Journal of Korean Powder Metallurgy Institute
Vol. 12, No. 5, 2005

Synthesis and Spark-plasma Sinetring of Nanoscale Al/alumina Powder by Wire Electric Explosion Process

Ji-Soon Kim*, H. T. Kim, A. P. Illyin[a] and Young-Soon Kwon
Research Center for Machine Parts and Materials Processing, School of Materials Science and Engineering, University of Ulsan, San-29, Mugeo-2Dong, Nam-Ku, Ulsan 680-749, Korea
[a]High Voltage Research Institute Tomsk Polytechnic University, Tomsk 634050, Russia
(Received September 15, 2005; Accepted October 13, 2005)

Abstract Nanoscale Al powder with thin layer of alumina was produced by Wire Electric Explosion (WEE) process. Spark-Plasma Sintering (SPS) was performed for the produced powder to confirm the effectiveness of SPS like so-called 'surface-cleaning effect' and so on. Crystallite size and alumina content of produced powder varied with the ratio of input energy to sublimation energy of Al wire (e/e_s): Increase in (e/e_s) resulted in the decrease of crystallite size and the increase of alumina content. Shrinkage curve during SPS process showed that the oxide surface layer could not be destroyed near the melting point of Al. It implied that there was not enough or no spark-plasma effect during SPS for Al/Alumina powder.

Key words : Nanoscale powder, Wire electric wire explosion, Al/alumina, Spark-plasma sintering.

I. Introduction

It is well known that nanoscale powder materials show different properties from other conventional bulk material. Development of new technologies for the production of nanoscale powder has become nowadays one of the most important topics.

The pulse energy technology has a number of principal advantages for nanoscale powder production: In the pulsed mode it is possible to provide high density of energy to a substance with a required dosage which can be controlled precisely. The energy supplied in the pulsed mode is used with higher efficiency. The process proceeds extremely fast. All the process can be regarded as adiabatic. Particle formation with designed characteristics would be possible.

In the High Voltage Research Institute (HVRI, Tomsk, Russia) 'wire electric explosion (WEE) process' has been developed for the production of nanoscale powder[1-5]. In this paper a brief explanation on this theory will be given in 'II. Theoretical Background.' Normally because of high affinity of nanoscale metal powder to gas species like oxygen it should be usually passivated to have surface oxide layer for further handling. This oxide layer can hinder the densification of nanoscale metal powder produced in spite of its ultrafine size.

Spark-Plasma Sintering is recently well-known as an effective densification process especially for hard-to-sinter materials and nanoscale powder. Possible reasons for the enhancement of densification are summarized in Reference[6]: (a) Electrical breakdown of surface oxide film and removal of contaminated layer on particle surface by spark generation and sputtering(surface cleaning effect), (b) destruction of

*Corresponding Author : [Tel : +82(52)2592244; E-mail : jskim@mail.ulsan.ac.kr]

surface oxide film and neck formation by local melting and evaporation of metallic region at the particle inside/oxide film interface, (c) focused current and Joule heat at the neck, (d) enhanced migration of atom or ion by temperature difference between neck and particle core (thermal diffusion effect) as well as by electrical field (field diffusion effect), and (e) plastic deformation by applied pressure.

In this study nanoscale Al/alumina powder was produced by WEE process varying the ratio of input energy to sublimation energy of Al wire (e/e_s) in a low vacuum chamber. Particle and crystallite size was measured by various methods and compared. Powder was observed by FE-SEM and analyzed with use of XRD and EPMA. Spark-Plasma Sintering was performed to confirm 'the plasma effect' enhancing the densification.

II. Theoretical Background

Wire Electric Explosion is a process which destroys a metallic or electrically conductive wire by passing a high density current (more than 10^{10} A/m^2) through it with use of LC-circuit. The main process information during the explosion can be obtained from waveforms of voltage and current (Fig. 1). Initially, the wire is heated-up and partly melted by resistance heating where a slight increase in the voltage waveform is observed. Further heating until t_1 makes the wire liquid state. From this moment the wire begins to expand intensively and thereby the electrical resistance increases abruptly by several orders. At t_2 the current in the circuit remains constant and a pause phase is built. At t_3 the breakdown of the explosion products takes place and the arc stage (secondary discharge) begins. If the residual voltage across the capacitor is small or equal to zero, the arc stage does not exist.

