Characterization of stability of ceramic suspension for slurry introduction in inductively coupled plasma optical emission spectrometry and application to aluminium nitride analysis

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Characterization of the stability of ceramic suspension for slurry introduction in inductively coupled plasma optical emission spectrometry (ICP-OES) and its application to the analysis of aluminium nitride (AlN) was reported in this paper. Stability and homogeneity suspensions of μm sized AlN and nm sized AlN, as the representatives selected, were characterized by sedimentation test, scanning electron microscope observation and zeta potential measurement. The zeta potential of the interface between the particle and the medium can be controlled by pH adjustment and adding 0.8 wt% polyethylene imine (PEI) for μm size AlN or 2.0 wt% PEI for nm size AlN, respectively. The analytical results obtained *via* slurry introduction were compared with those *via* nebulization of aqueous solutions prepared by fusion digestion. The nm size AlN can be directly analyzed by using slurry nebulization ICP-OES with aqueous standards calibration, and the impurities Cu, Fe, Mg, Mn, *etc.* in μm size AlN can also be determined by slurry method, but the results of some elements with high boiling points, such as Si, Y, *etc.*, show deviation from the reference values.

Introduction

The development and production of new ceramic materials requires sensitive analytical methods for the determination of impurities at trace levels. Inductively coupled plasma optical emission spectrometry (ICP-OES) is nowadays the main method for the trace analysis of the inorganic elements. In routine work, the sample should be prepared in the form of a solution and a nebulization technique for sample introduction is used. However, ceramics such as Al_2O_3 , TiO_2 , SiC , Si_3N_4 and AlN are difficult to digest into solution even using microwave-assisted digestion. Fusion dissolution causes a large factor of dilution and severe contamination from the fusion reagents and vessels. The critical requirements of high purity of the fusion reagents and time consumption limit it as a routine procedure for the analysis of these materials. An alternative approach is to prepare the sample as a slurry, which has been applied in GFAAS for a long time. Several papers of ceramics analysis by ICP-OES using slurry sample introduction have been reported.^{1–6} For the control of the purity of products for ceramics, determination of impurities is necessary. Technically, these materials must be of small grain size, even nanometer size. Accordingly, the slurry nebulization technique can be directly analyzed without the need for grinding, and therefore avoids time consumption and contamination.

A highly stable and homogeneous slurry is required in order to provide precise and accurate analytical results. In an excellent book, Conley⁷ described various aspects of dispersion of suspensions. Farinas *et al.*⁸ mentioned that the two main factors determining the capability of the slurry technique are the particle size of the starting powders and the stability and homogeneity of the suspension. They investigated the effect of the stability and homogeneity of the suspension on line intensity and measurement precision in ICP-OES. Varga *et al.*⁹

investigated the effect of pH of aqueous ceramic suspension on colloidal stability and precision of analytical measurements using slurry nebulization ICP-OES. Ebdon *et al.*¹⁰ reviewed slurry nebulization for plasmas and reported that preparation of a stable and homogeneous suspension was an indispensable step prior to slurry nebulization in plasma: they pointed out that there are only a few in-depth studies in the references regarding the stabilizing effect of dispersants.

It is also noticeable that although analytical atomic spectrometry has been used for the analysis of many advanced ceramic materials, details of sample preparation are very scarcely reported.¹¹ On the other hand, one should be more cautious when the slurry nebulization ICP-OES technique was used to analyze ceramic powders because the transport and nebulization efficiency are strongly influenced by the stability and homogeneity of the aqueous slurries.^{9,12}

Recently, Wang *et al.*¹³ reported the determination of metal impurities in titanium dioxide using slurry sample introduction with axial viewing ICP-OES and showed that preparation of a stable and homogeneous aqueous slurry is vital for the determination. TiO_2 aqueous suspension was stabilized by addition of polyacrylate amine (NH_4PAA) dispersant.

AlN is one of the typical ceramics having special properties such as high thermal conductivity, low dielectric constant, high electrical resistance, low density, and a thermal expansion coefficient that matches well with that of silicon.^{14,15} However, its properties are significantly affected by some impurities.^{14,15} Using slurry nebulization for ICP-OES analysis of AlN is a reasonable selection. The preparation of a stable and homogeneous slurry is thus considered as being the first important step.

