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The future of thermal plasma processing for coating

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ABSTRACT:The purpose of this review is to identify the areas in thermal plasma processing for coating fields where scientific and/or engineering advances would have been highly expected in the near future. In particular, we characterize three types of injection plasma processing(IPP) for coating, that is, thermal plasma CVD, plasma flash evaporation, and plasma spraying, and discuss the problems relating to each IPP. In order to demonstrate the prominent features of IPP, special attention will be given to radio-frequency(rf) and hybrid plasma processing, which will be discussed in conjunction with our recent research concerning the functional materials coatings. "Super-high rate and large area deposition of SiC and diamond by hybrid plasma CVD", "Large area deposition of high-quality YBCO films by rf plasma flash evaporation" and "Integrated fabrication of solid oxide fuel cell by hybrid plasma spraying" will be mentioned as three distinctive candidates, which should suggest the way of thinking for the future development of IPP in the field of functional materials coatings.

I. INTRODUCTION

Over the past two decades, thermal plasmas have been used for materials synthesis and processing. However, the development of injection plasma processing(IPP) for coating was commercially successful only in a spraying field. The major reason might be caused by the fact that only few researchers who have been engaged in thermal plasma processing intended to develop special plasma torches suited to various types of IPP, and a conventional direct current(dc) plasma torches have been used exclusively, because of their ease of operation and installation. Of course, the dc plasma jet has unique characteristics such as high energy density and high velocity, and has been used successfully for spraying. Unfortunately, however, the dwell time of the injected materials in the plasma is usually less than 1 msec, which is insufficient to be applied for a wide variety of coating process. Moreover, the steep temperature and velocity gradients occurring in the plasma generally result in non-uniformity in terms of heating, trajectory, and reactions in addition with the high heat flux to the substrate which leads to difficulties in controlling the substrate temperature. Recently, there have been a variety of approaches pursued to overcome such problems and achieve better control of the plasma for IPP by expanding, stretching, and spinning the dc plasma jet. Though the development of such novel dc plasma torches is anticipated in the future, they may not allow for the central feeding of materials for using the power input region efficiently, and for minimizing the non-uniformity. In these respects, rf and hybrid plasmas are highly recommended. The most important characteristics of these plasmas are their large volume and relatively low velocity. Moreover, they may allow central feeding of materials to minimize trajectory and reaction variations.

From the viewpoints mentioned above, the recommended research priorities will be focused on rf and hybrid plasma deposition technologies, and the current topics relating to them will be reviewed briefly in this paper.

II. CHARACTERIZATION OF IPP FOR COATING.

The present thermal plasma technology can be roughly classified into two fields, which originated from batch-type arc heating technology and combustion flame technology. IPP may be classified into a new branch of the latter case. Principally, the combustion flame technology is applicable to the IPP. However, it should be noted that the flame temperature of plasma is extremely high showing peculiar characteristics, and that the variable ranges of plasma parameters are strongly restricted compared with other conventional processing, which demand a substantial modification of the process design. Occasionally, intuition developed through the use of the conventional processes cannot necessarily be transferred to IPP.