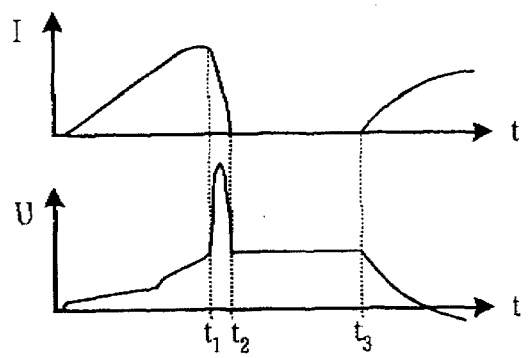

Fig. 1. Typical waveforms of current (I) and voltage (U) vs. time for WEE.

Three dimensionless complexes are proposed from the theory. These complexes allow us to describe many of characteristics both on the heating stage and on the stage of wire demolition. When exploding a wire made of single component metal, the constants characterizing the metal can be omitted and the following generalized variables can be used:

$$\varepsilon = \frac{C \cdot U_0^2}{n^2 \cdot d^4 Z} \cdot 10^{-18}, \frac{J}{m^4 \cdot Ohm} \qquad \lambda = \frac{l}{n \cdot d^2 Z} \cdot 10^{-6}, \frac{1}{m^4 \cdot Ohm}$$

$$v = \frac{\sqrt{L \cdot C}}{d} \cdot 10^3, \frac{s}{m}$$

where l, d, n are the length, diameter and number of exploding wire. C, L and Z are the capacity, inductance and wave impedance of the circuit. Uo is the charging voltage[7-14]. As it was found before[15], the average size of particles formed as a result of WEE is determined for Al:

$$\bar{a} = 0.3 \times 10^{-6} \cdot (e/e_s)^{-3}; [e_s = 33 J/m^3 (Al)]$$

where e is energy liberated in the wire and e_s sublimation energy of the exploding material. This dependence is obtained for the terminal conditions of

$$0.7 e_s < e < e_i, \quad e/e_a < 1, \quad 10^{-7} < t_b < 10^{-5}$$

where e_i is the ionization energy, e_a is the energy liberated in the arc, t_b is the time of energy transfer into the wire.

III. Experimental Procedure

WEE facility designed and constructed by HVRI

Table 1. Experimental conditions used in this study

Circuit	Capacitance	2.2~3.2 μF
	Charging voltage	18~30 kV
	R_k/Z	~0.2
Wire	Materials	Al
	Diameter	0.2~0.45 mm
	Length	100±50 mm
	Feeding speed	100 mm/s
Ambient Gas	Species	Ar
	Pressure	2 atm
Powder supply equipment	Fan speed	3000 rpm (4.5~5 m/s)
e/e_s	0.91 , 1.59 , 1.96	

was used for production of nanoscale Al powder. After setting up the facility the chamber was evacuated to 0.1Pa range, purged with Ar gas three times and then filled with Ar + O_2 gas. All experimental conditions used in this study were determined from the pre-experiments designed using the standard model theory, which are given in Table 1. As a process variable the ratio of the input energy (e) to sublimation energy of the exploding Al (e_s) was chosen finally. Particle size of obtained powder was measured by various methods like BET specific surface area, Hall-Williamson method (X-ray line broadening) and laser-diffraction particle size analyzer. Powder morphology was observed with FE-SEM. Phase analysis was carried out with use of XRD. The amount of oxygen in produced powder was determined by electron probe microanalysis (EPMA). To confirm the effectiveness of SPS produced Al/alumina powder was sintered at various temperatures with the heating rate of 100°C/min and the applied pressure of 50 MPa in vacuum.

