journal

J. Am. Ceram. Soc., 87 [4] 762–65 (2004)

Coating Fine Nickel Particles with Al_2O_3 Utilizing an Atomic Layer Deposition-Fluidized Bed Reactor (ALD–FBR)

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An atomic layer deposition–fluidized bed reactor (ALD–FBR) method has been developed to deposit ultrathin and conformal coatings on fine particles. Experiments of Al_2O_3 deposition on 150-μm-diameter nickel particles were conducted. The fluidized bed was constructed to operate under vacuum, and the fluidizing gas used was nitrogen. Trimethylaluminum and water were used as dosing reagents. The reactions were conducted at 450 K. Successful deposition of alumina films, with thickness controllable at the nanometer level, was observed based on transmission electron microscopy imaging, inductively coupled plasma atomic emission spectrometry, X-ray photoemission spectroscopy, particle-size distributions, and wavelength-dispersive spectrometry imaging.

I. Introduction

THE ability to coat particles with an ultrafine layer of another substance has recently been given more attention.[1–5] Many reasons for this type of coating can be given, but the overriding theme for each of them is the alteration of the surface properties of the particles without affecting the bulk properties. Atomic layer deposition (ALD)[6,7] provides a unique method for performing this task, because the films generated using this method are conformal and can be controlled down to the atomic level.

ALD is based on standard chemical vapor deposition (CVD) technology, except that it splits the binary reaction into two half-reactions that occur on the surface of the substrate. In the case of aluminum using trimethylaluminum (TMA) and water as reactants, the binary reaction is

$$2Al(CH_3)_3 + 3H_2O \rightarrow Al_2O_3 + 6CH_4 \quad (1)$$

Thus, the two half-reactions are

$$AlOH^* + Al(CH)_3 \rightarrow Al\text{-}O\text{-}Al(CH_3)_2^* + CH_4 \quad (1a)$$

$$Al(CH_3)^* + H_2O \rightarrow AlOH^* + CH_4 \quad (1b)$$

where the starred species are the surface species.[6,8] Note that this indicates growth of the film; were it to represent the initial growth on a particle surface, the alumina species on the right-side of reaction (1*a*) (as well as the first alumina species on the left-side of reaction (1*b*)) would be whatever the particle is comprised of, e.g., nickel. Because the substrate has a limited number of reactive sites, each reaction continues until all the sites have been reacted, and no further. This approach has been successful in coating very fine boron nitride (BN) particles on a very small (<0.1 g) scale[9,10] as well as flat silicon substrates;[8,11,12] however, until now, ALD on nickel has not been reported.

The theory and practice of fluidized bed reactor technology has been discussed for many years.[13] The practice of using a fluidized bed reactor to produce coatings via a deposition method was first described in the 1960s for nuclear fuels,[14] but relatively little effort went into this method until the late 1980s and early 1990s.[15–18] All these efforts describe chemical vapor deposition–fluidized bed reactor (CVD–FBR) technologies in one fashion or another; for a review, see Chen and Chen.[5]

The major goal of the research described here is to demonstrate and develop an understanding of ALD–FBR. Although ALD and FBR technologies have been discussed separately, combining the two has not been previously reported. The nickel particles were selected because of their relative ease of fluidization, whereas the alumina coatings were chosen because of the availability of reactants and prior work with alumina ALD.[6,8–10]

II. Experimental Procedures

As shown in Fig. 1, the apparatus for ALD–FBR is fairly complex. The reactor itself is composed of stainless steel and is encased by a clamshell-type furnace. The reactant bubblers are attached to the system via their vent lines, and are operated by the

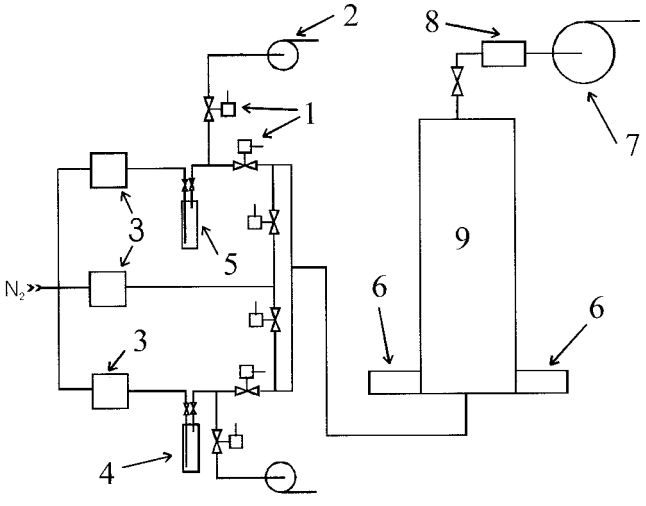

Fig. 1. Simplified schematic diagram of the ALD–FBR apparatus: (1) mass flow controller; (2) main vacuum pump; (3) reactor; (4) fluidized bed of powder; (5) distributor; (6) dosing line purge pumps.

