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Nanoscaled ceramic powders produced by laser ablation

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Abstract

Copper oxide, silicon carbide and alumina-zirconia nanopowders have been produced by laser ablation in different atmospheres. Particle morphology, phase transformation and powder composition were investigated by X-ray diffraction, transmission electron microscopy, high resolution electron microscopy, and infrared spectroscopy. Targets used for producing the corresponding nanopowders usually melt, evaporate, decompose and oxidize during laser ablation, which lead to phase transformations and composition changes. A model has been proposed to explain the formation mechanism of nanoparticles, especially the nanoparticles embedded in amorphous matrices. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Copper oxide; Silicon carbide; Alumina-zirconia solid solution; Nanopowders; Laser ablation

1. Introduction

Nanoparticles, which have an intermediate condition between atoms or molecules and bulk materials, are expected to possess novel electronic, optical, magnetic, transport, photochemical, electrochemical and mechanical properties [1-4]. Thus increasing attention has been given to the fabrication and characterization of nanoparticles during recent decades, various techniques such as physical or chemical vapor condensation [5-8], solgel [9], rapid solidification [10], liquid precursor processes [11], flame processes [12-14] and laser ablation [15,16] have been adapted to synthesize nanoparticles. Numerous studies in nanoparticles deeply increase the understanding of phenomena related to luminescence, catalysis, chemisorption, aerosol, powder metallurgy, ferrofluid etc. Nanoparticles of almost all-inorganic materials can easily be produced by laser ablation because all inorganic materials can be evaporated by high-intensity laser beams and be subsequently condensed into particles. Adjusting the synthesis conditions such as laser parameters, ambient atmospheres and gas flow rates can control particle sizes, morphologies and

* Corresponding author E-mail address: xcyangg@yahoo.com (X.C. Yang). compositions. Especially the particle surfaces can be kept free of contamination of solvents and other residuals, which make the nanoparticles usable in catalysts and gas sensors. Becker [17] generated metallic nanoparticles by laser ablation. In this paper, copper oxide, SiC and ZrO₂-Al₂O₃ systems were chosen based on their wide range of applications. For example, Cu₂O can be used as heterogeneous catalysts, photocatalyst for water splitting under visible light irradiation, pigments and sensors [18]; SiC is a good candidate for hightemperature structural ceramics and high-temperature electronic and optoelectronic devices [19,20]; and the Al₂O₃-ZrO₂ system can be widely used for oxygen sensors, high-temperature fuel cells, thermal barrier coatings, catalyst support and toughened ceramics [21,22].

2. Experimental

In our experiments, some ceramic nanopowders are prepared by laser evaporation of compressed micrometer powders with a 400 W Nd:YAG-laser (wavelength = 1.06 μ m) and subsequent recondensation of the laser-induced vapor in different atmospheres at 9×10^4 Pa. Nanoparticles generated by gas-phase condensation were collected on a glass fiber filter with an

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average pore size of several micrometer at room temperature using membrane separation technique when the aerosol was pumped out of the evaporation chamber. For the laser ablation, the following parameters were used: laser pulse width 0.5 ms, pulse repetition rate 34 Hz and laser light pulse power density $5600 \text{ W} \text{ mm}^{-2}$. The experimental set-up is schematically shown in Fig. 1. The laser beam was focussed on the target through a quartz window and made the target material evaporate. In order to ablate the whole surface of the target, the evaporation chamber was mounted on a computer controlled x-y manipulator. Gas was introduced in the evaporation chamber to change the atmosphere and pressure. In addition, it was also used to prevent the powders from depositing on the quartz window. The characteristics of the micrometer powders are shown in Table 1.

 Al_2O_3 -ZrO₂ micropowders containing 28.5 mol% Al_2O_3 (#A) and 31.0 mol% Al_2O_3 (#B) were mixed about 36 h, respectively. CuO, SiC and Al_2O_3 -ZrO₂ micropowders all were compressed into 30 mm diameter samples with a pressure of 1 MPa.

X-ray diffraction (XRD) patterns of these powders were recorded using a Siemens X-ray diffractometer (D5000) with CuK_{α} radiation at 40 KV and 30 mA. A Phillips CM200 transmission electron microscope (TEM) was used for determining particle morphologies and sizes. Microstructural characterization of nanoparticles was determined by a JEM 4000 EX high resolution TEM (HRTEM). IR spectra were recorded using a Nicolet FTIR-5dx Fourier transform infrared spectroscope.

3. Results

3.1. Copper oxide nanopowders

Fig. 2(a and b) give the XRD diagrams of copper oxide nanometer powders produced by laser evaporation in air and in argon, respectively. The results show



Fig. 1. Schematic diagram of the laser ablation apparatus.