IV. Results and Discussion

Table 2 shows the calculated and measured particle size. The expected particle size from the model theory ($\bar{a}$) is given together with the calculated particle size from the X-ray line broadening and the BET specific area ($\bar{d}$), and the avg. particle size measured by laser-diffraction. Powder 1 which was

Table 2. Particle Size Data Obtained from Theoretical Calculation and Various Measurements for alumina/Al Composite Powder Produced by Wire Explosion

	e/e_s	$\bar{a}$ nm	XRD nm	$\bar{d}$ nm	BET m^2/g	PSA nm
Powder 1	0.91	395	127	56	40	499
Powder 2	1.59	74	75	50	45	386
Powder 3	1.96	40	69	73	30	500

$$\bar{d} = \frac{6}{(density \times specific\ surface\ area)}$$

$\bar{a}=0.3\times10^{-6}\cdot(e/e_s)^{-3}$; [$e_s$=33J/$m^3$ (AL)]

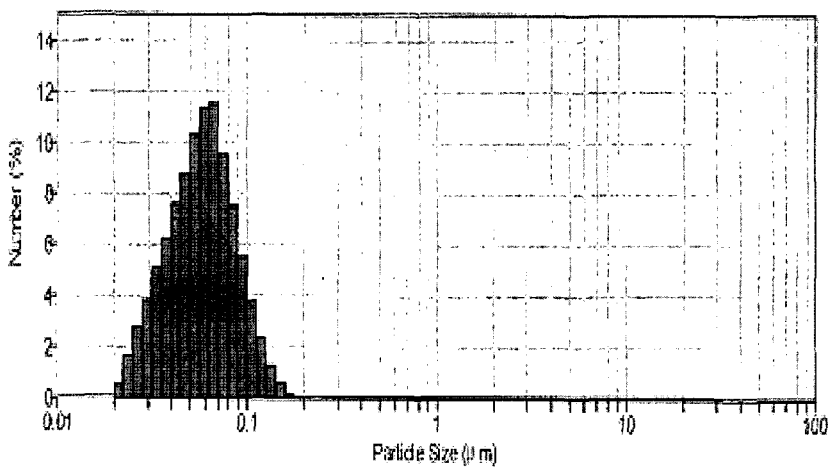

Fig. 2. Particle size distribution of Powder 2.

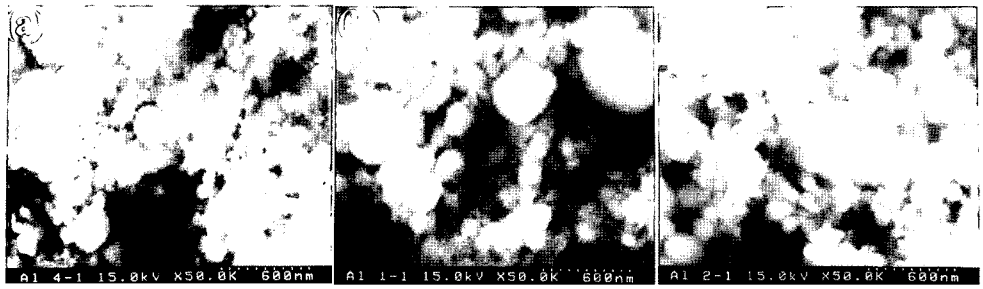

Fig. 3. FE-SEM images of Powder (a) 1, (b) 2 and (c) 3.

produced with the lowest e/e_s value has a large deviation from the expected value. Particle size of Powder 2 and 3 seems to be better matched with the calculated one compared to Powder 1. Fig. 2 shows a particle size distribution curve of Powder 2 determined by laser diffraction particle size analysis, which shows a unimodal size distribution with average size of 386 nm. This result seems to be resulted from the fact that laser diffraction method for measuring the particle size does not measure the separate crystallite. Agglomerates can be considered as one particle. FE-SEM images of powder produced are given in Fig. 3. All powder have spherical shape. Especially in Powder 1 large particles can be easily found. As given also in Table 2, it is evident that with increase in e/e_s value the particle size is finer and its distribution more homogeneous. It can be related with the difference in time and temperature for the given explosion by the electric energy pulse. In case of high energy input the wire can be heated faster to higher temperature in comparison with low energy. Stronger explosion could happen in shorter period for high e/e_s value than low e/e_s.

