Ultrasonic spray deposition of SiC nanoparticles for laminate metal composite fabrication

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1. Abstract

2. Nanoparticles have been increasingly used in functional and composite materials. One of the challenges, however, has been dispersing and controlling the nanoparticle clusters. In this study, the deposition of SiC nanoparticles via ultrasonic spraying process was investigated for a potential application in synthesis of laminate metal composites. The governing parameters of the ultrasonic spraying process which includes suspension and spraying parameters, and their influence on the deposited structure have been investigated. These parameters determine the driving force that transports the atomized droplets to the

1 substrate, the amount of liquid phase present on the substrate, and its evaporation rate. By
2 controlling these parameters, deposition structures ranging from a few SiC nanoparticles to
3 cluster sizes of 10 μm could be obtained. The potential of using ultrasonic spraying to
4 fabricate laminate composites reinforced at the interfaces with nanoparticles was
5 investigated. Composites with a uniform deposition of SiC at the interface showed better
6 mechanical properties than those with a nonuniform deposition when compared at the same
7 SiC loading.

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9 **4. Keywords:** ultrasonic spraying; nanoparticle; composite; deposition

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7. Introduction

Various techniques have been used in material coating or surface deposition, including tape casting [1], thermal spraying [2], plasma spraying [3], electrostatic spray deposition [4], spray deposition [5], spray pyrolysis [6], and ultrasonic spray deposition [7]. Among these techniques, ultrasonic spraying offers several unique and desirable characteristics. The ultrasonic spraying nozzle vibrates at high frequency using two piezoelectric discs and an amplifier. This makes the liquid leave the nozzle tip in the form of mist that has a narrow droplet size distribution and a very low spraying velocity (in the order of 1 m/s) compared with other spraying techniques [8]. It is a process that is favored by its simplicity and low cost, in addition to its flexibility in producing thin multilayered deposited structures [9]. It offers a relatively moderate deposition surface temperatures of 100–500°C [10]. Accordingly, a wide variety of substrate materials can be used [11] by tuning the spraying parameters. The technique also allows accurate control of the deposition rate [12] and deposition structure [7]. In a recent study, the deposition structures of ultrasonic and handheld spraying techniques were compared, and the ultrasonic spraying technique resulted in a smoother and more uniform deposition structure [13]. It has been used to fabricate fuel cell electrodes [14], thin films [15, 16], nanocatalysts [17], high temperature oxidation resistant coatings [16], and electrochromic windows [18]. The atomized droplet size, which significantly influences the deposition structure and the spray quality, is mainly determined by the liquid properties (surface tension and density) and the nozzle vibration frequency [19]. Moreover, spraying parameters, such as the nozzle vibration frequency, flow rate, deposition surface temperature [20], spraying air pressure [21], and spraying distance [12], affect the final deposition structure.

1 In this study, the ultrasonic spraying is used for spraying nano-suspension systems to
2 deposit nanoparticles on substrate materials. Nano-suspensions or nano-fluids are liquid with
3 homogeneously suspended nano-sized particles [22], which may be metals [23], oxides [24],
4 carbides [16], and carbon structured materials [25]. One of the main advantages of using
5 nanoparticle suspensions is the low tendency for particle agglomeration and sedimentation,
6 which will keep the particles suspended and dispersed throughout the operation and may
7 potentially improve the quality of deposited layer [22]. Nano-suspension spraying has been
8 used in many applications. It has been used to process granular nanoparticles using various
9 spraying techniques, where the suspension is sprayed and the droplet dries while traveling and
10 can then be collected [26-29]. During drying, the nanoparticles can be self-assembled in various
11 morphologies depending on the process conditions [30]. Moreover, spraying suspension of
12 CNT has been used to deposit a CNT network film on a substrate to fabricate a conductive film
13 for electronic applications [31, 32]. Hand spraying of CNT micro-ball suspension was used to
14 fabricate dye-sensitized solar cells [33]. Spraying of nano-suspension was also used to fabricate
15 solid oxide fuel cells using a conventional spraying atomizer [34]. In a recent study, ultrasonic
16 spraying was used to deposit graphene flakes films on polymer-coated glass. The researchers
17 chose the ultrasonic spraying technique as it produced relatively small droplets of a few
18 micrometers that allowed rapid solvent evaporation [35].

