempts for the development of a plasma torch in which powders are injected in the axial direction, although these are still in the research stage. Over the last few years, the high-velocity oxy fuel (HVOF) system, whose industrial use is rapidly increasing, can be considered to be a series of distribution control technologies for the use of axial directional feeding. Furthermore, with the dc plasma torch method, it has been clarified that  $10^{-3}$  s order periodic variations in plasma intensity always develop owing to the arc discharge characteristics. Therefore, dc plasma can be considered in reality to be a pulse discharge of 1 kHz. The real issue is that the fluctuation period is almost the same as the time required for injected particles to be heated and melted. Accordingly, even if the distribution related to powder injection is controlled, the heating history distribution cannot be controlled in the spraying method utilizing a dc plasma torch, unless some kind of relaxation process is

installed in the later stage. The distribution in region 2 is mainly caused by the rolling-in of the ambient gas together with the distribution of composition, temperature, and flow velocity of the plasma jet, and the heating characteristics are also different. In particular, in the case of a plasma jet in a turbulent flow state, many masses of low-temperature gases are present sporadically as floating clouds in the plasma [2]. Therefore, the generated plasma is not uniform, causing amplification of the dependence of the heating characteristics on trajectory. Figure 4 shows the relationship between the residence time and the impinging velocity of particles for plasmas generated by various types of plasma torches for spraying. It demonstrates the strong dependence of spraying parameters on the type of plasma generator, and the state of distribution is also strongly dependent on the type of plasma generator. Therefore, it is important to understand each plasma flow characteristic. The causes of distributions in region 3 are considered to be related to the surface conditions of the substrate, which influences the deformation and solidification of droplet particulate. The research on this topic is in the preliminary stage. In particular, heat transfer between a liquid droplet and a solid which are at a temperature difference of 2000–3000 K occurs through a nanoscale heat-transfer region. Hence, at present, even in the simulation described later, it is necessary to introduce the contact thermal resistance as a parameter.



**Fig. 4** Dwell times and velocities of droplets in different types of plasmas. (RFPS: radio-frequency plasma spraying, HYPS: hybrid-plasma spraying, APS: atmospheric plasma spraying, LPRFPS: low-pressure radio-frequency plasma spraying, LPPS: low-pressure plasma spraying).

Thus far, I briefly discussed the factors related to distribution; the developmental process of plasma generators for spraying in the past 10–15 years can be understood easily if it is reviewed in terms of trajectory and heating history distribution control. For instance, over the early stage of the introduction of low-pressure dc plasma spraying systems, the high particle speed over 400 m/s was the selling point of the system. In reality, however, the particle velocity was not so high. That is, the main effect of the pressure reduction is considered not to increase the particle velocity but to narrow the distributions mentioned above owing to expansion of the plasma tail flame, together with relaxation of the pulsing fluctuations of the plasma jet and uniform heating capability of the substrate. In recent years, in order to further control the various distribution parameters, the use of a radio frequency (RF) plasma torch is being considered in industries. The most notable feature of this system is that a plasma is generated in a fairly large diameter of 20–50 mm, and the powders can be fed in the axial direction into the plasma [3]. Therefore, the distribution due to the variation of trajectories and thermal histories can be made very narrow, and the spraying yield remains as high as 80 %. The dc-rf hybrid plasma spraying technology [4], which will be explained below, belongs to this group.

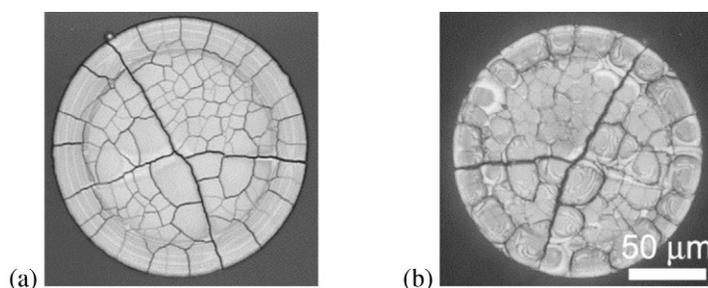
On the basis of the above background knowledge, the research stages of the spraying process can be classified into the following three phases.

- First phase: Experimental and theoretical studies to analyze a series of processes including thermal history and trajectory in which single particles are injected into a plasma jet, heated, and accelerated, and accelerated droplet particles collide with the substrate, and deform, solidify, and adhere to it.
- Second phase: Systematic study of plasma surface mutual reactions and various types of spraying parameters during the formation process of the sprayed coating of a single-phase substance due to a series of above-mentioned individual phenomena, and evaluation of the structure, composition, internal stress, and adhesive strength of the coating.
- Third phase: Evaluation of overall concurrence of spraying process and above-mentioned approach from the viewpoint of materials science for highly advanced application areas such as for composite materials including fiber-reinforced materials (FRM), multilayered material, graded materials, and cermets.