It is well known that the stability of a slurry depends substantially on the interactions between the suspended solid particles. A rapid phase separation (flocculation) occurs if the

Van der Waals attraction overcomes the electrostatic repulsion. The μm or nm AlN powder suspension is unstable in simple aqueous solution. Luo *et al.*¹⁶ used NH_4PAA as a dispersant to stabilize treated sub- μm AlN powder in aqueous solution. Castor oil has also been used as the dispersant of AlN slurry by Huang.¹⁷ Polyethylene imine (PEI), used as a universal cation dispersant, has been reported to disperse SiC ¹⁸ and ZrO_2 ,¹⁹ but it has not been yet used to disperse AlN powder.

In this work, representative μm and nm particle sizes of AlN powder and NH_4PAA and PEI dispersant were selected. Characterization of slurry stability and homogeneity was carried out. Influential factors on the stability were described. Slurry nebulization was applied to the analysis of μm size AlN and nm size AlN, and analytical results were presented and discussed.

Experimental

Instrumentation

All measurements were performed on a VISTA AX ICP-OES spectrometer with axial view configuration (Varian, Australia). The sample introduction system consists of a V-groove nebulizer and a reduced-volume Sturman–Masters type spray chamber made of poly(tetrafluorethylene) (PTFE). The operating parameters and selected analytical lines are listed in Table 1 and Table 2, respectively.

Material selected and slurry preparation

Two different sizes of AlN particle were selected for testing. The μm size AlN powder was synthesized by a self-propagation high temperature synthesis method and anti-hydrolysis treated simultaneously by using phosphoric acid (Shanghai Institute of Ceramics, CAS, China). The other one was nm size AlN (Hefei Kiln Nanometer Technology Development Co. Ltd, China).

Slurry was prepared by weighing AlN sample and then transferring it into a 100 ml volumetric flask containing dispersant NH_4PAA (Aldrich Chemical Co., USA) or PEI (DH Laboratory, UK). The pH was adjusted to the desired value with HCl or aqueous NH_3 . Just before nebulization, the slurry was agitated in an ultrasonic bath for 15 min to ensure a stable and good dispersion.

Characterization and dispersion of slurries

Zeta potential measurement. The zeta potential of the suspensions was measured by Zeta-Plus Analyser (Brookhaven Instruments, USA). Suspensions were prepared by adding different amounts of dispersant to AlN powders (0.01 wt.%). The suspensions were mixed ultrasonically just before zeta potential measurement.

Table 1 Instrumentation and operating conditions

Spectral range	167–785 nm
Viewing	Axial
Rf generator	40 MHz
Nebulizer	V-groove
Torch	All-quartz
Injector tube diameter	2.3 mm
Power	1.25 kW
Plasma flow	15 l min^{-1}
Auxiliary flow	1.5 l min^{-1}
Nebulizer flow	0.80 l min^{-1}
Replicate read time	3 s
Replicates	3
Instr. stabilization delay	20 s
Sample uptake delay	15 s
Sample uptake rate	0.8 ml min^{-1}

Table 2 Selected analytical lines

Element	Spectral lines/nm
Cr	205.560
Cu	324.754
Fe	238.204
Mg	279.553
Mn	257.610
Ni	231.604
P	213.618
Si	288.158
Ti	334.188
Y	360.074
Zr	339.198

Sedimentation measurement. Settling experiments were conducted using a 2 wt% AlN suspension with various amounts of NH_4PAA or PEI as the dispersant. The suspensions were ultrasonically treated for 30 min, and then settled in 10 ml graded tubes. The readings of sedimentation volume were recorded after two weeks.

SEM observation and particle size determination

The suspensions were settled on a copper slice under gravity until a thin sediment film was formed. The sediment was then dried in the air and observed with a scanning electron microscope (SEM) (JSM-6700F, Japan). To obtain high-quality micrographs, the sediments were coated with a thin gold layer prior to measurement. The particle size of μm AlN was determined by SICAS-4800 Photo-Sedimentometry (Shanghai Institute of Ceramics, CAS). The particle size of nm AlN is gained from the SEM image. The distribution of particles is illustrated in Figs. 1 and 2, respectively.

