Nanocomposite Derived from Core–Shell Nanoparticles via Creep Deformation of an Amorphous Silica Layer Below its Glass Transition Temperature

Yoshiaki Kinemuchi,† Atsuya Towata, and Masaki Yasuoka

National Institute of Advanced Industrial Science and Technology, 2266-98 Anagahora, Shimoshidami, Moriyama, Nagoya 463-8560, Japan

The microstructural design of ceramics is relevant to tune their properties. Nanostructuring can drastically modify ceramic properties because of enhanced interfacial effects, although the creation of such structures in ceramics is still challenging because of the interfacial reaction and grain growth at elevated temperatures during sintering. Here, we demonstrate densification of core–shell nanoparticles consisting of Fe₃O₄ (core particle, 20 nm diameter) and SiO₂ (shell layer, 2 nm thick) with over 90% of theoretical density below 500°C, which was achieved by facilitating plastic flow of amorphous SiO₂ under high pressure below its glass transition temperature. Thus, grain growth of the core nanoparticles was strongly suppressed, and the core nanoparticles remained separated by an amorphous layer in the final microstructure reflecting the original core–shell nanostructure. We also analyzed the densification behavior on the basis of a power law creep model, and estimated the pressures required to attain full density.

I. Introduction

Sintering is a practical way to obtain a bulk form of oxide materials, although it normally requires heating at higher than 1000°C. Such high temperature inevitably leads to grain coarsening during the process, which makes nanostructuring of most ceramics very difficult. However, Chen and Wang pointed out that coarsening during the sintering stage can be suppressed by adopting a heating profile, known as two-step sintering, in which grain-boundary diffusion dominates the densification progress. Although this novel sintering profile is effective at maintaining the grain size below 100 nm, the grains still gradually grow to a size more than double than that of the starting nanoparticles. A sintering temperature of typically 0.5 $T_m$ ($T_m$: melting point) in two-step sintering is regarded as the lowest bound for the densification of oxides via atomic diffusion, and thus external pressures are thought to be required to reduce the sintering temperature further. In fact, application of external pressure allows densities higher than 90% to be achieved with heating of 200°C for ZnO (0.2 $T_m$), 300°C for In₂O₃ (0.3 $T_m$), and 480°C for TiO₂ (0.35 $T_m$). A remarkable feature of such low temperature processes is their lack of grain growth: the grain size is mostly identical to the size of the starting nanoparticles (typically 20–40 nm) Furthermore, the grain size is stabilized below a certain threshold temperature, which is several hundred degrees higher than the temperature used for processing. Interestingly, this threshold temperature, 0.4 $T_m$, for ZnO as an example, is identical to the onset sintering temperature of the nanoparticles without external pressure, and therefore should be linked with grain-boundary diffusivity. In other words, these results suggest that densification without grain growth is practically difficult unless densification is achieved below 0.4 $T_m$.

Pressure-assisted densification below 0.4 $T_m$ is mostly caused by either plastic yield or power law creep. Both these phenomena are related to the yield of the material, but the latter shows time dependence. In the above examples of densification of oxides by applying external pressure, the densification occurred instantaneously upon pressing. Therefore, plastic deformation is the principal mechanism for the densification. As for the creep deformation of crystalline oxides, diffusional creep initiates plastic deformation which brings out superplasticity in some materials. Because the atomic diffusion drives this behavior, it is significant only at high temperature (>0.7 $T_m$), but the lower bound for deformation temperature reduces to 0.4 $T_m$ in the case of nanocrystals. This 0.4 $T_m$ again coincides with the onset temperature of grain growth in nanoceramics. As expected, grain growth occurred during creep tests, indicating that creep deformation does not freeze grain growth during densification of nanocrystals.