Unfortunately, the tragedy in the study of plasma spraying is that there have been only a few notable research results over the past 30 years for the first phase, and most of the research shifted to the second and third phases. To make matters worse, in the last two phases, significant results in the area of applications have been accomplished. The background on this is, first, there is a world-renowned spray apparatus manufacturer monopolizing the market since the spraying apparatus has been mainly developed hand-in-hand with aviation industries, and it is certain that we are behind in this area. Actually, there are not many reports on basic research that include the development of spraying systems. One of the reasons for this is that many studies end with the evaluation of the characteristics of the sprayed coating using parameters whose values are restricted owing to the use of conventional spraying apparatus. Second, it is essentially difficult to control various distributions such as those of particle injection velocity to plasma, thermal history, and trajectory arising from nonuniformity of plasma and acceleration using a traditional dc plasma spraying system. The coating layer represents the results of convolutions of these factors. Thus, researchers have refrained from the study of phase 1, perhaps believing that the fruits from phase 1 research are not worthy of the efforts required for such a difficult task. As described before, it is obvious that the difficulty in controlling the distributions has limited the application fields of conventional spraying processes. Therefore, if we can develop a method that reduces the degree of the above distributions, there is no doubt that we can steadily progress toward the advanced spraying technologies.

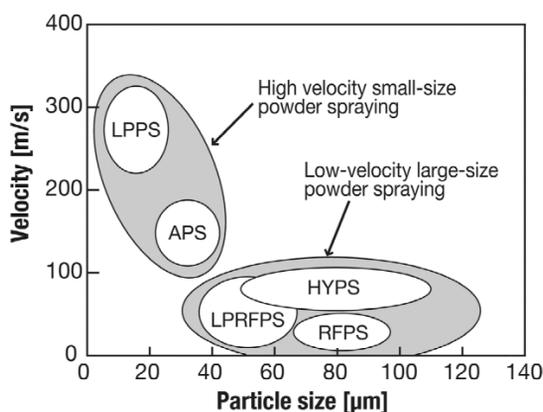
### **Velocity and size of spraying particles**

Many engineers working in this field seem to consider there is a close relationship between the spraying particle velocity and the quality of the coating, i.e., the faster the spraying particle velocity, the higher the coating quality. However, on observing the deformed  $\text{ZrO}_2$  particles in Fig. 5, it is obvious that the particle velocity does not affect the deformation solidification process as much as the extent the engineers believe. The particle velocity, at the maximum, is 70 m/s in this case, however, the ratio of the splat diameter to the droplet diameter was as high as approximately 5.0. This means that a particle of 50- $\mu\text{m}$  diameter deforms to a splat of 250- $\mu\text{m}$  diameter and 1- $\mu\text{m}$  thickness. Naturally, the spraying particle velocity cannot be too slow for solidification to occur before impacting the substrate. Hence, there should obviously be a lower limit for the sprayed particle velocity. Now, what determines the upper speed limit? It is the speed that causes splashing, which deteriorates the quality of the coating. The upper and lower limit values are determined by the physical properties of particles and heating history as well as the temperature and surface conditions of the substrate. In line with the fact that all process parameters have optimal values, there is an optimal value for spraying particle velocity. However, the splashing phenomenon is observed when the partially solidified particles are impinging. Therefore, it goes without saying that the complete melting is the premise.



**Fig. 5** Optical image of a YSZ splat; (a) top view and (b) bottom view through glass substrate.

Figure 6 shows the classification of plasma spraying processes in terms of impinging particle velocity and the particle size to be used. The latter is the size of a particle at which the particle is melted completely but not evaporated. Obviously, the novel and conventional plasma spraying processes are characterized as the low-velocity large-diameter particle spraying process and high-velocity small-diameter particle spraying process, respectively. For example, with the RF plasma spraying process, the residence time is long, 5–10 ms; it is advantageous as the spraying of large particles is possible. However, when a material with a high melting point is used for spraying, the particle with velocity of the order of 20 m/s or so may solidify before impinging to the substrate. This is one of the drawbacks of this method. With the dc-rf hybrid plasma spraying method, in which the low particle velocity problem in the RF plasma spraying method is compensated, and the particle velocity immediately above the substrate is controlled, ranging 40–70 m/s even at the atmospheric pressure by adjusting input power to the dc plasma jet. In the spraying of the Ti particles on a stainless substrate, the larger the particle size, the stronger the adhesion strength. With the regularly used 30- $\mu\text{m}$  particles, adhesion strength of only 40 MPa was reported, whereas we obtained a result as high as 200 MPa with 120- $\mu\text{m}$  particles [5]. This result was considered to be caused by the diffusion effect due to the substrate temperature increase immediately under the splats. This is an important case study in point, revealing the future of the spraying method in terms of industrial applications, and also suggesting the possibility of realizing a very difficult spraying process by using large-grain particles even under atmospheric pressure conditions.



