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AGLOMERATION OF Al_2O_3 NANOMETRIC AND SUBMICROMETRIC PARTICLES BY SPRAY DRYING FOR THEIR USE AS FEEDSTOCK IN THERMAL SPRAYING COATINGS

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KEYWORDS
Spray drying, agglomeration efficiency, granules morphology, nanometric and submicrometric alumina particles

ABSTRACT
This study focuses on optimizing the parameters of the spray-drying process for the agglomeration of both nanometric and submicrometric Al_2O_3 particles for their use as feedstock to manufacture thermally sprayed coatings. Initially, for an aqueous suspension with submicrometric alumina particles, d_{10} = 0.8 to d_{90} = 2.0 µm, named SA, was evaluated the effect of: *i)* The solids percentage in the aqueous suspension, *ii)* the feed flow rate and *iii)* the hot air rate used to evaporate the water in the suspension, on the agglomeration efficiency and the morphology of agglomerated obtained, utilizing a factorial experimental design with three factors and two levels. The agglomeration efficiency was calculated as the ratio between the weight percentage of granulated particles and the weight of solids in the sprayed slurry, while the morphology was analyzed by scanning electron spectroscopy SEM. The agglomeration results for the SA suspension indicate that the highest efficiency was achieved with a solid percentage in an aqueous suspension of 30 wt. % (10 vol.%), a feed rate of 3.1 ml/min and a hot air rate of 5.5 m^3/min at a temperature of 220 °C, obtaining spherical agglomerates. Nevertheless, different morphologies of agglomerate were obtained based on the others experimental runs, such as hollow spheres. Subsequently, these parameters were replicated for a suspension of alumina nanoparticles, d_{50}=80 nm, called NA, to obtain granules with a spherical morphology, composed of primary and secondary agglomerates whose size distributions correspond to d_{10} = 5 to d_{90} = 11 µm and d_{10} = 30 to d_{90} = 44 µm, respectively, with a total granulation efficiency of 80%, of which, 90% have a suitable range size to be used as raw material in the production of coatings by means of thermal spraying.

AGLOMERACIÓN DE PARTÍCULAS NANOMÉTRICAS Y SUBMICROMÉTRICAS DE Al_2O_3 MEDIANTE SECADO POR ASPERSIÓN PARA SU UTILIZACIÓN COMO MATERIAL DE ALIMENTACIÓN EN RECUBRIMIENTOS POR PROYECCIÓN TÉRMICA

KEYWORDS

Secado por aspersión, eficiencia de aglomeración, morfología de gránulos, partículas de alumina nanometricas y submicrométricas

ABSTRACT

Este estudio se centra en la optimización de los parámetros del proceso de secado por aspersión para la aglomeración de partículas de Al_2O_3 tanto nanométricas como submicrométricas para su uso como materia prima en la fabricación de recubrimientos proyectados térmicamente. Inicialmente, para una suspensión acuosa con partículas submicrométricas de alúmina, d_{10} = 0,8 a d_{90} = 2,0 µm, denominada SA, se evaluó el efecto de: i) el porcentaje de sólidos en la suspensión acuosa, ii) el caudal de alimentación y iii) la tasa de aire caliente utilizada para evaporar el agua de la suspensión, sobre la eficiencia de aglomeración y la morfología de los aglomerados obtenidos, utilizando un diseño experimental factorial con tres factores y dos niveles. La eficiencia de aglomeración se calculó como la relación entre el porcentaje en peso de partículas granuladas y el peso de sólidos en la suspensión pulverizada. Por su parte, la morfología se analizó mediante espectroscopia electrónica de barrido SEM. Los resultados de aglomeración para la suspensión SA indican que la mayor eficiencia se alcanzó con un porcentaje de sólidos en suspensión acuosa del 30 % en peso (10 % vol.), una velocidad de alimentación de 3,1 ml/min y un caudal de aire caliente de 5,5 m^3/min a una temperatura de 220 °C, obteniéndose aglomerados esféricos. No obstante, se obtuvieron diferentes morfologías de aglomerado en función de las otras corridas experimentales, como esferas huecas. Posteriormente, se replicaron estos parámetros para una suspensión de nanopartículas de alúmina, d_{50} = 80 nm, denominada NA, para obtener gránulos con morfología esférica, compuestos por aglomerados primarios y secundarios cuyas distribuciones de tamaño corresponden a d_{10} = 5 - d_{90} = 11 µm y d_{10} = 30 - d_{90} = 44 µm, respectivamente, con una eficiencia total de granulación del 80%, de los cuales, el 90% tienen un rango de tamaño adecuado para ser utilizados como materia prima en la producción de recubrimientos mediante proyección térmica.

