Room temperature impact consolidation and application to ceramic coatings: aerosol deposition method

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Coating processes that purely use collision pressure or impact force such as the aerosol deposition (AD) method and cold spray method have been attracting attention. These methods accelerate microparticles and ultrafine particles into a beam at velocities of several hundreds of m/s or more that impacts a substrate, thus forming dense films with good adhesion forces by only providing purely mechanical energy. It is thought that microparticles of metals and ceramics can thus be macroscopically bonded at room temperature while remaining in a virtually solid state. In fact, the AD method has been commercialized as an important coating process in the field of semiconductor fabrication equipment which has been confirmed to be able to form thin or thick dense films of ceramics with microcrystal structures on the scale of several tens of nm or less at room temperature that offer excellent electromechanical properties. This is called room temperature impact consolidation (RTIC), and is thought to have different principles of film growth from thermal spray coating and shock compaction techniques which obtain bonding by putting the raw material particles into a molten or semi-molten state. This paper describes the deposition mechanism of AD processes that use RTIC and the importance of this as a coating technique for the future.

Key-words : Aerosol deposition, Ceramic layer, Room temperature impact consolidation, RTIC, Brittle-ductile transition, Dynamic-recrystallization, Shock compaction, Fine powder, Battery, Dye sensitized solar cell, Hard coating

1. Introduction

Research into microparticle impact phenomena has been conducted for a long time in fields such as space science, high pressure physics, defense, and aerospace engineering with the aim of improving the shielding of spacecraft against meteorites and space debris, improving the armor performance of weapon systems, and also with the aim of synthesizing new materials. The shock loading and shock compression effects that are discussed within this research are due to shock waves that are transmitted within a material based on purely mechanical processes, and cause changes to the material structure that differ from normal mechanical action and heat action. As a result, it is not hard to envision microparticles that have collided with a substrate strongly adhering under certain conditions to cause some kind of film growth phenomenon.

At the start of the 1970s, Ide et al. attempted to use this kind of microparticle impact phenomenon in film growth technology, and began using the electrostatic particle impact deposition (EPID) technique for the first time in Japan as a technique for electrostatically accelerating microparticles. Furthermore, at virtually the same time, a device employing similar principles called macron beam (USA)3 was being studied as an experimental technique for nuclear fusion and ultrahigh pressure physics. Next, studies into methods of accelerating microparticles or ultrafine particles by gas carrier started in the 1980s, including the gas deposition (GD) method4 of Hayashi et al. in which metal ultrafine particles with a high surface activity formed by gas evaporation methods are mixed with a gas and accelerated through a fine nozzle and sprayed onto a substrate to form a coating, and the cold spray (CS) method of Papyrin, Alkimov, et al. in which metal microparticles in the solid state are mixed with gas and sprayed onto a substrate material under atmospheric pressure at ultrasonic velocities to form a film.

The GD method actively uses the fact that submicrometer ultrafine particles suspended in gas are virtually unaffected by gravity and reach the same velocity as the carrier gas in an extremely short time. By using an inert gas as the carrier gas, adhesion occurs between ultrafine particles formed inside a vacuum chamber while maintaining the surface activity of the ultrafine particles, and it is possible to form a metal film pattern with a thickness of 10 μm and line width 100 μm or more. In contrast, in the
CS method, low melting point metal particles with diameters of several μm or more that can be used for spraying are carrier ed by gas and sprayed onto a substrate material under atmospheric pressure. Although the device configuration basically closely resembles regular low-pressure thermal spraying equipment, it is not accompanied by the formation of plasma. The name comes from the fact that the films are grown at lower temperatures compared to thermal spraying methods, and recently there has also been research activity in Japan on the similar shot coating method.9) The GD method differs from thermal spraying equipment in that film growth does not occur unless the particle velocity is accelerated to over 500 m/s even for low melting point materials such as aluminum and copper, and an ultrasonic nozzle and a hot gas at around 500 °C is used, and this offers the advantage of film growth under atmospheric pressure. Although the growth of robust metal films of several millimeters or more in thickness in just a few minutes has been confirmed, the growth of films using purely ceramic materials has not been successful.10) Other methods that use gas carrier that have been studied include using the supersonic cluster beam deposition method in which the raw particle size is reduced to the cluster size to attempt to grow carbon material and SiC films and to create microstructures.11) Furthermore, in the field of thermal spray technology, research has started attempting to improve film properties and obtain new functions by fabricating nanocrystalline films by creating submicron ultrafine ceramic particles under high pressure like the gas evaporation method in chemical vapor deposition and spraying this onto the substrate at ultrasonic velocities, such as the hypersonic plasma particle deposition (HPPD) method.12,13) This can also be viewed as a nanocrystalline film growth technique that uses a “build-up process” similar to the GD method.

In contrast, there has recently been a focus on a process called the aerosol deposition (AD) method14–19 which is able to perform dense thick ceramic coatings at room temperature by carrier ing dried ceramic microparticles of particle diameter from μm to several μm in gas while still in the solid state and spraying them onto a substrate material under reduced pressure. Together with the previously studied CS method, this set of film growth techniques are also called kinetic spray methods in the field of thermal spraying.20,21) A major feature is that dense films can be formed by impacting the raw material particles into the substrate while still in the solid state instead of the molten or semi-molten state like in conventional thermal spraying techniques. From both a logical and practical perspective, this is a departure from conventional coating techniques, and holds the possibility of overcoming the problems that face conventional coatings. In the AD method in particular, a phenomenon has been noted where solid state room temperature ceramic particles deposit onto the substrate without pores at high density and high strength under conditions of absolutely no thermal assistance and without heating the substrate, and this is called room temperature impact consolidation (RTIC).14,16–18) This demolishes the conventional thinking that “ceramics are created by sintering raw material particles at high temperature”, and is expected to attract applications. Since it does not involve high-temperature annealing, it is expected to offer advantages such as being able to grow ceramic films that have nanoscale crystal structure and composite structures.

This report introduces RTIC which is the core of the AD method, the principles and characteristics of film growth using RTIC, and examples of practical applications, and explains development trends regarding these both inside and outside of Japan. It also introduces the current state of applications in fully solid-state batteries in which research has been progressing in recent years, flexible dye sensitized solar cells, and applications as a hard coating on resin substrate materials.