IPP for coating can be divided into three main categories as shown in Fig.1. The **thermal plasma CVD(TPCVD)** is characterized by the injection of gaseous or liquid reactants into the plasma. This processing may be considered to be the modification of low pressure plasma CVD(PCVD). However, the axially injected reactants are sometimes completely dissociated to the elements, and the substrate temperature is invariably lower than that of the tail flame. Therefore, the deposition mechanism is considered to be different from conventional CVD process which demands the rate-limiting step of surface reaction proceed by thermal energy of the heated substrate. A prominent feature of TPCVD is considered to be an extreamely high flux of radicals, which may effectively react at the deposition surface. For some cases, cluster deposition is considered to be an additional important feature, especially, for high-rate deposition. In the **thermal plasma flash evaporation** method, powders are used as raw materials and injected into the plasma. As this takes place, a chemical process must be followed by physical processes such as the melting and evaporation of solid particles. It may fairly be said that the ability to cause vaporization is the most important feature in this method. In order to expect the perfect evaporation of the powders, the size less than 10 μm must be fed continuously into the plasma. Recently, the powder feeder that can feed such fine powder continuously with the precision similar to that achieved by the mass flow controller for gas feeding, has been available commercially. This process is very fit for the multicomponet film deposition, since the composition controlled vapors can be easily generated in a plasma flame. Frequently, reactive plasma is used for the reaction with the vaporized elements. The advanteges of this processing are its simplicity, flexibility, and that by-products can be minimized, in addition to the prominent features of TPCVD. The last one shows **plasma spraying**. In this case, injected powder size must be large enough not to be vaporized, and small enough to be completely melted. Each droplet is flattened on impact at the substrate and solidified, and the coating consists of many layers of the flatterned particles. Essentially, the structure of the coating is determined by the heat content, the kinematic viscosity, and the velocity of droplets just before the collision. This method has been used for over two decades in applying metals and ceramics coatings. Noteworthy is that rf and hybrid plasma spraying made it possible to use relatively large-size powders which could not be used by conventional dc plasma spraying because of the shortness of the dwell time. The use of such large-size powders has been changing the concepts of plasma spraying, especially, the concepts relating to the porosity and the adhesive strength , and should open new fields of spraying applications.

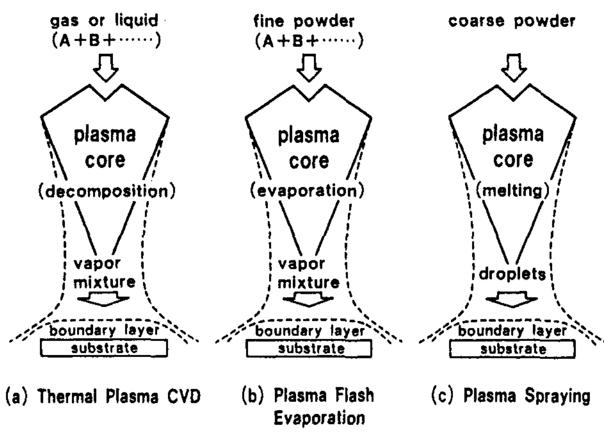

Fig. 1. Three main categories of IPP for coating.

III. Guiding principle for the development of IPP for coating.

Figure 2 shows our guiding principle for the development of IPP for coating. The meaning of this figure is as follows: From economical and engineering points of view, functional value of the coating necessarily requires the application of the coating methods which enable the deposition rate higher than some critical value. On the other hand, each coating method has its own characteristic deposition rate and is required to be applied for the deposition of more valuable coatings than those already achieved by each method. Typical examples developing so far in our laboratory are shown by the arrows. In the field of CVD, it has been aimed primarily to increase the deposition rate and deposition area without degradation of the film quality. In the case of SiC coating, we have achieved the deposition rates 2-3 orders of magnitude faster than the cases of usual CVD at relatively lower temperature(1-3). Regarding evaporation, we have been developing plasma flash evaporation(4-10), and have been investigating high-rate and as-grown deposition of high quality superconductor films superior than those prepared by other low pressure processing such as electron-beam evaporation and laser ablation. Regarding spraying, on the other hand, we have been developing novel spraying techniques(11,12), and have been investigating the possibility to apply them to new spraying fields, such as the formation of solid oxide fuel cell(13,14). These two directionalities, that is, the increase of the deposition rate over few orders of magnitude and the improvement of the conventional process to be applied for depositing high quality coatings possessing more functional value are considered to be the role of future IPP in the coating fields(15).