Table 3. Content of *Al*, *O* and Al_2O_3 content determined from EPMA result

	e/e_s	*Al* (mol %)	O (mol %)	*Al* (vol %)	Al_2O_3 (vol %)
Powder 1	0.91	64.6	35.4	71.8	28.2
Powder 2	1.59	75.8	24.2	84.7	15.3
Powder 3	1.96	86.6	13.4	92.8	7.2

Fig. 4 shows the result of XRD phase analysis. In addition to Al peaks alumina peaks were detected which implies that the oxide layer was formed on the powder surface. This could be confirmed from the result of electron probe microanalysis for the green compact of Powder 1-3 (Table 3). Oxygen content decreased with increase of e/e_s. Supposed that all oxygen were converted to Al_2O_3, the volume percent of Al_2O_3 in Powder 1-3 would be 28, 15 and 7%, respectively. Change in Al_2O_3 content as a func-

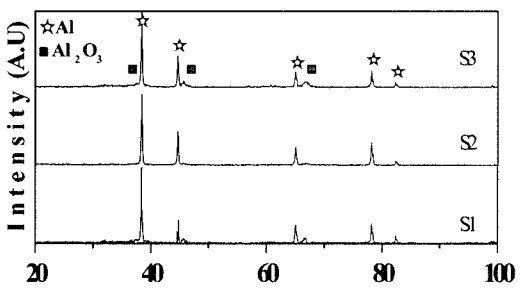

Fig. 4. XRD pattern of Powder 1-3.

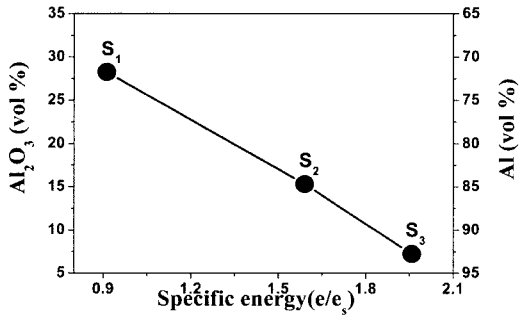

Fig. 5. Change in alumina content as a function of specific energy e/e_s.

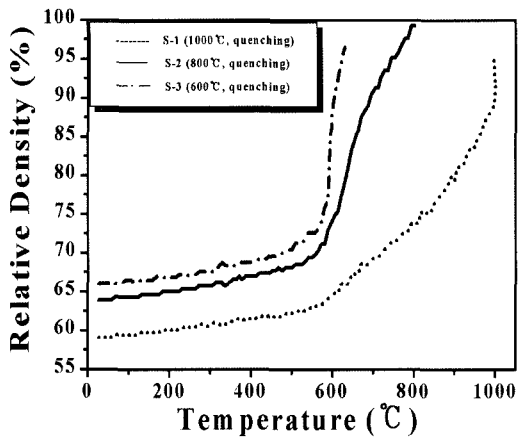

Fig. 6. Densification curve of Powder 1-3 during SPS process.

tion of e/e_s value is given in Fig. 5. Al_2O_3 content decreased almost linearly with increase of the e/e_s value, which can be related with short period during explosion process in case of high e/e_s value. From these results it could be concluded that a production of ultra-fine alumina/Al composite powder with a size of <100 nm and a controlled amount of alumina would be possible.

Fig. 6 is the densification curve of Powder 1-3 during spark-plasma sintering. Irrespective of alumina content the shrinkage started at nearly same temperature of 580°C. Increase in the amount of alumina led to a slow shrinkage rate. Powder 2 reached full density at 800°C and Powder 3 could not be fully densified even at 1000°C. SEM images of Powder 3 compact sintered at 580 and 600°C are given in Fig. 7. From this microstructural observation result the alumina layer on the particle surface keeps its form during the heating stage of sintering and is abruptly destroyed by melting of Al inside the individual particles. With increase of e/e_s value the thickness of oxide layer can be increased and the densification will be retarded. The alumina layer seems to be too stable and dense for the 'spark-plasma effect for surface cleaning' to enhance the densification.