**Fig. 6** Typical ranges of powder sizes and velocities achieved in various spraying techniques.

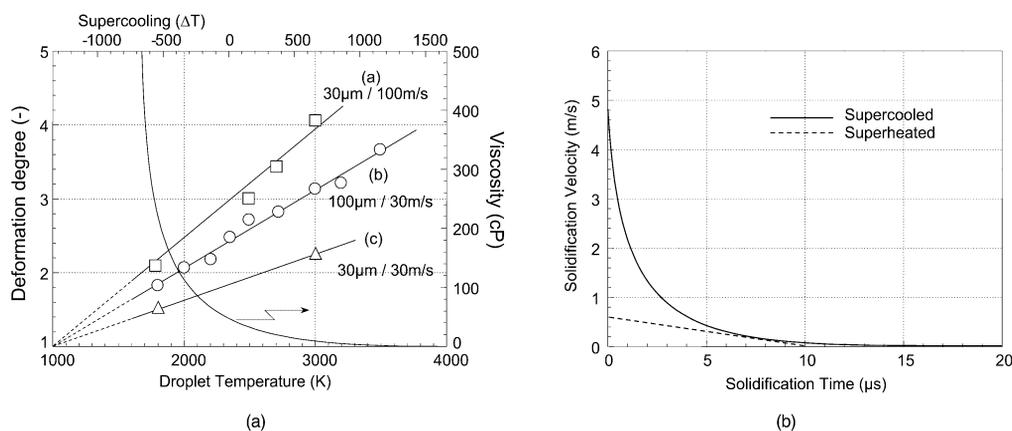
On the other hand, how impinging velocity, particle size, and temperature affect the deformation and solidification processes has not yet been analyzed systematically. But, if we restrict our discussion to the case where particles deform to a disk shape without splashing, it may be said that these factors

do not affect the extent of deformation so much in a sense that they are similar in terms of shape. However, they greatly affect the solidification process. In other words, for the particles having some level of velocity, the temperature and size are more important parameters than the velocity. In particular, when the solidification process is controlled by the heat transfer in the thickness direction, the deformation and solidification processes are naturally dependent on the thickness of the deformed particles, namely, the size of the particles. The quantitative understanding of velocity, size, temperature, and contact thermal resistance is an issue to be resolved in the future [6]. On the other hand, several results have recently been reported that there is a threshold temperature for the substrate that determines the occurrence of splash- and disk-type deformation. These are new topics in this field [7]. Phenomenologically, when solidification advances from the points of contacts of liquid droplets with substrate, splash-type deformation seems to develop. In the meantime, when solidification begins at the peripheral regions of the splat, disk-type deformation develops. In other words, when the contact thermal resistance is small, splash-type deformation develops. The detailed analysis of this behavior requires an understanding of nanoscale heat transfer; however, in general, the issue of this splash-type deformation is not a big problem if the substrate can be heated up to the temperature within the permissible range.

### Simulation and in situ measurements

Through the recent re-recognition of an importance of the first-phase research, the number of reports on simulations and in situ measurements related to the deformation and solidification processes of single spraying particles has been increasing [8]. However, many case studies are conducted independently by people who belong to the heat engineering fields and to the measurement fields, and there has been no report of an integrated understanding from both two approaches. For example, in nanoscale heat transfer, normal contact thermal resistance is not applicable in the heat conduction analysis, as a temperature difference of 2000 K or higher is present at the interface between the liquid droplet and the substrate. Thus, it is essential that in the future, information obtained by measurements should be used in numerical analyses to determine the physical quantities to be measured, i.e., an approach from both sides is essential.

Recently, researchers have succeeded even in modeling up to pore formation using stochastic approaches for coating formation [9]. However, it is important to understand that all of these models assume equilibrium solidification in which the contact thermal resistance is introduced as a fitting parameter, in a certain sense. Regarding the simulation, I would like to point out the necessity of clarifying the relationship between the deformation and solidification process of sprayed particles under the state of supercooling, since the phenomenon of supercooling, which should be naturally taken into consideration in the field of metallurgy in relation to solidification phenomena, has been neglected in the modelings reported so far. Figure 7a shows a part of the calculation results, in which the viscosity is represented in terms of a function of temperature, and supercooling solidification phenomenon is incorporated into the simulation [10]. Although the details of the calculations are not presented here, when the supercooling phenomenon is included, the extent of deformation dependence on particle temperature can be described by linear extrapolation of the equilibrium solidification curve. However, it has been demonstrated that the initial solidification rate differs by approximately one order of magnitude from the case of equilibrium solidification (Fig. 7b). In other words, even if the shape of deformation is the same, the metallurgical solidification structure differs greatly, and as a result, the coating characteristics may differ greatly, too.



**Fig. 7** Variation of deformation degree with the initial impinging temperatures for various droplets (a) and comparison of solidification velocity of a supercooled and superheated droplet (b).