Reagents and samples

All reagents were of guarantee grade. The solutions were prepared with Milli-Q water (18 M Ω cm). Calibration curves were established by use of aqueous standards. The multi-element standards were prepared from 1000 mg l^{-1} aqueous standards (Shanghai Institute of Measurement and Testing Technology, Shanghai, China). The blank and standards were prepared containing same amount of dispersant.

The reference data were taken from a fusion prepared clear solution of the same sample. Sample (0.1 g) was mixed with an alkaline flux (2 g, Na_2CO_3 + borax) and fused in a Pt crucible for 30 min. After cooling to room temperature, water was

Fig. 1 Aluminium nitride distribution diagram for μm particle size of slurry (determined by photosedimentometry).

Fig. 2 SEM micrographs of sediments resulting from 2 wt.% nm AlN suspension at pH 6.0: (a) without dispersants $\times 20\,000$; (b) with dispersants $\times 20\,000$; (c) without dispersants $\times 50\,000$; (d) with dispersants $\times 50\,000$.

added to cover the fusion cake and the sample was left overnight. The dissolved sample solution was transferred into a polyethylene volume flask and made up to a volume of 100 ml with water.

Results and discussion

Characterization and optimisation of suspension

The aim of the characterization of the slurry is to establish the optimised conditions for preparing a stable and homogeneous suspension. As a representative, AlN slurry was characterized with particle size distribution, sedimentation test and zeta potential measurement. Dispersant and its appropriate amount were taken on the basis of the characterized results. The stability of the suspension under optimised conditions was finally experimentally verified by the normalized spectroscopic signals *versus* time of slurry introduction.

The distribution data were determined by the photo-sedimentation experiments. Fig. 1 shows that most partitions of the μm -AlN powder are smaller than $7\,\mu\text{m}$. The mean diameter is $1.9\,\mu\text{m}$. Fig. 2 shows the morphology of the nm AlN particles during SEM observation. It shows that nm particle size of AlN is far smaller than $1\,\mu\text{m}$. Fig. 3 shows the relationship of the sediment volume of μm -AlN suspensions *versus* the concentration of NH_4PAA or PEI after resting for two weeks at pH 6.0.

Fig. 3 Sediment volume of 2 wt% μm aluminium nitride suspension as a function of dispersant concentration after two weeks.

As is shown in Fig. 3, the sediment volume reached a minimum at 0.8% for PEI and 1.0% for NH_4PAA , respectively. The starting point, namely a dispersant concentration of zero, was the simple aqueous slurry prepared without addition of PEI or NH_4PAA . It indicated that the aqueous μm size AlN suspensions with 0.8% PEI is in a well-stable state. It also shows that the stability effect of PEI is better than that of NH_4PAA . Therefore, PEI was selected as the dispersant that has been investigated in detail.

Farinas *et al.*⁷ have discussed the relationship between stability and the zeta potential. In this paper, we characterized the stability *via* measuring the zeta potential of the system to optimise the conditions for a stable suspension. Fig. 4 presents the dependence of pH on the zeta potential of μm particle size AlN slurry at different PEI concentrations. The zeta potential of the slurry has an important effect on the dispersion state of particles in suspensions, which represents the electrostatic interaction between particles in the dispersion. The presence of too much dispersant also leads to instability, since the electrostatic double layer is compressed by the large amount of dispersant. Therefore, it is vital to determine the isoelectric point (IEP) for the preparation of stable slurry. In the case where the IEP is determined, the appropriate pH region for slurry stability is experimentally determined in which suffi-

Fig. 4 Profiles of zeta potential *versus* pH for μm particle size AlN slurry at different PEI concentrations. ($\square$, 0 wt%; $\blacksquare$, 0.4 wt%; $\blacktriangle$, 0.8 wt%; $\triangle$, 1.5 wt%).

ciently high charged surface generates a strongly repulsive, so that the slurry is stable. The isoelectric points are found near pH 6.0 for no dispersant. Adding PEI moved the IEP towards the alkaline region. The experiment shows that the zeta potential at pH 5 ascends from about 20 mV for simple aqueous slurry to about 60 mV for a spiked slurry. From Fig. 4 it can be found that 0.8 wt% PEI is the appropriate amount for dispersing the μm size AlN powder and the zeta potential was essentially much more than 40 mV in the range of pH 2–8, which guides the appropriate pH range conditions for slurry preparation. The result agreed well with that of sedimentation test.