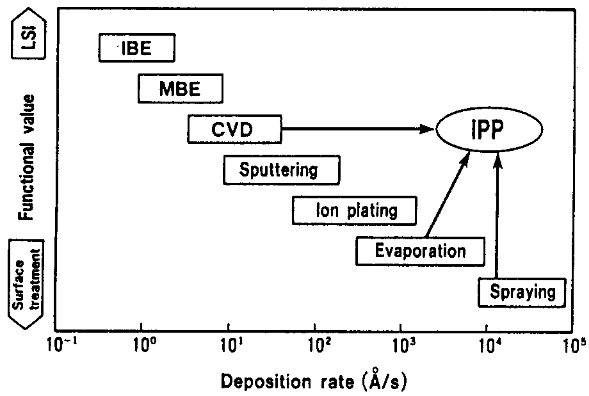

Fig. 2. Guiding principle of our research for the development of IPP in the coating field.

IV. PLASMA TORCHES FOR IPP.

As mentioned in the previous chapter, the most important key to success for IPP in various coating applications depends to a large extent upon the development of plasma torches which make it possible to generate relatively large size plasma, and to sustain a stable plasma, in particular, when raw materials are being axially injected. In these respects, an rf plasma torch and a hybrid plasma torch are strongly recommended. Figure 3 shows the schematic diagrams of these two torches, which have been developed and used in our laboratory. And Fig.4 shows the calculated temperature and flow fields in Ar plasmas, which will be generated in the torches shown in Fig.3, with coil current of 4 MHz-100A, sheath gas flow rate and swirl velocity of 40

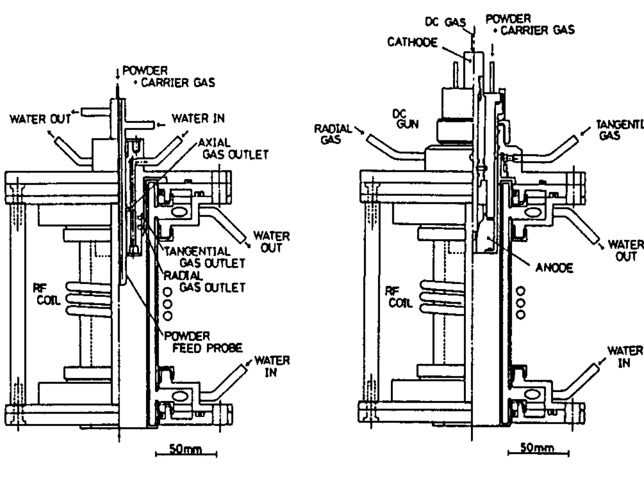

Fig. 3. Schematic diagrams of rf and hybrid plasma torches.

L/min and 10 m/s, carrier gas and dc plasma jet flow rate of 5 L/min, and dc jet power of 0.6 kW at the inlet boundary. The rf input power level is about 6.6 kW in each case.

In the rf plasma, the carrieer gas injection results in cooling the entrance region close to the center line. Moreover, the flow pattern shows the presence of large recirculation flow, by which a part of the carrier gas connot penetrate into plasma but creeps over the plasma boundary. Therefore, the injection nozzle must be located at the level of upper end of an rf coil at least(as shown in Fig.3) for injecting all raw materials into plasma, though higher carrier gas flow rate results in the formation of low temperature channel like a tunnel. Principally, the rf plasma is electrodeless discharge and the plasma is free from electrode contamination. Accordingly, reactive gases can be used as plasma gases for special cases. The dwell time is of the order of 10 ms and this torch is very fit for powder processing in IPP. On the other hand, the main feature of the hybrid plasma is that the large recirculation flow existing in the rf plasma is extinguished by the presence of the high-velocity channel caused by the dc arc jet. Therefore, if the raw materials can be carried by the arc jet flow, they can be expected to pass through the high temperature region higher than 9000 K, with the dwell time of about 5 ms. Moreover, the central channel is enveloped by the large high-temperature region, and the homogeneous heating of the injected materials is expected. Actually, our experience clearly demonstrates that the hybrid plasma has the potential to give higher efficiencies for practical processing than conventional rf plasmas, because the plasma flow of the arc jet instead of the usual carrier gas flow plays an important role as a lasting igniter and a strong propulsor. In spite of these advantages, the presence of a dc torch may be a source of contamination through electrode erosion. However, ine rt gas such as Ar can be used exclusively for the dc arc jet working gas because molecular and reactive gases can be fed into the sheath gas for increasing plasma enthalpy and reactivity. Therefore, contamination in the coating through electrode erosion can be minimized. Recently, the effectiveness of these two kinds of plasma torches for coating has been accepted by industries which have developed industrial scale torches with the power level higher than few hundreds kW.