In contrast with the creep of nanocrystals, the creep behavior of amorphous phases is relatively well-known, yet its feasibility for densification at low temperatures is uncertain. Nevertheless coating an amorphous layer onto nanocrystals may facilitate densification at low temperatures under external pressure. An example of densification of amorphous phases is the hot pressing of fused silica, which has been demonstrated above 1000°C; this temperature is, however, greater than 0.4 $T_m$ for most ceramic materials and thus clearly too high a temperature for the densification of nanocrystals without excessive grain growth.

To overcome the limit of 0.4 $T_m$ in this study, we first discuss the densification of 30-nm colloidal silica particles under external pressures below 500°C, and then demonstrate densification of core–shell nanoparticles via the creep deformation of the silica shell layer. These core–shell microstructures allow us to both maintain the nanosize of the core particles and space the core particles out. They offer a practical way of obtaining bulk nanostructured materials, and may reduce the interaction between core crystals which occurs in nanograin magnets, see Ref. [12] for example.

II. Experimental Procedure

Densification of colloidal silica (Aldrich, Ludox TM-40) was first tested. A transmission electron microscope, TEM (JEOL, JEM-2010, Japan), image of the powder showed that the particles were spherical, ~30 nm in size and had a largely monodisperse particle size distribution. (Fig. 1) The average particle size measured by dynamic light scattering (Malvern,
Zetasizer Nano ZS, U.K.) was 33 nm, in good agreement with the TEM observation. Nanoparticles were then obtained via freeze-drying of the colloid. The X-ray diffraction pattern (XRD, Rigaku, RINT2000, beam source CuKα, Japan) of these particles was characterized by a halo peak around 20°, indicating the amorphous phase. The particles were charged in a mold made of tungsten carbide which was loaded into a vacuum chamber equipped with a plunger (Sumitomo, SPS1050, Japan). Subsequently, the particles were densified by uniaxial pressing with the plunger below 500°C at less than 10 Pa chamber pressure. The uniaxial pressing was only applied during the constant temperature part of the heating program. Meanwhile, changes in the dimensions of the sample were monitored. To exclude elastic deformation of the experimental system (i.e., the punches and spacers rather than the sample) from the data, pressing was discontinued for a short time while the sample dimensions were measured. These data were used for the estimation of density during the process. Archimedes method was adopted to check the final density of samples after sintering. The density was calculated relative to a theoretical density of 2.2 g/cm³. The shrinkage rate of the nanoparticles without pressure was also analyzed using a dilatometer (Bruker AXS, TD5200S) in air. Thermo-gravimetric analysis (Rigaku, Thermo plus EVO II) of nanoparticles was also performed in air. After testing the SiO₂ creep, the feasibility of exploiting SiO₂ creep for nanostructuring was studied in a SiO₂–Fe₃O₄ nanocomposite. First, Fe₃O₄ core particles were prepared by hydrothermal synthesis from FeCl₃·6H₂O (Wako Pure Chemical Industries, Japan) and FeCl₂·4H₂O (Wako Pure Chemical Industries). Here, FeCl₃·6H₂O (1.39 g) and FeCl₂·4H₂O (0.57 g) were dissolved in 5 mL of water mixed with 5 g of ethylene glycol to obtain a precursor. Adding aqueous NaOH (5.0 g in 8 mL water) to the precursor led to precipitation of the reactants. The reactant mixture was then placed in a 25 mL Teflon-sealed autoclave and held at 180°C for 4 h to synthesize Fe₃O₄ nanoparticles. After washing the particles several times with ethanol and distilled water, the surface of the particles was modified by hydrothermal reaction at 120°C for 1 h in 20 mL water containing 1 g of aminopropyltriethoxysilane (Shin-Etsu Chemical Co., Ltd, Japan). The powder was again washed with ethanol and distilled water several times. Then tetraethylorthosilicate (Wako Pure Chemical Industries) was coated onto the particles by the Stöber method at room temperature. The thickness of the coating was adjusted to 2 nm, as shown in Fig. 2. The atomic ratio of Si/Fe measured by energy dispersive X-ray spectroscopy was 25.5/74.5 which corresponded to either a SiO₂/Fe₃O₄ molar ratio of 50.7/49.3 or volume ratio of 38.6/61.4. Assuming the formation of a homogeneous layer on the 30-nm core particles, the ratio of Si/Fe corresponds to a layer thickness of 2.6 nm, which is in reasonable agreement with TEM observation. For this composition, the theoretical density is estimated to be 4.0 g/cm³. Finally, the core–shell particles were densified based on the previously evaluated SiO₂ deformation. The microstructure of the sintered materials was observed by TEM after a conventional sample preparation procedure: slicing, grinding, dimpling, and ion-milling. Magnetization curves of both the nanocomposites and nanoceramics prepared from the Fe₃O₄ used as the core particles were measured using a Vibrating Sample (Riken Denshi, BVH-10H, Japan).