V. Conclusion

Wire Electric Explosion (WEE) method was briefly introduced, which was developed for the production of ultra-fine powder in the High Voltage Research Institute, TPU. Using this theory nanoscale Al/alumina powder with avg. size of <100 nm and a controlled amount of alumina phase was produced by varying e/e_s value. Powder with high content of alumina could not be densified even at 1000°C because the alumina layer keep unchaneged stable. The so-called 'surface cleaning effect' during SPS process could not be confirmed for nanoscale Al/alumina powder.

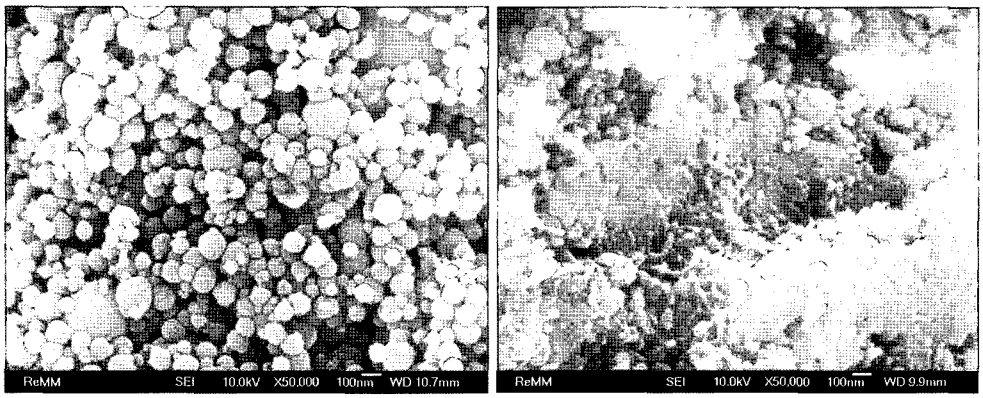

Fig. 7. SEM images of Powder3 compact sintered at 580°C(left) and 600°C(right) for 0 min.

Acknowledgments

"This work was supported by the Ministry of Commerce, Industry and Energy through the Research Center for Machine Parts and Materials Processing (ReMM) at University of Ulsan."

References

1. N. A. Yavorovsky : *Abstract of technical science candidate thesis,* Tomsk, Tomsk Polytechnical Inst., 1982.
2. V. I. Davydovich : *Abstract of technical science candidate thesis,* Tomsk, Tomsk Polytechnical Inst., 1986.
3. M. I. Lerner : *Abstract of Technical science candidate thesis,* Tomsk, Tomsk Polytechnical Inst., 1987.
4. N. A. Yavorovsky : Production method of ultradispersed powders of inorganic substances, *Patent of Russian Federation No. 20482 77@ B.L 1995, n. 32,* priority from 4.04.9 1.
5. N. A. Yavorovsky, V. I. Davydovich and B. A. Bill, Unit for the production of ultradispersed powders of inorganic materials by electrical explosion and chamber for explosion of metal preparation, *Patent of Russian Federation No. 20482 78, B.L 1995, n. 32,* priority from 18.07.9 1.
6. M. Omori, A. Okubo and T. Hirai : J. Japan Soc. of Powder and Powder Metallurgy, **45** (1998) 216.
7. M. F. Mahieux, *Comp, Rend.,* **257** (1963) 1083.
8. R. Reutel and J. Blackbern : *Exploding wires,* Moscow: Inostrannaya literature, (1963) 56.
9. E. I. Azarkevich : *JTF,* **43** (1973) 14 1.
10. E. I. Azarkevich, A. Kotov Yu., V. S. Sedoy : *JTF,* **43** (1975) 175.
11. Y. A. Kotov, V. S. Sedoy and L. I. Chemisova : *Design and implementation of intensive beam sources,* Novosibirsk: Nauka, (1976) 61.
12. V. S. Sedoy : *Abstract of Technical science candidate thesis,* Tomsk, Tomsk Polytechnical Inst, (1975) 24.
13. V. S. Sedoy and L. I. Chemizova : *Proc. on Conference Electric discharge in liquids and its application,* Kiev: Naukova Dumka, (1976) 36.
14. V. S. Sedoy : *JTF,* **46** (1976) 1707.
15. N. A. Yavorovsky and A. Kotov Yu. : *Phizika i khimiya obrabotki materialov (Physics and chemistry of material processing),* **4** (1978) 24.