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Development of Functionally Gradient Materials (FGMs) of Thermal Stress Relaxation Type

Saburo Kitaguchi*1 Nobuyuki Shimoda*1
Hideki Hamatani*1 Yasutomo Ichiyama*1
Tohru Saito*1

Abstract:

One of the technical tasks in the development of reusable spacecraft is the development of airframe heat-barrier materials and propulsion system structural materials that can withstand the punishing thermal environment to be encountered in the outer space. A functionally gradient material (FGM) proposed as a solution to this problem is expected to develop the desired thermal stress relaxation function. Research was made to develop optimum apparatuses and systems for continuously controlling the compositional gradient of a spray-coated ceramic-metal structure using the low-pressure plasma spraying (LPPS) process. This resulted in the development of the FGM fabrication technology. FGM test specimens successfully passed high-heat load environment evaluation tests at the National Aerospace Laboratory, Science and Technology Agency. These results are considered to prove the viability of the new FGM. In this paper, the microstructures of FGM coatings as analyzed by transmission electron microscopy are also discussed.

1. Introduction

Among the technical tasks in the development of reusable spacecraft, apart from the propulsion system development, is the development of airframe heat-barrier materials and propulsion system structural materials that can withstand the punishing thermal environment to be encountered in the outer space. If a metal and a ceramic are to be combined to create strength and toughness along with heat resistance, the most serious issue is the generation of thermal stress that results from the discontinuity of thermal expansion coefficient and Young's modulus from the metal to the ceramic when the composite is exposed to a temperature change. Functionally gradient materials (FGMs) are proposed as one solution to this problem. They are expected to deliver the thermal stress relaxation function as required in the service environment. The FGM is a composite material that has its microelements (such as metal, ceramic, fiber, and micropore constituents) systematically and continuously distributed and controlled so as to develop a function suited to the intended service environment[1].

The purpose of this research is to establish the technology of producing thermal stress-relaxation FGMs with excellent heat resistance and barrier properties by optimizing the thermal stress distribution to minimize fracture damages in the high-temperature-gradient environment in which the material surfaces are exposed to a large temperature variance. CVD, PVD, powder metallurgy, and other processes are studied as methods of fabricating FGM composite structures from the nanometer order to the micrometer order. The present study is designed to continuously control the composition of a sprayed metal-ceramic

*1 Technical Development Bureau

composite coating film by low-pressure plasma spraying (LPPS), so that it will continuously change its physical and other properties and to develop a thermal stress relaxation function in the intended high-temperature environment.

Discussed hereunder are the results of development of the FGM fabrication technology based on LPPS, of analysis of FGM composition and structure by optical microscopy and transmission electron microscopy, and of FGM evaluation tests simulating the actual environment.

2. Study of FGM Fabrication Technology

Plasma spraying supersedes all other spraying processes in the ability to use high-melting-point materials and to accurately control the coating thickness. LPPS, a process for spraying a coating material onto the substrate surface in a large vacuum chamber under an inert gas (such as argon) atmosphere, can overcome the problem of loss of bond strength due to the oxidation of both molten particles and substrate surface as observed with conventional hot spraying in air. The LPPS process is extensively applied as a highly reliable method of depositing superalloy coatings on turbine blades and other aircraft components.

Optimum LPPS apparatus and operating conditions were studied for spraying a mixture of two or more raw material powders that widely differ in melting point and specific gravity. The basic requirements of the FGM fabrication apparatus are that dissimilar molten metal and ceramic particles should be homogeneously mixed in the desired proportions on the planes normal to the thickness direction, and that the desired compositional pattern should be achieved with good reproducibility in the heat flow direction.

The basic considerations in the FGM fabrication operating conditions are that dissimilar raw material powders should be melted with such a high efficiency as to prevent the inclusion of unmolten particles, and that the stability of deposition yield onto the substrate should be maintained irrespective of the compositional proportions in the composite coating.

