1. INTRODUCTION

Thermal plasmas, normally generated by DC (direct current) arc or inductively coupled RF (Radio Frequency) discharge, can be described as a high enthalpy flame with extremely high temperature fields (1,000~20,000 K) and a wide range of velocity fields from several m/s [1-5] to supersonic values [6-7]. Since the resultant huge enthalpy can be realized for various kinds of plasma forming gases and easily controlled by electricity, thermal plasmas have been expected to facilitate not only fast chemical reactions but also rapid heat transfer in a variety of synthetic routes for nano-sized materials [8-11]. For example, reactive gases, such as, nitrogen and oxygen, can be chemically activated in the form of various radicals dissociated or ionized in their thermal plasma state. As reported in many other papers [8-10], these radicals can be directly used in the formation of nitrides and oxides with very small sizes. Moreover, many kinds of micron-sized solid precursors can be immediately heated up to their evaporation points when they are injected into thermal plasma flames. In this case, nano-sized particles can also be synthesized by quenching those vapors as shown in Fig. 1. These features of thermal plasma available for the synthesis of nano-sized materials, however, vary depending on the employed plasma torches [9,11]. For example, non-transferred DC torches with hot cathodes normally produce a hot ionized flame with temperatures in the range of 8,000~16,000 K at the torch exit [2]. The velocities of this flame can reach to hundreds m/s or to several thousand m/s depending on the torch nozzle structures at a given gas flow rate [2,12-14]. On the other hand, RF plasma torches produce relatively large flame of 5,000~10,000 K moving at mild velocities of up to several tens m/s [2,5,15-17]. In addition, the absence of electrodes may be favorable for the formation of reactive thermal plasma. Hence, actual synthesis systems have adopted plasma torches, maximizing their unique features, such as, flow fields, flame sizes, and torch structure itself, to the targeted nano materials. Among the torches adopted in this way, three kinds of plasma torches are illustrated in Fig. 2 as the typical plasma sources available for synthesis of nano-sized materials. Since the characteristics of these torches have been intensively studied with the main features of the generated thermal plasmas [1~5], we will address a brief review on their application results to various materials in this paper, such as, metals, ceramics, glasses, carbonaceous materials and other functional composites like metal-oxide catalysts and core-shell structured nano-materials.
For most kinds of metals with sizes of <50 nm, similar changes may take place due to the size effect on their properties. However, their practical applications are now limited because they are still expensive and difficult to mass production. In contrast, metal powders with relatively large sizes of 50 ~ 500 nm are increasingly in demand in various industries as the alternatives to conventional micron-sized ones. For example, Ni powders with sizes of 50 ~ 200 nm are very promising as the attractive electrode materials in high performance MLCC (Multi-Layered Ceramic Capacitor). For this reason, our review will be focused on the efforts to prepare metal powders with the sizes of 50 ~ 500 nm using thermal plasmas.

In recent decades, transferred DC plasma torches as shown in Fig. 2 (a) have been widely employed as an effective heat source for the production of nano metal powders with sizes around 50 nm. Since the target metals are used as electrodes in this type of plasma torch, the transferred arc plasma evaporates the electrode materials directly. Accordingly, nano-sized powders can be easily obtained from most kinds of metals by means of transferred DC plasma torch. For the same reason, however, the rate of generating nano-sized metal particles is strongly dependent on physical properties of metals used as electrode target. For example, S. Ohno et. al.'s [22] have recorded the generation rate of nano-sized particles for 16 metals as follow: Mn (64.2) > Ag (10.1) > Al (8.7) > Sc (6.3) > Cr (5.9) > Si (1.3) > Pd (1.1) > Fe (1.0) > Cu (0.8) > Co (0.7) > Ti (0.5) > Ni (0.3) > V (0.1) > Mo (0.01) > Ta (0.006) > W (0.004). In this enumeration, the numbers in parenthesis represent the relative ratios to the generation rate of iron metal, which is counted 1.0. The related data were obtained at the same input power and experimental conditions of 50% H2 - 50% Ar atmosphere [22]. From above experimental results and thermodynamic calculations on evaporation rates of each metal, they concluded that the driving force for the generation of particles from metals is much concerned with physical properties of metal, such as, heat of vaporization and melting points of metals. For the improvement of these generation rates, the injection of reducing gas, such as, N2 and H2, can be helpful regardless of their melting points [22-24]. In addition, it is also worth noticing that some patented apparatus uses the spherical target materials as anodes for their easy evaporation [24-26]. By adopting spherical shape anode targets, it has been explained that formation of melted slags can be minimized and hydrogen permeation into target materials is also expedited.