2. AD method

AD is a method of forming a coating by mixing microparticle and ultrafine particle raw material prepared in advance by some other method into gas to create an aerosol, and spraying this onto a substrate through a nozzle as shown in Fig. 1. If you imagine the method of spraying the particles as if from a sand blaster in a low-pressure environment, this is close to the reality. Normally, mechanically crushed ceramic powder of particle diameter 0.08 to 2 μm is used for the raw material microparticles. The ultrafine particles carrier ed by the gas are easily accelerated to several hundred m/s through the nozzle. The kinetic energy of the raw material particles accelerated by the gas carrier is converted into localized heat energy through the collision with the substrate, and it is thought that this realizes welding between the substrate and particles and between particles. However, the mechanism of this energy conversion cannot be said to be fully understood. Recently, it has become possible to form high density transparent ceramic coatings at room temperature at high growth speed by using a ceramic raw material powder with the AD method and adjusting the particle diameter, mechanical properties, etc. and selecting the appropriate film growth conditions for RTIC to occur. Heating of the substrate while spraying the raw material microparticles on the substrate and heat treatment after film growth are not performed. Furthermore, this phenomenon occurs in the same way also not only for ceramic materials but also for metal materials.18,22

Virtually no amorphous layers or external phases are seen between the crystal grains in the fine structure of the ceramic film formed by RTIC by the AD method as shown in Figs. 2(A)–2(C), and a dense film is obtained consisting of non-oriented microparticles of under 10 to 20 nm at room temperature in all cases. Furthermore, a clear lattice shape is found also inside the microcrystals of 10 nm or less, and although the interior of the film contains stress, etc., the film organization has a uniform structure extending from the substrate interface to the film surface. Furthermore, although the raw material particles have a monocrystalline structure with mean particle diameters of more than 80 to 100 nm in all cases, the formed films have a
smaller microcrystalline structure. The results of X-ray diffraction (XRD) and energy dispersive X-ray analysis also show that the formed films virtually maintain the crystal structure of the raw material powder with little variation in a room temperature atmosphere. Measurement of particle velocities, evaluation of kinetic energy, etc. has shown that the raw material particle crystals are mechanically fractured by the particle impact and become finer by plastic deformation, while a nanocrystalline thin film is formed by the inter-particle bonding that occurs at the same time. This is a perspective that was not grasped by coating methods that use conventional particle collisions. Furthermore, an anchor layer of thickness around 50 to 300 nm (varies depending on the hardness of the particles and substrate material) is formed at the interface between the film and substrate by the particle impacts, and this gives a high adhesion force of over 20 MPa.14–18,82)

The following summarizes the features of the AD method compared to conventional thin film processes.

1. Able to grow/form dense films without binder at room temperature.
2. High density and adhesion strength compared to conventional thin film techniques even at film thicknesses of over several μm.
3. High film growth rate (5 to 50 μm/min) (Conventional film growth techniques: 0.01 to 0.05 μm/min).
4. Able to obtain grown films with the same composition and crystal structure as the powder used in systems with complex compositions with greatly different evaporation pressures.
5. Able to obtain a wide range of film thicknesses (0.5 μm to 1 mm).
6. Fine detail patterns can be obtained such as by direct rendering, masking, or lift-off methods without using film etching processes.
7. Able to grow films in low vacuum (several hundred Pa to atmospheric pressure).

In films fabricated by RTIC using the AD method, the substrate temperature is not observed to increase at all from the impacts, and ceramic materials are also able to consolidate macroscopically at room temperature. Since this does not involve a sintering process, it can also be viewed as a type of binder-free ultra-dense ceramic green body.

3. Electrical and mechanical properties of AD films

We investigated the purity of raw material particles, compressive failure properties, and film growth conditions using the AD method, and were able to form high density alumina (α-Al2O3) thick films, piezoelectric/ferroelectric thick films, and yttria (Y2O3) thick films on various kinds of metal and glass substrates at room temperature. In
alumina films in particular, electromechanical properties equivalent to bulk sintered material were obtained with a Vickers hardness of 180 to 220 GPa, Young’s modulus of 300 to 350 GPa, volume resistivity of $1.5 \times 10^{15} \, \Omega \cdot \text{cm}$, and permittivity ($\varepsilon$) of 9.8. Furthermore, performance far better than sintered bodies was obtained with alumina films and aluminum nitride films formed on stainless steel, Cu, and Al substrates at room temperature having an electrical breakdown strength of 100 to 300 kV/mm or more, and films of thickness 5 µm formed on glass substrates having high transparency with an optical transmissivity of 98% or more. This is thought to be because optical scattering was suppressed and the ground boundary path became longer as the crystals became finer. Furthermore, there are no pores, and smoothness at the several nm level can be obtained by performing simple polishing. We also successfully fabricated uniform films across an area of 200 mm square. Recently, there have been several reports on the excellence of the insulating properties of this kind of film grown at room temperature. However, although the ferroelectric materials and ferromagnetic materials exhibited high withstand voltage similar to that of pure ceramics, when the crystal grain size in room temperature grown films is reduced too much to several tens of nm, the polarization domains become clamped by grain boundary stress and sufficient performance cannot be obtained. Although PZT room temperature grown films exhibited piezoelectric and ferroelectric properties when a high electric field of 1 MV/cm was applied, the piezoelectric constant ($d_{31}$) was 20 to 30 pm/V which is extremely low for practical applications. However, when these were annealed (in atmosphere at around 500 to 900 °C), growth of microcrystal grains and defect recovery were confirmed, and a large improvement in ferroelectric properties was observed. Relative permittivity of 1200 to 2500 and piezoelectric constants of $d_{31} = -164$ to $-360 \, \text{pm/V}$ were obtained from PNN-PZT piezoelectric films formed by the AD method for film thicknesses of around 10 µm. These values surpass properties previously reported from thin films methods such as the sol–gel method, hydrothermal synthesis methods, and screen-printing methods, and are excellent properties even compared to recent examples of sputtering reports when the speed of the film growth is considered. Furthermore, in the case of piezoelectric films, since the driving electric field strength increases as the film becomes thinner, there is demand for high piezoelectric constant and withstand voltage unlike when bulk material is driven, and this requires optimizing the density of the film structure and crystal grain sizes. The AD method makes this kind of fine structure control easy, and allows easy growth of dense thick films by adjusting the bulk powder even for piezoelectric materials with complex compositions, and makes it possible to reduce the annealing temperature by around 200 to 300 °C.

Furthermore, thick films having insulating properties and mechanical strength equivalent to or better than bulk material with a Vickers hardness of 92 GPa, volume resistivity of $10^{14} \, \Omega \cdot \text{cm}$ or more, breakdown voltage of 150 V/µm, and adhesion strength of 80 MPa or more could be formed by using yttria ($Y_2O_3$) powder which normally needs to be treated by hot isostatic pressing at 1700 °C or more and solidifying it at high density. Figure 3 shows the results of evaluation of the plasma corrosion resistance. Although the smoothness is excellent compared to thick bulk material and thermal spray coating even before exposure to plasma, after exposure to plasma, whereas absolutely no pores are observed in the AD yttria film, large pores are observed in films from other methods, and the plasma erosion speed and surface roughness are greatly improved. It has also been found that inter-particle bonding is chemically stable regardless of room temperature film growth. Currently, glass and aluminum alloy parts coated with yttria by this method have been fully commercially by TOTO Limited as a low dust plasma resistant material for semiconductor fabrication equipment.
and it has become an essential component technology for global semiconductor fabrication.33,34)