Table 1Characteristics of the micrometer powders

Sample	Phase	Purity (%)	Mean particle size (µm)
CuO	Monoclinic	99.9	2.0
SiC	Alpha	99.75	2.5
Al ₂ O ₃	Alpha	99.99	1.0
ZrO ₂	Monoclinic	99.9	1.5



Fig. 2. XRD diagrams of copper oxide nanometer powders produced in air (a) and in argon (b) by laser evaporation.

that copper oxide nanometer powder produced in air consists of CuO, Cu₂O and a minor amount of Cu, but only Cu and Cu₂O can be found in the nanometer powder produced in argon. Fig. 3(a and b) are TEM photographs of nanopowders produced in air and in argon, respectively. Comparing their morphologies, we found that the powder produced in air consists of nearly spherical particles, and these particles obey a lognormal size distribution with a mean size of about 12 nm as shown in Fig. 4. The powder produced in argon atmosphere, however, consists of needle-like particles with lengths of about 200 nm and widths of about 45 nm. To our knowledge, the structure of Cu₂O nanowires was not reported before.

3.2. SiC nanopowder

Fig. 5 gives the XRD diagrams of SiC micropowder and its nanopowders produced in argon (ASC) and N₂ (NSC). It indicates that the SiC micropowder is α -phase and the corresponding nanopowders are β -phase. A minor amount of crystalline SiO₂ was found in ASC.

IR spectra in Fig. 6 show that ASC and NSC have similar absorption peaks: the Si–O–Si bending vibrations around 470 cm⁻¹, the Si–O–Si stretching vibrations around 1100 cm⁻¹, the Si–C stretching modes





Fig. 3. TEM photographs of copper oxide nanopowders produced in air (a) and in argon (b).

around 870 cm⁻¹, the O–H bending vibrations at 1620 cm⁻¹ and the O–H stretching vibrations around 3300–3580 cm⁻¹. The O–H vibrations originate from H₂O adsorbed by KBr-containing samples. The strong absorption around 1100 cm⁻¹ in NSC shows that SiC was oxidized seriously in N₂ because the used N₂ contains high levels of oxygen impurity. In NSC a shoulder peak appears at 1200 cm⁻¹ besides Si–O–Si stretching vibration at 1075 cm⁻¹, but in ASC, the Si–O–Si

stretching vibration completely splits into a two-peak structure (1063 and 1202 cm⁻¹). Considering the existence of crystalline SiO₂ observed by XRD in ASC, the two-peak structure can be attributed to two different types of Si–O–Si bonds: crystalline SiO₂ at 1202 cm⁻¹ and amorphous SiO₂ at 1063 cm⁻¹ [23]. Fig. 7 gives the TEM photographs of the SiC nanopowders produced in Ar and N₂ atmospheres. SiC mean particle sizes in ASC and NSC are 20 and 24 nm, respectively.



Fig. 4. Particle size distribution of copper oxide nanopowder produced in air atmosphere.



Fig. 5. XRD diagrams of SiC micropowder and the according nanopowders produced in Ar and N_2 .

More amorphous substances can be observed in Fig. 7(b) than in (a), further showing that SiC was oxidized more seriously in N_2 than in Ar.

3.3. Nanopowders of Al_2O_3 -Zr O_2 solid solution

Fig. 8 gives XRD diagrams of samples #A and #B. Fig. 9 gives XRD diagrams of NS1 and NS2 that were produced from samples #A and #B by laser ablation in air atmosphere, respectively. Fig. 8 shows that samples #A and #B both consist of m-ZrO₂ and α -Al₂O₃. Fig. 9 shows that NS2 consists of t-ZrO₂ and α -Al₂O₃, but no Al₂O₃ diffraction peaks exist in NS1. IR spectra in Fig. 10 further demonstrate that no second phase Al₂O₃ as exists in NS1, but in NS2 exists a second phase Al₂O₃ as

indicated by a shoulder peak at 840 cm⁻¹ [24]. The absorption peak at 605 cm⁻¹ can be attributed to ZrO₂ because it is similar to the IR peak of the 20 mol% Al₂O₃ doped ZrO₂ nanoparticles reported in Ref. [25]. The absorption peaks at 1573 and 1360 cm^{-1} can be attributed to CO₂ impurities. The O-H stretching vibrations around 3470 cm⁻¹ result from H₂O adsorbed by the KBr-containing samples. The existence of the second phase Al_2O_3 in NS2 shows that the Al_2O_3 -ZrO₂ system has a solid solution limit with increasing Al₂O₃ content in the starting samples. In our processing conditions, the solid solution limit is about 28 mol% Al_2O_3 . The solid solution limit of the Al_2O_3 –ZrO₂ system produced in air is a little smaller than that produced in Ar (33 mol%) [26]. This can be explained using the following reaction equations:

$$Al_2O_3 \xrightarrow{ZrO_2} 2Al'_{Zr} + V_0^{-} + 3O_0^{\times}$$
$$ZrO_2 + xAl^{3+} \rightarrow Zr_{(1-x)}Al_xO_{(2-x/2)} + x/4O_2 \uparrow$$

It can be seen that oxygen gas in air retards the formation of the solid solution.

