Nanoscopic Analysis of Cold Sprayed GaN Particle Deposition Behavior

著者	Zhou Shaoyun
学位授与機関	Tohoku University
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ぞう　しゃおゆん
氏　　　　　　名　Zhou Shaoyun
研究科，専攻の名称　東北大学大学院工学研究科（博士課程）機械機能創成専攻
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(コールドスプレー法による GaN 粒子付着挙動のナノスコピック解析)

論 文 審 査 委 員　主査　東北大学教授　小川　和洋　東北大学教授　足立　幸志
東北大学教授　千葉　晶彦　　教授　Thomas Klassen
（Helmut-Schmidt-Universität）
東北大学准教授　市川　裕士

論文内容要約

Carbon neutrality by 2050 cannot be realized through ordinary efforts. Against this backdrop, many countries have formulated a strategy that specified 14 promising fields to accelerate efforts toward structural changes in the energy and industrial sectors and undertake bold investments for innovation. Simultaneously, concerning the extreme demand for energy, renewable and exploitable energy supplies are essential, such as nuclear fusion or solar energy. Significant research work has been done to reduce pollution and its environmental effects.

Based on carbon recycling, the photocatalysis technique shows promising pathways toward solar energy conversion, energy storage, and environmental remediation. As inspired by natural photosynthesis and through harvesting solar energy as the source of renewable energy, photocatalysis has been regarded as green and sustainable technology that attracted the interest of scientists worldwide. photocatalysis will make significant impacts in the areas of (1) water splitting into hydrogen (H_2) and oxygen (O_2), (2) CO_2 reduction to energy fuels, (3) degradation of pollutants, (4) selective organic transformations, and (5) bacterial disinfection, respectively. For photocatalyst reaction, reusability and correlated conversion efficiency are crucial considerations. As for reusability, immobilization of the photocatalyst as a thin film would be easier for separation between photocatalyst and pollutant. Moreover, the microstructure morphology of the surface is a critical factor that governs photocatalyst efficiency. Above all, fabricating the high deposition efficiency of photocatalyst in film states would be the primary objective. Compared to TiO_2 and ZnO, GaN has outstanding chemical stability in both acidic and basic solutions, and its continuous H_2 production and low degradation in activity. Besides, considering several disadvantages remained in conventional methods to fabricate GaN coatings, low-pressure cold spray (LPCS), appears to be a promising alternative technique that is a well-established technique and offers the possibility of morphology adjustment to contribute to higher photocatalytic performance. Therefore, fabricating the high deposition efficiency of nano-porous GaN photocatalyst coating by a low-pressure cold spray process would be the primary objective.

The cold spray is a novel and promising solid-state material deposition process, which was initially developed as a coating technology in the 1980s. During the cold spray process, coating builds up layer-by-layer in the solid state, originating from particle kinetic energy rather than thermal energy. Accordingly, this allows for the avoidance of defects such as oxidation, phase transformation, and thermal residual stress. Thus, thermally sensitive materials and dissimilar materials could also be used during the cold spray process. Moreover, for a technological breakthrough in cold spray viability, the deposition mechanism has always been a focal research topic continuously investigated. So far, most studies are dedicated to pure metal coatings and have already achieved good results. The most crucial requirement for metal deposition occurs only when the particle velocity exceeds critical velocity. Also, it has been revealed that the bonding is dominated by nano-scale metallurgical reactions originating from localized high-strain-rate plastic deformation. Consequently, the natural oxide films are destroyed to induce metallic bonding by creating new metal-on-metal interfacial contacts. Notably, the natural oxide films have already proved that inhibit metal deposition. Conversely, scarce studies have focused on brittle ceramic materials owing to the difficulties in plastic deformation. Thus, for wide-industrial applications, considerable efforts are still needed to understand the mechanism between ceramic and other materials.

For the research background, there are three main issues to be overcome:

(1) The difficulty of the high-velocity impact of brittle ceramic particles via the low-pressure cold spray process is a huge challenge due to poor plasticity.

(2) Achieving GaN coatings via a low-pressure cold spray process for its photocatalytic property has been unexplored before.