4. RTIC and film growth mechanisms

Apart from the AD method, several other film growth techniques that use the collision adhesion phenomenon of solid particles have been reported previously. Figure 4 shows coating methods that use collision adhesion of dry microparticles and ultrafine particles organized by particle diameter and particle velocity of the raw material particles, film growth atmosphere temperature, and material properties (ceramic, metal, etc.). These are broadly divided into methods that use electric field acceleration (EPID method and macron beam method) and methods that use gas carrier (AD method, CS method, GD method, etc.). Generally in these film growth methods, the kinetic energy of the microparticles is released concentrated into a small area in a short amount of time by collisions with the substrate or between particles, and this is thought to increase the temperature above the material melting point and to cause bonding between the particles.4,10) However, in these methods, the microparticles are thought to remain bonded in a virtually solid state overall, and it is thought that the principles differ from film growth methods by thermal energy assistance of microparticles like thermal spraying techniques. Furthermore, although the CS method is able to form metal films and cermet films, it cannot form dense ceramic films. Figure 4 shows the AD method compared to the CS method in terms of particle impact velocity and particle diameter, and although the kinetic energy is clearly smaller, it is able to form dense ceramic films and metal films, and this is not sufficiently explained by the difference in the magnitude of the kinetic energy described above. Furthermore, it is not clear whether the bonding state between microparticles in the microparticle films (films formed by bonding between microparticles) formed by each method is the same, and in fact there are few examples of reports discussing the mechanisms of dissipation of the energy from particle impact. When the film growth results are looked at phenomenologically, there are large differences between them.

4.1 Effect on film growth of raw material particles

Since room temperature grown films formed by the AD method do not undergo high-temperature annealing, they cannot be expected to have excellent properties without removing contamination from the raw material particle surface and defects inherent in the particles from normal commercial ceramic powder. As a result, it is extremely important to perform a detailed investigation and adjustment focusing on the raw material particle properties when applying this method for various materials. The particle diameter and mechanical properties of the raw material particles have also been found to have a large effect on the film growth speed and film density.

In particular, there is an effective process window for the raw material particle diameter for obtaining a dense ceramic film. When films are grown by using spherical ultrafine particles of α-Al2O3 of mean particle diameter around 50 nm synthesized by chemical methods, then even when the particles are accelerated to 400 m/s which is above the particle velocity described above, a pressed compact is formed and a grown film cannot be formed even if the particle diameter is fine, as shown in Fig. 5(A). However, when a film is grown by using sub-micron order particle diameter α-Al2O3 microparticles with irregular particle shapes, RTIC occurs at a particle velocity of around 200 m/s and a dense and transparent grown film can be formed as shown in Fig. 5(B).16-18) Fine particles change direction to parallel to the substrate when the carrier gas flow impacts the substrate as shown in Fig. 6. This is thought to be because the velocity with which microparticles that have a small mass impact the substrate is greatly reduced due to tracking the flow of the carrier gas flow, similar to the classifier unit in an impactor, etc., and RTIC does not occur since the velocity falls below the critical particle velocity (Vc).

Furthermore, in the case of α-Al2O3 in this experiment, if large raw material particles are used consisting of single crystals of particle diameter 5 μm or more, then film growth does not occur when the film growth speed is increased, but etching of the substrate occurs similar to regular sandblasting, as shown in Fig. 5(C). This is thought to be caused by changes in the failure properties accompanying the increased raw material particle diameter, and is thought to be a kind of size effect. Furthermore, a trend where the film growth rate decreases as the particle velocity increases has been observed,15) and it is found that the actual phenomenon cannot be explained purely in terms of the magnitude of the particle kinetic energy. Furthermore, when dry mill processing is performed on the raw ingredient particles, although the film growth speed greatly increases by over 10 times as mill processing time increases,36) the film density decreases suddenly at some point. As a result, there is an optimal mill processing time for obtaining both film growth speed and film density. Although the particle diameters of the raw material particles become finer when mill processing is performed, a mechanochemical effect also acts at the same time which causes large changes in the
re-aggregation properties, mechanical physical properties, surface activity, and defect structure of the particles, and since this also changes the defect structure and amount of defects that are left inside the film, this is thought to have a complex effect on the film growth properties and electro-mechanical properties of the grown film.

4.2 Similar particle consolidation phenomena

The characteristic features of RTIC are, macroscopically, that ceramic powders are strongly bonded and consolidated at room temperature, and the crystal grains in the raw material powder become finer during this process. A phenomenon that is similar in terms of this is a powder forming process called shock compaction. When a high-pressure shock wave passes through a powder compact, the crystal grains become finer while at the same time bonding between powder particles also occurs. This phenomenon has been investigated for a long time as a powder consolidation in which crystals become finer under static high pressure in a high-pressure environment. In metallurgy, it is discussed particularly as a process mechanism of cold forging. There have been attempts to explain these mechanisms based on dislocation theory, and for brittle materials like ceramics, virtually all of the discussion has been about high-pressure fields under medium to high temperatures. In these processes where high pressures are applied, a change from brittle failure to plastic deformation has been observed in ceramic powder compacts, which is called the brittle-ductile transition (BDT), and various explanations have been studied from a crystal mechanics perspective such as the nucleation process and movement of dislocations, etc. However, there are differences in the individual interpretations of the crystals becoming finer depending on the material and process temperature range as described later, and it is difficult to say that this fully explains RTIC.

4.3 Densification mechanisms

In order to understand this kind of film growth technique that utilizes impact consolidation of solid particles, it is important to first measure the kinetic energy during...
particle impact. If the particle diameter is 10 μm or more, although it is possible to directly image the particles and perform velocity evaluation such as using a high-speed camera or streak camera, measurement is not possible in practice for particle diameters of 1 μm or smaller. Therefore, a unique measurement technique has been developed that creates a packet in a particle stream using a moving slit, and calculates the impact velocity of the particle packet from the offset in the position when the packet reaches the substrate which is moving together with the slit from the flight time after the particle packet passes through the slit. As a result, the particle impact velocity of the AD method was found to be in the range of 150 to 400 m/s under normal film growth conditions. Recently, researchers on the CS method have reported detailed results for this from several additional experiments and fluid dynamics simulations. The maximum temperature increase and maximum impact pressure during particle impact were found from simulations using the finite element method (FEM) based on the Johnson-Holmquist state equations using the particle impact velocities measured experimentally in this way. At the typical particle impact velocity (normal direction to the substrate) that occurs in RTIC as found by experiments on α-Al₂O₃ microparticles of 300 m/s, the maximum temperature increase did not exceed 500 °C, and the maximum impact pressure was 3 GPa, as shown in Figs. 7(A) and 7(B). At this level of particle kinetic energy, it is difficult to say that enough energy is provided to cause the entire particle to become molten during impact with the substrate or to cause sintering between particles, particularly for the case of ceramic materials, and it is expected that complicated mechanisms act in the energy conversions that cause densification and bonding between particles.