T. M. Besman—contributing editor

Manuscript No. 187223. Received January 4, 2002; approved January 29, 2003.
Funded by the National Science Foundation Center for Ceramics and Composite Materials (University of New Mexico/Rutgers University) and Integrated Sciences (Tulsa, OK).

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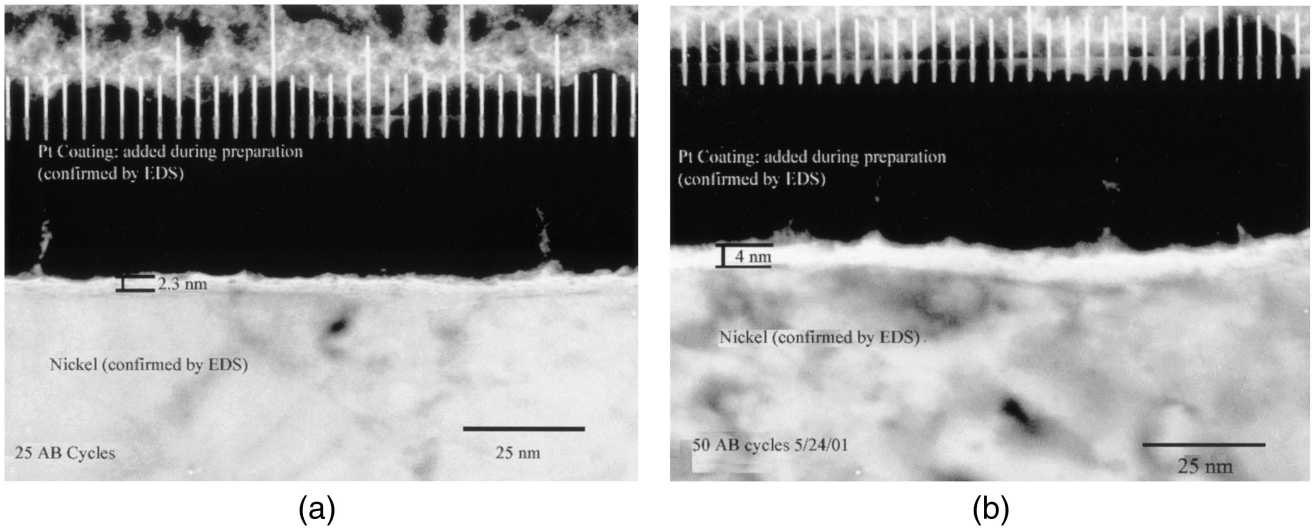

Fig. 2. TEM images of Al_2O_3-coated nickel particles. The first picture shows 25 AB cycles, yielding 2.3 nm. The second picture shows 50 AB cycles, yielding 4 nm.

driving force of their vapor pressure. The reactor itself is maintained at a vacuum using a large pump (Model 2063AC, Alcatel Vacuum Technology, Paris, France), and the dosing lines can also be pumped down using smaller separate vacuum pumps (Model 2008A, Alcatel Vacuum Technology, Paris, France). The fluidizing gas flow is maintained using a mass flow controller (MFC) (MKS Instruments, Andover, MA). An additional MFC can control a separate purge flow through the dosing lines, which is only used to clean the system after operation. The dosing line entrance into the reactor is just beneath the removable porous metal distributor plate. Operationally, the bed (while being fluidized) is operated at three times minimum fluidization velocity. The method used to calculate minimum fluidization velocity for the conditions encountered in our system is described elsewhere.[19,20]

Micrograph images of Al_2O_3-coated nickel particles are performed using transmission electron microscopy (TEM; Model EM430, Philips, Eindhoven, Netherlands), operating at 300 kV. The chemical composition of the surface is analyzed using X-ray photoelectron spectroscopy (XPS; Axis Kratos Analytical, Hofheim, Germany). Wavelength dispersive spectroscopy (WDS) and inductively coupled plasma–auger electron spectroscopy (ICP–AES) were performed using an electron microprobe (Model JXA 8600, JEOL, Tokyo, Japan) and an (ICP–AES 3410+, Applied Research Laboratories). Particle size analysis was performed using a particle size analyzer (Model 3225 Aerosize, TSI Inc., Shoreview, MN).