2.1 Study of FGM fabrication technology

As shown in **Photo 1**, ZrO_2-8wt%Y_2O_3 (YSZ) with excellent heat barrier properties is used as the ceramic to be arranged on the outermost surface that is subjected to a thermal load, and a Ni-20wt%Cr alloy (NiCr) with excellent elevated-temperature properties is used as the metal to be arranged on the other surface that is subject to cooling.

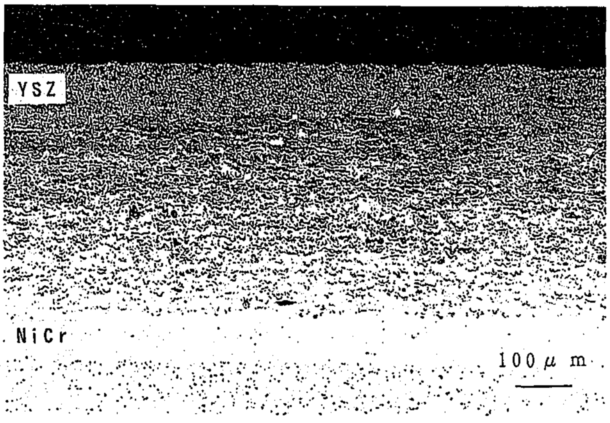

Photo 1 Section through FGM coating deposited by LPPS

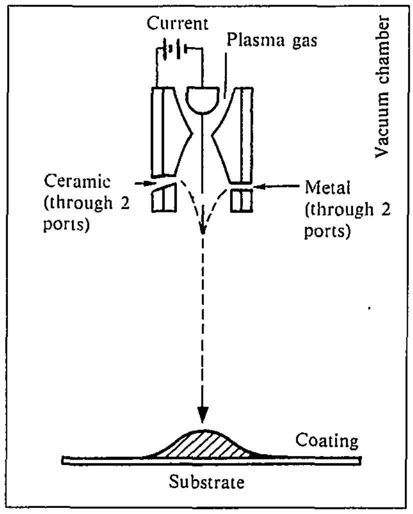

Fig 1 Schematic illustration of low-pressure 1-gun, 4-port spray system

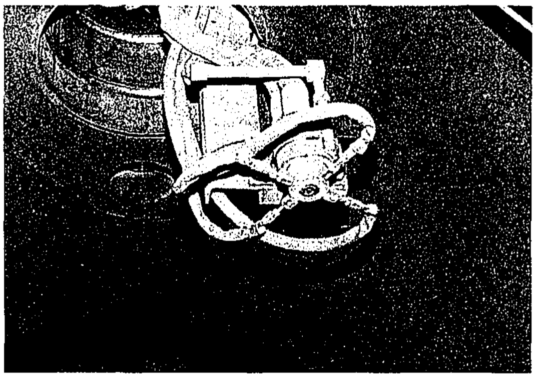
Photo 2 General view of 4-port spray gun

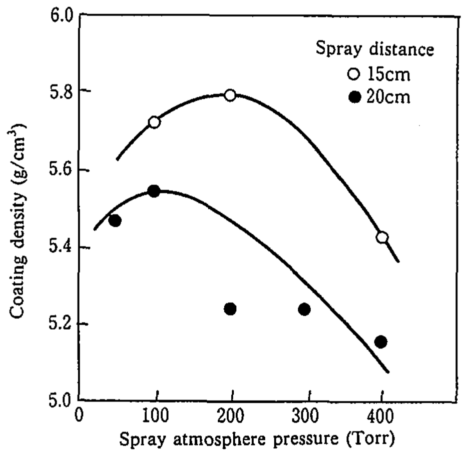

Fig 2 Relationship between spray atmosphere pressure and YSZ coating density

The main features of the spraying system newly developed for FGM fabrication are as shown in **Fig. 1** and **Photo 2**. The spray gun is of the four-port type in which the ceramic and metal powders are simultaneously introduced into the plasma jet through two surrounding ports each. The same type of powdered material is delivered through the diametrically opposite ports so that