19 In this study, the ultrasonic spraying technique was applied to accurately control the
20 deposition structure of nanoparticles needed to produce layered metal composites reinforced by
21 nanoparticles at the interfaces. Previous studies demonstrated that laminated composites can be
22 designed to improve several characteristics, including damage tolerance [36], impact toughness

[37], fatigue behavior [38], corrosion resistance, wear resistance, formability, and ductility [39].

In manufacturing of metal laminate composites reinforced with nanoparticles, several studies were found, each of which employed techniques involving manual spreading of the reinforcements [40], immersing the substrate in suspension systems [41], and air gun spraying to deposit nanoparticles [42]. The challenge, however, has been in trying to precisely control the spatial distribution of the reinforcement elements.

In this study, the deposition of silicon carbide (SiC) nanoparticles using ultrasonic spraying method was investigated for the purpose of synthesizing a multilayer composite made of AZ31 magnesium alloy. The study entailed understanding the effects of suspension and spraying parameters on the deposited microstructure. The size and amount of nanoparticles in the ethanol suspension affect the initial atomization droplet size, which was calculated using a theoretical model. The effects of the spraying parameters (flow rate, substrate surface temperature, air pressure, and nozzle to substrate distance) on the deposition morphology were investigated to identify appropriate parameter ranges to make the multilayer composite. Finally, an AZ31 magnesium alloy laminate composite reinforced by silicon carbide (SiC) nanoparticles was fabricated, and the potential use of ultrasonic spraying technique for laminate composite synthesis was discussed.

8. Experimental procedure

Ultrasonic spraying is a promising technique that can coat surfaces with various nanoparticles and chemicals, and in so doing, precisely control the deposited microstructure. In this study, an ultrasonic deposition system (Exacta-Coat Ultrasonic Coating System, Sono-Tek Corp.) as shown in Fig. 1 was used to perform the spraying. The system features a sonic syringe

1 that controls the flow rate of the suspension and provides bursts of vibration to prevent the
2 suspended particles from developing sedimentation and agglomeration.

3 The spray-deposited structure can be influenced by various processing parameters, which
4 may be classified into two categories: suspension and spraying parameters. The suspension
5 parameters are the suspended particle type, size, and SiC concentration. Suspension
6 concentrations of 0-16 wt.% of SiC were used to study the effect on the surface tension for two
7 different particle sizes, 80 and 800 nm. For the 800 nm SiC, it was challenging to keep the
8 suspension homogeneous during the spraying process due to the particles developing
9 sedimentation and tendency to clog the spraying tubes and system. On the other hand, the 80
10 nm SiC particle suspension could be kept stable for days, which made it favorable for the
11 spraying process. Nanoparticles were mixed into ethanol and sonicated for six hours in an
12 ultrasonic bath to achieve a stable and homogenous suspension [43]. The surface tension was
13 measured using the pendant drop method [44]. The important spraying parameters that could
14 affect the deposition structure are the deposition surface temperature (T), the spraying suspension
15 flow rate (Q), the spraying air pressure (P), and the nozzle distance (D) [8]. Each parameter was
16 investigated by analyzing the deposited structure qualitatively under a scanning electron
17 microscope (SEM). For spraying, a low suspension concentration was prepared using the 80 nm
18 SiC particles with a concentration of 0.1 wt.% SiC.

19 Fig. 2 shows a schematic overview of the spraying process and the spraying path. A
20 total of 12 passes were used for each sample with a nozzle velocity of 10 mm/sec. The spacing
21 between the centers of two adjacent lines was 2 mm, which provided small enough spacing so

that the spray area overlapped and the final deposited structure was uniform. The detailed spraying conditions and parameters are summarized in Table 1.

A laminate composite of magnesium alloy (AZ31) sheets and SiC nanoparticles were fabricated. The AZ31-SiC laminate composite was comprised of 15 layers of AZ31 sheets (80–100 μm thick) sprayed with SiC at the interface. The chemical composition of the AZ31 sheet is provided in Table 2. Composites with different SiC loadings of 0, 0.15, 0.3, and 0.6 wt.% were synthesized.