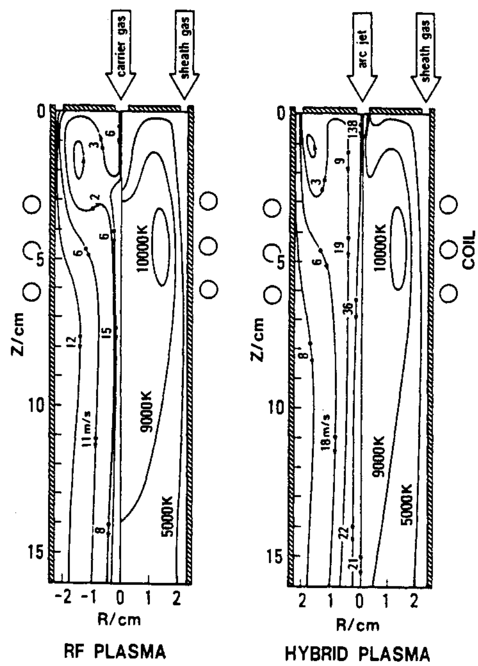

Fig. 4. Stream-line patterns and temperature distributions of rf and hybrid plasmas.

In order to demonstrate the prominent featuers mentioned above, the application of the two types of torch to the thermal plasma processing for coating will be shown in what follows.

V. REVIEW OF OUR RECENT RESEARCH

[a] Hybrid plasma CVD(Super-high rate and large-area deposition of SiC and diamond)(1-3)

As shown in our previous papers, thick and dense SiC layers were successfully deposited at a rate above 200 nm/s on a graphite substrate from $SiCl_4$ and CH_4 under soft vacuum of about 200 Torr, by using a 25 kW hybrid plasma reactor, that is, super high-rate TPCVD.

Recently, in order to apply this process for large-area deposition, we have been developing a cyclic-TPCVD(C-TPCVD) system consisting mainly of a hybrid plasma torch and a deposition chamber in which a 300 mm outside-diameter rotating doughnut-type graphite stage is set up(Fig.5). The plasma torch is mounted 130 mm off-axis from the center of the rotating stage. Most striking fact is that nano-crystalline SiC layers with the grain size around few nm, which depends upon the substrate temperature as shown in Fig.6, and with the hardness higher than that of the sintered block of SiC, could be successfully deposited on the substrate put on a 40 rpm rotating stage with the conversion efficiency higher than 70%. In addition, from the actual processing points of view, it must be noted that the substrate temperature can be regulated without auxiliary heating or cooling devices in this system, since the substrate temperature is governed by the balance between heat flux from plasma to the rotating large-area stage and the radiation loss from the stage, and the temperature is determined by the plasma power and the stage area. Very recently, we have attempted to apply this technique for depositing diamond from Ar-H_2-CH_4 system under soft vacuum of 250 Torr and investigated its potential for depositing diamond on the substrate larger than 12 inch diameter at least. Preliminary experimental results showed that the actual deposition rate at the rotating speed of 40 rpm is estimated to be about 1 nm/cycle, which corresponds to the total deposition rate above 0.2 g/hr. and about 2 % conversion from CH_4 to diamond. The marked difference of the conversion efficiencies between SiC (70%) and diamond(2%) deposition may be attributed to each deposition mechanism. As mentioned in our previous papers(1-3,16,17) cluster deposition and radical reaction at the surface may be principal mechanisms for the growth of SiC and diamond layers, respectively, by TPCVD.