1. INTRODUCTION

Thermally sprayed ceramic coatings from nanometric and submicrometric agglomerated particles are widely used to protect metallic substrates because of their good performance under demanding mechanical, tribological, and thermal conditions, as well as in biomedical and environmental applications, among others [1-5]. The agglomerated powders commercially available for manufacturing thermally sprayed ceramic coatings are processed mainly by the spray drying process [6-9], because this technique allows obtaining particle sizes between 10 and 110 µm, which is an ideal size distribution for an adequate flux in feeder systems for thermal spraying processes [1,10,11].

In the spray-drying process, an aqueous suspension of nanometric or submicrometric particles, which may contain additives, such as binders or deflocculants, is atomized through a nozzle, which allows control of the size, distribution, trajectory, and speed of the drops. Then, each drop, made up of a mixture of precursor or liquid, particles, and additives, is exposed to a flow of hot air in the drying chamber, which provides the necessary heat to evaporate the aqueous phase of the drops. Owing to the interactions that occur between the particles in the drying chamber (collision, electrostatic, and added agglutinating effects), granules with different morphologies and size distributions are formed. Subsequently, the agglomerated particles, dragged by the flow of hot air, are transported to a classifying cyclone, where those with greater mass fall into a collecting container located in the lower part of the cyclone; on the other hand, fine particles (which generally do not agglomerate) are drawn up through the gas exhaust pipe where they are collected by a filter [12-20].

The morphology and size distribution of the agglomerated particles depend on the content of solids in the suspension; to achieve an adequate flow during the process, contents between 40% and 50% of solids by volume are reported for micrometric-scale solids and between 10 and 15% by volume for nanometric particles [21-23].

Considering the above, this study intends to understand the effect of variables related to the suspension and spray-drying equipment on the amount, by weight, of agglomerates obtained with the appropriate size and shape to be used as raw materials in the production of coatings by thermal spraying process.

2. MATERIALS AND METHODS

Two alumina powders, with a d_{50} of 1.2 µm and 80 nm, named as submicrometric and nanometric powder respectively were used in this research. The submicrometric powder is the TCH-63 trade mark, manufactured by Lianyungang Zhong Ao Aluminium Co., Ltd, while the nanometric powder is manufactured and distributed by US Research Nanomaterials, Inc.

The spray-drying processes were carried out in a Toption TP-S15 equipment, which is constituted by: 1. Magnetic stirrer and suspension 2. Peristaltic pump, 3. Suspension and atomizing air inlet, 4. Atomization nozzle, 5. Drying chamber of parallel currents, 6. Collecting vessels, 7. Classifying cyclone, 8. Exhaust pipe and 9. The control panel (Figure 1).

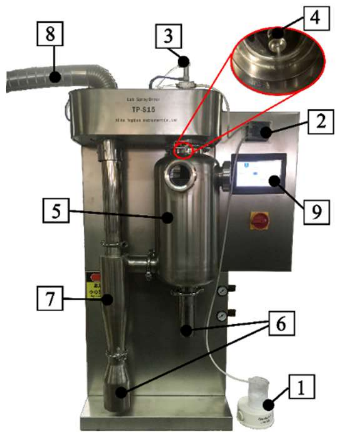

Figure 1. *Equipment used for spray drying.*

During the spray-drying process, the suspensions were kept under continuous stirring to ensure a homogeneous distribution of the particles in the liquid phase, which promoted an almost constant solid/liquid ratio in each drop.

The experimental methodology was divided into 3 phases: 1. Evaluation of the effect of the feeding rate, concentration of solids in the suspension, and flow of hot air on the agglomeration of SA slurry; 2. The scaling of the results obtained in the previous step for the suspension NA and 3. Characterization of agglomerates obtained in phases 1 and 2.

2.1. Phase 1: Evaluation of agglomeration parameters for SA suspension

A factorial experimental design (2^3) was used to determine the effect of the agglomeration process parameters on the granulation efficiency, which is defined as the ratio between the weight of the final granules and the number of solids present in the suspension. The experimental design analysis was carried out using the free-use statistical software R™ [24].