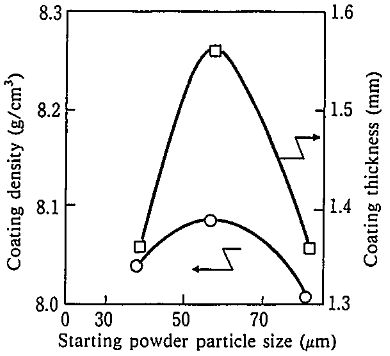

Fig 3 Effect of NiCr starting powder particle size on coating density and thickness

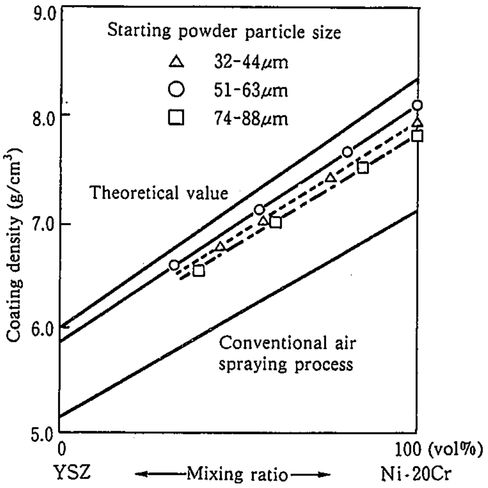

Fig 4 Effect of YSZ/NiCr mixing ratio on coating density

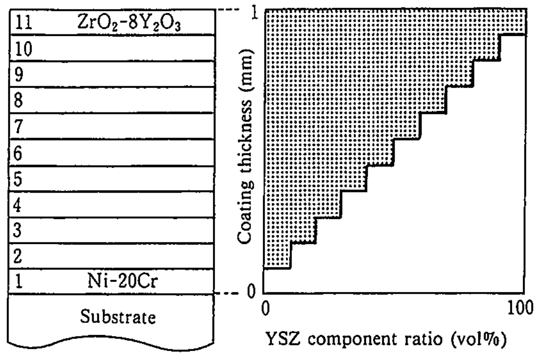

Fig 5 Program setup of YSZ/NiCr powder feed ratio

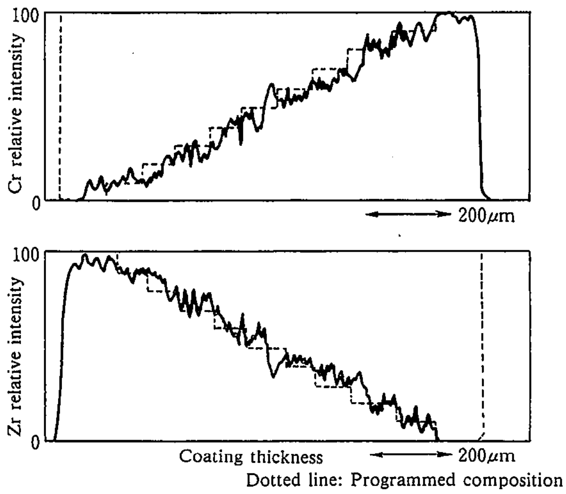

Fig 6 Analyzed coating composition as compared with programmed coating composition

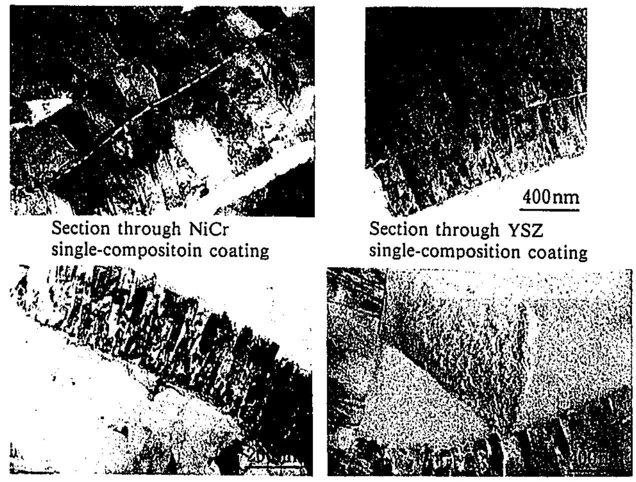

Photo 3 Cross-sectional microstructure of NiCr-YSZ mixed-composition coating

dissimilar particle mixture can be uniformly distributed in the plasma jet while maintaining the necessary axisymmetry with respect to the center of the spray gun. In the optimization of spraying conditions, an original medium-pressure spraying region where the optimum spray atmosphere pressure is in the neighborhood of 200 torr as shown in **Fig. 2** was developed to improve the density of the high-melting point YSZ coating.