There is much to learn from the calculations related to deformation and solidification processes during the collision of not only single sprayed particles but also multiple particles with the substrate, and we are amazed when we observe graphically dynamic images. However, if we examine the calculation conditions in a little more detail, I feel it necessary to mention that there are many incidences in which conditions do not match those in actual processes. Naturally, simulations and experiments are complementary, and for achieving progress in this field, “beautiful measurement experiments” are essential. Especially, I would like to stress here that “average or mean values” of the velocity, temperature, and size of droplets have little help for understanding the actual deposition phenomena. The reason may be sufficient to show the fact that you will observe wider distributions of them even when you select the particles by inserting the plate with 1-mm hole just in front of the substrate. Accordingly, at this stage, it is strongly anticipated to gather the data relating 1:1 correspondence between the velocity, temperature, and size of a single droplet just before impinging and the morphology and structure of the splat [11]. We are moving from an era in which study of the dependence of external parameters yields some information, to an era in which new information is obtained only from the quantitative studies on the dependence of internal parameters. Furthermore, we are in the era in which such a study is possible by novel instruments.

## PLASMA SPRAY CVD AND PVD

In PS-CVD, gaseous or liquid reactants are injected and completely dissociated to the atom elements as precursors. In most of the cases, as the substrate temperature is significantly lower than that of the tail flame, the rate-limiting step of the deposition is considered to be in the plasma/substrate boundary. Therefore, unlike surface reaction observed in the conventional CVD, the prominent feature of PS-CVD is transport of high radical flux. For some cases, cluster deposition is expected as an additional important feature, especially when extremely high rate deposition is attained [12]. For example, SiC coatings have been successfully deposited by PS-CVD from  $\text{SiCl}_4 + \text{CH}_4$  gas mixture at a rate of 1 mm/h with the deposition efficiency of over 70 %, due possibly to the  $\text{CH}_x$  radical formation and also to the thermophoretic effect in the plasma/substrate boundary [13]. By using hybrid plasma, microcrystalline Si with a defect density of  $7.2 \times 10^{16}/\text{cm}^3$  was produced from  $\text{SiH}_4 + \text{Ar}$  plasma at an ultrafast rate of over 1000 nm/s, which is about 2000 times faster than that achieved by the conventional CVD [14]. Computer simulations have suggested the effective roles of clusters with the size of  $\sim 1$  nm and of the thermophoresis in the plasma/substrate boundary to achieve such ultrafast depositions [15,16].

Furthermore, the deposition of complex oxides such as optical materials was also attained by this technique, supporting the possibility of high rate deposition assisted by hot cluster formations [17]. On the other hand, in the case of diamond synthesis, it is plausible that molecules such as  $\text{CH}_3$ ,  $\text{C}_2\text{H}_x$  are the precursors and the deposition rate is controlled by extraction of hydrogen near the surface. As a result, despite the deposition efficiency of only several percent, high deposition rates faster than  $10\ \mu\text{m}/\text{h}$  is realized by the high flux of atomic hydrogen [18]. Commercially, large-area diamond films with a diameter of 6 in and thickness of 1–2 mm are already produced by a 300 kW dc plasma system. Another interesting example is that thick (over  $20\ \mu\text{m}$ ) cBN films were obtained by using  $\text{BF}_3\text{-Ar-H}_2$  gas mixture plasma under 50 Torr with the PS-CVD method although the thickness of cBN films hardly reaches  $1\ \mu\text{m}$  by the conventional low-pressure (several mmTorr) deposition [19].

In contrast, PS-CVD at medium pressure of around several Torr can be a unique approach to expand the potential of plasma spray processing. The effectiveness of this processing may be in that various precursors can be created stably through chemical reactions in the plasma, promoting the functionalities of the products. In addition, owing to the characteristics of medium-pressure plasma, such precursors are transported/treated in rather high-density plasma flow, which increases the throughput and thereby retains the potential of plasma spraying as an affordable process technique. Because of such characteristics different from those of low-pressure and thermal plasmas, this plasma process may be distinctively called “mesoplasma” spraying. The deposition of the epitaxial silicon films at high rates via mesoplasma CVD is a recent example [20]. As such, a variety of developments in mesoplasma spraying technology are highly expected as a key technology in the future.

