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研究課題名（和文）Elucidating the deposition and film formation mechanism of plasma-assisted aerosol deposition (PAD) process

研究課題名（英文）Elucidating the deposition and film formation mechanism of plasma-assisted aerosol deposition (PAD) process

研究代表者

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研究成果の概要（和文）：In this project, I developed the single particle (coating built-up unit) concept to investigate the PAD mechanism. The behavior of the single particle deposition was investigated by using a multi-layer high-speed shutter (to avoid the huge number of particle depositions).

研究成果の学術的意義や社会的意義
The single particle concept was promising to clarify the coating formation and bonding mechanisms of the new coating region of PAD. It was helpful to promote technology development and enable the formation of thick and dense coatings on different shapes of objects from flat to 3D.

研究成果の概要（英文）：Plasma assistance aerosol deposition (PAD) is a coating technology the process is based on the utilization of plasma assistance for the fine particles at very high speed. However, it is difficult to understand the PAD bonding mechanism during coating formation due to the deposition of a huge number of particles at the same time. In this project, I developed the single particle (coating built-up unit) concept to investigate the PAD mechanism. The behavior of the single particle deposition was investigated by using a multi-layer high-speed shutter. The PAD spray mechanism goes through the plasma surface activation of the particle without melting. Then the activated fine particles are accelerated by high-velocity gas flow to impact and stuck on the substrate via room temperature impact consolidation mechanism. During the deposition, the activated surface layers acted as a glue and increased the binding between the deposited particles, thereby improving the deposition efficiency.

研究分野：Material processing and microstructure control

キーワード：Plasma assistance AD　Single particle　Bonding mechanism　Deposition mechanism

１．研究開始当初の背景 Background of the initial start of the research

Aerosol deposition (AD) hard coatings are used in semiconductor and several thin film applications. But the low deposition rate and difficulty of 3D coverage limits AD applications in thick film fields. In AIST, we successfully improved the deposition rate 20 times and enabled the 3D coverage by plasma assistance to AD (PAD). However, the deposition and film formation mechanism of PAD is not completely clear yet. Thus, it is difficult to clarify plasma assistance, particle adhesion and complete PAD mechanism during coatings formation, where huge number of particles are sprayed and deposited on substrate on same time under high velocity.

２．研究の目的 Research Objectives

The objective of this study is proposing a new concept to clarify the PAD mechanism via elucidating the mechanism of individual single particle (coating build-up unit), from flight in plasma to impacting on substrate and coating formation to establish an innovative technology. The focus was given to use Al_2O_3 powder, as standard material used for PAD development and elucidating the adhesion mechanisms of the individual single particle (starting coating build-up unit). Furthermore, the process optimization towards development of homogeneous coatings on different shapes and accurate evaluation of the fabricated coating properties were investigated in comparison with the coatings fabricated by conventional plasma spray technique.

３．研究の方法 Methods of Research

The inflight behavior was investigated via the development of individual single particles concept, via:

- Deposition of only single particle on the substrate by using multi-layer high speed shutter in front of the substrate and elucidating the adhesion phenomenon on the substrate.
- Investigating the relation between the plasma and the PAD process parameters: plasma power, plasma gas type and its flow rate, chamber pressure, spray distance to realize stable PAD deposition on different substrates and different shapes.
- Investigating the phase composition and grain size, surface microstructure and grain boundary, mechanical properties (hardness, young modules) of fabricated PAD coatings compared to conventional coatings.

４．研究成果 Research results

4-1 Elucidating the Al_2O_3 single particle impacting behavior during PAD process:

Figure 1 shows the surface morphology and cross-sectional images of single particles. It reveals that, upon impacting the ceramic particle goes through particle fracture and deformation on the substrate via impact consolidation. The initial stage of deposition started with a very thin layer of less than 100 nm. During the further deposition, the undulations of the interface became larger, and particles were buried in the substrate.

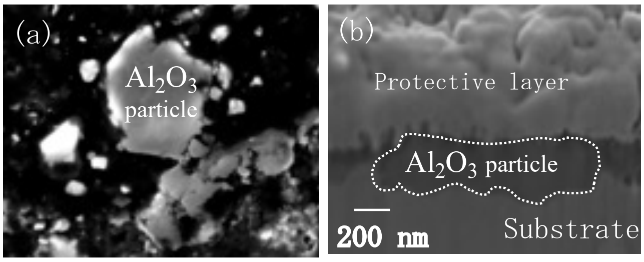

Figure 1, Secondary electron images of the deposited single Al_2O_3 particles deposited by PAD (a) surface microstructure (b) cross-section images after FIB cutting.

