Status of Thermal Spray Technology in Japan

K. Taní and H. Nakahira

This article summarizes the present status and prospects for future progress of the thermal spraying business and technology in Japan. Organizations that have supported thermal spraying business and technology consist of coating contract shops, producers and suppliers of spray equipment and consumables, and large companies that have been using thermal spray technology in their production lines. Moreover, outside, noncommercial organizations such as universities, government, or local industrial institutes and academic societies for thermal spraying are reviewed. In terms of thermal spraying equipment, in particular, the installation of atmosphere-controlled plasma spray and high-velocity oxygen/fuel spray (HVOF) are investigated. Typical examples include industrial applications that are performed mainly by coating contract shops and large companies. In emerging spraying process technologies, synthesis of new materials using atmospheric plasma spray and atmosphere-controlled plasma spray, laser-assisted spraying, and new plasma torches are presented.

1. Introduction

THERMAL spraying in Japan is currently developing into one of the most effective surface-modifying techniques for industrial applications. This technique is widely used for various purposes, including for example, cathodic protection for steel structures such as bridges and offshore structures and wear and corrosion resistance for industrial machinery components. Furthermore, functional coatings for advanced technology are also being developed. To achieve this, the performance and property retention abilities of sprayed coatings composed of metallic, ceramic, or cermet materials are becoming increasingly important. Research and development for industrial applications has been carried out primarily due to the cooperation of end users and coating manufacturers.

In this article, a thorough review of the profile of the thermal spray business, developments in industrial applications, and the fundamental research for thermal spraying in Japan are summarized.

2. Profile of the Thermal Spray Market

In discussing the trends in thermal spraying technology in Japan, one of the most salient issues to be considered is the market size of the thermal spray industry. It generally comprises the following activities: contract coating jobs, the production and supply of spray equipment and consumables, and in-house production and application of coatings by large companies in the automotive and aircraft industries. It is reported that approximately 160 or more companies practice thermal spraying, and most of them are coating contract shops.^[1] As yet, not all of the figures for this industry have been included in the statistical data

Key Words: applications in Japan, commercial markets, process trends, status report, thermal spray trends

in this market survey, only those of individual companies, and therefore, the sales totals of contract coating jobs, spray equipment (including consumables such as powder, wire, and rod), and in-house production by large companies have not been identified precisely. However, in 1990, an investigation was carried out by an economic research organization,^[2] in which the sales figures in the thermal spray industry were estimated (Fig. 1).

The estimated annual sales, except for spray equipment including consumables, was about \$758 million (US dollars) in 1990. In this estimation, the sales of coating contract services of the top ten shops reached \$135 million (US dollars), and that of the lower ranking 150 or so shops was \$217 million (US dollars). The remainder, which is estimated at \$406 million (US dollars), is presumed to be the value of in-house production jobs by large companies. According to another source, [3] the sales of thermal spray equipment, systems, and consumables such as powder, wire, and rod reached about \$154 million (US dollars) per year in 1989. This achievement was due to the good business climate of the preceding 4 or 5 years in Japan in which the growth rate of the thermal spray business was 10 to 13%/year. However, the business situation deteriorated in the latter half of 1991, so that the growth rate for the next 1 or 2 years will drop to less than 10%/year.



Figure 1 Estimated sales in the thermal spray industry.^[2]

K. Tani, Thermal Spraying Technology R & D Laboratories, Tocalo Co., Ltd., Kobe, Japan; and the late H. Nakabira, Tocalo Co., Ltd., Kobe, Japan.

3. Activities of Business Circles and Professional Societies

The thermal spray industry is generally considered to be composed of two circles: the business sector and academic societies that support the scientific base of thermal spray technology. Figure 2 shows their activities. The thermal spray business has developed from the achievements of coating contract shops and suppliers of equipment and consumables, which have jointly organized a group named the Japan Thermal Sprayers Association. This group consisted of 66 companies as of Feb 1991, almost all of which were small or medium in size. Some shops have developed thermal spray techniques through contract jobs that have evolved into industry-wide standards. Moreover, some shops have their own capabilities for research and development and for the exchange of technical information overseas. Producers and suppliers also play an important role in developing new information on thermal spraying.