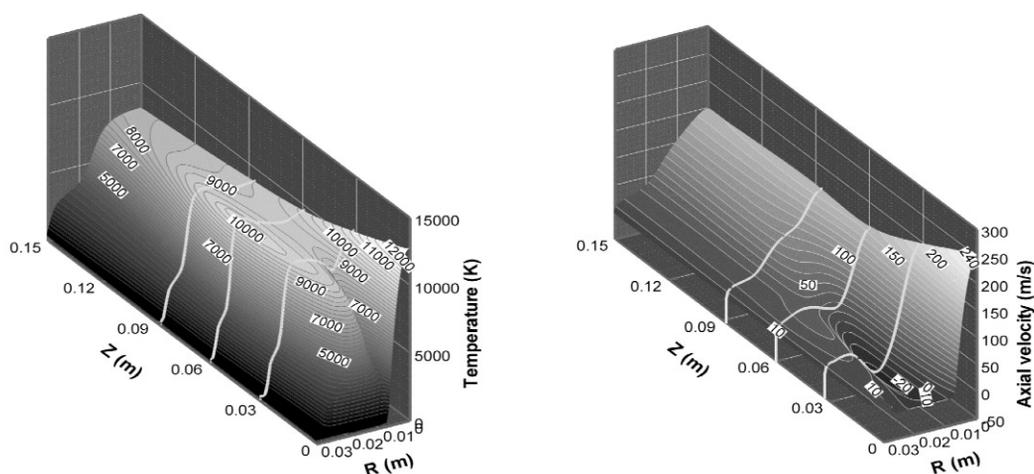
In the PS-PVD method, atoms or clusters are utilized as precursors through evaporation of fine powders injected. Therefore, the most important feature in this method is the ability to vaporize powders completely (generally as small as  $10\ \mu\text{m}$  in diameter) and continuously in the plasma. Along with the merits of the analogous “flash evaporation” technique that facilitates deposition of the compounds with totally different vapor pressures, the advantages of PS-PVD processing are its flexibility and the minimum formation of by-products. In addition, higher vapor fluxes can be achieved by an increase in the powders to be injected, with increasing the plasma power inputs. However, the sizes of the powders have to be carefully selected according to their residence time in the plasma, since rather large particles may remain at the liquid phase without being evaporated. Furthermore, high rate carrier gas is in general required to inject smoothly finer particles, intending complete evaporation within the plasma flow. This gas velocity, however, needs to be carefully controlled since the plasma is remarkably disturbed and becomes unstable, deteriorating inevitably the quality of the coatings [21]. This method has been employed to deposit a variety of materials, including 123 oxide superconductors. In particular, an interesting result observed is that hot cluster deposition facilitates the epitaxial growth of the 123 phase [22], although such peritectic phase formation from incongruent melt is in general difficult to be controlled in the case of the powder spraying technique. Similarly, PS-PVD has successfully demonstrated the deposition of thick SiC films at rates well greater than  $300\ \text{nm}/\text{s}$ , using ultrafine SiC powder as a starting material. Such SiC has shown the enhanced thermoelectric properties by N-doping [23]. This process is often compared to the laser ablation process. Several makers have tipped that the PS-PVD will become advantageous over laser ablation owing to its “large area” and “ultra-fast” characteristics, once fine powders with high fluidity and precisely controllable powder feeding system both become conveniently accessible.

## COMPREHENSIVE PLASMA SPRAY PROCESSING: CASE STUDY FOR THERMAL BARRIER COATINGS

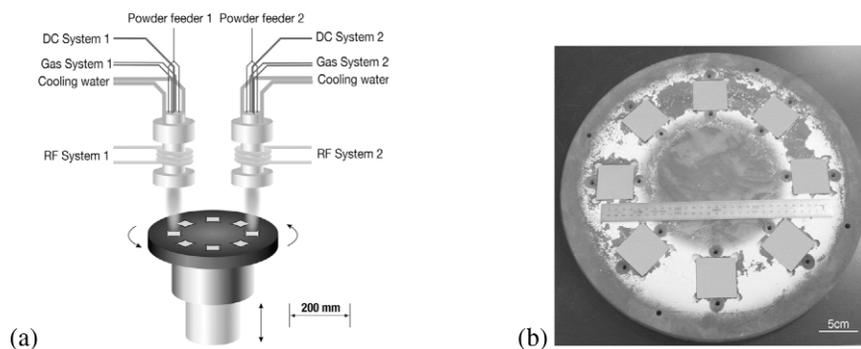
The development of novel TBCs by twin hybrid plasma spraying (THPS) is one of the best case examples of integrating all the potentials of different plasma spraying techniques, that is, composite coating production with the plasma powder spraying and PS-PVD processes. The use of TBCs together with the development of super alloys and cooling systems enables the continuous improvements in the effi-

ciency and durability of gas turbine engines. Practically, the thickness of over several hundreds of microns is required for TBCs, so that deposition rate and cost-efficiency have become the momentous criteria in choosing the proper manufacturing method. Over the last decade, various processes have been adopted for TBC deposition and are divided into two main types; one is vapor deposition technique, such as electron-beam PVD (EB-PVD), plasma-enhanced CVD, and laser CVD, and the other is molten particle deposition typically represented by atmospheric plasma powder spraying. In short, TBCs made by the former are characterized by columnar microstructures, while splat structures are commonly obtained by the latter. Owing to this structural difference, the thermal and mechanical properties of such TBCs vary considerably. The vapor-deposited TBCs have the merits of excellent strain tolerance, excellent surface finish, good erosion resistance, and relatively long lifetime. However, these merits are gained at the expense of rather high thermal conductivity and high production cost. On the other hand, molten-particle-deposited TBCs exhibit the lowest thermal conductivity, high processing efficiency, and low cost, but are less durable. Thus, the coatings with all the above advantages as added values will be the next-generation TBCs. In this respect, thermal plasma spraying is an attractive, promising, and natural choice for novel coating technologies as it inherently possesses the potential to achieve all the characteristics by both molten particle spraying and vapor deposition.