Therefore, the PAD spray mechanism goes through the plasma surface activation of the particle without melting. Then the activated fine particles are accelerated by high-velocity gas flow to impact and stuck on the substrate via room temperature impact consolidation mechanism. During the deposition, the activated surface layers acted as a glue and increased the binding between the deposited particles, thereby improving the deposition efficiency. Based on this finding the process window was optimized to fabricate thick and dense Al_2O_3 coatings as follows:

4-2 Dense ceramic coatings on flat and complex shaped objects:

Dense coatings were fabricated on flat as well as complex objects for wide range of 3-D applications as shown in Fig. 2. The obtained coatings were homogeneous with a uniform nanocrystalline structure with no obvious cracks or pores at the microscale. Furthermore, homogeneously uniform coating with a strong adhesion has been fabricated successfully on cylindrical substrates with 6.3 mm diameter. The phase analysis revealed that the fabricated PAD coatings consisted mainly of α-Al_2O_3 phase which is same as starting powder phase [1, 2].

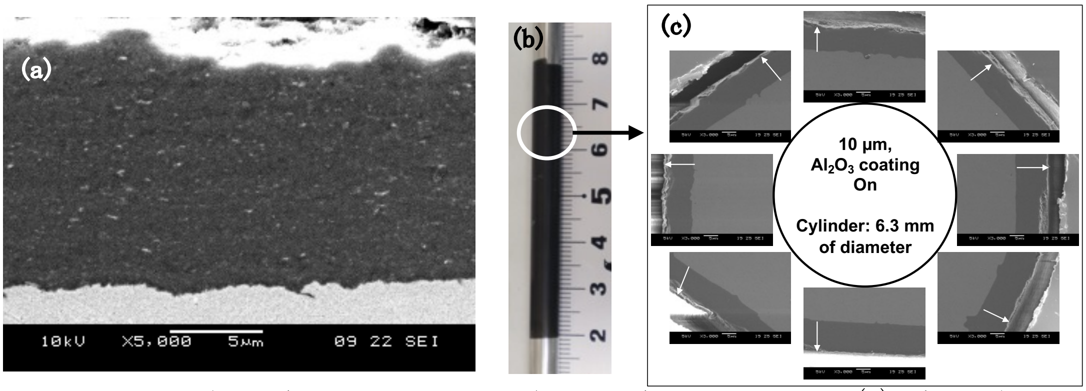

Figure 2, Secondary electron images of the PAD Al_2O_3 coatings on (a) flat substrates, (b) 3D shaped cylinder of 6.3 mm of diameter, and (c) cross-section of (b).

This indicated that, melting of Al_2O_3 particles was unlikely during the PAD process, thus if the particles melted, the metastable γ-phase would have appeared in the phase composition. The measured crystallite size of the prepared PAD coating was 6.7 ± 2.8 nm. We confirmed that the crystallite size in the film was approximately 7 times smaller than the crystallite size of the raw material powder (45 ± 6.3 nm). This reveals that the average crystallite size of the prepared PAD coating is like that of the previously reported conventional thin AD coating [3]. In a previous study, the crystallite size of an AD coating measured using the Hall method was typically in the range of 10-20 nm. Furthermore, during PAD spraying the plasma activated the surface of the particles then the activated particles impact and stuck with the substrate and the activated surface act as glue and improved the deposition efficiency and 3D capabilities.

4-3 Statistical evaluation of mechanical properties of dense PAD coatings:

To realize the practical applications, fundamental and accurate evaluation of their mechanical properties and determine the influence of their microstructure on the mechanical properties is required. Therefore, the mechanical properties of the fabricated PAD Al_2O_3 coating were evaluated in comparison with the conventional APS coating by the nanoindentation test. The Vickers hardness of PAD coatings was approximately 1400 Vickers hardness (approximately 15 GPa) [3].
The hardness and elastic modulus were derived from the load displacement curve using the Oliver and Pharr technique and compared with conventional plasma spray coatings. The variation of mechanical properties, which were obtained using the nanoindentation method, of PAD coatings was extremely small and smaller than that of plasma-sprayed coatings Fig. 3. Therefore, statistical evaluation of distribution of the mechanical properties by using the Weibull plot:

$$lnln\, 1/(1-p) = mlnH - mlnx\_0$$

Thus, Weibull coefficient (m) is the slope of the Weibull plot, and it is representing the variation in each characteristic. The observed homogeneity in the mechanical properties of PAD is attributed to the fine coating structure at the nanoscale, less pores, and cracks than plasma-sprayed coatings, and it was clear that:

- Hardness and modulus distributions of HAD coatings are very narrow.
- HAD Weibull coefficient showed an extremely smaller variation in mechanical properties.
- Variation in elastic modulus of HAD is close to the bulk body, with a nice uniformity.