Basic scientific research on spraying phenomena and on the characterization of sprayed coatings, etc., are essential to developing the thermal spraying industry. Besides coating contract shops, large companies such as steel manufacturers (*e.g.*, Nippon Steel and Kawasaki Steel) and heavy-machinery companies (*e.g.*, Hitachi, Ishikawajima-Harima Heavy Industries, Mitsubishi Heavy Industries, and Toshiba) have also researched and developed the technology. Moreover, they regard thermal spraying as a component technology. For heavy-machinery manufacturers, the purpose of thermal spraying is not only for the surface treatment of machine components, but also for the development of new materials using spraying technology. For example, automakers have been developing original applications in various engine components (*e.g.*, oxygen sensors, turbochargers, and disk brakes).

Many professional societies have promoted research and development in thermal spray technology by contributing fundamental research. Significant contributors include:

- High Temperature Society of Japan
- The Iron and Steel Institute of Japan
- The Japan Institute of Metals
- Japan Society of Corrosion Engineering
- The Japan Society of Mechanical Engineers





- The Japan Society for Precision Engineering
- Japan Thermal Spraying Society
- The Japan Welding Society

The High Temperature Society of Japan is one of the major academic societies for thermal spray research and development. Its thermal spray division is composed of three committees: technical information on thermal spray, testing and characterization, and corrosion engineering. Technical meetings are held twice a year. This society is the leader of the organizing committee for ITSC'95, which will be held in Kobe. The Japan Thermal Spraying Society and the Japan Welding Society are also major organizations in the thermal spray field, and technical meetings of each society are held twice a year.

Technical articles and information have been contributed to various transactions and journals, and therefore, the work and impact of academic societies is growing. Thus, although thermal spraying has developed as an effective surface-modification technique, its systematization has been perfected solely through experience, in contrast to more disciplined and established technologies. Theoretical analysis of coating quality and spray phenomena should be systematized technologically. By increasing the technical potential of thermal spraying, up and coming technical fields will be required to be integrated with thermal spray technology. The character of thermal spraying technology should be considered to be interdisciplinary to bring about the integration of science and technologies such as materials science, physics, chemistry, mechanical engineering, etc., and to assist in the development of the industry.

This situation has been recognized so clearly that research and development are performed in organizations, including both coating manufacturers and academic organizations such as universities, colleges of technology, national laboratories, and government or local industrial research institutes. For example, high-energy thermal spraying technologies using low-pressure plasma spray, high-velocity oxygen/fuel spray, and a laser source are being researched at the Welding Research Institute of Osaka University. The invention of functionally gradient materials (FGM) is being researched at the National Research Institute for Metals and at the Steel Research Laboratories of Nippon Steel. Radio-frequency plasma spray process combined with conventional DC plasma also are being studied at the University of Tokyo.

4 Installation of Atmosphere-Controlled Plasma Spray and HVOF

Plasma spraying in a controlled atmosphere is known by several terms including vacuum plasma spray (VPSTM), low-pressure plasma spray (LPPSTM), or low-pressure plasma spray coating (LPC). More than 20 units have been installed in Japan.^[4] The equipment is mainly used by heavy-machinery manufacturers, steelmakers, and a few coating contract shops and is classified by its two uses: research and development and commercial production.^[4] A variety of research and development themes are followed, whereas commercial applications at present primarily involve the MCrAIY coating used on components in aeroengines and stationary industrial gas turbines. Some of the commercially used HVOF equipment is Jet KoteTM and Diamond JetTM. Jet KoteTM has been used mainly to produce WC cermet coatings for over 6 years. Diamond JetTM was introduced to Japan in 1989 for its high-velocity combustion flame. More than 40 units have been installed, mainly in coating contract shops. Its typical application is in the deposition of WC cermet coatings. Other types of HVOF equipment have also been introduced from Europe and the United States; however, these have not been commercially used for production in coating contract shops. Detonation gun equipment developed in Russia has also been installed in a few companies. It has been reported that one of its applications is a chromium carbide cermet coating for heat exchanger tubes in coal-fired boiler facilities for erosion resistance against fly ash.^[5]