The experimental setup used for composite synthesis is shown in Fig. 3. The die was made of H13 tool steel and was lubricated by spraying a thin layer of boron nitride to prevent potential reaction between the sample and the die at elevated temperatures. The consolidation was performed in two stages. First, a pre-compaction pressure of 50 MPa was applied to the stacked layers at room temperature. Then the temperature was raised to the mushy zone of the AZ31 alloy (between the solidus and liquidus temperature) [45] while 50 MPa of pressure was maintained. The stacked layers were hot pressed under 50 MPa for 20 minutes at 610°C, at which temperature the liquid phase is about 9%. The obtained composites were cut using a diamond saw and were polished to the final dimensions (0.9 mm in thickness and 1.2 mm in width) needed to perform the three-point bend test. The flexural stress and flexural strain were recorded using the materials testing system.

9. Results and discussion

The droplet size is one of the main parameters that affects the deposited microstructure and is mainly determined by the ultrasonic frequency of the nozzle and the suspension properties (surface tension and density) [19]. The droplet size can be approximately estimated by Eqn. (1)

[8], which represents a model that predicts the diameter of the atomized droplet exiting from the ultrasonic nozzle used in various studies [7, 8, 46]:

$$d_d = 2 \frac{\sqrt[3]{2}}{\pi} \left(\frac{\pi \sigma}{\rho f^2} \right)^{\frac{1}{3}} \quad (1)$$

where, σ and ρ are the surface tension and the density of the suspension, respectively; and f is the ultrasonic nozzle frequency. Note that the surface tension and density have opposite effect on the atomized droplet size.

Fig. 4(a) shows the relation between surface tension and particle loading for two different SiC particle sizes (80 nm and 800 nm). The surface tension increased as the SiC loading increased. Zhu et al. [47] reported a similar observation. Since the particles tend to agglomerate at the gas-liquid interface, it increases the concentration of particles at the surface. At the gas-liquid interface, two forces, repulsive force (electrostatic) and attractive force (van der Waals), compete with each other [48] and can affect the surface free energy of the suspension. At a low concentration, the particles are farther away from each other, and therefore, the particle interaction is lower, resulting in a lower surface tension according to Saeid et al. [49]. On the other hand, as the concentration increases, the distance between the particles becomes shorter, which increases the attractive force and results in surface free energy increase [49]. The observation also agrees with findings from other researchers [50].

It was observed that the suspension properties were significantly affected not only by the amount of the suspended particles but also by their size. When the same amount is loaded, the smaller particle size increases the total free surface area, which results in increase of the total surface free energy [48]. Moreover, the surface tension of the suspension affects the deposited

1 structure. The morphology of the deposited structure becomes more uniform at a lower surface
2 tension due to enhanced wetting that helps to enlarge the droplet spread area upon contacting the
3 surface and allows merging of these droplets [51].

4 Using Eqn. (1), the droplet sizes for various conditions were calculated as shown in Fig.
5 5. It can be noticed that the change in droplet size is reversed depending on the size of the
6 suspended particle. As mentioned earlier, the surface tension and density have the opposite
7 effect on atomization droplet size as the particle loading is increased. Since the change in
8 surface tension is much lower for larger particles as the loading is increased, the droplet size
9 decreased for larger particles with increasing loading (see Fig. 5(a)). However, for the typical
10 range of **suspension concentration** used in spraying, atomization droplet size is largely
11 determined by the nozzle frequency as shown in Fig. 5(b). Since the spray system has a fixed
12 nozzle frequency of 120 kHz, the expected droplet size is in the order of 15 μm .

13 The final deposited droplet size may **vary** depending on the evaporation and drying
14 dynamics of the droplet when it contacts the heated surface [52]. **Because** the prediction of the
15 final droplet size **before colliding into the substrate is complex, the deposition patterns of single**
16 **droplets were experimentally measured.** A single pass spray was applied on the heated
17 substrate with a fast spraying speed of 100 mm/sec. The spraying was performed using a 0.1
18 wt.% SiC **(80 nm)**-ethanol suspension at 300°C, under air pressure of 0.5 kPa, and **with** a
19 suspension flow rate of 0.25 ml/min. SEM images of the single droplets are shown in Fig. 6.