When the film growth mechanisms by RTIC in ceramic materials is considered based on the experimental facts and simulation results described above, then from the raw material particle diameters used, it is not possible to realize enough densification for high transparency to occur unless the impacting ceramic microparticles at least undergo plastic flow like a metal. As a result, the density is thought to increase by the microparticle crystals undergoing fast deformation involving shifting of crystal planes and movement of dislocations, etc. and by the crystal structure becoming finer when they impact the substrate, and it is thought that it is possible for new surfaces to form and for mass transfer to occur and form bonding between particles based on the impact force accompanying this. Figures 8(A)–8(C) shows results that experimentally confirm the state of densification due to this particle fracturing. When PZT (piezoelectric material) that contains heavy elements such as lead is mixed with alumina microcrystals that contain light elements such as aluminum and oxygen and sprayed onto a substrate to form a composite film of PZT/alumina at room temperature, and the structure of this is observed by transmission electron microscope (TEM), the PZT which contains the heavy elements appears black and the alumina which contains light elements appears white, and the distribution of the two materials inside the film can be observed from differences in the brightness. As a result, black lamellar PZT regions were observed parallel to the substrate surface in the cross-section TEM micrograph shown in Fig. 8(B) and this kind of layered structure was not observed in the film surface shown in Fig. 8(A). When the volume of this lamellar region was found by assuming an ellipsoidal shape, it roughly matched the volume ratio of the individual raw material particles. Furthermore, fine crystal structure with particle diameters of around 20 nm like the TEM micrograph shown in Fig. 2(C) were observed inside the regions of each deformed raw material particle inside the film as shown in Fig. 8(C). At this time, the size of crystallites in the film reduced to less than 1/10th of the sizes of crystallites in the original raw material particles. Although the crystallinity worsened as a result with the peak width at half maximum broadening in observations by XRD, the crystals in the film maintained the original crystal structure.

Furthermore, in order to confirm whether or not this kind of fracturing phenomenon of ceramic microparticles accompanying plastic deformation would occur simply by application of quasi-static pressure at room temperature, a raw material particle compression failure test apparatus was developed that can perform compression failure
testing individually on individual raw material particles by linking a nano-indenteter and atomic force microscope (AFM) on a high-precision stage, and the quasi-static failure behavior of the ceramic raw material microparticles was evaluated as shown in Figs. 9(A) and 9(B). As a result, for raw material particle diameters of less than around 1 micron, sudden deformation occurred once the elastic deformation region was exceeded in the relationship between the indenter displacement and compressive force applied to the particle, and although the compression vs. displacement curve indicated partially brittle failure behavior, plastic particle deformation was confirmed by scanning electron microscope (SEM) and TEM observation after compression testing at room temperature as shown in Figs. 9 and 10. Furthermore, when the compressive failure strength of the raw material particles was calculated based on the raw material particle diameters measured by AFM and SEM at this time, it was around 2 to 3 GPa, which was a good match to the impact pressure of 3 GPa applied to raw material particles during impact with the substrate as found by FEM simulation based on the substrate impact velocity of particles as found experimentally by the time of flight difference method shown earlier. Furthermore, the important point of the results of the compressive failure testing of individual raw material particles as shown in the TEM micrograph in Fig. 10 is that the compression was applied slowly under conditions of maintaining thermal equilibrium at room temperature, and the plastic deformation of the microparticles occurred at room temperature. That is, room temperature BDT occurred, which is described later. However, when raw material particles with good crystallinity and particle diameters of 5 μm or are used, brittle failure occurs like regular ceramic particles, and the ceramic particles break into fine fragments which rebound elastically, and the impacting particles etch the substrate as shown in Fig. 9(B).

Many additional experiments have been applied to various brittle materials for the RTIC specific to this method described above, and it is thought that the crystal structure becomes finer by fracturing and deformation by impact on the substrate and film surface. It is therefore thought that the formed films have a dense nanometer scale crystal structure that contains virtually no amorphous phase at room temperature. This is a perspective that was unknown in coating methods using conventional particle impact such as thermal spraying techniques that require molten particles.

4.4 Discussion of RTIC

The AD method is able to produce dense highly transparent ceramic films at room temperature. In this “room temperature consolidation” of ceramic microparticles, it was found that plastic flow of ceramic microparticles of particle diameters under a few microns occurs under impact loads of around several GPa. Questions for uncovering the key for more deeply understanding this phenomenon are (1) whether this actually occurs at room temperature, and (2) whether the bonding between particles and bonding between the particles and substrate is caused by the impacted contact interface rising above the melting point, and (3) whether the formation of new surfaces by
fracturing of particles during impact is able to promote bonding even at room temperature.

For this, bright plasma optical emissions can be observed near the substrate sprayed with particles during film growth by the AD method. An explanation for the film growth mechanism that arises from these optical emissions is that the particle surface becomes hot and melts locally during impact of microparticles. However, a phenomenon called fracto-emissions is known where electrons are physically ejected when two solid surfaces impact or rub together.60),61) Electrons are also emitted from the substrate material surface by the impact of microparticles in the case of the AD method, and these electrons are thought to excite the carrier gas causing optical emissions. In fact, the optical emissions when the carrier gas is He match the optical emission spectra of He, and the optical emissions spectra from melting of the particles themselves is not observed, as shown in Fig. 11. However, it has been confirmed that impact optical emissions no longer occur if the carrier gas is changed to a gas that is not readily ionized at around 100 Pa, such as by changing from He to N₂.35) As a result, it is difficult to think that the particle surface melts and becomes hot enough to deform by the particle collisions in the AD method.

As described earlier, the consolidation of ceramic microparticles under the application of high pressure has been investigated from different perspectives in various different fields in the past. In the conventionally known shock compaction method, a high speed projectile is impacted at over 1 km/s into powder packed into a die like an anvil, which thus applies impact pressures of 10 to 100 GPa which are at least an order of magnitude larger than the AD method, and refining and consolidation of particle crystals is observed that resembles RTIC. Kondo et al. explained that the heat energy dissipates locally from the shock wave passing through the particle at this time using a “skin model”.62) In the case of ceramic materials, a prerequisite for the mechanisms of plastic flow and bonding between particles in the basic shock compaction method is softening and sintering phenomenon of the ceramics by an increase in the temperature at the interfaces between particles due to the shock wave. Furthermore, the idea of self-heated shock compaction63) has also been proposed for obtaining crack-free dense sintered bodies by synchronizing the timing of thermal relaxation and pressure application by reducing particle diameters. This idea does not include the idea of plastic deformation and chemical bonding of ceramics at room temperature. However, unexplained bonding mechanisms still exist. In contrast, the impact velocity and impact pressure of particles in the AD method are both lower than the shock compaction methods described above by at least one order of magnitude, and the input energy is clearly lower in the conventional shock compaction method. Because of this, it is difficult to consider both as the same phenomenon. We proposed the hypothesis that “when the particle diameter of ceramic particles becomes below several microns, plastic flow occurs at room temperature under the high pressure load of the particle impact, and new surfaces are formed on the particle surface because of this which promotes bonding between particles even at room temperature due to the activation. As a result, dense highly transparent ceramic films can be obtained at room temperature”.64) Recently, there have been several reports on the possibility of plastic deformation at room temperature of the ceramic materials in (1), that is, BDT at room temperature depending on the particle diameter. As a representative example, it is known from observation of nanoindentation of brittle materials such as Si and Ge that when the indentation depth of the indenter is at the sub-micron level, impressions from plastic deformation without crack formation are observed in the surface of brittle materials regardless of room temperature or not.53),65) Furthermore, in the field of machining it has long been known that a plastic working state is obtained and smooth machining surfaces free of brittle failure marks such as pits can be obtained in high-precision cutting work of brittle mate-