In Fig. 9, ZrO_2 diffraction peaks can be identified as tetragonal or/and cubic ZrO_2 since it is not easy to distinguish between them using XRD due to the severe peak broadening [27]. The solid solution of Al_2O_3 in ZrO_2 induced ZrO_2 lattice distortion and made the according diffraction peaks shift to larger diffraction angles. The crystalline sizes of zirconia in NS1 and NS2 are about 5.1 and 4.2 nm, respectively, and the crystalline size of alumina is about 6.1 nm as calculated from the broadening of the t (111) and γ (440) diffraction peaks by using Scherrer formula [28]:



Fig. 6. IR absorption spectra of the nanopowders produced in Ar and N2.



Fig. 7. TEM photographs of the SiC nanopowders produced in Ar (a) and N_2 (b).



Fig. 8. XRD diagrams of samples #A and #B used for laser evaporation.

$$d = \frac{k\lambda}{\beta \cos \theta}$$

where *d* is the crystalline size, *k* is a constant number (k = 0.9), λ is the X-ray wavelength (1.5406 Å), θ is half the diffraction angle for the reflection measured. β is the full width at half maximum (FWHM) for the reflection measured.

Fig. 11 gives TEM micrographs of NS1 and NS2. It shows that the particles are nearly spherical and the powders have little aggregation. Some particles embedded in a glass matrix were found. Particles in NS1 and NS2 both obey lognormal distributions as shown in



Fig. 9. XRD diagrams of NS1 and NS2.

Fig. 12. NS1 has a medium diameter of 8.3 nm with a geometric standard deviation of 1.51, and NS2 has a medium diameter of 9.9 nm with a geometric standard deviation of 1.42, respectively. HRTEM image in Fig. 13 shows that almost all particles are single crystal. That is, the crystalline size calculated from Scherrer formula should be nearly equal to the corresponding medium particle size measured from TEM. However, our results indicate that the calculated crystalline sizes are far smaller than the measured medium particle sizes. The difference originates from the instrumental effects [29] and microstrain effects in nanoparticles [30]. The particle marked as A in Fig. 13 shows a core-shell structure, where a single crystal of alumina–zirconia



Fig. 10. IR absorption spectra of NS1 and NS2.

solid solution was embedded in a melting aluminazirconia matrix.

4. Discussion

4.1. Particle morphology, agglomeration, and size distribution

TEM observation shows that nanoparticles smaller than a critical size are spherical and have a strong agglomeration. The critical diameter is about 20 nm, as suggested by Granqvist and Buhrman [5], while larger particles display growth habit and have little agglomeration as shown in Fig. 3(b) and in Fig. 7(a). Other TEM observations also show similar results [5,26]. Van

der Waals force of attraction among particles increases with decreasing particle size, so smaller particles agglomerate more strongly. Powders prepared by laser ablation have little hard agglomeration, i.e. particle sintering as observed in our previous research [31]. Lognormal size distributions are obeyed in our powders. This is consistent with Ref. [5], where the lognormal distribution function was used to describe the size distribution of ultrafine metal particles produced by evaporation from a temperature-regulated oven containing a reduced atmosphere of an inert gas. Refs. [32,33] reported that metal nanopowders generated by sputtering or by plasma-discharge all obey lognormal size distributions. Thus it is rational to infer that nanoparticles produced by vapor-condensation methods obey lognormal size distributions, regardless of evaporated



Fig. 11. TEM micrographs of NS1 and NS2.



Fig. 12. Size distributions of nanoparticles in NS1 and NS2.



Fig. 13. HRTEM image of nanoparticles in NS1.

techniques used and particles growth processes involved. The origin of the lognormal distribution were further explained by Granqvist' research group [34]. It is very interesting that copper oxide particles synthesized in Ar atmosphere are needle-like, however, copper oxide particles produced in air are nearly spherical, indicating an important effect of atmosphere on particle morphologies.