III. Results and Discussion

Several runs of different numbers of AB cycles, giving different film thickness at ~0.1 nm per AB cycle, are performed to verify the method. Runs were performed with 25, 50, 100, and 200 cycles. TEM images of coated particles are then obtained; the results are shown in Fig. 2. The 25-cycle run yields a coating of 2.3 nm, while the 50-cycle run yields a coating of 4 nm. The XPS data accumulated shows that the 75 and 100 cycles have thicker coatings based on peak areas (Table I). These results show the expected trend, i.e., as the number of cycles increases, the thickness of the Al_2O_3 layer increases. This can be seen from the ratio of area for Al 2s and Ni 2p peaks. As the number of cycles increases, the intensity of Al 2s increases; simultaneously, the intensity of Ni 3p decreases.

Table I. ALD Observations and Calculations

Sample	Thickness (observed)	Thickness (calculated)	$A_{Al\ 2s}$	$A_{Al\ 2p}$	$A_{Ni\ 2p}$	$A_{Al\ 2s}/A_{Ni\ 2p}$
25 AB cycles	2.3 nm	3.0 nm	1.0	0.9	2.8	0.3
50 AB cycles	4.0 nm	4.6 nm	1.4	1.4	1.3	1.1
75 AB cycles		8.1 nm	2.5	2.2	1.3	1.9
100 AB cycles		11.1 nm	3.1	2.7	0.7	4.6

ICP-AES gives parts of aluminum per million parts of nickel. The sample is initially dissolved in HF. Using the average particle size of the nickel particles, combined with their density and the assumed density of the alumina film (also taking into account the stoichiometry of aluminum in the film), a film thickness could be calculated. This method was chosen because it is very quick and easy to perform, and yields acceptable data given the above analyses (most notably the TEM images). For a 50 AB cycle run, the average film thickness is 4.6 nm, very close to the observed 4 nm. ICP–AES runs on the 25-, 75-, and 100-cycle films yielded 3, 8.1, and 11.1 nm, respectively. A graphical representation of ICP–AES results is shown in Fig. 3.

WDS mapping of the surface of the coated particles shows that all particles have been coated. This is important because it shows

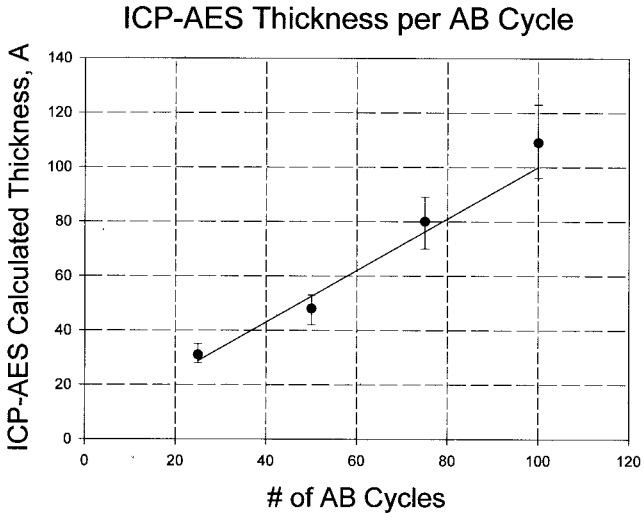

Fig. 3. Graphical representation of ICP-AES calculated thickness versus the number of AB cycles performed. The slope of the line is approximately one, indicating that ~.01 nm of Al_2O_3 is being deposited per cycle. Error bars were created by taking the high and low values for observed particle diameters (see Fig. 5).