Since the anode electrodes are made of consumable target materials in these applications, however, they should be replenished after each batch of metal nano-powders, and consequently, the production process using transferred DC plasma torch becomes often non-continuous. As an alternative to this batch process, non-transferred DC or RF plasma torches have been equipped in continuous production system of nano-sized powders. Fig. 2 (b) shows a typical usage of non-transferred DC plasma torches for continuous production of metal powders. In this figure, the targeted materials are injected into thermal plasma flame as a precursor powder while the torch electrodes are used only for maintaining the formation of arc plasma [27-28]. For effective heating of the precursors, injection ports can be located on the inner surface of cylindrical anode nozzle [29]. With the injection ports at torch exit, which is conventionally used for plasma spray coating applications, however, it is hard for this type of DC torch to enable most of the injected precursors to be fully evaporated during their flight of plasma flame. As reported in other papers [30-32], there are many trajectories far from full evaporation of injected metal precursors in this case. Although smaller particles are relatively easily evaporated, some parts of the precursors injected into the plasma flame can be still reproduced without full evaporation due to their ineffective trajectories [33].

As a heat source to alleviate incomplete heating problems of injected precursors, RF plasma torches have
attracted much attention. Since this type of torch needs no electrode for sustaining plasma, axial injection of precursor along the centerline of RF torch is possible as illustrated in Fig. 2 (c). Accordingly, high temperature region of RF plasma can be effectively used in heating up the solid precursors if they are injected along the centerline of the torch. The absence of an electrode is also advantageous for the synthesis of high purity materials. Thanks to these advantages in in-flight treatment of injected solid precursors, RF plasma torches have been widely adopted to make a variety of small sized metal powders [34-40]. For example, Al, Ni, and W metals with micron-sizes can be reformed into small particles with average diameters around 50 nm at the plate power level of 60~70 kW and the feed rate of 19~20 g/min [34]. Compared with a non-transferred DC plasma torch, however, the competitive advantages of a RF plasma torch come from not only its high enthalpy available along the centerline of the RF plasma torch but also relatively long residence time of axially injected precursors. From the numerical simulations using metal or ceramic particles with sizes of 20 ~ 60 µm, such as, Fe, Ni, Cu, W and Al₂O₃, their complete evaporation has been expected to take times of 4.5 ~ 8.5 ms along the centerline of the RF plasma torch [35-37]. In other words, if the solid precursors are injected at the velocity of 20 m/sec, evaporation times of 4.5 ~ 8.5 ms require torch lengths of 100 ~ 170 mm. Since these lengths are easily attainable by an RF plasma torch combined with an extended cylindrical reactor [38], many kinds of metal and oxides with micron sizes are expected to be immediately heated up to their evaporation points by the RF plasma torch system. The extended cylindrical reactor can be designed to expand and decelerate the RF plasma flame by enlarging its diameter compared with RF torch diameter as shown in Fig. 3 [41]. In the designed system of Fig. 3, the RF plasma torch plays a role of heat source for melting or evaporation of the precursors injected along the centerline of the torch. Moving axially along the centerline, however, some of the heated precursors can spread out radially due to the convection and diffusion processes existing in plasma flow. After issuing out the exit of RF plasma torch, these radially dispersed trajectories can escape the hot region of plasma flame, which flows axially along the centerline of reactor. As a result, the precursors escaping from this hot region
of plasma flame may be cooled down rather than heated up. Consequently, radial expansion of RF plasma flame in a reactor may provide these precursors with extended residence time in hot region of plasma flame. In order to estimate these effects, a lot of modeling and experimental works have been conducted for the RF plasma torches coupled with reactors coaxially [42-46]. From these works, it has been confirmed that high temperature region can be expanded radially with the deceleration of RF plasma flows in a reactor having a diameter larger than one of RF plasma torch. However, the extent of the high temperature region, e.g., isothermal lines corresponding to critical temperatures, such as, 3,000 K for the boiling point of Ni, is not so large compared with the diameters of RF plasma torches. For example, expanded diameters of 3,000 K isothermal lines range from 60~70 mm for the RF plasma torches with a diameter of ~50 mm [42-46]. Accordingly, a cylindrical reactor with a slightly enlarged diameter can be helpful for effective use of RF plasma enthalpy by concentrating the expanded high temperature region. Apart from reactor design, however, heating process of injected metal precursors is significantly dependent on various operation parameters, such as, plasma input power, feeding rate, and precursor sizes. For example, Ni particles with sizes of 60 µm have been calculated to remain mostly unevaporated at torch exit when their feeding rate is increased over 30 g/min with a RF input power of 5 kW [37]. Whereas, small sizes of the injected precursors are normally in favor of complete evaporation with the increase of RF input power. In other words, high powered RF plasma torch system may be preferred for mass treatment of small sized precursors. Recently, RF plasma torch systems with plate power level of 200~300 kW have been commercialized together with high performance feeder for micron-sized powders [38].