5. Coating Applications

5.1 Steel and Nonferrous Industries

The major industrial sectors for which thermal spraying has been applied are

- Steel rolling and finishing
- Aluminum rolling and finishing
- Pulp and paper
- Aeronautics
- Energy
- Automotive
- Others

The steel industry is a large market. Various types of rolls are used in steel rolling and finishing facilities. Typical applications include the continuous annealing line (CAL), continuous annealing and processing line (CAPL), and the continuous galvanizing line (CGL). Figure 3 illustrates a typical layout of a continuous annealing line.^[6] Many thermal sprayed hearth rolls are presently in use in heat treatment furnaces. Table 1 provides a few examples of their coating specifications. An important function of the coating is promoting buildup and pickup resis-

tance for roll surfaces against steel sheet at elevated temperatures. In Japan, the surface quality and mechanical properties of cold rolled or galvanized sheet are highly developed in response to the severe specifications of customers such as automakers.^[7] Consequently, the quality of roll surfaces is essential to keeping productivity high. For these reasons, plasma sprayed cobalt- or nickel-based superalloys, oxide/metal composites, and a chromium carbide cermet are used.^[8]

A HVOF sprayed tungsten carbide cermet coating also is widely used on the process rolls in a continuous galvanizing line for wear and pickup resistance. The WC-Co coating has excellent durability against the molten zinc-aluminum hot dipping bath. Figure 4 shows the typical layout of a continuous galvanizing line.^[9] Protective coatings for the rolls in a galvanizing pot, such as the sink roll, have been developed,^[10] and they have contributed to the production of high surface quality galvanized sheet products.

Besides applications in the steel industry, similar ones have been established in nonferrous metal rolling industries. For example, in aluminum rolling processes, WC cermet coatings are effective for buildup or pickup resistance against aluminum sheet products^[11,12] when they are applied on the bridle and deflector rolls. The coating contributes to the performance retention of roll surfaces and increases productivity by decreasing downtime at such facilities.

5.2 Aeronautical Industry

The principal use of sprayed coatings in the aeronautical industries are applications in various turbine engine components for commercial aviation. An atmospheric plasma sprayed zir-

Table 1Examples of Coating Specifications forHearth Rolls

Composition	Maximum service temperature, °C
Co-based alloy-Cr ₂ O ₃ cermet	~1100
Co-based alloy-ZrO ₂ ·SiO ₂ cermet	~1000
Co-based alloy-oxide carbide cermet	~1050
Cr ₃ C ₂ -NiCr	~950
Z_{rO_2} ·SiO ₂	~900



Figure 3 Schematic of a typical layout of a continuous annealing line facility.^[6]



Figure 4 Schematic of a typical layout of a continuous galvanizing line facility.^[9]

	COMBUSTION CHAMBER	NiCrAlY/ZrO ₂ -MgO (THERMAL BARRIER) Cr ₃ C ₂ -25NiCr (WEAR RESISTANCE)
	BLADE, VANE	CoNiCrAIY/DIFFUSION TREATMENT NiCrAIY/2CaO·SiO ₂ -nCaO·ZrO ₂ (HOT CORROSION RESISTANCE) CoNiCrAIY/ZrO ₂ ·8Y ₂ O ₃ (THERMAL BARRIER)

Figure 5 Coatings for heavy-duty gas turbine components.

conia ceramic coating is widely accepted as a thermal barrier coating. A plasma sprayed copper-nickel-indium coating is commonly used to help minimize fretting wear. However, these specifications have already been completed to the achievements of major engine manufacturers in the United States and Europe. A vacuum plasma sprayed MCrAIY coating for engine blades and vanes is also used in the same applications.

