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論 文 内 容 要 旨

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_2 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_2 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 Al_2O_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 Al_2O_3 species. Such a pretreatment is very effective in preventing Ni oxide formation and encouraging the formation of stable Al_2O_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 Al_2O_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 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 compete 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 the of the 25Y−cermet coating, a weight gain was observed at high temperatures, which reached 0.013 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 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 Cr_2O_3 layer is an important part of the studied process. It was assumed that the Cr_2O_3 layer was formed on the top of the Cr_2O_3 in the same way as for the bond coat, in which CeO_2 easily absorbed oxygen, oxidized Al, and formed Al_2O_3 species inside the coated layers. In a similar way, Al depletion occurred, and Cr_2O_3 was formed on the top of the coated layers. The resulting Cr_2O_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 CeO_2 addition. The obtained oxidation results indicate that 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.

論文審査結果の要旨

先進火力発電用ガスタービン (GT) 動静翼に必要不可欠な遮熱コーティング(Thermal Barrier Coating: TBC)においては，高温環境下での使用により，トップコート (TC) /ボンドコート (BC) 界面に熱成長酸化物層（Thermally Grown Oxide: TGO）が形成し，各層における熱膨張係数の違いから熱応力によるコーティングのはく離や脱落が危惧される。そのため，各層間の熱応力緩和や耐はく離性の向上が急務の課題となっている。はく離抑制のためには，TC と BC の比率を段階的に変化させた傾斜機能材料 (Functionally Graded Materials: FGM) が有効であるが，TC はセラミックスであり大気圧プラズマ溶射 (Air Plasma Spray: APS) による施工が望ましく，BC は金属であり施工中の高温酸化を抑制するため減圧プラズマ溶射 (Low pressure plasma spray: LPPS)による施工が望ましく，両材料の融点，機械的特性等が異なるため，1 つのプロセスで TC と BC を混合させた層を得ることは難しい。本論文では，上記の問題を解決するために，粒子を溶かさずに固相のまま成膜可能なコールドスプレー(CS)法を応用し，セラミックスと金属から成るサーメット粉末の利用によって傾斜機能 TBC の開発に関する基礎的かつ基盤的知見を得ている。本論文は，これらの研究成果をまとめたものであり，全編 6 章からなる。

第 1 章は序論であり，本研究の背景，目的および本論文の構成を述べている。

第 2 章では，CS 法を用いた CoNiCrAlY 合金ボンドコートの施工に関し，軟質な純 Ni との組み合わせによる成膜を可能にしている。ボンドコート材料としては，これまで多くの GT 動静翼に使用されてきた CoNiCrAlY 合金を対象とするが，硬いを CS 法で施工することは困難であった。軟質な金属材料との組み合わせは，安価な窒素ガスにおける成膜も可能とし，工業的に大きく貢献する成果である。しかし，過度の Ni 含有は，高温中での使用により NiO の高温酸化物を生成し，長時間の利用によっては界面強度を低下させる点を指摘している。

第 3 章では，第 2 章における高温酸化の問題を解決するために，セラミックス材料である CeO_2 を CoNiCrAlY 合金と混合された造粒サーメット粉末を開発し，硬いセラミックス粒子によるピーニング効果と造粒粉末による破砕のし易さから成膜に成功している。さらに，本ボンドコート材料では，CeO_2 添加によりボンドコート内部に成長するくさび状酸化物が生成・成長し，このくさび状酸化物によって，基材との界面強度の向上にも成功している。本成果は，CS 法によるボンドコート材料の成膜効率を向上させることのみならず，界面強度向上による TBC の長寿命化にも大きく貢献する知見である。

第 4 章では，　傾斜機能(FG)を有する TBC 成膜のため，トップコート材料であるイットリア安定化ジルコニア(YSZ)と CoNiCrAlY の比率を変化させ混合したサーメット粉末を開発している。これまでに YSZ を CS 法で成膜した事例はなく，本研究の結果は世界に先駆けた研究成果である。また，YSZ と CoNiCrAlY の比率を変化させた粉末は，YSZ が 75%までは成膜可能であることを示している。ただし，各層間における接合強度が，不安定な高温酸化のために不十分である点を指摘している。

第 5 章では，第 4 章で認められた界面強度不足を解決するために，第 3 章で使用した CeO_2 粉末を FG-TBC 層に混合したサーメット材料を開発している。CeO_2 添加により，界面強度および皮膜の破壊じん性値が向上し，さらに遮熱性を向上させる気孔率の増加も確認している。本成果は，FG-TBC 実用化の可能性を示すことができ，工学的かつ工業的に大きく貢献する結果である。

第 6 章は結論である。

以上要する本論文は，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を提案・実証することにより，ガスタービンの効率向上ならびに長寿命化を可能にさせる有益な成果であり，機械システムデザイン工学ならびにコーティング工学の発展に寄与するところが少なくない。

よって，本論文は博士(工学)の学位論文として合格と認める。