III. Results and Discussion

(1) Densification of Silica

The sintering curve of the SiO₂ nanoparticles is shown in Fig. 3, along with the strain rate. The significant shrinkage at 900°C is responsible for the sintering, while a gradual increase in the density is observed below this temperature. The peaks in the strain rate below 900°C are thought to be because of the small size of the nanoparticles, which means that diffusion via the surfaces becomes predominant at relatively low
temperatures. Similar peaks have been found for other nanosized ceramic powders. The sintering behavior is identical with that of porous silica glass whose glass transition temperature, \( T_g \), increased linearly with sintering temperature. According to this linear relation, the \( T_g \) of our sample is estimated to be about 700°C, which is 500°C lower than that of pure quartz glass. The hydroxy groups in the colloidal silica are one reason for the low \( T_g \), as they are known to disrupt the network structure of the glass. Indeed, weight loss related to decomposition of hydroxy groups was observed in the thermogravimetric analysis (Fig. 4). Interestingly, the decomposition is mostly governed by temperature, although loss of 0.2–0.3 wt% was found during 1 h of isothermal treatments at 300°C and 500°C. This means that materials properties change mainly depending on temperature and only slightly with time under isothermal conditions. In addition, the viscosity at \( T_g \) is normally of the order of \( 10^{12} \text{ Pa s} \), implying poor fluidity below this temperature. In fact, densification below \( T_g \) was negligible as shown in Fig. 3.

Densification of the silica nanoparticle compact by external pressure shows exponential behavior (Fig. 5). The threshold pressure for densification was largely similar, regardless of temperature, however, the slope above the threshold reduced with decreasing temperature. In general, the deformation mode of glass follows Newtonian flow, in which a linear relation of deformation rate with pressure is observed. The densification of fused silica glass obeys Newtonian flow above \( T_g \), which enables the compact to be densified at \(-1000\)°C in this system, as observed in Fig. 3. Sintering by this mechanism is referred to as viscous sintering, and theoretical consideration of this form of sintering can be found in several models. However, the densification behavior below \( T_g \) is uncertain. The change in glass structure at high pressure, where the density of silica increases from 2.2 g/cm³ above a few GPa of pressure, may partly influence the densification behavior because such high pressures will exist at the point contacts between particles in the initial sintering stage.

![Fig. 3. Densification behavior of spherical SiO₂ without high pressure. Density (ρ) and strain rate (dε/dt) are shown as a function of temperature (T). Even below the glass transition temperature (~700°C), gradual densification can be observed as shown in the inset.](image)

![Fig. 4. Weight change in SiO₂ powder from room temperature (RT) to 1000°C at a heating rate of 10 K/min (a), from RT to 300°C with prolonged heating (b), and from RT to 500°C with prolonged heating (c). The change in residual water during prolonged heating (d) is estimated based on the total weight loss and weight loss during temperature holding at the corresponding temperature.](image)
The effect of time on densification is shown in Fig. 6. In the all conditions studied, an obvious increase in the density with the progress of time was observed, indicating creep deformation contributed to the densification. The increase in densification rate with temperature suggests variation in viscosity with temperature.