Currently in Japan, few engine manufacturers have developed turbine engines themselves. Consequently, new aspects in the development of sprayed coatings for aeroengines are not expected. However, surface-treated blades and vanes are used extensively as components in heavy-duty gas turbines for power generation.^[13] Figure 5 shows examples of coatings applied to components in heavy-duty gas turbines. These components are sprayed with a NiCoCrAlY alloy by low-pressure plasma spraying followed by diffusion heat treatment.

Recently, an advanced thermal barrier coating composed of a $2CaO \cdot SiO_2 - nCaO \cdot ZrO_2$ bondcoated with NiCrAlY^[14] has been developed. It uses vertical microcracks in the coating to improve

thermal shock resistance. Moreover, an amorphous phase (SiO_2) and a coexisting CaO compound are effective in corrosion resistance against ashes such as vanadium compounds and sodium sulfates. Stationary industrial gas turbines are required to use a lower quality fuel oil containing impurities such as sulfur and vanadium compounds, and therefore, this coating is considered a new thermal barrier and hot corrosion-resistant coating for turbine components.

5.3 Paper Industry

In the paper industry, mirror-finished WC cermet coatings have been applied to the rolls at the coater section of a paperboard-making facility.^[15] This application was developed to replace hard chromium plating. The WC cermet coating, which is superior to chromium plating in wear resistance, has made it possible to install doctoring blades onto the roll surface at all operating times. The retention of a dust-free surface has been significantly advanced.^[16] The retention of surface cleanliness for rolls in paper mills is still a serious problem; consequently, a hy-



Figure 6 Ceramic coatings for oxygen sensors in the automotive engine.^[18]



MATERIAL : PLASMA-SPRAYED AI-SI / POLYESTER

Figure 7 Abradable coating for turbocompressor housing.^[19]

brid surface coating combined with wear-resistant materials and cohesion-preventing agents is being developed.

Surfaces of yankee dryer cylinders for tissue papermaking facilities are coated with a molybdenum matrix nickel alloy. The coated surface is wear resistant against doctor blades and exhibits heat conduction behavior that is more uniform than a cast iron substrate. This coating technique^[17] was introduced from the United States in 1990. A yankee dryer is so large that the spraying and finishing processes are generally required to be performed on site.

5.4 Automotive Applications

Thermally sprayed coatings are widely used in automotive engine components, and automotive companies have developed original applications in house. A typical component is an oxygen sensor composed of a sintered zirconia solid electrolyte for detecting the oxygen concentration in exhaust gas. A schematic view of the cell and a diagram of the control system are shown in Fig. 6.^[18] A platinum electrode of the cell is coated with plasma sprayed zirconia or magnesia-alumina spinel for protection against gas stream erosion.^[19]

Thermally sprayed abradable coatings have been used in aircraft engines for the air seal and improvement of turbine efficiency. Their application in the compressor housings of automobile turbochargers was also developed in 1989.^[19] Figure 7 shows a view of the turbocompressor housing in which an abradable coating has been applied.^[20] The optimum coating material is an aluminum-silicon/polyester composite.^[21] Commercial automobiles incorporating this new type of turbocharger have been on the market since 1989.^[22]

6. New Process Technology

6.1 Development of Functional Materials

National institutes and laboratories and large enterprises have been researching the application of thermal spray as a national project. Some of the components of the solid oxide fuel cell (SOFC), which is used in power generation, are formed by thermal spray.^[23] The performance of spray-formed components, such as their gas permeation and polarization behavior, are being researched.^{124,25]} The invention of functional gradient materials that have properties including a chemical composition that gradually varies are also being investigated.^[26] In thermalspray methods, the practicability of two types of processes has been researched. One is the separate spraying of zirconia-yttria and NiCrAlY using a dual-torch system^[27] and the other is zirconia-yttria and 80Ni20Cr using the same torch in a reduced atmosphere (20 torr).^[28]