In a hybrid plasma [24], the large recirculation eddy present in the conventional RF plasma is extinguished by the high-velocity channel of the arc jet. The central channel of the plasma is also heated by the high-temperature jet, and the dc plasma jet can act as a lasting igniter and a strong propulsor to enable the axial injection of powder, which may improve the uniformity of the powder thermal history compared to the radial feeding method. A more homogeneous plasma flow than that of conventional RF plasma is another merit of the hybrid plasma, as is found in the temperature and axial velocity fields in a 100-kW hybrid plasma estimated by computer simulation shown in Fig. 8. Such high power capacity of the hybrid plasma system enables the full melting and/or evaporation of yttria-stabilized zirconia (YSZ) with high melting temperature and utilizes its unique chemical and physical properties for TBC topcoat. On the other hand, as powders are used for both plasma powder spraying and PS-PVD processes, composite coatings can be formed by one torch deposition owing to inevitable distributions of powder size, velocity, and plasma conditions, i.e., the combination of melting and evaporation process of the injected powders. However, real engineered composites should be obtained by a precise and active control of the film structures, and this was made possible with a novel 300-kW THPS system shown in Fig. 9a. This system is equipped with two hybrid-plasma torches in a chamber, and substrates on a rotary substrate holder are exposed by turns to the two plasma flames, which is capable of plasma powder spraying and PS-PVD process. That is, an alternate layering of the intended structures with any materials can be realized by assigning different processes separately to each of the two hybrid-plasma torches. Figure 9b shows the photograph of the as-deposited YSZ coating by this cyclic deposition technique. It is seen that YSZ coating was performed on the 8 substrates simultaneously, exhibiting uniform top appearance over the  $5 \times 5$  cm substrate.



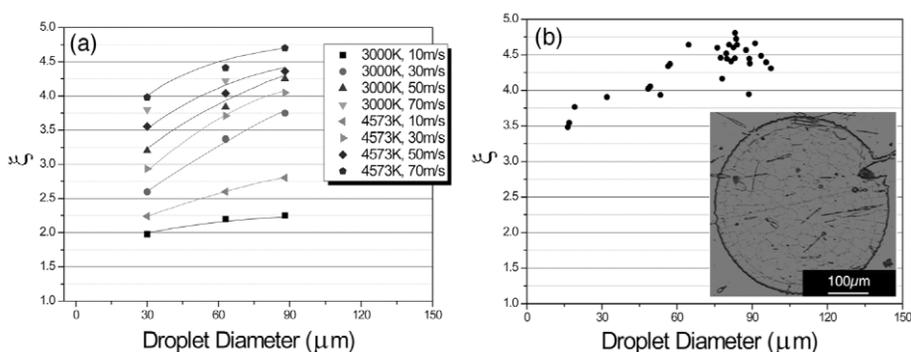
**Fig. 8** Temperature (left) and axial velocity (b) field of a 100 kW hybrid plasma. The white lines denote the 3-turn coil positions. The central high temperature and high velocity channel is caused by the dc jet.



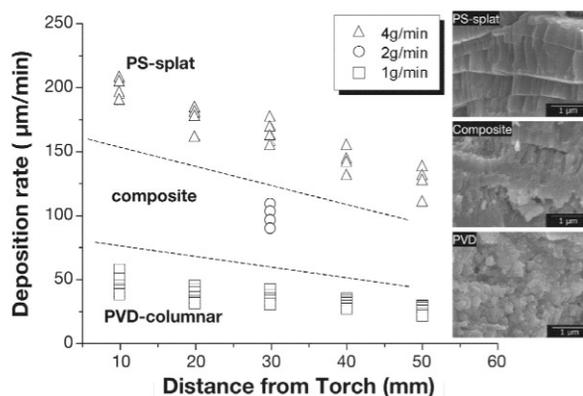
**Fig. 9** Schematic of a 300-kW THPS system (a) and photograph of the as-deposited YSZ coatings on a rotating holder (b).