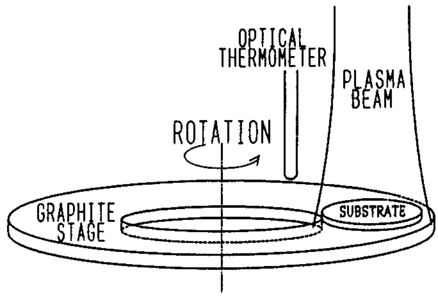

Fig. 5. Schematic diagram of cyclic thermal plasma CVD(C-TPCVD).

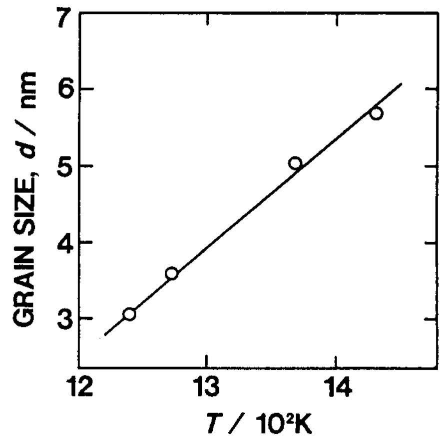

Fig. 6. Effect of substrate temperature on the grain size of the nano-crystalline SiC coating.

Unitil now, large-area SiC and diamond films have not been obtained by TPCVD, because the substrate had been fixed in a plasma tail flame and had to be water-cooled. By using C-TPCVD developed here, however, we have succeeded to overcome the shortcomings of the plasma flame reactor and prepare uniform films on large-area substrates for the first time. The key for the success is considered to be the introduction of high power(50 kW) hybrid plasma system combined with the substrate movement system. In the future, it will be demonstrated that 2-dimensional movement of the substrate should be so helpful for the practical large-area coating by TPCVD.

[b] RF plasma flash evaporation.(Large-area deposition of high-quality YBCO films.)(4-10)

The so-called flash evaporation had been developed for the vacuum deposition of compounds whose constituents contain the elements with large different vapor pressures, and applied especially for the deposition of III-V semiconductors. In this method, powder or chips of the multi-components are sprinkled onto a superheated evaporator to achieve complete evaporation of the multi-components. RF plasma flash evaporation developed by our group has the same principle except that the super-heated evaporator is replaced by rf plasma, and the vacuum chamber is replaced by a soft-vacuum plasma reactor. By these replacements, it was expected that the plasma flash evaporation has peculiar and promising characteristics, such as deposition under high radical flux, large-area deposition, and high-rate deposition in addition with the characteristics of the conventional flash evaporation. In order to develop this method and apply it for the deposition of YBCO superconducting films, we had to overcome two big problems, that is, continuous feeding of aggromerated fine powder into plasma with the precision similar to that achieved by the mass flow controller for gas feeding, and the precise controll of substrate temperature under high heat flux from plasma flame, since the crystal structure and the superconducting characteristics of YBCO films are greatly affected by the deposition rate(R_d) and the substrate temperature(T_s).

Recently, we suceeded to overcome such problems by developing a new-type powder feeder and a substrate holder. By using the improved apparatus, the growth characteristics of YBCO films deposited on (100)MgO and (100)$SrTiO_3$ substrates under 200 Torr were studied as functions of T_s and R_d. It was found that these parameters, as well as the substrate material, governed the growth direction. On (100)MgO, c-axis orientation was observed at T_s > 700°C and 620°C < T_s < 660°C. Moreover, the c axis was oriented at a slower deposition rate(R_d = 40 nm/min), and the a-axis and ab-axis at faster deposition rates:70 and 100 nm/min,respectively, as shown in Fig.7. On the other hand, on (100)$SrTiO_3$, all the films obtained in the range of these experimental conditions revealed only c-axis orientation, while the crystallinity varied slightly at each T_s. The film deposited on (100)$SrTiO_3$ at a temperature of 690°C and a deposition rate of 70 nm/min exhibited a maximal superconducting critical zero point of 90 K as shown in Fig.8.