6.2 Reactive Low-Pressure Plasma Spraying

The synthesis of composite materials is performed by reactive low-pressure plasma spraying, which forms a nitride by a plasma-assisted reaction. For example, titanium nitride/titanium composite coatings that improve wear resistance and strength at elevated temperatures,^[29] an aluminum-based hybrid material that is reinforced with aluminum nitride and silicon carbide whickers,^[30] and intermetallic compound coatings (IMC) that are composed of an intermetallic compound matrix and nitride^[31] have been developed. One intermetallic compound coating material is being examined as a high-temperature oxidation-resistant material.^[32] For example a titanium-palladium alloy coating is being developed for titanium bulk material using an argon atmosphere vacuum plasma spraying process. An excellent wet corrosion resistance comparable to titanium bulk material has been reported.^[33]

6.3 Radio-Frequency Plasma Spray

Radio-frequency (RF) plasmas have a large high-temperature zone of several centimeters in diameter. The process is performed in an ambient atmosphere, and the velocity of the plasma stream can be as low as several meters per second.^[34] When used for plasma spraying, a sufficient melting of sprayed particles similar to a conventional DC plasma is obtained.^[35] Moreover, combining the RF technique with conventional DC plasma may minimize the formation of porosity within a coating. For example, the synthesis of TiAl₃, MoSi₂,^[36] as a functional gradient material, and spray-formed yttria-stabilized zirconia as a solid electrolyte, and LaCoO₃ and NiO as electrodes for solid oxide fuel cells^[35] are being researched using this process.

6.4 Laser Spray

The modification of sprayed coatings by a laser source is also one of the important themes for research and development organizations in Japan. One is the deposition of a reactive metal such as titanium;^[37] another is the modification of deposited layers by remelting or diffusion with a substrate.^[38-42]As an example of precision thermal spraying, a laser spraying process and a micropowder feed unit are being used in the fabrication of electronic circuitry by depositing thin films of metal and/or ceramics onto a circuit card.^[43]

6.5 Multi-Electrode Plasma Spray

The development of a central powder feed plasma gun is the ultimate achievement, and such a major breakthrough is needed to bring plasma spray coating to new levels of acceptance. A three-electrode plasma torch^[44] and gas tunnel plasma spraying are being researched.^[45]

7. Miscellaneous

7.1 Research on Spraying Phenomena

The analysis of spraying phenomena is important in optimizing spraying conditions. One of the prevailing research themes is measuring the velocity of plasma jets and sprayed particles.^[46-47] Flame-temperature distribution and impact force of sprayed particles are also being studied. The relationship of the plasma jet temperature and its length, the influence of melting conditions of particles, and the influence of particle velocity on adhesion strength have been quantified.^[48]

7.2 Testing and Characterization

There are many unknown factors in the characteristics of thermally sprayed coatings. The determination of cohesive strength between sprayed particles, adhesive strength to the substrate, and residual stress in a coating are typical targets of research. In these fields, newly emerging testing and characterization techniques have been researched. The evaluation of adhesion strength using a glue-free tensile pin test procedure^[49] and a centrifugal device combined with an acoustic

emission testing method have been proposed.^[50]Residual stress analysis is also performed using X-ray diffraction methods.^[51] Physical properties such as thermal conductivity and anisotropy are active research topics.^[52,53]These values are very useful for the design and evaluation of gradient materials.

8. Conclusions

The status of business sectors and academic societies that are the supporting and driving force for the future of thermal spray science and technology has been reviewed. Spray coating applications and the profile and future prospects were investigated. The thermal spray market in Japan has been estimated at more than 100 billion yen (about \$770 million US dollars) per year in the first half of 1992. It is certain that present thermal spray techniques have advanced to the point where they are now looked upon as reliable manufacturing processes. Up to now, the progress of thermal spraying in Japan has owed a lot to the technologies of the United States and Europe. However, in the steelmaking and automotive industries, Japan has superseded the technologies of other countries in the area of thermal spraying. Therefore, thermal spraying activities in Japan may have to develop more innovative applications based on the above achievements to maintain a leadership role.