20 It can be observed that nanoparticles form coffee ring patterns upon deposition and tend
21 to cluster at the gas-liquid interface of the droplet [53]. Ring-like stains are commonly seen in
22 the drops containing dispersed solutes. When the particles are homogeneously dispersed in the

suspension droplet, the droplet spreads and the suspension begins to evaporate as soon as it collides with the surface. At the gas-liquid contact line, the suspended particles begin to deposit and cause the pinning of the contact line. Upon further evaporation, the droplet shrinkage is hindered in the horizontal direction, but it is allowed in the vertical one. The pinning of the contact line causes the migration of the liquid to the contact line to replenish the evaporated liquid. As a result, the particles carried by the liquid deposit and cluster at the contact line [54]. The size of the deposited droplet patterns varies in a wide range with a minimum of few microns to a maximum of about 50 μm . Most of the patterns, however, ranged between 20 and 50 μm , which are larger than the initially estimated atomized droplet size of 15 μm , since the droplets spread due to the momentum as soon as it contacts the surface.

The effect of the flow rate on the deposited structure is shown in Fig. 7. The samples were sprayed using a 0.1 wt.% SiC (80 nm)-ethanol suspension at the heat plate temperature of 350°C, under the air pressure of 0.5 kPa, and at the flow rates of 0.25–1.00 ml/min. As the flow rate increased, the SiC cluster size increased. Fig. 7(d) and (f) show that the SiC particles form a continuous line of segregated particles, which is interrupted by large clusters of SiC nanoparticles. The formation of such clusters during evaporation depends on the evaporation time of the suspension during its transportation to the substrate and after deposition. As the flow rate increases, the amount of liquid phase transported during spraying is higher, resulting in a longer evaporation time. The presence of a relatively large amount of the liquid phase on the deposition substrate allows the suspended particles to segregate and cluster at the contact lines. In contrast, spraying at a lower flow rate will help improve the uniformity and homogeneity of the deposited microstructure. The deposited structure will be favored with relatively smaller

discontinuous nanoparticle clusters with a narrower clusters size distribution (Fig. 7(a)). For the 0.25 ml/min sample, the deposited nanoparticle cluster size varied from a single particle (80 nm) up to 20 μm . For the 1.00 ml/min sample, small clusters were observed in the range of few particles up to 70 μm . Naoki et al. [55] reported similar results where they studied the effect of the spraying time on the uniformity of the deposited structure. They reported that the shorter the spraying time (a smaller spraying amount) resulted in an evenly coated surface with a uniform structure while the longer one resulted in a non-uniform, highly textured deposited layer [55].

As the flow rate increases, the deposited structure becomes more porous. In a typical spraying environment, the deposited structure is formed by the accumulation of the sprayed particles of each spraying pass. The morphology and texture of the dried deposited layer affect the drying dynamics of the successive sprayed layer [56]. When the dried deposited layer surface is rough (with high peaks and low valleys), the freshly deposited droplets dry on the peaks and do not fill the cavities on the surface due to the surface tension forming porous structures [55].

The effect of the deposition surface temperature is shown in Fig. 8. The spraying was performed using a 0.1 wt.% SiC (80 nm)-ethanol suspension under an air pressure of 0.5 kPa, and with a suspension flow rate of 0.25 ml/min. At lower temperature, the suspension evaporation is slow and leads to agglomeration of the sprayed droplets. While evaporating, the nanoparticles begin to form larger clusters, which are continuous in the spraying direction and have lateral peripheral branches that grow perpendicular to the spraying direction as shown in Fig. 8(a) and (b). These peripheral branches are caused by fingering instability [52]. The instability occurs at the three phase contact line (gas, liquid, and particle) [57]. At higher

temperatures, the evaporation rate is higher, thus leading to the reduction of the droplet size during travel [58]. A complete evaporation of relatively fine droplets may occur before they even reach the surface [59], which results in a loss of particles and prevents deposition. Moreover, the heated surface generates thermophoretic forces in an upward direction against the droplet movement. These forces contribute to the drag forces that hinder the droplet freefall and cause the droplets to deviate from their expected trajectory. For smaller droplets, the deviation from the droplet trajectory is greater than that of the relatively larger ones [12]. If complete evaporation occurs, the suspended particles do not have enough inertia to reach the substrate, and therefore, they are carried away from the substrate. The inertia of the traveling droplet needs to be above a critical value in order to overcome the thermophoretic forces and to be successfully deposited on the surface [7]. As seen in Fig. 8(e) and (f), the substrate is nearly free from any particle deposition at 400°C.