(3) Besides, scarce studies have been reported on the deposition mechanisms for nitride ceramic coatings, especially GaN coatings by the low-pressure cold spray process.

The main objectives of this thesis are:

(1) To demonstrate the possibility of fabricating GaN coatings via a low-pressure cold spray process.

(2) To develop deposition efficiency for the photocatalytic property.

(3) To elucidate the deposition mechanism of GaN coatings under ductile substrate for wide-industrial applications.

Frontier conclusions were drawn in detail in separated sections.

In Chapter 2, the feasibility of fabricating low-pressure cold sprayed nano-porous GaN coatings were successfully demonstrated for the first time. On the basis of splat test results and quantitative analyses under different spray temperatures and pressures, 400°C and 0.6 MPa were determined to be the best spray conditions of temperature and pressure. Upon the impact on the substrate, owing to the dissolution by van der Waals forces and electrostatic forces, the agglomerated micrometer-sized GaN particles consequently disintegrated. Concurrently, a higher number of deposited disintegrated particles would be detected near the nozzle axis of the traversed area. Furthermore, the comparatively higher impact energy obtained for particles that originate from the highest gas pressures and temperatures would improve the fragmentation of the agglomerated particles and significantly enhance the deposition efficiency for the low-pressure cold spray process. Concurrently, based on the cross-sectional observation by FIB at the tilt of 45°, no discernible permanent deformation of the substrate was characterized.

Subsequently, in an effort to further validate the best spray condition from splat tests, multi-pass tests were carried out under stainless-steel substrates for 16 passes at six spray conditions. The difference in average thickness and roughness were measured at different gas temperatures and pressures. Thereafter, various substrate pretreatment was utilized to obtain different substrate roughness for the coatings formation process, they are as received, sand-blasted, laser cleaning, and sand-blasted + laser cleaning, respectively. The results indicated that the relatively higher roughness of the substrate surface could provide higher roughness and thickness for the properties of the coatings.

In Chapters 3 and 4, the deposition mechanism between nitride ceramic particles and metallic substrate via low-pressure cold spray process by compressive air and N_2 gas is compared and elucidated. According to scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), and transmission electron microscope (TEM)) observation and analysis, the main deposition mechanism involving four phenomena is proposed, and further examination of the interfacial oxide layer effects on nitride ceramic coatings and the function of the interfacial amorphous layer is obtained. Based on these conclusions, these novel findings may provide evidence for GaN-metal joints. Moreover, the proposed methods to explain the mechanism may be extended to other ceramic-metal combinations and subsequently provide effective methods for adhesion between them.

The coating is formed through severe fragmentation and coordinated deformation of the micro-sized agglomerated and super-agglomerated particles, resulting in solid particle/particle bonding. Furthermore, compared to as-received substrates, sandblasted substrates possess a higher roughness, improving the mechanical interlocking for the first layer formation.

Due to the advantages of ease of operation and significant contrast, Fresnel imaging mode is an effective means to differentiate particle boundaries and cavities. Based on the results, the nano-sized GaN particles remain around 70 nm from feedstock to coating. No significant indication of grain refinement suggested that the cold spray deposition mechanism of brittle particles does not mainly rely on that.

Before cold spray, the original oxide layer thickness of the nano-sized particles of feedstock is rather insignificant, except for only 1.34 nm of the initial oxide layer for agglomerated particles surface. Besides, the stainless-steel substrate surface exhibits a 12.10 nm thick oxide layer. Subsequently, the oxide layer thickness of inner deposited GaN particles is approximately 4.20 ± 0.47 nm after cold spray. Crucially, the original oxide layer on the stainless steel 304 substrate was drastically damaged by the successive impacts exerted by the GaN particles. Meanwhile, a new oxide layer, around 18.1 nm thick, is formed at the coating/substrate interface. Referring to thermochemical data of pure substances, the possible oxides are demonstrated. According to the tests and analysis, after cold spray, the newly-generated oxide layer detected near the interface (particle/particle and particle/substrate) is mainly composed of Ga_2O_3 and distributed in the coating part.