Finally, it should be noted that prepared metal powders with very small sizes should be passivated for safety before their exposure to atmosphere.

3. THERMAL PLASMA SYNTHESIS OF NANO-SIZED NON-METAL POWDERS

Similar to the synthesis of nano-sized metal powders, size reducing of a solid precursor by thermal plasma may be the simplest way to obtain nano-sized non-metal powders. Some kinds of materials can be successfully reformed into nano-sized powders in this way. As a typical example, Fig. 4 shows the transformation of micron-sized glass powders into nano-sized ones. In this figure, one can see that the sizes of glass precursors are reduced down to < 500 nm after their in-flight treatment using RF thermal plasma [41,47]. In this special case, RF plasma torch was used as a powerful heat source to evaporate the micron-sized glass frits for their re-synthesis into very small particles. With the same purposes, other kinds of single phase oxides, such as, ZrO₂, SiO₂, Al₂O₃ and TiO₂, have been tested by various types of plasma torches [48-52]. In these applications, however, changes of their crystalline structures have been observed with successful size reduction, such as, amorphization of SiO₂ and phase transition in TiO₂. For some specialty nano-powders, however, these changes in crystalline structures can be enhanced intentionally by modification of plasma torch system. For example, B. Bora et.al.’s have used a supersonic DC plasma torch for achieving specialty Al₂O₃ nano-powders with amorphous crystalline structures [53]. In their experiment, a supersonic Laval nozzle was attached to a non-transferred DC plasma torch in order to obtain high quenching rate requested for amorphization of the in-flight treated Al₂O₃ precursors [53-55].

These size reducing processes of refractory non-metal solid precursors, however, often show a limitation for large scale application because the dense loading effect on the evaporation of injected materials becomes severe as feeding rate is increased for mass production [37]. Actually, it has been estimated by M. Kambara et. al.’s
that solid fine powders can be evaporated at 1 kg/h by a 100 kW class RF plasma system. At the same power level, however, they insisted that liquid and gaseous precursors can be treated at 10 and 100 kg/h, respectively. Accordingly, the choice of precursors needs to be determined in the basis of economical worth. For example, some kinds of nano-materials are obtainable in a large scale by means of direct decomposition of liquids or gaseous precursors using thermal plasmas. Carbonaceous nano-materials, such as CNT (carbon nanotubes) and specialty CB (carbon black), may be the most notable examples. Traditionally, CNTs with high purity have been obtained using the transferred DC arc discharge generated by graphite electrodes [57-60]. Due to the limitations of the batch process inherent in this type of plasma system, however, there have been many efforts to produce CNTs continuously by decomposing liquid or gas phase hydrocarbons with non-transferred DC or RF plasma torches [61-64]. For example, Choi et al. reported that continuous production of CNTs can be processed by injecting CH$_4$ gas and Ni-Y catalyst into the flame of non-transferred DC plasma torch [61]. In this experiment, multi-walled CNTs are mainly produced with high purity as shown in Fig. 5 at very high growth rate. Besides CNTs, the high enthalpy of thermal plasma has also been employed as a main heat source to decompose hydrocarbons into hydrogen rich fuels and solid carbon black, so called, plasma black [65-70]. As reported in many other papers and patents [65-70], plasma black can be formed like crinkled papers having well-developed graphite crystallites since they are produced at high temperatures over 2,000 K by thermal plasmas. Fig. 6 shows an example of this specialty plasma black, which was obtained from methane decomposition by a non-transferred DC plasma torch [70].