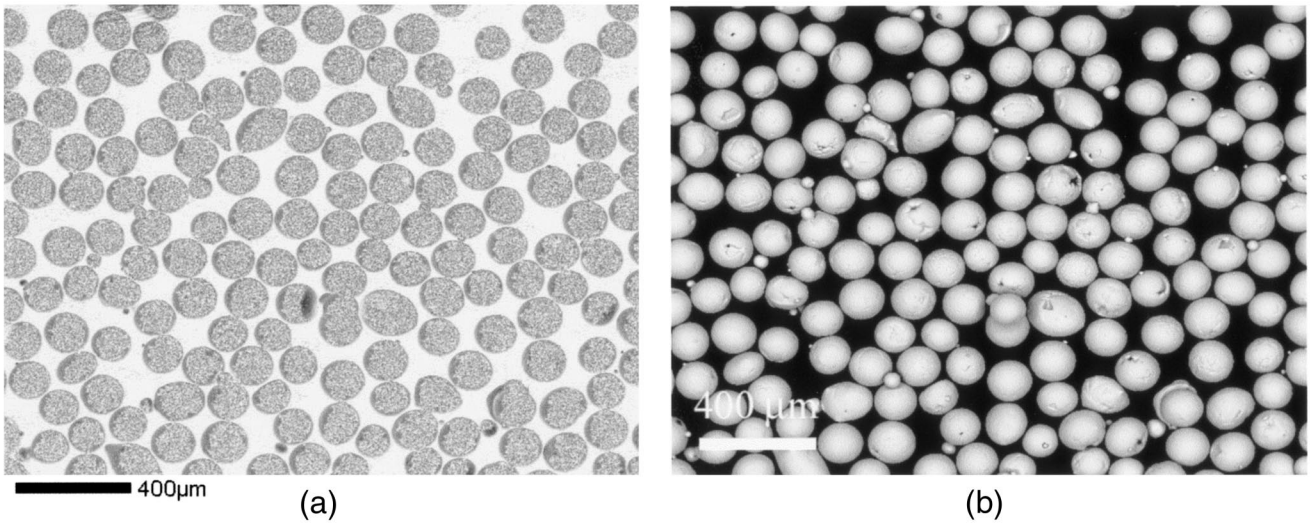

Fig. 4. (a) WDS pattern for aluminum; (b) simple SEM image of the same frame of nickel particles.

that ALD is a site-specific surface reaction; it takes place on all available surfaces (as long as the surface is reactive). By pulsing each reactant twice, complete surface coverage is achieved before switching reagents. Spectrum for 50 AB cycles is shown in Fig. 4.

Particle-size distributions are observed for the nickel particles used with no coating, and 25, 50, 75, and 100 AB cycles. The distributions are all virtually identical; the mean particle size for every run, including the "no-coating" run, are all within experimental error of each other, ranging from 151–152 ± 1 μm. The curves for no coating and 100 AB cycles are shown in Fig. 5, with the others left out for clarity. Both curves are normalized to one. This result indicates that the particles are not coated as agglomerates during the coating process, rather as individual particles.

IV. Conclusions

An atomic layer deposition–fluidized bed reactor (ALD–FBR) method has been developed to coat fine nickel particles with an ultrafine, conformal coating of Al_2O_3. This coating method provides a method to encapsulate fine particles with an atomic-level thickness controlled film.

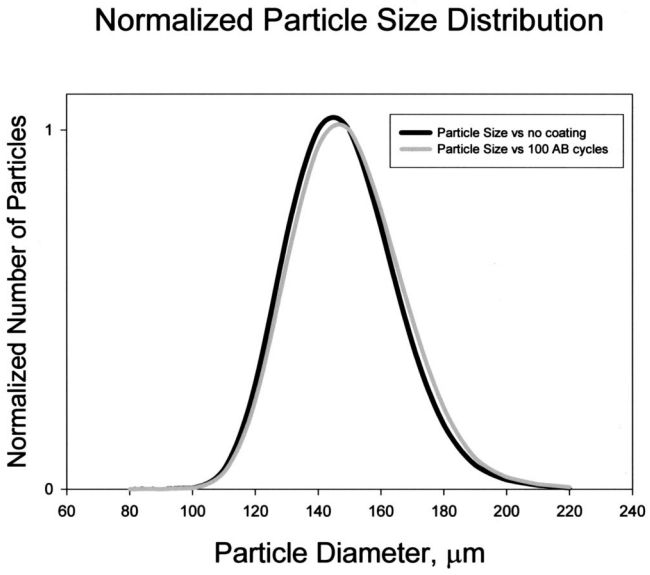

Fig. 5. Normalized particle size distributions for 150 μm fine nickel particles, uncoated and coated with ~100 nm of aluminum.

Transmission electron microscopy images show the conformal nature of the films, as well as indicating the level of control for the thickness of the film. X-ray photoelectron spectroscopy and inductively coupled plasma-auger electron spectroscopy data indicate that varying the number of cycles performed can control the thickness of the films. Wavelength dispersive spectroscopy spectral mapping shows that each particle is coated in approximately the same way, i.e., the particles are all coated equally.

Acknowledgments

The authors thank Dr. Clint Dutcher for his time, resources, and valuable discussion. The authors would also like to thank Dr. John Drexler in the Department of Geology at the University of Colorado for his analytical expertise. Additionally, the authors thank the National Science Foundation's GAANN fellowship program.

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