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学位論文題目	A New Concept in Functionally Graded Thermal Barrier Coatings Using Cold Spray Technique (コールドスプレー法を用いた傾斜機能遮熱コーティングの新構想)
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## 論文内容要約

In gas turbine plants, increased turbine inlet temperatures are required to improve the thermal efficiency of the plant and reduce the emission of greenhouse gases. However, gas turbine blades can experience damage and failure at high temperatures. To prevent this from happening, surfaces of the gas turbine blades must be protected by TBCs. However, the observed failures of these conventional TBC systems mainly result from the thermal expansion mismatch between the ceramic and metal coating layers. To overcome this mismatch, FGMs have been introduced into the TBCs, resulting in novel materials called FG-TBCs. These materials are sprayed in the form of multi-layered coatings, the composition of which varies in the thickness direction from 100% metal (applied directly to the substrate) to 100% ceramic for the top coat. Until now, several processing techniques have been explored to fabricate FG-TBCs, including plasma spraying, powder metallurgy, and in situ syntheses. Despite these studies, the optimum process for the fabrication of FG-TBCs still remains unknown. In this research, the cold spray technique was used to fabricate FG-TBCs in one step due to some advantages of this method. However, there are also some disadvantages that limit the utilization of the cold spray technique for fabricating FG-TBCs for bond coats and top coats, such as the necessity of using expensive He gas and difficulty to fabricate brittle materials. Therefore, the chapters in this thesis were devoted to solving the problems related to the utilization of the cold spray technique.

In the TBCs, CoNiCrAlY utilized in bond coating is one of the most commonly used materials to improve the adhesive force and resistance to anti-hot corrosion between the bond coat and the top coat. Recently, the cold spray technique has been very useful in fabricating CoNiCrAlY bond coats. However, large amounts of expensive helium gas are required to fabricate bond coats with satisfactory properties. To solve this problem, the effect of the Ni metal powder addition on the properties of the obtained CoNiCrAlY coatings was investigated in Chapter 2. In order to reduce total production costs and improve the deposition efficiency of the CoNiCrAlY coatings, pure Ni metal powder was added to CoNiCrAlY, and the resulting powder was cold-sprayed using N<sub>2</sub> as a carrier gas. Furthermore, high-temperature oxidation behavior of the obtained Ni-containing CoNiCrAlY coating was investigated.

In order to reduce total production costs and improve the deposition efficiency, Ni-CoNiCrAlY coatings were successfully deposited on Ni-based superalloys by cold spraying using N<sub>2</sub> gas. The obtained results showed the possibility of producing CoNiCrAlY coatings at low kinetic energies by using Ni metal powders. However, undesired Ni oxide species were formed on the

$\text{Al}_2\text{O}_3$  TGO layer after heat treatment due to the excessive Ni contents. These Ni oxides can lead to faster delamination between the top coat and bond coat in TBCs. Therefore, pretreatment in the environment with low oxygen partial pressures is required to prevent the formation of Ni oxides and encourage the formation of stable  $\text{Al}_2\text{O}_3$  species. Such a pretreatment is very effective in preventing Ni oxide formation and encouraging the formation of stable  $\text{Al}_2\text{O}_3$ . Consequently, TBCs with Ni–CoNiCrAlY bond coats deposited after pretreatment should have longer lifetimes than those manufactured without pretreatment. However, the pretreatment procedure is very complex and not suitable for fabricating FG–TBCs in one step using the cold spray technique.

In Chapter 3, C–CoNiCrAlY (ceria/CoNiCrAlY) cermet powders were used as bond coat materials. In Chapter 2, Ni powders were utilized to reduce the total production cost and improve the deposition efficiency for the CoNiCrAlY bond coats. However, it was found that excessive Ni oxide species were formed on the  $\text{Al}_2\text{O}_3$  TGO layers after heat treatment due to the excessive Ni contents. Therefore, in Chapter 3, the effect of ceria ceramic powder addition to the CoNiCrAlY coatings was investigated. In previous studies, small amounts of ceria were added to the bond coat materials to improve the bond strength between the bond coat and top coat caused by the wedge-like TGO layer. However, the cold spray technique is not suitable for fabricating ceramic/metal coatings. To solve this problem, cermet powders were introduced in this chapter to deposit the C–CoNiCrAlY powders.