The critical parameters to achieve a specific structure by the use of a single-torch system are identified. In the case of plasma powder spraying, empirically, a better adhesion strength is achieved by rather large powders if full melting of the constituent is maintained. As shown in Fig. 10, both computer simulation and experiments on large YSZ (with size of 63–88  $\mu\text{m}$ ) powder spraying confirms that a flattening degree as large as 5 was reached when the droplet size is near 100  $\mu\text{m}$  in a 100-kW hybrid plasma [25]. The good agreements between the numeric simulation results and the single splat deformation experiments in turn confirm that the viscosity and thermal resistance value obtained from in situ measurement [11] are reasonable. On the other hand, in the PS-PVD process, powder-feeding rate is found to be the first important parameter that affects the evaporation degree of powders. Figure 11 shows the variation of the deposition rate and coating structures with the powder-feeding rate and distance from the torch [26]. At a relatively high powder-feeding rate of 4 g/min, the coating was composed mostly of splats as a result of complete melting of the powders and deposition at the liquid state. Whereas, when the powder-feeding rate was lowered to 1 g/min, only the aggregation of nanoparticles is observed, which is the typical structure of vapor deposition by PS-PVD. This variation in microstructure demonstrates clearly the powder-loading effects. On this basis, when the powder-feeding rate was controlled to 2 g/min, a peculiar layered composite structure was achieved, in which the sprayed splats are enweaved between the PVD structure layers. A more interesting result is that the PVD struc-

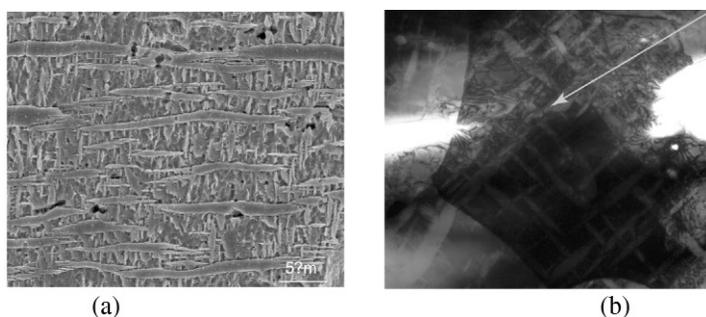
ture is achieved at a quarter of the deposition rate for the sprayed films, when reducing the feeding rate to one-fourth of that for the spraying. This is clear evidence of quite a good deposition efficiency of PS-PVD. A denser microstructure was also achieved in the thick PS-PVD coating of YSZ with a thickness of around 550  $\mu\text{m}$  deposited on water-cooled stationary substrate at ultra-high speed of over 150  $\mu\text{m}/\text{min}$  as shown in Fig. 12. It is interesting to note that interlaced structures were revealed in such dense YSZ coating after etching with 50 % HF for 3 min. From transmission electron microscopy (TEM) observations, a similar interlaced twin variant structure was observed clearly and identified as 't' phase. More detailed analyses are required to understand the formation mechanism of such structures. Nevertheless, the coating with this interlaced structure has higher nanohardness and elastic modulus than those of powder-sprayed and EB-PVD coatings [27]. Another important result is that the coating has shown much higher reflectivity against the infrared than the powder-sprayed coating, due probably to the layering structure at several micron intervals, parallel to the coating surface [28]. This suggests that the coating can reflect the infrared light effectively and therefore suppress radiation heating of underlying base materials particularly when exposed at elevated temperatures.



**Fig. 10** Effect of droplet diameter on the flattening degree (substrate temperature = 723 K): (a) numerical simulation and (b) experimental results.

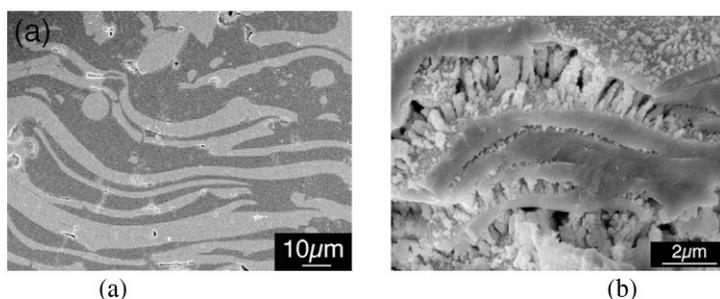


**Fig. 11** Variations of deposition rates and the coating structures with the powder-feeding rates at different torch-to-substrate distance.



**Fig. 12** FE-SEM micrograph of PS-PVD YSZ after etching (a) and TEM image without etching (b).

In twin torch depositions, composite coating with the combination of PS-PVD  $\text{Al}_2\text{O}_3$  and plasma powder spray YSZ was produced. Figure 13a shows the well-flattened YSZ splats (white) in the vapor-deposited  $\text{Al}_2\text{O}_3$  matrix (black) [26]. Understanding the individual droplet deformation and solidification in the middle of the coating is as important for the structure control purpose as the first splat formation behavior at the splat/substrate interface mainly for the adhesion control purpose. This technique facilitates the direct observation of such droplet deformation in the coating with ease. Figure 13b shows the peculiar layered structure attained in the YSZ/YSZ composite coating deposited by plasma powder spraying and spray PVD with small powder. Such porous YSZ composite was deposited at high rate of  $>50 \mu\text{m}/\text{min} \times 500 \text{ cm}^2$  and achieved significantly reduced thermal conductivities of 0.7 W/mK.