The relationship of the zeta potential of a nm particle size AlN slurry *versus* pH at different PEI concentrations is plotted in Fig. 5. The IEP of nm particle AlN is pH 8.9, different from the above mentioned IEP of μm size AlN. The μm size AlN powder has been treated with phosphoric acid in order to limit AlN hydrolysis, whereas nm particle AlN has not been treated by acid. Similarly to the μm size AlN, the IEP of nm particle AlN also moved towards a basic region (about pH 10.2). The zeta potential was increased initially with the increase of dispersant concentration, then a plateau value was achieved. The zeta potential at pH 6 changes from 30 mV for without any dispersant to 40 mV for 2 wt% PEI. The experiments show that 2 wt% PEI is the appropriate amount for dispersing the nm particle size AlN; also in range of pH 2–8, the zeta potential is almost kept constant. The nm particle size AlN has a large specific surface area and requires more PEI to disperse the particles, compared with μm particle size of AlN.

The dispersing effect of the PEI is also verified by comparing the SEM micrographs of sediments resulting from 2 wt% nm size AlN suspension without dispersant at pH 6 in Fig. 2 (Fig. 2(a), (c), magnification of $\times 20\,000$ and $\times 50\,000$, respectively) and with 2 wt% dispersant PEI at pH 6 (Fig. 2(b), (d), magnification of $\times 20\,000$ and $\times 50\,000$, respectively). Obvious differences can be observed. Large flocs are observed in the sediments of suspensions without PEI, while, particles of the sediments with 2 wt% PEI are not associated with each another, confirming that particles are well dispersed in the suspension.

Effect of slurry stability on the line intensity

Preparing the AlN slurries in aqueous solution without dispersant was unsuitable owing to the agglomeration or flocculation effect. When the AlN powder was simply dispersed into the water, flocculation of the powder happened quickly. Slurry stability was experimentally tested as shown in Figs. 6 and 7. The two particle sizes of AlN slurry with no dispersant at IEP

Fig. 5 Profiles of zeta potential *versus* pH for nm particle size AlN slurry at different PEI concentrations. (□, 0 wt%; ■, 1.0 wt%; ▲, 2.0 wt%; △, 3.0 wt%).

Fig. 6 Profiles of normalized intensity *versus* time for nm particle size AlN slurry at pH 8.9 (a) with 2.0 wt% PEI dispersant and (b) without dispersant (■ Al; ● Fe; ▲ Si).

(zeta potential is zero) display unstable character. The normalized intensities of matrix Al and impurities Fe and Si obviously decreased with time, as is shown in Figs. 6(b) and 7(b). Comparatively, the nm AlN slurry with dispersant PEI (2.0 wt%) (Fig. 6(a)) displays stable line intensities in a period of 60 min. The μm size of AlN also displays stable line intensity. However, the intensity of matrix Al and impurities Fe, Si decreased with the time after 15 min (Fig. 7(a)). Normally, the analysis was soon followed by the preparation of the slurry; however, it is customary to subject the slurry to an ultrasonic bath for 15 min just before nebulization to ensure that is well dispersed and stable.

Atomization difference between nm and μm size AlN

The rigorous studies reported that slurry particles larger than 5 μm (in some reports 2 μm) do not reach the plasma and result in a loss of signal.¹⁰ In the case of the routine procedure with nebulization of a clear aqueous solution, aerosol behaviour of transportation and atomization in the central channel of the ICP torch has been thoroughly studied. However, slurry particles have a quite different behaviour from aerosol: evaporation of the particles may be the bottleneck. Raeymaekers *et al.*¹ and Van Borm *et al.*²⁰ studied the influence of particle size of Al_2O_3 and SiO_2 on transportation and atomization efficiencies. The analytical results with slurry nebulization for nm size AlN (from Hefei Kiln Nanometer Technology Development Co. Ltd) were listed in Table 3, together with the

Fig. 7 Profiles of normalized intensity *versus* time for μm particle size AlN slurry at pH 6.0 (a) with 0.8 wt% PEI dispersant and (b) without dispersant (■ Al; ● Fe; ▲ Si).