In the applications above mentioned, thermal plasmas are mainly used as a heat source for evaporation of solid precursors or decomposition of gaseous precursors. In other words, plasma forming gases will take little part in the synthesis process of nano-sized particles except the role of heat transfer media. If the reactive gases, such as, oxygen and nitrogen, are used as one of the main constituents to form a plasma flame, however, chemical reactions between the radical reactive species and the heated precursors can be conducive to synthesis of nano-sized materials. Many kinds of oxides, carbides and nitrides have been synthesized in this way [10,71-74]. For example, nano-sized Al$_2$O$_3$ or TiO$_2$ particles can be easily obtained by in-flight treatment of Al metal or titanium hydrides in oxidative thermal plasma [71,72]. Since the oxidation reaction of metal is normally exothermic, these processes can be more energy efficient.

![Fig. 5. High-resolution TEM Images of CNTs Prepared by Non-transferred DC Plasma Torch: (a) Open-tip CNTs, (b) Encapsulated Tip and Partially Filled CNTs, (c) wall Structure of a Cylindrical Multi-walled CNT, and (d) wall Structure of a Bamboo-like Multi-walled CNT [61].](image)
effective compared with size reduction of micron-sized Al₂O₃ or TiO₂ precursors into nano-sized particles. In addition to these nano-sized oxide powders, a variety of carbides with submicron sizes, such as, nano-sized SiC, WC and TiC, have been prepared using reactive thermal plasmas [73-77]. In these applications, liquid or gaseous hydrocarbons, such as methane, can be adopted as a cheap and commercially useful carbon source [73-74, 77]. As for the cation sources for those covalent and metallic carbides, metal powder itself or chemicals containing each metal cation can be used, depending on the thermodynamics of targeted materials and the types of plasma torches. In a similar way, nano-sized nitride powders have been synthesized by nitrogen thermal plasma [76,78-79]. For example, ultrafine AlN powders can be synthesized from in-flight treatment of Al powder by thermal plasma containing N₂ gas [78-79]. Moreover, Si₃N₄ nano powders have been reported to be prepared by the RF thermal plasma with N₂ content more than 60 vol % of the plasma forming gas [76].