References

- 1. S. Baba, Ed., A Glance of Thermal Spray Job Shops, Weld. Tech., Vol 39 (No. 8), 1991, p 116-125, in Japanese.
- 2. T. Sugimoto, H. Higashiya, and Y. Miura, Ed., "The Current Status and Future Prospect of Thermal Spray Market," Yano Research Inst., Ltd., Nagoya, Japan, 1991, p 3-6, in Japanese.
- 3. M. Tsumuraya, Booz, Allen & Hamilton Inc., Japan, private communication.
- 4. R. Shida, Marubeni-Plasma Technik, private communication.
- M. Okamoto, Study of Ceramic Coating for Coal-Fired Boiler Tubes, *Therm. Nucl. Power*, Vol 41 (No. 6), 1990, p 767-777, in Japanese.
- 6. S. Ban, M. Ohkura, M. Miyahara, K. Ohnishi, Y Fujimura, and A. Teramoto, A New Continuous Annealing Line and Properties of its Products, *R & D* Kobe Steel Eng. Rep., Vol 33 (No. 4), 1991, p 62-65, in Japanese.
- 7. T. Kanamaru, Hot-Dip Galvanized Steel Sheet, J. Surf. Finish. Soc. Jpn., Vol 42, 1991, p 152-159, in Japanese.
- 8. N. Mifune and H. Nakahira, "The Application of Plasma Process to Hearth Rolls in A Continuous Annealing Line," 2nd Nat. Thermal Spray Conf., Cincinnati, 1988.
- 9. T. Asamura, Recent Developments of Surface Finishing Technology for Sheet Products, *Tetsu-To-Hagané*, Vol 77 (No.7), 1991, p 861-870, in Japanese.
- 10. Y. Harada and K. Tani, Japan patent 1-225761.
- 11. Y. Harada and K. Tani, US patent 4,912,835, Apr 3, 1990.
- 12. Y. Harada and K. Tani, Japan patent 64-87006.
- 13. K. Takahashi and I. Tsuji, The Application of Plasma Spray Technology to Heavy Duty Gas Turbines, *J. High Temp. Soc. Jpn.*, Vol 16 Suppl, 1990, p 227-281, in Japanese.
- 14. H. Taira, M. Ikeda, Y. Harada, and H. Hagiwara, US patent 5,032,557, July 16, 1991.
- 15. H. Nakahira, "Unusual Application by Jet Kote," 11th Int. Thermal Spray Conf., Montreal, Canada, 1986.
- 16. Y. Harada and K. Tani, Japan patent 1-150667.