![Fig. 11. Plasma emission spectrum observed during AD process.](image-url)
rials if the cutting depth is in the sub-micron order or shallower.\textsuperscript{66,67} However, the mechanism of this is focused on the phenomenological and it is not fully understood physically, and there are many explanations that assume that an extremely narrow region at the machining point heats up to near the melting point such as due to friction. Furthermore, we have also seen several reports related to room temperature BDT of ceramic particles by reducing the particle sizes after the above hypothesis was presented. Michle\textsuperscript{68,69} et al. machined Si and $\alpha$-Al$_2$O$_3$ into micropillars of various diameters and orientations by focused ion beam (FIB) and perform compression tests on these, and reported that room temperature BDT occurred depending on the pillar size and crystal orientation. Furthermore, Edalati\textsuperscript{70} et al. reported that severe plastic deformation occurred in partially stabilized zirconia by torsional strain under high hydrostatic pressures. From the perspective of explaining the mechanisms of film growth by the direct AD method, Sarab\textsuperscript{71} et al. from the Sandia National Laboratories in the USA reported plastic deformation behavior at room temperature in $\alpha$-Al$_2$O$_3$ microparticles the same as ours under SEM observation of microparticle compression failure testing the same as ours. Furthermore, Assadi\textsuperscript{72} et al. discussed size effects in brittle materials based on the movement conditions for dislocations using molecular dynamics simulations, and expanded this to the relationship between the possibility of room temperature BDT and film growth conditions using the AD method, and supported our hypothesis. There are still some unexplained areas for whether or not the bonding between particles and bonding between particles and the substrate in (2) occurs at room temperature.

4.5 Bonding mechanism of particles on RTIC

Figure 12 shows high resolution TEM images of the grain boundary between PZT and $\alpha$-Al$_2$O$_3$ formed by this process. Virtually no amorphous layer is seen, with either one or the other of the lattice patterns clearly observed down to near the grain boundary, and virtually no interdiffusion is observed. Furthermore, there is also no linear crystal grain boundary as seen in thermal equilibrium processes such as those in sintered ceramics, and the boundary structure is irregular. It is thought that bonding probably does not occur in a state close to thermal equilibrium locally as seen in shock compaction, but that the bonding state is closer to pressure bonding as seen in the field of bonding.\textsuperscript{18,82} In the field of mounting, the method of surface activated room temperature bonding\textsuperscript{73,74} by exposure to Ar ions has been commercialized, and room temperature bonding of brittle materials such as glass, Si, and LiNbO$_3$ has also been reported. It is possible that it could be explained by this kind of mechanism.

We believe that a chemically active nascent surface is formed at the time of particle collision and fracture, and that the nascent surfaces are close to each other at the atomic level to form chemical bonds between particles. In order to verify this, an experiment as shown in Fig. 13 was conducted. Large raw material particles having a particle diameter of several microns or more having normal brittle crushing characteristics at room temperature (that is, particles that cannot form a film by this process) are sprayed onto the substrate. At this time, a ceramic substrate obtained by sintering the same alumina particles as the sprayed raw material particles is used as the first substrate. The raw material particles colliding with the first substrate are crushed while etching the substrate, and as a result, fine fragment particles having a new surface are formed. The fine debris particles bounce off the first substrate and are discharged from the chamber exhaust port along the flow of the carrier gas. At this time, the fine debris particles on which the new surface was formed were captured on the second glass substrate disposed at a location sufficiently away from the base material. The distance between the second substrate and the first substrate is set so that the speed of the fine debris particles riding on the air current is less than the critical speed required for film formation. As a result, the fine debris particles deposited on the glass substrate are firmly bonded to the glass substrate. As the time further increased, as shown in Fig. 13, it was confirmed that a film having a low film density but a thickness of about 1 $\mu$m could be formed. This result suggests that the chemically active new surface formed by particle collision fracture contributes to the interparticle bonding in the AD process.

From the results of the above series of experiments, there is a possibility that the mechanism of particle bonding can be explained by surface chemistry with surface activation by forming a new surface by particle collision. Figure 14 is an explanatory model of the normal temperature impact solidification phenomenon in the AD method based on such a hypothesis. Particles that collide with the substrate by the AD method (Fig. 14①) propagate cracks in the particle crystal due to the impact pressure (Fig. 14②) and are finely crushed (Fig. 14③). As a result, an active new surface is formed on the fracture surface of the crushed particles (Fig. 14③), and at the same time, fine crystal fragments having such a new surface are mutually bonded on the substrate by inertial force and collision pressure. By moving and rotating, densification
proceeds (Fig. 14④), and the new surfaces recombine and solidify (Fig. 14⑤). In the AD method, an active surface is formed by particle crushing and rebinding between particles can be realized without ion beam irradiation as in the surface activated bonding method described above. However, it is necessary to examine the authenticity in more detail from the viewpoints of both experiments and simulations.

5. Application to energy and environment related devices

Although the AD method could also be called the “powder spray method” and requires a reduced pressure environment, since it is able to form crystallized thin films and thick films at high speed without needing expensive equipment in ultra-high vacuum or processes involving heating to high temperatures compared to conventional thin film techniques, it is expected that applications will expand to various energy related components in the future such as solar cells, lithium (Li) ion batteries, fuel cells, and superconductors.

Sekisui Chemical Co. Ltd. has developed a flexible dye sensitized solar cell with a conversion efficiency in excess of 8% as shown in Fig. 15 by room temperature forming of a highly adhesive porous titanium layer by roll-to-roll film growth by the AD method on resin film substrate, which has successfully commercialized. This application has proven that the AD method can grow not only...
dense films, but also porous films, and that bonding between titanium particles that is also good electrically can be obtained with high adhesion strength even by room temperature film growth. Furthermore, since the AD method is a low vacuum process, it shows that a continuous process is possible that includes the dye impregnation process and the film packaging process in atmosphere by differential evacuation. Furthermore, the development of fully solid-state batteries has also been spurred on by the AD method. We performed trial fabrication of fully solid-state thin film Li ion batteries by stacking layers of thin films of oxide cathode material (LCO and LMO), solid oxide electrolyte materials (LATP), and anode material (LTO) by a fully room temperature process using the AD method and the AD method, performing annealing at around 500 °C, and stacking a solid state electrolyte (LiPON) and Li metal anode. Furthermore, Kanemura et al. formed a cathode material on a pellet of solid-state electrolyte by using the AD method and annealed it at 750 to 800 °C, and successfully reduced the interface resistance to 1/100 to 1/1000. In addition, examples have also been reported of not only forming the solid-state electrolyte layers using the AD method, but also trial manufacturing of button batteries by forming cathode and anode electrode active materials on single crystal electrolyte (LLZO) with a high ion conductivity of 1 × 10–3 S/cm on par with liquid electrolytes by using the AD method from the perspectives of safety and reliability from preventing the occurrence of Li dendrites.