**Fig. 13** FE-SEM micrograph of PS-PVD  $\text{Al}_2\text{O}_3$  and powder spray YSZ composite coating (a) and layered YSZ coating deposited by PS-PVD and powder spray using twin torch deposition (b).

## SUMMARY

We have only entered the beginning stage for the basic study of spray coating technology. This means that it has potential for further development. In this sense, it is not appropriate to determine the present position of spraying technology in terms of currently available technologies, especially in fields where high-level coating processes are required. Even so, it is surprising that there are many analytical studies on the performance of the coatings produced by the currently available technologies. As mentioned in the beginning, for the development of the novel coating process, it is essential to adopt an integrated approach from the fields of processes, evaluations, analysis design, and so on. I strongly feel the necessity of the launch of a joint industry and academia project with participants from many different fields with various specialties. In this sense, discussions among researchers from different fields will become more important in the future.

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## REFERENCES

1. "Decomposition of organic halides by radio frequency ICP plasma", Patent, JP2732472 (1998).
2. E. Pfender, J. Fincke, R. Spores. *Plasma Chem. Plasma Process.* **11**, 529 (1991).
3. T. Okada, H. Hamatani, T. Yoshida. *J. Am. Ceram. Soc.* **72**, 2111 (1989).
4. T. Yoshida, T. Okada, H. Hamatani, H. Kumaoka. *Plasma Sources Sci. Technol.* **1**, 195 (1992).
5. T. Yoshida. *Pure Appl. Chem.* **66**, 1223 (1994).
6. P. Fauchais, M. Fukumoto, A. Vardelle, M. Vardelle. *J. Therm. Spray Technol.* **13**, 337 (2004).
7. M. Fukumoto, M. Shiiba, H. Kaji, T. Yasui. *Pure Appl. Chem.* **77**, 429 (2005).
8. C. Moreau, J.-F. Bisson, R. S. Lima, B. R. Marple. *Pure Appl. Chem.* **77**, 443 (2005).
9. M. Xue, J. Mostaghimi, S. Chandra. *Proc. of Thermal Spray 2004*, Osaka, Japan, 10–12 May (2004).
10. Y. K. Chae, J. Mostaghimi, T. Yoshida. *Sci. Tech. Adv. Mater.* **1**, 147 (2000).
11. K. Shinoda, T. Koseki, T. Yoshida. *J. Therm. Spray Technol.* **14**, 511 (2005).
12. T. Yoshida. *Mater. Trans., JIM* **31**, 1 (1990).
13. H. Murakami, T. Yoshida, K. Akashi. *Adv. Ceram. Mater.* **3**, 423 (1988).
14. Y. K. Chae, H. Ohone, K. Eguchi, T. Yoshida. *J. Appl. Phys.* **89**, 8311 (2001).
15. P. Han, T. Yoshida. *J. Appl. Phys.* **91**, 1814 (2002).
16. P. Han, T. Yoshida. *J. Appl. Phys.* **92**, 4772 (2002).
17. S. A. Kulinich, J. Shibata, H. Yamamoto, Y. Shimada, K. Terashima, T. Yoshida. *Appl. Surf. Sci.* **182**, 150 (2001).
18. H. Q. Yin, K. Eguchi, T. Yoshida. *J. Appl. Phys.* **78**, 3540 (1995).
19. S. Matsumoto, W. Zhang. *Jpn. J. Appl. Phys.* **39**, L442 (2000).
20. M. Kambara, H. Yagi, M. Sawayanagi, T. Yoshida. *J. Appl. Phys.* **99**, 074901 (2006).
21. X. H. Wang, K. Eguchi, C. Iwamoto, T. Yoshida. *Sci. Tech. Adv. Mater.* **3**, 313 (2002).
22. K. Terashima, K. Eguchi, T. Yoshida, K. Akashi. *Appl. Phys. Lett.* **52**, 1274 (1988).
23. X. H. Wang, A. Yamamoto, K. Eguchi, H. Obara T. Yoshida. *Sci. Tech. Adv. Mater.* **4**, 167 (2003).
24. T. Yoshida, T. Tani, H. Nishimura, K. Akashi. *J. Appl. Phys.* **54**, 640 (1983).
25. H. Huang, K. Eguchi, T. Yoshida. *J. Therm. Spray Technol.* **15**, 72 (2006).
26. K. Eguchi, H. Huang, M. Kambara, T. Yoshida. *J. Jpn. Inst. Metal* **69**, 17 (2005).
27. J. Q. Li, H. Huang, K. Eguchi, T. Yoshida. Unpublished data.
28. T. Ma, M. Kambara, H. Huang, T. Yoshida. Unpublished data.