The inlet temperature of the drying air, which was 220 ºC to avoid PVA degradation, a nozzle diameter of 1 mm to prevent the formation of clusters during atomization, and a suspension atomization pressure of 0.2 MPa, were taken as fixed parameters. The factors and levels evaluated in the experimental design, in addition to the experimental runs, are listed in Table 1 and Table 2, respectively.

Table 1*. Factors and experimental domain.*

Factors	Experimental domain	
	Level (-)	Level (+)
A: Suspension feed rate [ml/min]	3.1	5.8
S: Solid concentration in the suspension [wt. %]	15	30
V: Hot air ventilation rate [m^3/min]	3.9	5.5

Table 2*. Matrix of experiments of a full factorial design 2^3.*

Test	A	S	V
1	+	+	+
2	+	+	-
3	+	-	-
4	-	-	+
5	-	+	+
6	-	+	-
7	-	-	-
8	+	-	+

For the elaboration of the SA suspension, a mixture of polyacrylates diluted in water at 2 wt. % was used as a deflocculant to improve the dispersion of the solids and prevent their sedimentation; in addition, an aqueous solution of polyvinyl alcohol (PVA) diluted to 2 wt.% was used as the liquid phase of the suspension, which will help the conformation of the agglomerates during drying [9]. The weight percentages of the SA suspension components are listed in Table 3.

Table 3*. Components of SA suspension.*

Solid concentration* [wt.%]	Deflocculant [wt.%]	PVA Solution [wt.%]
15	0.25	84.75
30	0.50	69.50

* The weight percentages of the solids are equivalent to 5 vol.% and 10 vol.%, respectively.

In other investigations, the reported percentages in the weight of solids for spray-drying SA suspension were between 30 and 40 wt. %, however, during phase 1 of this study, an attempt was made to emulate the volume percentage reported in the literature for nanometric scale alumina, which stand between 10 and 15 vol.% [21,23].

The suspension feed rate and hot airflow evaluated in this study were determined from previous experiments that revealed the operability limitations of the spray-drying equipment used.

2.2. Phase 2: Agglomeration from NA suspension

Based on the results of phase 1, the spray drying parameters for a NA suspension were defined. It is intended to obtain nanostructured agglomerates suitable for use as raw materials in the thermal spraying process, with a size range of 5–75 µm. This range is based on the literature on raw materials for ceramic coatings fabricated using the thermal spraying process [1]. For the nanostructured agglomerates obtained in phase 2, the granulation efficiency, which was defined in phase 1, and the efficiency within the expected size range, determinate as the ratio between the weight of the agglomerates with the desire size distribution and the solids concentration of the suspension, were evaluated.

2.3. Phase 3: Agglomerate characterization

The morphology of the agglomerates obtained in phases 1 and 2 was studied by means of image analysis. The images were acquired by scanning electron microscopy (SEM) using Jeol JSM-6490LV equipment. Moreover, the agglomerates obtained in phase 2 were classified according to their size using sieves of Tyler series number 200 (75 µm) and 500 (25 µm).

3. RESULTS AND ANALYSIS

3.1. Spry drying of SA suspension

3.1.1. Granulation efficiency

Figure 2 presents the results of the equipment granulation efficiency during phase 1. Test 5 presented the highest efficiency (A=3.1 ml/min; S=30 %; V=5.5 m^3/min), with granulation between 40 and 45 wt. % of the material fed. This is due to three main reasons: *i)* the solid percentage in the suspension was higher; therefore, the number of particles in the atomized drop was greater; *ii)* the hot air flow was superior, which allowed better elimination of the aqueous phase; *iii)* the lower the flow of the atomized suspension, the lower the volume of liquid to evaporate per unit of time, which facilitates the drying and consequent agglomeration of the material. Based on the above, it can be deduced that the evaporation of the liquid contained in each formed drop was the most relevant factor for the granulation of the suspension studied.