The starting powder particle size-dependence of the melting properties of the NiCr powder was studied next. As shown in **Fig. 3**, a high-density coating was obtained with a high deposit ratio when the average particle size was 57 μm. According to this result, a ceramic-metal mixture was sprayed and the effect of the mixing ratio on the composite coating density was investigated. The findings obtained followed the rule of mixtures, as shown in **Fig. 4**. The average metal powder particle size of 57 μm was thus found to provide high densification.

The control of the rate of change in composition in the heat flow direction is directly related to the thermal stress relaxation function. Systematic control with clear intent is therefore emphasized. For example, spraying was programmed with the YSZ/NiCr powder feed ratio shown in **Fig. 5**, and the mixture was automatically sprayed according to the program. The actual and programmed coating film compositions agreed well as shown in **Fig. 6**. This means that the coating film composition can be precisely controlled to meet the coating requirements with diverse constitutional profiles.

3. Study of Spray Coating Microstructure

In the spray coating process, the starting powder is delivered into the high-temperature plasma, and is heated, melted and propelled by the plasma onto the substrate, where it is sequentially deposited and solidified. The microstructure of the sprayed FGM coating consists of three constitutional regions: the YSZ single-composition region, NiCr single-composition region, and NiCr-YSZ mixed-composition region.

TEM reveals characteristic solidification patterns of the FGM coating. As shown in **Photo 3**, the FGM coating section exhibits a columnar grain structure solidified in a direction normal to the substrate surface if the coating is composed of YSZ or NiCr alone. In the mixed-composition region, NiCr exhibits an equiaxed grain structure. As molten YSZ is deposited, NiCr is remelted and surrounded by YSZ with low thermal conductivity. The solidification of NiCr is presumed to proceed at lower rates than in the NiCr single-composition region.

NiCr alone was sprayed by changing the starting powder particle size, and the transgranular solidification structure in the resultant NiCr coating was observed on the sections normal to the coating direction. The grain size was recognized to depend on the starting powder particle size, as shown in **Photo 4**. These results suggest that the transgranular structure of spray coating can be controlled according to the starting powder particle size and the spray thermal hysteresis.

(a) Starting powder particle size: 27 μm　(b) 45μm　(c) 57μm　1μm

Photo 4 Microstructure of NiCr on plane normal to coating direction

Table 1 Results of laser irradiation thermal shock test

Material	Irradiation surface diameter (mm)	Irradiation time (s)	Critical laser output density Pc (W/mm^2)
Non-FGM	10	1.0	> 8.5
FGM	10	1.0	20

4. Results of FGM Evaluation Tests Under Thermal Load

The laser irradiation thermal shock test method can determine heat damage properties under transient thermal load conditions with small specimens (30 mm in diameter). It is highlighted as a new evaluation method in the FGM field[2]. The thermal shock properties of FGMs made by the LPPS process were investigated by using Nippon Steel's 5-kW CO_2 laser. The specimen was placed on the table, laser irradiated for 1 s, and cooled in air. The laser output divided by the irradiation area of the specimen is called the laser output density, and the minimum laser output at which the specimen is cracked is called the critical laser output density. The laser irradiation area was determined from the burn pattern of an acrylic plate. When a FGM coating is compared with a uniform non-FGM coating, the critical laser output density with the FGM coating is about two times as high as that with the non-FGM coating, as shown in **Table 1**.