- S. Melkert and G. Renner, "Wear and Temperature Characteristics of Thermal Sprayed Yankee Dryers," Proc. 1st Nat. Thermal Spray Conf., Orlando, 1987, p 227-281.
- T. Shimizu, The Application of Ceramics and Cermet Thermal Spray Technique for Automotive, *Thermal Spray. Tech.*, Vol 9 (No. 4), 1990, p 49-56, in Japanese.
- T. Itoh and A. Uchikawa, Technical Trend of Oxygen Sensors, J. Soc. Auto. Eng. Jpn., Vol 43 (No. 4), 1989, p 21-27, in Japanese.
- M. Ito, S. Ikawa, K. Murayama, and M. Sano, "Development of Abradable Flame Spray Coating Technology," SAE Tech. Pap. Series, SAE, 910400, 1991, p 1-9.
- N. Miyamoto, M. Nakagawa, T. Tomoda, K. Shimoda, and Y. Hirata, "Development of Abradable Seal Sprayed Coating for Turbo Compressor Housing," Proc. of Ann. Meet. Jpn. Soc. Auto. Eng. Inst., Vol 902, 1990, p 2.81-2.84, in Japanese.
- K. Takama, T. Isogai, T. Kawai, and A. Onishi, Development of CT26-Type Twin Entry-Ceramic Turbochargers, *Toyota Eng.*, Vol 40 (No. 1), 1990, p 113-119, in Japanese.
- 23. Y. Ohno, Y. Koga, A. Monma, K. Tsukamoto, and F. Uchiyama, Electrode Materials for Power Generation (Fuel Cell)—An Application of Sprayed Layers to the Functional Devices, J. Surf. Finish. Soc. Jpn., Vol 41, 1990, p 996-999, in Japanese.
- 24. S. Nagata, Y. Kasuga, K. Hayashi, Y. Kaga, Y. Ohno, and H. Sato, Experimental of 500W Solid Oxide Fuel Cell, *Trans. Inst. Elect.* Eng. Jpn. B, Vol 110 (No. 2), 1990, p 111-120, in Japanese.
- 25. K. Marumoto, S. Aya, and Y. Matsui, Characterization of Solid Oxide Fuel Cell Components by Gas Permeability Measurement, *Trans. Jpn. Soc. Mech. Eng. B*, Vol 56 (No. 532), 1990, p 268-273, in Japanese.
- M. Sasaki and T. Hirai, Fabrication and Properties of Functionally Gradient Materials, J. Jpn. Ceram. Soc., Vol 99 (No. 6), 1991, p 1002-1013, in Japanese.
- T. Fukushima, S. Kuroda, and S. Kitahara, "Formation of Graded Coatings by Thermal Spraying," Proc. Aut. Meet. Jpn. Weld. Soc., Vol 45, 1989, p 230-231, in Japanese.
- S. Kitagichi, N. Shimoda, T. Saito, H. Takigawa, and M. Koga, The Application of Low Pressure Plasma Spray for Fabrication of Functionally Gradient Materials, J. Jpn. Powder and Powder Metall., Vol 37 (No. 7), 1990, p 10-13, in Japanese.
- N. Asahi and Y. Kojima, Low Pressure Plasma Spray Coating, J. High Tem. Soc. Jpn., Vol 10, 1984, p 249-256, in Japanese.
- 30. Y. Tsunekawa, H. Yoshida, M. Okumiya, and I Niimi, Aluminum Matrix Composites Containing Carbide Whiskers Fabricated by Reactive Low Pressure Plasma Spraying, J. Jpn. Light Met., Vol 40, 1990, p 885-890, in Japanese.
- Y. Tsunekawa, Y. Kohno, M. Okumiya, and I. Niimi, Titanium Aluminide Matrix Composite Layers by Reactive Low Pressure Plasma Spraying, J. Jpn. Light Met., Vol 41, 1991, p 164-169, in Japanese.
- M. Yamaguchi, F. Nakamura, and Y. Shirai, Plasticity of Al₃Ti and Possibility of Its Being Improved, *J. Jpn. Light Met.*, Vol 38 (No. 4), 1988, p 228-237, in Japanese.
- 33. T. Suizu, Y. Harada, Y. Takatani, T. Tomita, and G. Hashizume, Corrosion Behavior of the Ti-Pd Coating Using a Vacuum Plasma Spray System, *Corrosion Eng.*, Vol 40 (No. 1), 1991, p 14-18, in Japanese.
- A. Notomi, Y. Takeda, M. Kodama, and T. Yoshida, "Study on Thermal Spraying by Radio-Frequency Plasma," Proc. Ann. Spring Meet. Jpn. Weld Soc., Vol 44, 1989, p 106-107, in Japanese.
- 35. H. Hamatani, T. Kumaoka, T. Yahata, and T. Yoshida, An Integrated Fabrication Process for Solid Oxide Fuel Cells Using Hybrid Plasma Spraying, J. Jpn. Inst. Met., Vol 55, 1991, p 1240-1248, in Japanese.