Table 3 Mean value and precision for determination of micro and trace elements in nm particle size AlN^a

Element	Alkaline fusion/ $\mu\text{g g}^{-1}$	Slurry method/ $\mu\text{g g}^{-1}$
Cr	295 $\pm$ 5	288 $\pm$ 10
Fe	425 $\pm$ 6	429 $\pm$ 4
Mg	6 $\pm$ 3	3 $\pm$ 2
Mn	14 $\pm$ 2	13 $\pm$ 2
Ni	144 $\pm$ 12	150 $\pm$ 8
Si	610 $\pm$ 16	619 $\pm$ 15
Ti	37 $\pm$ 3	40 $\pm$ 4

^a Mean value $\pm$ SD ($n = 5$).**Table 4** Mean value and precision for determination of micro and trace elements in μm particle size AlN^a

Element	Alkaline fusion/ $\mu\text{g g}^{-1}$	Slurry method/ $\mu\text{g g}^{-1}$
Cu	28 $\pm$ 2	29 $\pm$ 2
Fe	808 $\pm$ 16	778 $\pm$ 20
Mg	16 $\pm$ 4	19 $\pm$ 3
Mn	10 $\pm$ 1	6 $\pm$ 3
Ni	12 $\pm$ 2	12 $\pm$ 2
P	250 $\pm$ 8	249 $\pm$ 7
Si	1079 $\pm$ 41	380 $\pm$ 21
Ti	27 $\pm$ 1	15 $\pm$ 2
Y	1890 $\pm$ 25	1145 $\pm$ 60
Zr	1200 $\pm$ 31	1045 $\pm$ 60

^a Mean value $\pm$ SD ($n = 5$).

reference values expressed in terms of “alkaline fusion”. The reference values were determined from the same sample prepared *via* fusion with pure Na_2CO_3 + borax, and the blanks have been deducted. Table 3 shows that the impurities in nm size AlN slurry could be directly determined with calibration of aqueous standards.

The analytical results for another sample, μm size AlN (from Shanghai Institute of Ceramics), are listed in Table 4 together with the reference values also taken from the alkaline fusion procedure described above. For μm size AlN slurry, as shown in Table 4, the results for elements Cu, Fe, Mg, Mn, Ni and P were in good accordance with the fusion method. However, the results for Y, Si and others deviated from the reference values. In our opinion, result deviation might be chiefly attributed to incomplete evaporation of these elements with high boiling point in the μm size AlN.

Calibration techniques

As can be seen in Table 3, the prepared slurry of nm size AlN can be directly analyzed using slurry nebulization with aqueous standards calibration. All the results were in good accordance with the reference values.

As is shown in Table 4, for μm size AlN, the analytical results of impurities Cu, Fe, Mg, Mn, *etc.*, were in agreement with the reference values and can thus be accurately determined by the slurry method with aqueous standards calibration. However, the results of Si, Y, *etc.* obviously deviated. The method of standard additions for calibration was tested with only limited effect and no improvement occurred. The analytes added into the slurry exist in the form of ions; however, the analytes in solid particles exist in a quite different chemical form. Therefore, the evaporation and atomization behaviour of the analytes in the aqueous phase is somewhat different from that in solid particles. Moreover, the larger size of the particle, the greater the difference in behaviour. For nm size AlN, the

difference is so small that it could be negligible. For the μm size particles result deviation might be mainly attributed to their high boiling point and incomplete evaporation from the larger size AlN in the plasma channel. It is not too much to say that the slurry procedure with aqueous calibration for μm particle size AlN could be acceptable as a semi-quantitative method for screening the raw material in production control.

Conclusions

1. In order to prepare a stable and homogeneous suspension for slurry nebulization of ceramic samples in ICP-OES, characterization for stability of suspension is necessary. Different sizes of the material need the addition of different optimized amounts of the dispersant and adjustment of different pH to achieve an appropriate zeta potential for stabilization.

2. The nm size AlN can be directly analyzed using slurry introduction ICP-OES with aqueous standards calibration.

3. Some impurities, such as Cu, Fe, Mg, Mn, *etc.*, in μm size AlN can also be determined by the slurry method, but some elements with high boiling point, such as Si, Y, *etc.*, cannot be accurately determined. The method of standard additions is not available to the slurry nebulization ICP-OES for calibration for the analysis of the μm size AlN slurry.

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