In other work, there have been studies that attempt to increase the heat dissipation performance of circuit boards for power modules and power LEDs by directly forming a highly insulating highly adhesive thick film of A12O3 or ALN on metal heat sinks by room temperature film growth using the AD method and U. (Balu) Balachandran et al. at Argonne National Laboratory have produced dense ceramic films of lanthanum-doped lead zirconate titanate (PLZT) on various substrates by room temperature AD. AD-PLZT film capacitors exhibit excellent volume and specific gravity capacities when compared to currently used polymer film capacitors. The measured properties indicated that PLZT-based ceramic film capacitors meet the requirements of modern high temperature capacitors. A PLZT film having a thickness of 8 μm formed on a flexible aluminum metallized polyimide film at room temperature by the AD method has a maximum applied electric field Emax = 1.25 MV/cm, dielectric constant ≥85, dielectric loss ≥0.012, Energy density ≥13.2 J/cm3, high dielectric constant, low dielectric loss, small dependence on applied electric field, high recovery energy density, and its temperature variation meets the requirements of X 8 R rating. This has been confirmed. This can be expected as utilization of the high insulating property of the AD film formed at room temperature.

In addition, the investigation has started into various attempts to increase the performance of energy related components such as reducing the internal resistance of solid oxide fuel cells (SOFC) by turning the electrolyte layer into a thin film, increasing the life of SOFC by increasing the density of the interconnect layer by using the AD method, stable fixing to the substrate of photocatalysts for decomposition of NOx, and using the characteristics of RTIC in the AD method in thermoelectric conversion elements to increase performance indicators by reducing thermal conductivity by making the crystal structure finer, making the films thinner, etc.

6. Application to reducing the weight of resin/ceramic components

In the mobile phone market, there has been a focus on changing case material from metal to zirconia ceramic and resin materials in order to improve value-adding, and support wireless power supply and 5G. However, the problems have been that thin ceramics break easily when dropped, and zirconia is heavy. If a lightweight resin with excellent shock resistance could be coated in a hard ceramic film with excellent coloring and aesthetics, it is expected to have a large market as a back cover for mobile phones. The possibility of this by using room temperature coatings by the AD method has been investigated, and it has been confirmed that a Vickers hardness of 1000 Hv or more similar to quartz can be obtained that is scratch resistant while have a surface aesthetic similar to pottery, as shown in Fig. 16. Furthermore, it has been noted that the adhesion strength and density can be greatly improved by using a silica hybrid layer in which resin and silica ultrafine particles are covalently bonded as an intermediate layer, and it has been shown that a hard AD alumina thick layer with good transparency even in the visible light range can be formed with good adhesion on resin substrate. In the future, it is also possible that this could greatly contribute to improving the durability of scratch resistant coating films on resin spectacles and reducing the weight of window materials for automobiles.

7. Overseas research trends related to the AD method

Although research is being pursued overseas such as in Korea, China, Taiwan, America, and Germany research and development is particularly active in Korea.
From around 2005 in Korea, the group of Prof. Nam of Kwangwoon University, the group of Dr. Kim of the Korea Institute of Ceramic Engineering and Technology, and the group of Dr. Cho et al. of the Korea Electronics Technology Institute have been actively researching film growth mechanisms\(^9\)\(^{\text{88-102}}\) and their application to electronics mounting techniques from the perspective of room temperature zero compression ceramics technology, as well as insulating materials and dielectric materials such as alumina, and composite materials with CNT, polymers, and nano-diamonds\(^{103-109}\) under the umbrella of a national project related to ceramics and energy. Furthermore, the group of Prof. Lee et al. of Hanyang University, the group of Prof. Ahn of Seoul National University, and the group of Proj. Yoon et al. of Korea University have been investigating the mechanisms and applications to functional materials such as titania within the fields related to thermal spraying and nano-particles.\(^110\)\(^{\text{110-117}}\) Furthermore, the group of Dr. Park et al. of the Korea Institute of Materials Science has been developing an energy harvester using AD piezoelectric thick films,\(^118\) and have been actively researching plasmas corrosion resistant coatings,\(^\text{123,124}\) for fuel cell applications,\(^\text{124,119-121}\) and thermoelectric device applications\(^\text{123}\) jointly with Seoul University and major Korean private corporations, and have also been studying titania coatings\(^\text{125-127}\) like the group of Prof. Yoon et al. for photocatalyst applications, etc. Furthermore, Dr. Hahn of the same group and others have been researching medical related material applications such as artificial joints and dental materials such as implant applications using apatite coatings.\(^\text{128-131}\) In addition, S.-W. Kim of Ajou University, J.-M. Oh of Kwangwoon University, S. Kim of LG Innotek, etc., are considering the deposition of monoclinic CsPbBr\(_3\) fluorescent composite supported on the surface of \(\alpha\)-Al\(_2\)O\(_3\) particles on a resin film by AD method.\(^\text{122}\) As a result, a flexible high-brightness fluorescent sheet excellent in high-temperature stability has been successfully produced. This is a good example of AD method for composite film formation. In particular, the application of plasma corrosion resistant materials for semiconductor manufacturing equipment, which was successfully commercialized in 2007 by TOTO Limited,\(^\text{133}\) was reported not only by this group but also by the group of Sungkyunkwan University in Korea and Samsung Electronics.\(^\text{134}\) This successful case of commercialization by a Japanese company attracted a great deal of interest among private companies and activated research and development activities around the world. In the future, it is thought that the properties of films formed at room temperature will be improved by optimizing the raw material particle synthesis methods in comparison to conventional fabrication methods, and that somehow extracting the excellent properties of room temperature processes using the AD method and turning them into practical applications is an important direction.