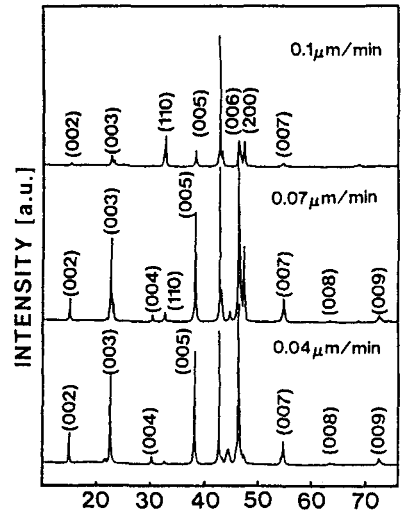

Fig. 7. X-ray diffraction patterns of the YBCO films deposited on (100)MgO substrates at T_s = 680-690°C.(R_d =(a)100, (b)70, and (c)40 nm/min)

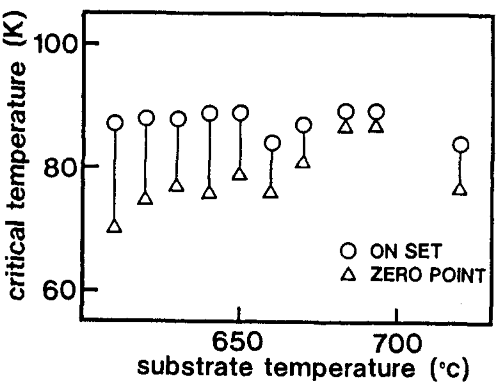

Fig. 8. Effect of T_s on T_c of the YBCO films deposited on (100)$SrTiO_3$ substrates.

Based on these basic studies, as-grown c-axis highly oriented YBCO films with T_c = 91 K and J_c = 6.8 x 10^5 A/cm^2 at 77 K in zero magnetic field have been obtained with a relatively high deposition rate above several hundreds nm/min on $SrTiO_3$ substrate over 7 x 7 cm^2. At this stage, we considered that such prominent feature might be caused by high net flux of atomic oxygen and the deposition of YBCO cluster. Actually, our preliminary experiments confirmed that the order of the atomic oxygen flux is around 10^{18} atoms/cm^2.s, and the existence of few nm YBCO clusters near the substrate surface. These results demonstrate that the new process can fabricate high performance films of advanced functional muticomponent materials like the superconductor at lower cost and in a shorter time than conventional processes, although the processing must be strictly controlled compared with those for the cases of structural ceramics like SiC.

[c] Novel plasma spraying.(Integrated fabrication of solid oxide fuel cell.)(11-14)

Plasma spraying has been used for over two decades in applying to metals and ceramics coatings. In conventional atmospheric dc plasma spraying(APS), however, the structure of the coating is somewhat porous and the bonding strength is not so satisfactory. To overcome these shortcomings, a relatively new technology, namely low pressure plasma spraying(LPPS) has been developed recently. Unfortunately, LPPS also has shortcomings, that is, lower momentum and heat transfer to the particles than for APS, and there still remain many problems concerning spraying of ceramics such as ZrO_2. From the points of view mentioned above, we planned to develop rf plasma spraying(RFPS) and hybrid plasma spraying(HYPS). The large plasma volume and the capability for axial injection were expected to reduce the trajectory variation and to reduce the porosity. However, relatively large-size powders must be used to prevent evaporation because of the longer dwell time of powders in such plasmas. Therefore, if APS and LPPS are named "high-velocity, small-size powder spraying", RFPS and HYPS may be named "low-velocity, large-size powder spraying". Our recent calculation concerning the deformation and solidification of sprayed particle suggested that spraying of large-size powders will make it possible to deposit dense and adhesive coatings compared with the conventional spraying of small size powders. Very recently, this hypothesis was clearly veryfied by experimental investigations in which three different size Ti powders were sprayed on mirror polished SS304 steel and the adhesion strength of the coatings were examined by tensile tests. Figure 9 shows the result which clearly demonstrates the particle size dependence of the tensile strength. Interestingly, the tensile strength is propotional to the particl size, and 40 Mpa, which is a reasonable value for the case of conventional spraying, is evaluated for 30 μm powder spraying.