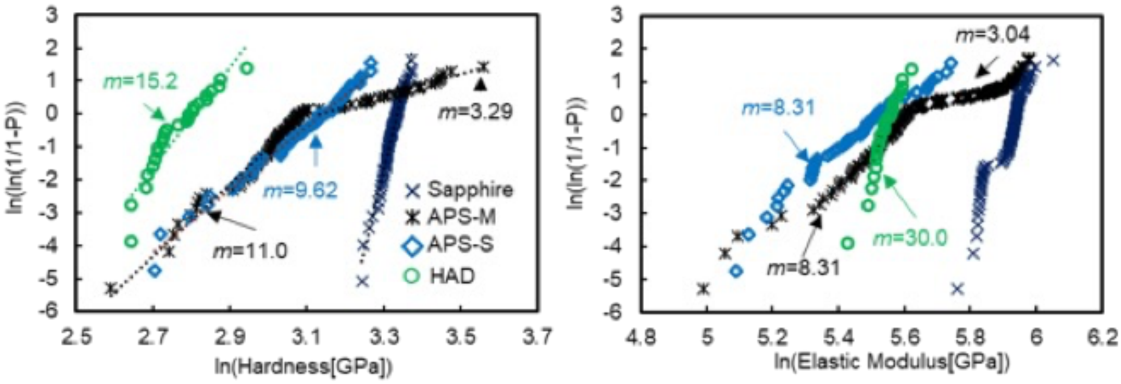

Figure 3 Weibull distribution of the hardness of APS and PAD Al_2O_3 coatings.

4-4 Dense Al_2O_3 coatings on different substrate materials and mechanical properties:

Utilization and optimization plasma activation significantly enhances the deposition of ceramic coatings on wide range of substrate materials. Highly dense and well-adhered Al_2O_3 coatings without obvious observable cracks and bulk-like properties were successfully fabricated on different substrate materials of SUS 304, Aluminium, Al_2O_3 and glass, via PAD of fine particles [4, 5].

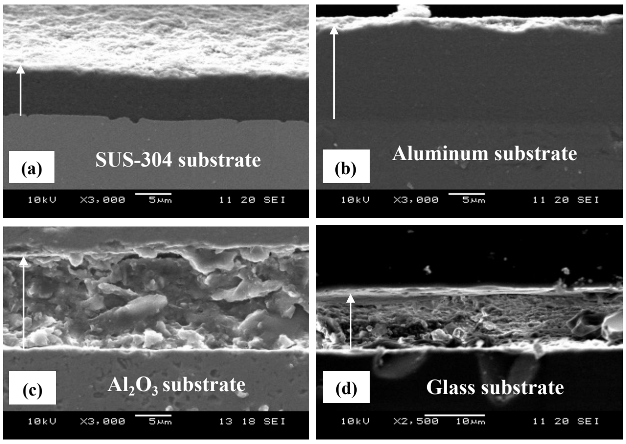

Figure 7 Secondary electron image of the cross-section microstructure of the coatings fabricated on different substrate materials of, (a) SUS-304, (b) Al, (c) Al_2O_3 and (d) glass.

The substrate material and its hardness significantly influenced the first deposition step, which determined the coating adhesion and properties. Coating hardness and the dominate bonding mechanism are related to substrate hardness, can be explained as follow:

- Metallic substrates are ductile, so enable strong film anchoring due to plastic deformation of its surface by the 1st impacting particles.
- Hard ceramic substrates microscopically did not show the classic anchoring layer. It is related to the sur-face roughness; thus, the interface was smoother compared to the metallic substrates. In addition, the ductility is another factor, thus hard ceramic substrate seems not ductile enough to enable the plastic de-formation of their surface with the 1st impacting particles.
- Hard ceramic substrate may require higher particle velocities to form a clear adhering layer.