Fig. 9 shows the effect of spraying air pressure on the deposited microstructure. The samples were sprayed using a 0.1 wt.% SiC (80 nm)-ethanol suspension at 350°C, with a suspension flow rate of 0.25 ml/min, and at air pressure settings of 0.25, 0.5, and 1.0 kPa. At the lowest air pressure (0.25 kPa), no SiC particles were observed on the substrate. This may be due to the lack of the force driving the nanoparticles to deposit on the substrate. As the droplet travels towards the substrate, the droplet velocity decays due to the air drag and thermophoretic forces [12]. At lower air pressure, the droplets take longer time to reach the substrate, which leads to partial or complete evaporation during travel. This can result in loss of particles as discussed earlier. The sample sprayed under an air pressure of 0.5 kPa showed a wide range of nanoparticle cluster size distribution as shown in Fig. 9 (a) and (b). As the air pressure

increased to 1.0 kPa, only relatively larger nanoparticle clusters were present on the deposition surface, while smaller sized clusters were nearly absent. It is speculated that the violent air streams from higher air pressure blew away the weakly attached deposited clusters [55]. The nozzle distance from the deposition substrate had an effect similar to the effect of the air pressure. There was no deposition of nanoparticles if the nozzle was either too close ($D = 15$ mm) or far ($D = 50$ mm) from the substrate. As a result, only a limited nozzle distance range was available for each combination of spraying parameters.

The potential of fabricating AZ31-SiC laminate composites via ultrasonic spraying was assessed by performing a three point bend test on synthesized composites. The eventual deposited amount of SiC on the substrate was measured for the spraying condition used to fabricate the composites ($T=350^{\circ}\text{C}$, $P=0.5$ kPa, and $Q=0.25$ ml/min). A direct measurement of the deposited amount for each coupon, which requires 6-24 spray passes, was not possible since the amount deposited fell below the resolution of the balance (0.0001 g). For this reason, the suspension was sprayed for 200 passes on 10 coupons, and the average deposition per pass was determined [60]. The measured deposition amount per pass for the set of conditions, $T=350^{\circ}\text{C}$, $P=0.5$ kPa, and $Q=0.25$ ml/min, was 0.0255 g/m².

The flexural stress and strain were calculated from the measured force and displacement data using Eqns. (2) and (3) [61].

$$\sigma_f = 3PL / 2wh^2 \quad (2)$$

$$\varepsilon_f = 6d_c h / L^2 \quad (3)$$

σ_f and ε_f are the flexural stress and flexural strain, respectively. P is the load, L is the support span, w and h are the width and depth of the specimen, respectively, and d_c is the deflection at

the middle of the span. Fig. 10 shows the flexural strength and strain of the consolidated samples with different SiC (80 nm) loadings (0.15–0.6 wt.% SiC). The samples were sprayed at 350°C, with a flow rate of 0.25 ml/min under a pressure of 0.5 kPa and from a distance of 25 mm. The addition of SiC at the interface between the consolidated layers increased the yield strength of the composite. The ultimate flexural strength, however, was only marginally improved compared with the unreinforced sample. The SiC reinforcement strengthened the composite until the yield, but did not change the hardening behavior since it was primarily governed by the AZ31 substrate material properties. An excessive amount of SiC loading at the interface resulted in degradation of mechanical properties as observed for 0.6 wt.% SiC sample in Fig. 10. Too thick of a layer of SiC nanoparticles prevented bonding of the AZ31 sheets.

To compare the effect of the deposition layer morphology on the mechanical properties of the composite, a sample was synthesized with high flow rate (1.0 ml/min) while the other parameters were kept the same. Such spraying conditions led to a nonuniform layer with large porous nanoparticle clusters (see Fig. 7), and the synthesized composite showed poor mechanical properties (see Fig. 10). As mentioned in earlier discussion, a high flow rate resulted in the formation of large SiC clusters and a highly porous deposition microstructure. The large clusters introduced uneven distribution of nanoparticles at the interface, and porous sites may act as crack nucleation points, which contribute to early failure of the composite.