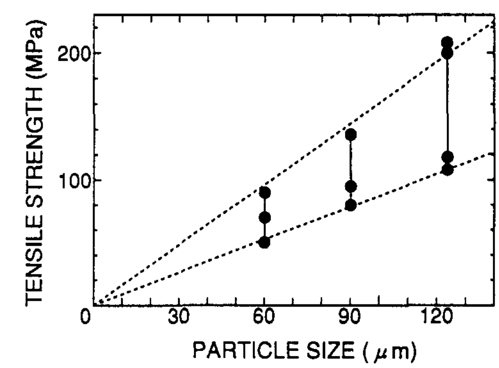

Fig. 9. Effect of sprayed Ti powder size on the adhesion strength between sprayed Ti layer and SS304 substrate.

With these points as background, we have been developing an integrated fabrication process for solid oxide fuel cells(SOFC) with RFPS and HYPS. Fundamental studies concerning particle velocity and deformation showed that the novel plasma spraying processes were mainly characterized by their superior capability for homogeneous heating and spraying large size powders with relatively low particle velocity, and that even the lower particle velocities in RFPS(20 m/s) and HYPS(40-70 m/s) compared with those in APS (100-200 m/s) were found to be sufficient for deformation of impinging molten particles on the substrate. However, RFPS imposed a severe limitation on the substrate position because it led to a short flying distance for the molten particles, especially, for the case of ZrO_2. In this repect, HYPS was considered to be superior to RFPS. With 75 μm YSZ powder, use of HYPS made it possible to get not only dense YSZ coating with relative density higher than 98% but also good gas permeability, lower than 10^{-7} $cm^4/g.s$(2500 mmHg). Moreover, NiO-YSZ cermet and chemically stable $LaCoO_3$ and $(LaSr)MnO_3$ could be prepared as electrodes by Ar-O_2 HYPS. Fig.10 shows preliminary result of the EMF measurement of a 200 μm-thick sample. This electric power density, 500 mW/cm^2, is not particularly high, but the value is acceptable for the film which have enough mechanical strength. Though the detailed cell performance has not been investigated yet, these experimental results have proved that HYPS must be a strong candidate for new aspects of the production of SOFC, especially from economic and engineering points of view.

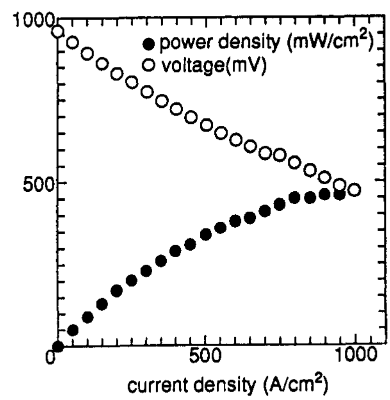

Fig.10. A typical result of the electromotive force measurement of 0.1 mm thick YSZ film deposited by Ar-O_2 HYPS.

VI. SUMMARY

In this paper, we discussed the role of IPP in the coating field, and briefly reviewed the promising IPP for coating. "High-rate and large-area thermal plasma CVD" and "Thermal plasma flash evaporation of muticomonent system" were proposed as two distinctive candidates for the future development of IPP for coating, especially in high performance ceramics technology, though the scientific understanding of the processes is an early stage. Without a doubt, another promising IPP relating to ceramics technology exists in the field of plasma spraying. The novel spray coating techniques such as RFPS and HYPS will open new spraying fields in the near future.

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