4-5 Evaluation of the through-thickness effect on mechanical properties:

The hardness and young' s modulus distributions along the through-thickness direction showed a significant difference across the coating-substrate interface and tended to show a slight decrease by 10-15% as the measured position went close the surface [6]. Increasing the hardness and young' s modulus on the substrate side near the interface is presumably related to the peeing effect of the substrate as well as the increase of interface roughness during the room temperature impact consolidation (RTIC) and deformation of the hard ceramic particles on the substrate. The decrease in the coating' s mechanical properties along the through-thickness direction is related to the particle deformation tendency during the coating build-up. At the beginning stage of the deposition, initial particles are impacting on a metallic substrate which is ductile enough to facile plastic deformation and the deposited layer can have an enough hammering effect by the subsequent impacting particles. The hardness and young's modulus in this location are 15.6 GPa and 246 GPa, respectively, and the highest through the thickness in case of the stainless-steel substrate. However, the later particles are impacting on a hard ceramic surface (initially formed HAD Al_2O_3 layers), which hardly undergo plastic deformation or led to less particle deformation. Furthermore, the effect of Nozzle on the particles velocity during PAD process was investigated towards process stable deposition [7].

Research summary:

A new concept of single-particle investigation was developed to clarify and realize a better understanding of the new coating regium of PAD. Furthermore, this research results significantly promoted to expand the process development into deposition on different shape objects and different materials as important factors towards practical process development and application. In addition, accurate statistical evaluation of the coating's properties compared to the conventional techniques was introduced.

Furthermore, the research results pave the way for future developments in understanding the bonding mechanism with different substrate materials.

(1) **Mohammed Shahien**, Kentaro Shinoda, Jun Akedo, Hybrid aerosol deposition as an outstanding prospective for dense barrier ceramic coatings deposition on different substrates, Proceeding of the International Thermal Spray Conference and Exposition (ITSC 2022), 2022, pp. 709-715.

(2) **Mohammed Shahien**, Kentaro Shinoda, Masato Suzuki, Yong Fan, and Norihiko Iki, Hybrid Aerosol Deposition Process and Its Applicability Towards Carbon Neutrality, Proceeding of the 9th Tsukuba International Coating Symposium (TICS 9), 2022, pp.27-28.

(3) Kosuke Sanami, **Mohammed Shahien**, Atsushi Yumoto, Jun Akedo, Kentaro Shinoda, Evaluating the Mechanical Properties of Dense Hybrid Aerosol Deposition Alumina Coatings Using the Nanoindentation Method, Journal of Thermal Spray Technology, Vol 32, 2023, pp. 729-736

(4) **Mohammed Shahien**, Kentaro Shinoda, Jun Akedo, Hard Dense Ceramic Coatings on Different Substrate Materials, Proceeding of the 9th Tsukuba International Coating Symposium (TICS 9), 2022.

(5) **Mohammed Shahien**, Kentaro Shinoda, Jun Akedo, Hybrid aerosol deposition as an outstanding prospective for dense barrier on different substrates, Journal of Thermal Spray Technology (Under Review).

(6) **Mohammed Shahien**, Kentaro Shinoda, Hybrid Aerosol Deposition of Dense Al2O3 Coatings and Evaluation of the Through-Thickness Effect, Proceeding of the International Thermal Spray Conference and Exposition (ITSC 2023), PP. 443-449

(7) Yuki Akedo, Eishi Kubota, **Mohammed Shahien**, Masato Suzuki, Jun Akedo, Takayasu Fujino, Kentaro Shinoda, Effect of Convergent-Divergent Nozzle on Fine Particle Velocity in low-pressure Induction Plasma Jet in Plasma-Assisted Aerosol Deposition, Journal PLASMA CHEMISTRY AND PLASMA PROCESSING, (Under Review).

５．主な発表論文等

〔雑誌論文〕　計6件（うち査読付論文　4件／うち国際共著　1件／うちオープンアクセス　3件）

１．著者名	４．巻
Sanami Kosuke、Shahien Mohammed、Yumoto Atsushi、Akedo Jun、Shinoda Kentaro	32
２．論文標題	**５．発行年**
Evaluating the Mechanical Properties of Dense Hybrid Aerosol Deposition Alumina Coatings Using the Nanoindentation Method	2022年
３．雑誌名	**６．最初と最後の頁**
Journal of Thermal Spray Technology	729～736
掲載論文のDOI（デジタルオブジェクト識別子）	**査読の有無**
10.1007/s11666-022-01518-6	有
オープンアクセス	**国際共著**
オープンアクセスではない、又はオープンアクセスが困難	該当する