At the Kakuda Research Center of the National Aerospace Laboratory, Science and Technology Agency, the YSZ-NiCr FGM is tested in a high-temperature-gradient environment simulating the actual service environment. More specifically, the performance of the YSZ-NiCr FGM is evaluated by the high-temperature gradient field test in which an FGM specimen is irradiated with an 30-kW Xe arc lamp under vacuum and by the high-temperature gas flow test (see **Photo 5**) in which a FGM specimen is directly exposed in a low-pressure chamber to a high-temperature and high-velocity simulated air stream obtained by the combustion of oxygen, hydrogen and nitrogen adjusted in mixing proportions. Each FGM specimen is forcibly cooled on the other surface by liquid nitrogen or the like. The FGM specimens are repeatedly heated locally in the former test method, and are generally heated in the latter test method. The FGM specimens performed well in both tests. These test results can be interpreted as meaning that the properties of FGM coatings deposited by the LPPS process are validated under the specified test conditions. **Photos 6** and **7** respectively show an FGM specimen after the high-temperature gradient field evaluation test and its cross section.

5. Conclusions

Research and development made on the technology of fabricating FGMs by LPPS led to the establishment of an optimum FGM spraying process. The particle grain structure of FGM coatings was observed by TEM. The thermal stress relaxation function

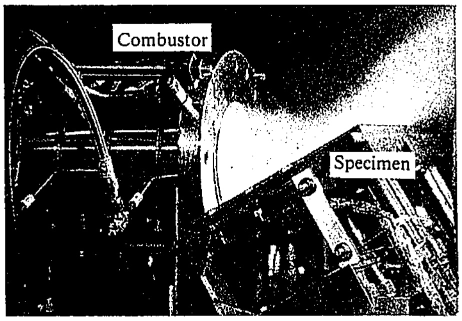

Photo 5 General view of high-temperature gas stream evaluation test (joint research by National Aerospace Laboratory of Science and Technology Agency and Nippon Steel)

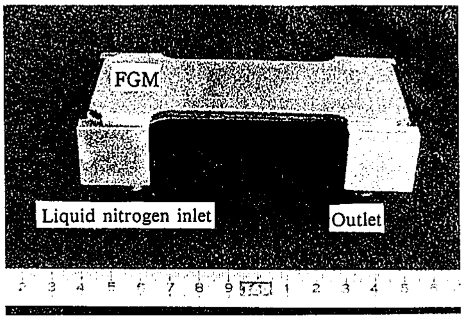

Photo 6 Specimen after high-temperature-gradient field evaluation test (joint research by National Aerospace Laboratory of Science and Technology Agency and Nippon Steel)

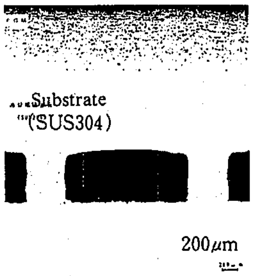

Photo 7 Section through specimen after high-temperature gradient field evaluation test

of the FGM coatings was demonstrated in evaluation test methods simulating the actual environment of use.

(1) A one-gun, four-port spraying system was developed for spray coating a YSZ-NiCr FGM, and spraying conditions were established in the medium-pressure region where the spray atmosphere pressure is in the neighborhood of 200 torr. The spaying system and conditions proved extremely effective in mixing and melting different starting powder materials for the deposition of YSZ-NiCr mixed-composition coatings.

(2) When the coating is composed only of YSZ or NiCr, the microstructure is a columnar grain structure having directionality normal to the substrate. When the coating is composed of both YSZ and NiCr, the microstructure is an equiaxed grain structure, which is due probably to the remelting of NiCr by the heat of molten YSZ particles accumulating in the surrounding area.

(3) FGM coating specimens were exposed to a wide temperature difference between the top and bottom surfaces in simulated environment evaluation tests. In these tests, the coating specimens demonstrated the thermal stress relaxation function as originally planned, in terms of thermal fatigue properties under repeated high heat irradiation and heat resistance and barrier properties in a high-temperature and high-velocity simulated air stream.

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