- S. Takeuchi, T. Okada, T. Yoshida, and K. Akashi, Development of a Novel Spray Coating Technique with a Radio-Frequency Plasma Torch, J. Jpn. Inst. Met., Vol 52, 1988, p 711-718, in Japanese.
- M. Yoneda, A. Utsumi, K. Nakagawa, J. Matsuda, M. Katsumura, M. Aoki, et al, Fundamental Study on Laser Spraying (Report 2)— Thermal Spraying of Pure Titanium, Rep. Gov. Indust. Res. Inst. Shikoku, Vol 21 (No. 1), 1989, p 9-16, in Japanese.
- M. Yoneda and M. Katsumura, Laser Hybrid Processing, J. Jpn. Weld. Soc., Vol 58, 1989, p 427-434, in Japanese.
- Y. Furuya, Y. Yoneyama, and M. Ohsawa, "Surface Modification by YAG Laser Processing," Proc. Ann. Aut. Meet. Jpn. Soc. Precision Eng., 1990, p 159, in Japanese.
- T. Suzuki, M. Itoh, M. Nakahashi, and H. Takeda, Improvement of Plasma Sprayed ZrO₂ Properties by Laser Processing, J. Jpn. Ceram. Soc., Vol 97 (No. 5), 1989, p 571-577, in Japanese.
- 41. S. Hiramoto, M. Ohmine, and T. Morita, Laser Consolidation of Plasma Sprayed Coating of Ni-Cr Self-Fluxing Alloys Containing Carbides, J. High Temp. Soc. Jpn., Vol 16 (No. 5), 1990, p 216-224, in Japanese.
- 42. T. Senda and C. Takahashi, Structural Change in Plasma Sprayed Alumina Coatings by Laser Melting (Part 1)—On Continuous Wave Mode Treatment, J. Jpn. Ceram. Soc., Vol 99 (No. 6), 1991, p 503-507, in Japanese.
- F. Uchiyama and K. Tsukamoto, "A Proposal for Ceramic Circuit Card," Proc. Ann. Meet. Inst. Elect. Eng. Jpn. 1990, p 4-16, in Japanese.
- 44. H. Maruo, Y. Hirata, and J. Kato, "Development of a New Plasma Spraying Torch with Axial Powder Feeding," Proc. 12th Int. Conf. Thermal Spraying, London, 1989, p 50-1-9.
- A. Kobayashi, S. Kurihara, and Y. Arata, Effect of Spraying Condition on Gas Tunnel Type Plasma Spraying, J. High Temp. Soc. Jpn., Vol 15 (No. 5), 1989, p 210-216, in Japanese.
- 46. A. Noutomi and Y. Takeda, Characteristics of Plasma Spray Jet and Particle Behavior, Current Advances in Materials and Processes, *Iron Steel Inst. Jpn.*, Vol 3, 1990, p 319, in Japanese.
- 47. S. Kuroda, T. Fukushima, S. Kitahara, and H. Fujimori, Measurement of Temperature and Velocity of Thermally Sprayed Particles using Thermal Radiation, J. Jpn. Weld. Soc., Vol 8 (No. 1), 1990, p 132-138, in Japanese.
- 48. S. Kitahara, T. Fukushima, and S. Kuroda, Nat. Res. Inst. Met. Tech. Rep., Vol 11, 1990, p 371, in Japanese.
- 49. Y. Inoue, T. Ono, A. Noutomi, A. Izuha, M. Toyoda, and M. Tsukamoto, Adhesive Strength Evaluation of Plasma Sprayed Coating by Tensile Pin Test—Applicability of Stress Singularity Parameter for Evaluating Adhesive Strength of Coating Films, J. Jpn. Weld. Soc., Vol 9, 1991, p 167-173, in Japanese.
- 50. S. Watanabe, S. Miyake, and M. Murakawa, "A Trial in Measuring Adhesion of Sprayed Coating Using Centrifugal Force," Proc. Ann. Aut. Meet. Jpn. Thermal Spraying Soc., Vol 54, 1991, p 71-76, in Japanese.
- K. Tanaka, N. Mine, K. Suzuki, and R. Kawase, X-Ray Residual Stress Measurement of Alumina Detonation Coating, J. Mater. Sci. Jpn., Vol 40, 1991, p 96-101, in Japanese.
- 52. K. Tani, H. Nakahira, K. Miyajima, and Y. Harada, Thermal and Elastic Anisotropy of Thermally Sprayed Coatings, *Mater. Trans. Jpn. Inst. Met.*, Vol 33, 1992, p 618-626.
- 53. Y. Tsunekawa, H. Harada, M. Okumiya, and I. Niimi, Heat Transfer in Thermal Barrier Coating with Gradient Constituents Fabricated by Low Pressure Plasma Spraying, . J. Jpn. Inst. Met., Vol 54, 1990, p 1256-1260, in Japanese.