In order to reduce the total production cost and improve the deposition efficiency, C–CoNiCrAlY coatings were successfully deposited on Ni-based superalloys by cold spraying using  $\text{N}_2$  gas. Cermet powders are very efficient in depositing ceramic materials and fabricating C–CoNiCrAlY coatings at low kinetic energies. The C–CoNiCrAlY cermet powder was effective in improving the bond strength caused by the wedge-like TGO layers at operating temperatures. The wedge-like TGO layer formed by ceria enhanced the bond strength between the TC and BC, but the added ceria (as compared to the original Ce addition) produced fast oxidation rates, which resulted in the complete oxidation of all sides after 300 h. The growth rate of the wedge-like TGO layer was very high. Therefore, it can be concluded that further studies, in which oxidation growth rates are controlled by varying the amount of added ceria, should be conducted.

In Chapter 4, mechanically agglomerated and sintered YSZ/CoNiCrAlY cermet powders and the corresponding cold-sprayed coatings were investigated to confirm the possibility of using them as materials for FG–TBCs. The effect of cermet powders was confirmed for the cold spraying described in Chapter 3. In this chapter, the cermet powders containing well-distributed YSZ particles were utilized to investigate the mechanical properties and coating mechanism by the cold spray technique.

The YSZ/CoNiCrAlY cermet powders were successfully deposited by the cold spray process. The obtained results showed homogeneous microstructures because the feedstock powders were mechanically blended and agglomerated to form spray particles. No metal oxidation was observed for the cold-sprayed deposited surfaces, and the hardness of the coatings deposited by cold spraying exceeded that of the powders by almost a factor of 5, which indicated that the Y-cermet coating was characterized by increased hardness compression due to its deposition by cold-spraying. However, different mixtures of the Y-cermet powders exhibited dependences of the hardness and deposition efficiency properties on their YSZ contents. Therefore, different manufacturing conditions

are required to obtain high-quality coatings, depending on the YSZ contents. It was confirmed that the cold spray technique is a suitable method to manufacture FG–TBCs using Y-cermet powders (especially considering its low costs and simplicity). However, some remaining issues, such as pore formation and generation of cracks under high pressure, must be resolved before this process can be implemented commercially.

In Chapter 5, possible reasons for simple delamination at high temperatures and the related issues were investigated. The ceria was already confirmed to improve the adhesive strength and control the direction of cracks in Chapter 3. Therefore, in this chapter, the ceria powder was applied to improve the bond strength of the cermet coating layer.

In the case of the 25Y–cermet coating, a weight gain was observed at high temperatures, which reached  $0.013 \text{ g cm}^2$  after 20 h of oxidation. On the other hand, the delamination did not occur for the C25Y–cermet coating despite the long oxidation time. The corresponding weight gain for the C25Y–cermet coating was small compared to that for the 25Y–cermet coating (about  $0.08 \text{ g cm}^2$  after 300 h of oxidation), which became stabilized at longer oxidation times. The added ceria showed high efficiency in preventing simple delamination, high weight gain, and formation of pores. However, the related mechanism describing the effect of added ceria on these properties still needs to be investigated. The formation of the  $\text{Cr}_2\text{O}_3$  layer is an important part of the studied process. It was assumed that the  $\text{Cr}_2\text{O}_3$  layer was formed on the top of the  $\text{Cr}_2\text{O}_3$  in the same way as for the bond coat, in which  $\text{CeO}_2$  easily absorbed oxygen, oxidized Al, and formed  $\text{Al}_2\text{O}_3$  species inside the coated layers. In a similar way, Al depletion occurred, and  $\text{Cr}_2\text{O}_3$  was formed on the top of the coated layers. The resulting  $\text{Cr}_2\text{O}_3$  prevented the influx of diffused oxygen and the related weight increase. The obtained results exhibit low oxidation rates (compared to that for the 25Y–cermet coating), thus preventing delamination. However, other possible oxidation mechanisms may also exist. In addition, coatings containing 25 and 50 Y–cermet powders with well-distributed YSZ particles were successfully deposited for the FG–TBCs by cold spraying. In the case of the FG–layer, no delamination was observed due to the oxidation caused by the  $\text{CeO}_2$  addition. The obtained oxidation results indicate that  $\text{CeO}_2$  addition produces a significant effect on the delamination and oxidation properties that result in weight increase.

In summary, the cold spray system was proven to be a suitable technique for fabricating FG–TBCs. The cermet powders and ceria are significant components that improve strength and lifetimes of the FG–TBCs produced by this method. However, additional studies are required to successfully apply this process to the FG–TBCs commercial manufacturing.