(2) Analysis of Silica Densification

Even below \( T_g \), densification of silica, which was strongly dependent on pressure and temperature, was observed. Figure 7 shows the same data as shown in Fig. 5 but plotted against the pressure reduced by the yield stress. Here, the yield stress at different temperatures was estimated from reported Vickers hardness data\(^{10} \) using Tabor’s indentation law\(^{26} \) which describes the relationship between the average contact pressure during indentation and the yield stress of materials subjected to the test. The data converge into a universal curve which increases with roughly the third power of pressure. This curve corresponds to the initial deformation of silica, thus the contribution of deformation by yield is thought to be rather large. Based on the indentation law, Arzt formulated the densification behavior by yield as follows:\(^{5} \)

\[
\sigma_y \leq \frac{4 \pi}{3aZ \rho} P_e \tag{1}
\]

Here, \( \sigma_y \) is the yield stress, \( a \) is the contact area, \( Z \) is the coordination number, \( \rho \) is the density, and \( P_e \) is the external pressure. If the above criterion is satisfied, densification proceeds by yield. It is noted that both \( a \) and \( Z \) vary with the progress of densification. For the random packing of spherical particles,\(^{27} \) \( Z \) gradually increases with densification, which can be numerically expressed as a function of \( \rho \) as discussed below.

\[
a = \pi(\rho - \rho_0) \tag{2}
\]

\[
\begin{cases}
Z = Z_0 + 9.5(\rho - \rho_0) & [\rho < 0.85] \\
Z = Z_0 + 2 + 9.5(\rho - 0.85) + 881(\rho - 0.85)^3 & [\rho \geq 0.85] 
\end{cases} \tag{3}
\]

\( Z_0 = 7.3 \) and \( \rho_0 = 0.64 \). Substituting these values of \( Z \) and \( a \) into Eq. 1 allows us to predict the densification due to yield.

Our starting nanoparticles possessed spherical shape (Fig. 1), but the initial compaction density was 0.60 ± 0.01 which was slightly lower than that expected for random packing (0.64),\(^{27} \) suggesting agglomeration of particles. This difference in initial packing causes quantitative disagreement, especially during the initial sintering stage; however, the trend does not change, regardless of compaction density. Therefore, we adopted the model without modification, as shown in Fig. 7. The model predicts a gradual increase in density with pressure, indicating that the yield deformation does not account for the densification of SiO\(_2\). Although the sintering temperature is far below \( T_g \), it is worth mentioning the possibility of viscous sintering. Under external pressure, with negligible capillary force, densification is predicted to obey the following equation:\(^{28} \)

\[
\dot{\rho} = \frac{3P_e}{4 \eta}(1 - \rho) \tag{4}
\]

Here, \( \dot{\rho} \) is the rate of densification and \( \eta \) is viscosity. Integration of Eq. 4 results in the following expression:

\[
\ln \frac{1 - \rho_0}{1 - \rho} = \frac{3P_e}{4 \eta} t \tag{5}
\]

Here, \( t \) is time. This model also predicts increasing density with pressure, although the curve of \( \rho \) against \( P_e \) for the model follows an increasing convex upward function at a given time; this does not agree with our experimental observations, indicating that viscous sintering is unlikely to be occurring here.

As the influence of pressure on density shows power law behavior, we later discuss the densification based on the
power law creep model. This is thought to be adequate because of the time dependence of density at constant temperature (Fig. 6). The basic idea of power law creep densification relies on the strain rate \( \dot{\epsilon} \) being proportional to the \( n \)th power of pressure:

\[
\dot{\epsilon} = \dot{\epsilon}_0 p^n
\]  

(6)

Here, \( \dot{\epsilon}_0 \) is material constant and \( p \) is the local pressure at the contact. In the case of densification, the local pressure is a function of microstructure. If spherical pores are distributed in the material, \( \dot{\rho} \) can be expressed by the Wilkinson model as follows:

\[
\dot{\rho} = \frac{3}{2} \dot{\epsilon}_0 \frac{p(1-p)}{[1 - (1-p)^{1/n}]^n} \left( \frac{3}{2n} P_e \right)^n
\]  