10. Conclusions

In this study, the dispersion and control of the deposited SiC nanoparticles were investigated using the ultrasonic spraying process. The ultrasonic spray deposition is governed

by the suspension properties and the spraying parameters. The conclusions from this work can be summarized as the following:

- The atomization droplet size was largely affected by the nozzle vibration frequency while the suspension parameters only had a limited influence. According to Eqn (1), The change in suspension concentration up to 16 wt.% SiC only resulted in droplet size variation of approximately 1 μm .
- The deposited nanoparticle cluster size and morphology were affected by two main factors: the driving force that transports the atomized droplet from the nozzle to the substrate, and the evaporation behavior of the droplet (the amount of liquid phase present on the substrate and its evaporation rate). The amount of the liquid phase on the substrate and its evaporation rate were determined by the flow rate and the deposition surface temperature. The driving force is mainly determined by the air pressure and the nozzle to substrate distance.
- Having a large amount of liquid phase present on the substrate and low evaporation rate increased the nanoparticle cluster size and resulted in nonuniform deposition microstructure. Although a minimum inertia for the droplet is required for deposition of nanoparticles, violent air streams may destruct the deposited structure.
- The use of ultrasonic spraying of nanoparticles showed a promising potential to fabricate laminate composites. AZ31-0.3 wt.% SiC composites with uniformly deposited microstructure at the interface showed an improvement in the flexural yield strength by 49% compared with the unreinforced AZ31, while composites with nonuniform structure or thicker deposition layer exhibited deterioration in mechanical properties.

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Figure captions

Fig. 1: Ultrasonic spray deposition system.

Fig. 2: (a) Schematic overview of the spraying process and (b) spraying path.

Fig. 3: Experimental setup used for consolidation of the metal laminate composites.

Fig. 4: The effect of SiC loading and particle size on the surface tension of ethanol-SiC suspension system.

Fig. 5: (a) Prediction of the atomization droplet size, and (b) prediction of the droplet size from the atomization using different atomization frequencies.

Fig. 6: An atomized droplet deposited by a single pass experiment.

Fig. 7: Effect of flow rate on the deposition structure (a, b) 0.25 ml/min, (c, d) 0.5 ml/min, and (e, f) 1.0 ml/min.

Fig. 8: Effect of temperature on the deposition structure, (a, b) 200°C, (c, d) 350°C, and (e, f) 400°C.

Fig. 9: Effect of air pressure on the deposition structure, (a, b) 0.5 kPa and (c, d) 1.0 kPa.

Fig. 10: Flexural yield and ultimate strength of the consolidated AZ31-SiC composites.

Table captions

Table 1: Summary of spraying parameters and their values.

Table 2: Chemical composition of the AZ31 sheets.

Tables

Table 1: Summary of the spraying parameters and their values.

<i>Parameters</i>	<i>Values</i>
Material and particle size	SiC nanoparticles (< 80 nm)
Suspension medium and concentration	Ethanol + 0.1 wt.% SiC
Substrate thickness	80 μm
Sonication time	6 hours
Spraying type	Path spraying
Spraying speed	10 mm/sec
Spraying lines spacing	2 mm
Temperature (T)	200, 350, and 400°C
Flow rate (Q)	0.25, 0.5, and 1.0 ml/min
Air pressure (P)	0.25, 0.5, and 1.0 kPa
Distance (D)	15, 25, and 50 mm

Table 2: Chemical composition of the AZ31 sheets.

<i>Chemical Composition Limits of AZ31 in wt.%</i>											
	Al	Zn	Mn	Ca	Cu	Fe	Ni	Si	Others Each	Others total	Mg
Min.	2.5	0.7	0.2	--	--	--	--	--	--	--	Bal.
Max.	3.5	1.3	1.0	0.04	0.05	0.005	0.005	0.05	0.1	0.3	Bal.

Fig.1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Spraying condition:

$T = 350^{\circ}\text{C}$ $D = 25 \text{ mm}$ $P = 0.25 \text{ kPa}$

0.25 ml/min

0.5 ml/min

1.0 ml/min

Flow rate increases

Fig. 8

Spraying condition:

$Q=0.25$ ml/min

$D=25$ mm

$P=0.5$ kPa

200°C

350°C

400°C

Temperature increases

Fig. 9

Spraying condition:

$Q = 0.25 \text{ ml/min}$ $D = 25 \text{ mm}$ $T = 350^\circ\text{C}$

0.5 kPa

1.0 kPa

Air pressure increases

Fig. 10