１．著者名	４．巻
Mohammed Shahien, Kentaro Shinoda	5
２．論文標題	**５．発行年**
Hybrid Aerosol Deposition of Dense Al2O3 Coatings and Evaluation of the Through-Thickness Effect	2023年
３．雑誌名	**６．最初と最後の頁**
Proceeding of the International Thermal Spray Conference and Exposition (ITSC 2023)	443-449
掲載論文のDOI（デジタルオブジェクト識別子）	**査読の有無**
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オープンアクセス	**国際共著**
オープンアクセスとしている（また、その予定である）	－

１．著者名	４．巻
Mohammed Shahien, Kentaro Shinoda, Masato Suzuki, Yong Fan, and Norihiko Iki	12
２．論文標題	**５．発行年**
Hybrid Aerosol Deposition Process and Its Applicability Towards Carbon Neutrality	2022年
３．雑誌名	**６．最初と最後の頁**
Proceeding of the 9th Tsukuba International Coating Symposium (TICS 9)	27-28
掲載論文のDOI（デジタルオブジェクト識別子）	**査読の有無**
なし	無
オープンアクセス	**国際共著**
オープンアクセスではない、又はオープンアクセスが困難	－

１．著者名	４．巻
Mohammed Shahien, Kentaro Shinoda, Jun Akedo	12
２．論文標題	**５．発行年**
Hard Dense Ceramic Coatings on Different Substrate Materials	2022年
３．雑誌名	**６．最初と最後の頁**
Proceeding of the 9th Tsukuba International Coating Symposium (TICS 9)	45
掲載論文のDOI（デジタルオブジェクト識別子）	**査読の有無**
なし	無
オープンアクセス	**国際共著**
オープンアクセスではない、又はオープンアクセスが困難	－

１．著者名 Mohammed Shahien, Kentaro Shinoda, Jun Akedo	４．巻 DVS 380
２．論文標題 Hybrid aerosol deposition as an outstanding prospective for dense barrier ceramic coatings deposition on different substrates	５．発行年 2022年
３．雑誌名 Proceeding of the International Thermal Spray Conference and Exposition (ITSC 2022)	６．最初と最後の頁 709-715
掲載論文のDOI（デジタルオブジェクト識別子） 10.31399/asm.cp.itsc2022p0709	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 －

１．著者名 Kosuke Sanami, Mohammed Shahien, Atsushi Yumoto, Kentaro Shinoda, Jun Akedo	４．巻 DVS 380
２．論文標題 Evaluation of Mechanical Properties of Dense HAD Al2O3 Coatings by Nanoindentation method	５．発行年 2022年
３．雑誌名 Proceeding of the International Thermal Spray Conference and Exposition (ITSC 2022)	６．最初と最後の頁 453-460
掲載論文のDOI（デジタルオブジェクト識別子） 10.31399/asm.cp.itsc2022p0453	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 －

〔学会発表〕　計4件（うち招待講演　0件／うち国際学会　4件）

１．発表者名 Mohammed Shahien, Kentaro Shinoda
２．発表標題 Hybrid Aerosol Deposition of Dense Al2O3 Coatings and Evaluation of the Through-Thickness Effect
３．学会等名 The International Thermal Spray Conference and Exposition (ITSC 2023), Canada（国際学会）（国際学会）
４．発表年 2023年

１．発表者名 Mohammed Shahien, Kentaro Shinoda, Masato Suzuki, Yong Fan, and Norihiko Iki
２．発表標題 Hybrid Aerosol Deposition Process and Its Applicability Towards Carbon Neutrality
３．学会等名 The 9th Tsukuba International Coating Symposium (TICS 9), Tsukuba, japan（招待講演）（国際学会）（国際学会）
４．発表年 2022年

1．発表者名 Mohammed Shahien, Kentaro Shinoda, Jun Akedo
2．発表標題 Hard Dense Ceramic Coatings on Different Substrate Materials
3．学会等名 The 9th Tsukuba International Coating Symposium (TICS 9), Tsukuba, japan（招待講演）（国際学会）（国際学会）
4．発表年 2022年

1．発表者名 Mohammed Shahien, Kentaro Shinoda, Jun Akedo
2．発表標題 Hybrid aerosol deposition as an outstanding prospective for dense barrier ceramic coatings deposition on different substrates
3．学会等名 The International Thermal Spray Conference and Exposition (ITSC 2022)（国際学会）
4．発表年 2022年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

－

6．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

7．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

8．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関