The high-resolution transmission electron microscopy (HRTEM) characterization revealed localized amorphization near the particle/particle boundaries and particle/substrate interface. The domains located relatively far from the particle/particle and particle/substrate interfaces in the coating sample, as well as the nano-sized GaN feedstock, exhibited defect-free crystal fringes, whereas a high density of dislocations is displayed close to the interface regions. Therefore, high strain rates induced the formation of amorphous structures at their fringes and a relatively high density of dislocations. Furthermore, the dislocations demonstrated that nano-sized GaN particles endure plastic deformation during the cold spray process. Dislocation is a lattice imperfection of crystalline materials. Based on the TEM observations and references, the dislocations were driven by the severe particle impact induced by the cold spraying. Meanwhile, given that the diameter of the initial nano-sized GaN particles detected reduced insignificantly, plastic deformation of nano-sized particles is conceivable and generated by dislocation movement during the cold spray process.

The phenomenon of local heteroepitaxy needs to fulfill the requirements of aligned parallel lattice planes and similar interplanar distances. Generally, when lattice mismatch is lower than 10%, it can be considered heteroepitaxy. Thus, the presence of a local heteroepitaxy that facilitates the adherence of GaN particles to stainless steel surfaces was revealed.

Therefore, local heteroepitaxy detected between the GaN and stainless steel with the formation of Ga_2O_3 is regarded as a critical factor that promotes the adhesion between the coating and substrate. Besides, sufficient O_2 concentration of propellant gas would improve the formation of Ga_2O_3 near the interface. Suppose the oxide layer is considered to constitute a barrier to metallurgical bonding for metal-to-metal contact through the cold spray. In that case, the oxide layer at the ceramic particle/metallic substrate interface may not be. As a result, interfacial oxidation may be significant in bonding between ceramic particles with metallic substrates.

Above all analysis results, at the nanoscale, the deposition mechanisms of GaN coatings under metal substrates are dominated by four aspects. First of all, mechanical interlocking could be improved by the increase of substrate roughness. Secondly, boundary amorphization is induced by a high strain rate and rapid cooling down. Thirdly, the chemical oxidation reaction proven the presence of newly-generated Ga_2O_3 layer which detected near the interface of the nitride ceramic coatings and metal substrate via low-pressure cold spray process for the first time. And finally, local heteroepitaxy phenomenon which induced by low lattice mismatch and parallel lattice planes are obtained and considered beneficial effect for the particle deposition.

In Chapter 5, the NOx decomposition test was conducted to evaluate the photocatalytic performance compared to cold-sprayed GaN coatings and GaN powder. Besides, the spray information, including roughness and thickness, was measured at corresponding gas spray conditions. Higher decomposition of NO gas was evaluated for the cold-sprayed specimen under UV light (10-400 nm) (approximately 33%) than for the GaN powder (at 24%), which can be reasonable to speculate that the evolution of the coating surface morphology with the surface area enhancement and no degradation in the photocatalytic property. The obtained nano-porous GaN coatings exhibited a high specific surface area and visible light absorption presumably resulting from the fragmentation of original GaN feedstocks. Therefore, improvement of the photocatalytic performance of the GaN coatings was effectively achieved by increasing the roughness or thickness via a low-pressure cold spray process. Besides, x-ray diffraction (XRD) was applied to study the crystal structure of the GaN powder and coatings samples. The crystalline orientation associated with each peak was identified and presented, 11 peaks correspond to the crystalline phase's different orientations and are well-matched to the pdf cards of the hexagonal wurtzite structure GaN (JCPDS, No. 74-0243). Above all, no phase transformation was detected from initial feedstock states to coatings states of the cold spray process, which also demonstrated no degradation of photocatalytic performance. To comprehend the evolution of the width in the diffraction peak, Williamson–Hall method was used for estimating the lattice strain and crystallite size. Consequently, the Williamson-Hall method exhibited rather significant changes in the crystallite size from GaN powder to coatings. However, a substantial increase in the intrinsic strain after cold spray induced a broadening of the XRD peaks.

Finally, the novel conclusions of the studies performed in the abovementioned framework were drawn in Chapter 6. This novel finding obtained can effectively support a more expanded range of ceramic/metal combinations in the future.