4. THERMAL PLASMA SYNTHESIS OF SPECIALTY NANO-COMPOSITE POWDERS

In spite of various attempts mentioned above, reactive thermal plasma is limited to only a few kinds of nano-sized powders because of the difficulty in achieving reproducible processes [10]. Additionally, the composition of the plasma forming gas should be optimized experimentally to each application in order to match the stoichiometry of synthesized ceramics, such as, oxides, carbides and nitrides [76]. For these reasons, in-flight treatment of solid precursors may be preferred in some practical applications due to their reproducibility as well as simplicity of the plasma material process although the treatment capacity is often short of the industrial requirements. Among them, supported metal catalysts and core-shell structured nano-powders may be promising. For example, solid solution NiO-MgO catalysts with very small sizes have attracted much attention in CO₂ reforming of methane because of their high activity and selectivity as well as excellent stability during this reforming process [80]. Since the high performance of these catalysts comes from the structural features of NiO-MgO solid solution as well as the increased Ni metal surface, many efforts have been focused on finding the preparation methods to enhance the degree of solid solution at the increased content of Ni metals [80-83]. As a new route for this purpose, we introduced in-flight thermal plasma treatment of mixture precursors consisting of Ni metal and MgO oxide particles [84]. In our experiment using a RF plasma torch, it was found that mixture of Ni metal (~5 µm) and MgO oxides (~200 nm) can be reformed into nano-sized Ni particles (< 100 nm) attached to MgO nano-rods with diameters of 10-20 nm as shown in Fig. 7. In these reformed composites, the formation of a solid solution between Ni particles and MgO nano-rods was confirmed from the XRD data. Thanks to these structural properties of as-prepared composites as well as the reduced sizes of the Ni metal, as-synthesized NiO-MgO nano-powders showed not only high catalytic activity but also negligible carbon coking during the partial oxidation reaction of methane at 750 °C for 24 hr. As reported in other papers, high catalytic activity can be attributed to the small sized Ni metal particles, which are dispersed on the MgO nano-rods in Fig. 7. On the other
hand, the enhanced resistance to carbon coking seems to be caused by the structural advantages originating from the formation of a NiO-MgO solid solution. From these experimental results, we expect that simultaneous treatment of Ni metal and MgO oxides can meet two requirements of oxide supported Ni catalysts (i.e., very small Ni metal particles and the formation of NiO-MgO solid solution). In this case, it is believed that Ni metals (~5 \( \mu m \)) injected with MgO powders may experience the preferential evaporation during their RF plasma heating. For MgO precursors, however, the heat transfer from the RF plasma seems to be just enough for their changes of shape into nano-rods. As a result, MgO nano-rods can work as a nucleation seed for Ni vapors during the quenching process, which leads to very small Ni particles dispersed on the surface of MgO nano-rods as shown in Fig. 7. In addition, the consecutive consolidation process starts at the temperatures near the melting points of each element, and accordingly, the formation of NiO-MgO solid solution can also be expected on the interfaces between MgO nano-rods and Ni droplets at those temperatures [84]. Instead of refractory oxide support, such as MgO, H. Zea et al. [85] have prepared carbon supported metal catalysts using a non-transferred DC plasma torch. Unlike MgO support, however, the in-flight heating of carbon injected with Pd metal resulted in the loss of carbon surface area due to the removal of all oxygen groups from carbon supports by plasma treatment. In addition, they also reported that mixture precursors consisting of PdAg metal and Al2O3 oxides leads to significant metal loss in as-prepared catalysts because of the burial of metal particles into Al2O3 pores during their plasma treatment [85-86]. Compared with the melting points of MgO (2,852 \(^\circ\)C) and Al2O3 (2,072 \(^\circ\)C), these results indicate that oxide supports with high melting points are favorable in the thermal plasma synthesis of supported metal catalysts without metal loss.

This burial phenomenon of metal particle into ceramic pores with relatively low melting points can be, however, very useful in making a unique nano-material with core-shell structures. As disclosed in K. Nishmura et al.’s patent [87], mixture precursors of Ni metal and BaTiO3 can be easily reformed into Ni core - BaTiO3 shell structure by the RF thermal plasma. In this case, Ni metal burial into BaTiO3 oxide can take a place as discussed previously since BaTiO3 has a relatively low melting point of 1,625 \(^\circ\)C. Fig. 8 shows the TEM image of these Ni core - BaTiO3 shell structures, which is reproduced similarly to the approach in K. Nishmura et al.’s patent [87] using RF plasma torch system. In the same fashion, inorganic materials with low melting points, such as, glass, can also be used as the shell of a metal core [88]. These core-shell structured materials may be promising as the advanced nano-materials in MLCC or secondary battery. From the above results, it can be concluded that mixture precursors consisting of metal and ceramic materials can be reformed into nano-sized powders with a metal core - ceramic shell structure depending on the melting points of the shell materials. For the refractory ceramics with relatively high melting points, however, metal vapors tend to be nucleated on their surfaces, and then, to experience some kinds of high temperature reactions with heated ceramic surface, such as solid solution, sintering and other kinds of high temperature chemical reactions.
As a different example of the core-shell structured materials, it may be notable that transferred arc discharge on the mixtures of carbonaceous materials and metal powders can produce nano metal particles encapsulated by a carbon cage [89-91]. For example, Fe metal particles can be easily encapsulated by carbon layers as shown in Fig. 9 [90]. However, Si metal has been failed to fill the hollow carbon cages due to its strong tendency of carbide formation [91]. In these processes, the formation of carbon nanocapsules filled with Fe particles is attributed to the precipitation of carbon species solved in Fe metal droplets during their co-condensation [89]. If the carbide formation is preferred during the co-condensation, however, it is hard for the impregnated carbon species to escape from the metal lattices without carbon-metal reaction. It is interesting to compare this carbon caged metal particles with metal core - ceramic shell structures. In the case of metal core - ceramic shell structures, ceramic or glass materials with relatively low melting points absorb the metal particles, firstly, and then, their increased viscosity seems to play a role of cage to inhibit the emission of metal particles during quenching process. Different from ceramic or glass materials, carbon has no liquid state but its boiling point is very high over than 3,000 °C. Accordingly, it is more natural for the solid carbon to be impregnated into metal droplets, and then, precipitated in the form of carbon cage during their co-condensation processes.