4.2. Phase transformation

Inorganic materials evaporated by high-intensity laser beams transform into gas phases. Afterwards, the gas phases condense into solid states (clusters or nanoparticles) again due to high supersaturation. The condensed phases usually exist in the form of the corresponding low-temperature phases. For example, the condensed phase is cubic SiC after laser evaporating α -SiC. In NS1 and NS2, however, zirconia and alumina are in metastable phases. This can be explained by the fine crystallite size, high solid solution content and high cooling rate. Garvie et al. reported that the m-t transformation temperature of pure ZrO₂ decreases with decreasing crystalline size. When it decreases to ~ 30 nm, t-ZrO₂ can exist at room temperature [35]. Luo and Stevens reported that the crystalline size of the 3Y-TZP particles must be > 10 nm to retain tetragonal structure, smaller crystals would exist in cubic structure [36]. Previous investigations also showed that when doped with 2-7 mol% Y2O3, ZrO2 exhibits tetragonal structure, when doped with 7-12 mol% Y_2O_3 , ZrO_2 exhibits cubic structure [37]. Thus the ZrO_2 in our powders should exist in the form of the cubic structure due to the small crystalline size (<10 nm) and the high solid solution content (28 mol%).

4.3. Change of composition

Transition metal oxides often decompose at hightemperature. For example, CuO decomposed completely into Cu_2O and metallic Cu in argon atmosphere. In air atmosphere, however, the high oxygen partial pressure retarded the decomposition of copper oxide. Thus the copper oxide powder produced by laser ablation is a multi-phase mixture. Compositions of the mixture can be adjusted by controlling atmospheres.

Some non-oxides are easily oxidized if oxygen exists in the reactor. For example, SiC was partially oxidized into SiO₂ in our experiments. The existence of SiO₂ is harmful to SiC high-temperature properties. There are two types of SiO₂ in SiC powders produced by laser ablation: crystalline and amorphous SiO₂. Their forming mechanisms are as follows:

$SiC(s) \rightarrow SiC(g)$	(1)
SiC (g) + $O_2 \rightarrow SiO_2$ (g) + CO_2	(2)

SiC (g) \rightarrow SiC (nuclei) \rightarrow SiC (nanoparticles) (3) SiO (g) \rightarrow SiO (nuclei) \rightarrow SiO (arystalling) (4)

$$SiO_2 (g) \rightarrow SiO_2 (nuclei) \rightarrow SiO_2 (crystalline)$$
(4)

SiC (solid) + $O_2 \rightarrow SiO_2$ (amorphous) + CO_2 (5)

In N₂ atmosphere, the expected SiC–Si₃N₄ composite powder was not obtained because the reaction of SiC and O₂ impurity as mentioned above is much more active than that of SiC and N₂. It will be possible to obtain the composite powder by increasing the purity of N₂ or using the active gas ammonia instead of the inert gas N₂.

4.4. Forming mechanism of nanoparticles

High-energy laser can evaporate almost all inorganic materials during laser ablation. The evaporated materials condense into nanoparticles by collision and coalescence or nucleation and growth.

Fig. 14 shows a simple model of particle formation. When the laser beam ablates the target, a part of its



Fig. 14. A simple model of particle formation.

energy is absorbed due to interactions of the laser photons with the electrons of the target, and plasma creates at the surface leading to a nearly complete absorption of the incident laser energy [38]. The absorbed energy induces a temperature gradient in the target, which depends on the heat conductivity of the target and the laser intensity. Then the target is heated, melted and evaporated. The evaporated material expands like a small explosion and forces the melted material out of the crater with a high velocity. The quick solidification of the melted material keeps it amorphous. When the melted material leaves the crater and solidifies, some nanoparticles condensed from the evaporated phase penetrate into the melted phase due to the collision between them. According to the model, we can explain Fig. 11, where particles embedded in glass matrices have been observed. The core-shell structure shown in Fig. 13 formed when a single particle was embedded in an amorphous matrix.

5. Conclusions

Nanopowders such as copper oxide, silicon carbide and Al₂O₃-ZrO₂ were synthesized by laser ablation under different atmospheres. Nanoparticles smaller than 20 nm are spherical and have a strong agglomeration, while larger particles display the growth habit and have little agglomeration. Lognormal distribution is a universal rule for nanoparticles produced by vapor condensation. Atmosphere has an important effect not only on particle morphologies but also on particle compositions. The solid solution limit of Al₂O₃ in ZrO₂ produced in air (28 mol%) is a little smaller than that produced in Ar (33 mol%). The ZrO_2 in our powder is suspected to be the cubic structure due to the small crystallite size (< 10 nm) and the high solid solution content (28 mol%). A model has been proposed to explain the forming mechanism of nanoparticles, especially the nanoparticles embedded in amorphous matrices.

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