8. Summary

We have shown the phenomenon of consolidation of ceramic and metal raw material powder into a thin film state at room temperature (RTIC) by the AD method, and the possibility of this as a new coating method for contributing to higher function materials for a variety of applications including energy and environmental materials and medical related materials. The important points for understanding this phenomenon are (1) even for ceramic particles, as the particle diameter becomes smaller, there is a particle size range where the particles undergo plastic deformation even at room temperature, and (2) sufficient impact velocity can be obtained for plastic deformation of microparticles in this size range by spraying microparticles onto a substrate under reduced pressure. When these two conditions are met, a dense film is formed. Although various new process techniques have previously been investigated by making the raw material particles smaller and using nano-particles, etc. in order to reduce the sintering temperature and create new functions, in this method this is implemented by using cheap sub-micron order raw material particles as the starting material. RTIC can be treated as a process dominated by the application of pressure that has the advantages of being able to easily create ceramic materials with nanocrystal structures and nano-composite structures that are difficult to fabricate by conventional sintering processes, and is deeply interesting from the perspective of searching for new materials. Furthermore, in order to fully understand this film growth technique and use it in an even wider range of applications, it is necessary to study RTIC at an even deeper level, and in order to do this it is necessary to clarify the relationship between surface chemistry understanding and dislocation theory, and also the relationships between the conventionally known impact sintering, BDT mechanism, and dynamic re-crystallization, and to deepen our systematic understanding.