Besides metal-ceramic or metal-carbonaceous materials, ceramic-ceramic nano composites can also be made by in-flight treatment of their mixture precursors. Fig. 10 shows ternary IZTO (indium zinc tin oxide) nano powders synthesized by RF thermal plasmas [92]. In this case, three kinds of oxides, such as, In₂O₃, ZnO and SnO₂, are injected into a RF plasma flame with the preset cation ratios of 6:2:2. From this in-flight treatment, IZTO powders with a single phase of In₂O₃ structure can be achieved [92]. Since those three oxides have the relatively low melting points of < 2,000 °C, their surface can be heated up to
high temperatures enough for solid solution and sintering reactions between each oxide. In this experiment, In$_2$O$_3$ takes a 60 ca. % of precursors, and consequently, these solid solution and sintering reactions may be based on In$_2$O$_3$, such as the incorporation of ZnO and SnO$_2$ into In$_2$O$_3$ structure, which leads to a unified IZTO powders with a single phase of In$_2$O$_3$ structure. However, thermal plasma synthesis of ternary nano-powders is still unreliable in stoichiometry, and accordingly, more research is needed to clarify the thermal plasma synthesis mechanism of ternary and higher nano-materials.

5. CONCLUSION

In recent decades, nano-sized materials have been widely synthesized using thermal plasma torches. Depending on the features of the target materials and employed plasma torches, various synthesis routes have been presented. For example, a single phase metal particle with sizes around 50 nm can be produced directly from bulk metal using transferred DC arc plasma. For the same purpose, non-transferred DC or RF plasma torches have also been adopted. In these cases, however, nano-sized metal particles are normally obtained by in-flight treatment of solid metal precursors with sizes of under several tens micro-meter.

In-flight treatment of solid precursors may be preferable in the preparation of nano-sized glass powders and single phase oxides, such as, ZrO$_2$, SiO$_2$, Al$_2$O$_3$ and TiO$_2$. Among them, single phase oxides can be prepared by reactive thermal plasma synthesis. However, their reproducibility and stoichiometry problems should be solved for practical applications. In spite of this limitation, reactive thermal plasmas are still important in the synthesis of nitrides and carbides with very small sizes. For specialty nano-powders, such as, oxide supported catalysts and core-shell structured nano-materials, in-flight treatment of metal-ceramic mixture precursors can be applied. Depending on the physical properties of ceramic materials, such as melting points, the treated products can become a metal core - ceramic shell structured particle or a metal catalyst dispersed on ceramic supports. For the ceramic powder of BaTiO$_3$, with relatively low melting point, the mixed Ni metals can be buried into BaTiO$_3$ droplets and reformed into Ni core - BaTiO$_3$ shell structured nano-composite. Similar results can be obtained in the form of Ni core - glass shell structures. For the refractory MgO particles, however, they seem to experience the change of shape into nano-rods instead of evaporation, and then, support highly dispersed Ni particles with the formation of NiO-MgO solid solution.

Carbonaceous materials, such as CNTs, carbon black and nano metal particles encapsulated in a carbon cage, can also be produced by transferred DC arc discharge as well as other types of torches. However, it should be noted that the properties of produced carbonaceous materials depend on the used plasma torch systems. Based on these review results, it can be concluded that the advantages of thermal plasmas, such as, high enthalpy flows combined with a rapid quenching rate, can be very promising in the synthesis of not only a single phase material but also binary or higher nano-materials.

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