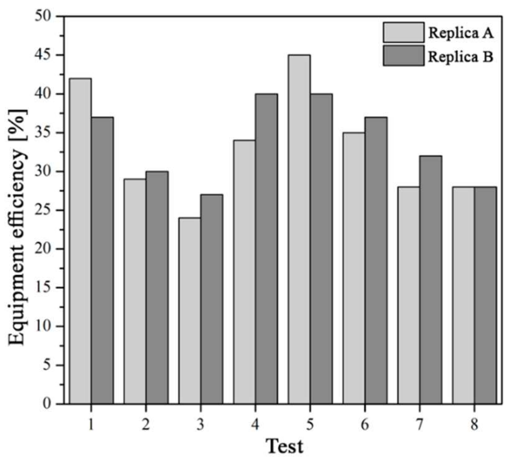

***Figure 2**. Experimental granulation efficiency for SA suspension.*

In contrast, test 3 (A=5.8 ml/min; S=15 %; V= 3.9 m^3/min) showed the lowest efficiency, with only 25 wt. % of material granulated regarding to the feed particles; this was due the atomized droplets did not dry completely, which causes them to adhere to the wall of the drying chamber. It should be noted that the parameters corresponding to the percentage of solids and ventilation in this test were the lowest in the design of experiments, while the suspension feed rate was the highest.

It was established that when the atomized droplets have high volumes of the aqueous phase, the heat transfer provided by hot air (ventilation) may be insufficient to remove the moisture contained in the fed suspension [25]. This was reflected when a high feed rate was used with a low concentration of solids in the suspension, where a large part of the material remained attached to the wall of the drying chamber of the equipment, thereby preventing its recovery and decreasing the granulation efficiency of the equipment.

3.1.2. Agglomerate morphology

Figure 3 shows the agglomerates obtained in tests 3 and 5. The morphology of the particles obtained in test 3 was irregular, hollow, and with thin walls, as shown in Figure 3a, which occurs when the internal pressure of the agglomerate causes the expansion of the drop; at the same time, the solids inside move towards its surface owing to the migration of the liquid due to capillarity; eventually, the liquid phase evaporates, causing a collapse of the granules owing to the release of the internal pressure of the agglomerate [22]. Because of the low wall thickness of the granules and their irregular shape, it was concluded that the number of particles in each of the drops was insufficient to obtain a dense and consistent agglomerate capable of withstanding the shear forces present during the drying process, which is responsible for molding the granules in a spherical shape.

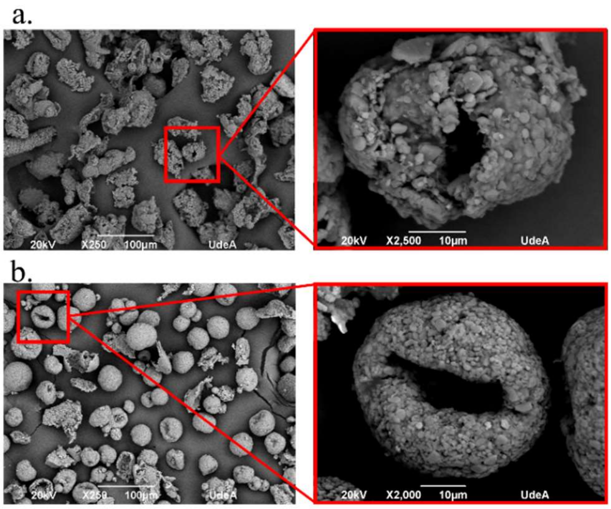

Figure 3. *Micrographs for the granules obtained, with their respective magnification. a) Test 3. and b) Test 5.*

In Figure 3b (test 5), the effect of high solid concentration, lower volume of liquid phase present in the drop, and higher hot air flow on the morphology of the granule can be seen. The number of particles in each of the drops was greater than that in test 3; thus, granules with a greater wall thickness were formed, reducing the internal gas escape generated by the evaporation of the liquid phase. The pressure gradient between the interior of the agglomerate and the atmosphere causes the breaking of some granules, allowing the gases to escape, thus obtaining apple-shaped agglomerated particles [11,25]. From the parameters of test 5 (A=3.1 ml/min; S=30 %; V= 5.5 m^3/min), a large quantity of dense particles with spherical morphology and sufficient mechanical resistance to withstand the shearing forces produced on their surface by contact with hot air were obtained because of the higher solid concentration. Additionally, owing to the low feed rate, the thermal energy supplied by hot air was sufficient to effectively remove the aqueous phase from the atomized particles entering the drying chamber.

It can be concluded that the parameters in test 5 presented the best agglomeration efficiency and allowed obtaining granules with spherical morphologies, which allows a better flowability when they were used as raw materials in thermal spray equipments [26].