References
1) T. Ide, Y. Mori, N. Ikawa and H. Yagi, Precis. Eng., 57, 122–127 (1991) [in Japanese].
2) Y. Mori, T. Ide, I. Konda, H. Yagi and H. Tsuchiya, Technol. Repts. Osaka Univ., 39, 255 (1989).
3) F. Fukuzawa, Ohuyo-Butsuri, 60, 720–721 (1991) [in Japanese].
4) C. Hayashi, Ohuyo-Butsuri, 54, 687–693 (1985) [in Japanese].
5) C. Hayashi, S. Kashu, M. Oda and F. Naruse, Mat. Sci. Eng. A-Struct., 163, 157–161 (1993).
6) P. Alkimov, V. F. Kosarev and A. N. Papyrin, Dokl. Akad. Nauk SSSR, 315, 1062–1065 (1990).
7) A. N. Papyrin, A. P. Alkhimov, V. F. Kosarev and S. V. Klinkov, Proc. of ITSC2001, 423 (2001).
8) K. Sakaki, Yousya-gijutsu, 21, 29–38 (2002) [in Japanese].
9) S. Sudou, N. Shindo, H. Ando and Y. Ito, Ceramics, 37, 46–48 (2002) [in Japanese].
10) R. C. Dykhuisen, M. F. Smith, D. L. Gilmore, R. A. Neiser, X. Jiang and S. Sampath, J. Therm. Spray Techn., 8, 559–564 (1999).
11) E. Barborini, P. Piseri, A. Podesta and P. Milani, Appl. Phys. Lett., 77, 1059–1061 (2000).
12) F. Di. Fondo, A. Gidwani, M. H. Fan, D. Neumann, D. I. Jordonoglou, J. V. R. Heberlein, P. H. McMurry, S. L. Girshick, N. Tymiak, W. W. Gerberick and N. P. Rao, Appl. Phys. Lett., 77, 910–912 (2000).
13) N. P. Rao, N. Tymiak, J. Blum, A. Neuman, H. J. Lee, S. L. Girshick, P. H. McMurry and J. Heberlein, J. Aerosol Sci., 29, 707–720 (1998).
14) J. Akedo and M. Lebedev, Jpn. J. Appl. Phys., 38, 5397–5401 (1999).
15) J. Akedo, Ohayo-Butsuri, 68, 44–47 (1999) [in Japanese].
16) J. Akedo, J. Am. Ceram. Soc., 89, 1834–1839 (2006).
17) J. Akedo, J. Therm. Spray Techn., 17, 181–198 (2008).
18) J. Akedo edit., “Aerosol deposition (AD) process: the basic and applications”, CMC publishing (2008) [in Japanese].
19) J. Akedo, Kinzoku, 75-3, 16–23 (2005) [in Japanese].
20) H. Park, J. Heo, F. Cao, J. Kwon, K. Kang, G. Bae and C. Lee, J. Therm. Spray Techn., 22, 883–891 (2013).
21) M. Momotani, N. Mori, S.-M. Nam, H. Kakimoto, S. Wada, T. Tsumura and J. Akedo, Key Eng. Mat., 301, 117–120 (2006).
22) Y. Sato, Y. Uemichi, K. Nishikawa and S. Yoshikado, IOP Conf. Ser.: Mater. Sci. Eng., 18, 092056 (2011).
23) H.-M. Cho and H.-J. Kim, IEEE Electr. Device L., 29, 991–993 (2008).
24) Y. Kim, C.-W. Ahn, J.-J. Choi, J. Ryu, J.-W. Kim, W.-H. Yoon, D.-S. Park, S.-Y. Yoon, B. Ma and B.-D. Hahn, Sci. Rep., 7, 6637 (2017).
25) J. Akedo and M. Lebedev, Appl. Phys. Lett., 77, 1710–1712 (2000).
26) J. Akedo, J.-H. Park and Y. Kawakami, Jpn. J. Appl. Phys., 57, 07LA02 (2018).
27) T. Miyoshi, J. Appl. Phys., 46, 7018-7023 (2007).
28) Y. Kawakami, H. Yoshikawa, K. Komagata and J. Akedo, J. Cryst. Growth, 275, e1295–e1298 (2005).
29) Y. Kawakami, S. Aisawa and J. Akedo, NEC TOKIN Tech. Rev., 32, 46–52 (2005).
30) NEDO project reports: Strategic development of energy use rationalization technology/leading research and development of basic technology for effective use of energy, “Research and development on energy rationalization technology of ceramic industry process using impact binding effect” (2004).
31) J. Iwasawa, R. Nishimizu, M. Tokita, M. Kiyohara and K. Uematsu, J. Ceram. Soc. Jpn., 114, 272–276 (2006).
32) TOTO Co. Ltd. Products: http://www.toto.co.jp/E_Cera/J.Cera/ad/203.htm.
33) Nikiiko BP, The Nikki-kei monozukuri, 1, 21–23 (2006) [in Japanese].
34) Abstract of the Inoue-Harushige Award: http://inouesho.jp/jyusyou/39/doc/02.pdf.
35) J. Akedo and M. Lebedev, Jpn. J. Appl. Phys., 40, 5528–5532 (2001).
36) J. Akedo and M. Lebedev, Jpn. J. Appl. Phys., 41, 6980–6984 (2002).
37) D. K. Potter and T. J. Ahrens, Appl. Phys. Lett., 51, 317–319 (1987).
38) H. Hirai and K. Kondo, Science, 253, 772–774 (1991).
39) L. E. Murr, A. W. Hare and N. G. Eror, Nature, 329, 37–39 (1987).
40) C. L. Seaman, S. T. Weir, E. A. Early, M. B. Maple, W. J. Nelis, P. C. McCandless and W. F. Brocious, Appl. Phys. Lett., 57, 93–95 (1990).
41) T. Negishi, T. Ogura, T. Masumoto, T. Goto, K. Fukuoka, Y. Syono and H. Ishii, J. Mater. Sci., 20, 399–406 (1985).
42) K. Kondo, Kotai-butsuri, 19, 127–135 (1984) [in Japanese].
43) D. E. Grady, Mech. Mater., 29, 181–203 (1998).
44) K. Kondo, A. Sawaoaka and S. Sito, “High-Pressure Science and Technology”, Ed. By K. D. Timmerhaus and M. S. Baebler, Plenum Press, New York (1979) pp. 905–910.
45) K. Kondo and T.-J. Ahrens, Phys. Chem. Miner., 9, 173–181 (1983).
46) K. Kondo and A. Sawaoaka, J. Appl. Phys., 52, 1590–1591 (1981).
47) K. Kondo, Kouatsu-no-Kagaku-to-gijutsu, 4, 138–147 (1995) [in Japanese].
48) H. Stunitz, J. D. Fitz Gerald and J. Tullis, Tectonophysics, 372, 215–233 (2003).
49) T. T. Zhua, J. Bushbya and D. J. Dunstanb, J. Mech. Phys. Solids, 23, 235–253 (1990).
50) A. R. Yund and J. Tullis, Contrib. Mineral. Petr., 108, 346–355 (1991).
51) H. Miura, T. Sakai, H. Hamaji and J. J. Jonas, Scripta Mater., 50, 65–69 (2004).
52) M. Brede and P. Haassen, Acta Metall., 36, 2003–2018 (1988).
53) J. Lankford, W. W. Predebon, J. M. Staehler, G. Subhash, B. J. Pletka and C. E. Anderson, Mech. Mater., 29, 205–218 (1998).
54) Y.-B. Xin and K. J. Hsia, Acta Mater., 45, 1747–1759 (1997).
55) M. Levedev, J. Akedo, K. Mori and T. Eiju, J. Vac. Sci. Technol. A, 18, 563–566 (2000).
56) S. D. Johnsoana, D. Schwera, D.-S. Park, Y.-S. Park and E. P. Gorzkowska, Surf. Coat. Tech., 332, 542–549 (2017).
57) L. Zhu, T.-C. Jen, Y.-T. Pan and H.-S. Chen, J. Therm. Spray Techn., 26, 1859–1873 (2017).
58) M. Yoshida, H. Ogiso, S. Nakano and J. Akedo, Rev. Sci. Instrum., 76, 093905 (2005).
59) D. Hanfl, J. Exner, M. Schubert, T. Stocker, P. Fuierer and R. Moos, J. Ceram. Sci. Technol., 06, 147–182 (2015).
60) J. T. Dickinson, L. C. Jensen and A. Jahan-Latibari, J. Vac. Sci. Technol. A, 2, 1112–1116 (1984).
61) L. Scudiero, J. T. Dickinson and Y. Enomoto, Phys. Chem. Miner., 25, 566–573 (1998).
62) K. Kondo, S. Soga, A. Sawaoaka and M. Araki, J. Mater. Sci., 20, 1033–1048 (1985).
63) T. Taniguchi and K. Kondo, Adv. Ceram. Mater., 3, 399–402 (1988).
64) J. Akedo, PAT No. 3265481 (2001).
65) T. T. Zhua, J. Bushbya and D. J. Dunstahn, J. Mech. Phys. Solids, 56, 1170–1185 (2008).
66) T. Sugita, K. Ueda and K. Endo, Precis. Eng., 52, 2138 (1986) [in Japanese].
67) M. Miyashita, Precis. Eng., 56, 5 (1990) [in Japanese].
68) F. Ostlund, K. Rzepiejewska-Malyska, K. Leifer, L. M. Hale, Y. Tang, R. Ballarini, W. W. Gerberich and J. Michlern, Adv. Funct. Mater., 19, 2439–2444 (2009).
69) A. Montagne, S. Pathak, X. Maeder and J. Michlern,
120) J.-J. Choi, J. Ryu, B.-D. Hahn, W.-H. Yoon, B.-K. Lee, J.-H. Choi and D.-S. Park, J. Am. Ceram. Soc., 93, 1614–1618 (2010).
121) J.-J. Choi, J.-H. Choi, J. Ryu, B.-D. Hahn, J.-W. Kim, C.-W. Ahn, W.-H. Yoon and D.-S. Park, J. Alloy. Compd., 545, 186–189 (2012).
122) W.-H. Yoon, J. Ryu, J.-J. Choi, B.-D. Hahn, J. H. Choi, B.-K. Lee, J.-H. Cho and D.-S. Park, J. Am. Ceram. Soc., 93, 2125–2127 (2010).
123) J.-H. Jung, B.-D. Hahn, W.-H. Yoon, D.-S. Park, J.-J. Choi, J. Ryu, J.-W. Kim, C. Ahn and K.-M. Song, J. Eur. Ceram. Soc., 32, 2451–2457 (2012).
124) H.-S. Ryu, T.-S. Lim, J.-H. Ryu and S.-H. Hong, J. Electrochem. Soc., 160, C42–C47 (2013).
125) J. Ryu, D.-S. Park, B.-D. Hahn, J.-J. Choi, W.-H. Yoon, K.-Y. Kim and H.-S. Yun, Appl. Catal. B-Environ., 83, 1–7 (2008).
126) M.-W. Lee, J.-J. Park, D. Y. Kim, S. G. Yoon, H. Y. Kim, D. Kim, S. C. James, S. Chandra, T. Coyle, J.-H. Ryu, W.-H. Yoon and D.-S. Park, J. Aerosol Sci., 42, 771–780 (2011).
127) H.-S. Ryu, D.-S. Park and S.-H. Hong, Surf. Coat. Techn., 219, 82–87 (2013).
128) B.-D. Hahn, D.-S. Park, J.-J. Choi, J. Ryu, W.-H. Yoon, B.-K. Lee and H.-E. Kim, J. Am. Ceram. Soc., 92, 793–799 (2009).
129) B.-D. Hahn, J.-M. Lee, D.-S. Park, J.-J. Choi, J. Ryu, W.-H. Yoon, B.-K. Lee, D.-S. Shin and H.-E. Kim, Acta Biomater., 5, 3205–3214 (2009).
130) B.-D. Hahn, J.-M. Lee, D.-S. Park, J.-J. Choi, J. Ryu, W.-H. Yoon, B.-K. Lee, D.-S. Shin and H.-E. Kim, Thin Solid Films, 518, 2194–2199 (2010).
131) B.-D. Hahn, D.-S. Park, J.-J. Choi, J. Ryu, W.-H. Yoon, J.-H. Choi, Y.-L. Cho, C. Park, H.-E. Kim and S.-G. Kim, Appl. Surf. Sci., 257, 7792–7799 (2011).
132) S. Kim, M.-Y. Cho, I.-S. Kim, W.-J. Kim, S.-H. Park, S. Baek, J.-M. Oh and S.-w. Kim, Adv. Mater. Interfaces, 1900359, 1–8 (2019).
133) J. Iwasawa, R. Nishimizu, M. Tokita, M. Kiyohara and K. Uematsu, J. Am. Ceram. Soc., 90, 2327–2332 (2007).
134) H. Choi, K. Kim, H. Choi, S. Kang, J. Yun, Y. Shin and T. Kim, Surf. Coat. Techn., 205, S125–S128 (2010).

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