3.2. Spray drying and agglomeration from NA suspension

3.2.1. Granulation efficiency and size classification.

Based on the granulation results for the SA slurry the NA suspension was prepared with 30 wt. % solids (10 % by volume). The suspension was spray-dried using test 5 parameters. A granulation efficiency of 80% was obtained with a material loss of 20 %, which was dry, but not agglomerated. This indicates the correct elimination of the aqueous phase of the atomized droplets. The results of the classification of the agglomerates obtained by means of the series of Tayler sieves are presented in Table 4.

***Table 4**. Size classification of agglomerates made from NA suspension*

Sieve fraction	Agglomerated [wt.%]
+200 (>75 µm)	10
-200 +500 (75 – 25 µm)	30
-500 (<25 µm)	60

3.2.2. Morphology and size efficiency

Considering that the appropriate particle size for the raw material of the thermal spraying process is between 5 and 75 µm [1], the morphology and size distribution of the granules of the sieve fractions smaller than 75 µm were evaluated by image analysis from SEM photos and; the results are presented in Figure 4 and Table 5, respectively.

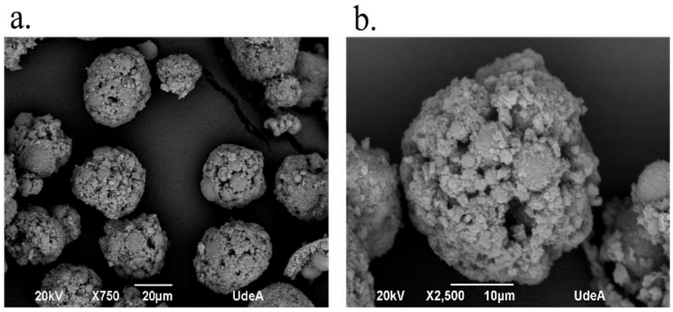

***Figure 4**. Agglomerated obtained from the spray drying of a NA suspension a) Size fraction -200 and b) Zoom for a single particle.*

***Table 5**. Granule size distribution in the ranges -200 +500 and -500 of the Taylor series.*

	-200 +500 [µm]	-500 [µm]
d_{10}	30	5
d_{90}	44	11

It can be seen in Figure 4 that the agglomerated particles have a spherical morphology. In addition, when zooming in, it is to be noted that the agglomerates are made up of smaller granules with diameters between 5 and 10 µm, Figure 4b. In other words, the granules obtained were composed of primary and secondary agglomerates, the latter being a conglomerate of the former. Based on the size distribution resulting from the image analysis and the morphology observed in Figure 4b, it can be concluded that the -500 fraction granules mainly correspond to primary agglomerates.

As can be seen in Table 5, the granules obtained in fractions -200 +500 and -500 were within an appropriate range to be used as raw material in the thermal spraying process (between 5 and 75 µm). The material in this size range is equivalent to 90% by weight of the agglomerated material, which corresponds to 80% by weight of the atomized nanoparticles. Therefore, the overall efficiency for the desired particle size was 72%.

4. CONCLUSIONS

From the atomization of the SA suspension, it was determined that an increase in the percentage of solids in the suspension, decrease in the rate of atomized suspension, and increase in the flow of hot air supplied to evaporate the liquid phase of the suspension increased the efficiency of granulation and the sphericity of the granules.

A concentration of 30 wt.% of solids (10% by volume) and an amount of deflocculant of 0.50 wt.%, respect to the weight of the dry material, allowed the suspension to be stable and flow correctly throughout the process. The hot airflow in the drying chamber is of great importance for the drying and transport of particles, both in the drying chamber and in the cyclone, after being atomized. An air flow of 5.5 m^3/min brought an increase in the granulation efficiency, as well as in the sphericity of the granules.

A low suspension feed rate (3.1 ml/min) allows the atomized droplets to take better advantage of the thermal energy delivered to them by hot air flow to achieve complete drying, which improves granulation.

Finally, granules obtained from the NA suspension containing 30 wt. % of solids (10% by volume) that were fed and atomized with a 3.1 ml/min rate and dried with a current of hot air with a 5.5 m^3/min flux, have a spherical morphology. 80 wt.% of the nanoparticles present in the NA atomized suspension were agglomerate and 72 wt.% of the granules obtained had a range of size consistent with that required to be used as raw material to produce coatings by oxyacetylene flame spraying.

For future studies, optimization of the obtained spray-drying parameters is suggested to increase the agglomeration efficiency within the appropriate size range of the nanostructured agglomerates.

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