(7)

Because of the assumption of microstructure, Eq. 7 is applicable to the final sintering stage, when \( \rho \geq 0.9 \). Equation 7 reduces to the expression for Newtonian flow densification for \( n = 1 \), i.e., becomes identical to Eq. 4, thus \( \dot{\epsilon}_0 \) equals to \( 1/(3n) \). Another expression for power law creep densification is an equation based on a random packing model (Arzt model):

\[
\dot{\rho} = 5.3 (\rho^2 \rho_0)^{1/4} \dot{\epsilon}_0 \sqrt{\frac{a}{\pi}} \left( \frac{P_e}{3} \right)^n
\]  

(8)

where:

\[
p = \frac{4\pi P_e}{a Z \rho}
\]

Equation 8 is regarded as adequate expression to the initial and intermediate sintering stages: \( \rho < 0.9 \). As both models rely on different considerations of the microstructure, the rates predicted by the models are not the same at the transition density of 0.9 (the rate given by random packing model turns out to be faster than that of spherical pore model). This requires a scaling adjustment of the rate curves to apply both models simultaneously, as shown in Fig. 8. Because of this scaling, the physical meaning of \( \dot{\epsilon}_0 \) in the models is reduced, while another material property, \( n \), uniquely governs the shape of the rate curve. From the curve, we can understand the sudden drop in densification rate because of the neck growth in the initial sintering stage, the gradual reduction in the rate during the intermediate stage, and the cessation of sintering in the final stage. The lines in Fig. 6 show the results of fitting the models to the data. Here, the density evolution was obtained by the integration of the deformation rate. We found the exponent, \( n \), remained in the range between 2 and 3. This exponent should relate to the microstructural evolution under pressure (as it also describes analogous events such as dislocation climb in crystals). However, few studies of the deformation below \( T_g \) have been reported. Consequently, we cannot be sure of the physical meaning of the number itself. We must also keep in mind that the change in viscoelastic properties under isothermal conditions, which is expected to occur from the thermogravimetric analysis, is incorporated in \( n \). Hence, at the moment, we accept it as an empirical number which can be used to predict the deformation.

(3) Application of Creep Deformation to Nanostructuring

Now, we are ready for practical application of the model to nanostructuring based on the fitted parameters. Figure 9 shows the estimated density evolution under various pressures. Here, the initial density was evaluated from the data shown in Fig. 5. The computational results indicate that the final density is mostly determined by the initial density at lower temperature, and therefore the required pressure for the same density is higher when the temperature is lower. For example, a pressure of 1.8 GPa is required to attain high density at 300 °C, whereas two third of that pressure is enough at 500 °C. We also have to mention that the estimation may include large error when the initial density falls below 0.74 as rearrangement of particle may contribute to the densification in the initial stage of sintering.

Following the prediction, core-shell nanoparticles consisting of Fe3O4 cores and SiO2 shells (Fig. 2) were densified at 300 °C or 500 °C under pressures of 2 or 1.2 GPa,
respectively, for 1 h. Pressure was only applied during the constant temperature part of the heat treatment. The resultant densities (as a fraction of the theoretical maximum density) were 0.954 at 300°C and 0.986 at 500°C, indicating the validity of the original prediction. No obvious cracks were observed by the naked eye. The X-ray diffraction pattern indicates no grain growth of the core particles. (Fig. 10) According to the phase diagram of these phases, Fe2SiO4 may form at low oxygen partial pressure. Although we used a graphite heater, which meant that there would be low oxygen partial pressure during heating, no traces of the secondary phase were found in the XRD patterns.

Observation by TEM also supported the above results. TEM images (Fig. 11) confirmed the homogenous distribution of amorphous phase between core particles. The high-resolution TEM image shows Fe3O4 grains with lattice fringes and an amorphous layer in between them. The SiO2 layer is roughly 2–3 nm thick, which is similar to the thickness of the shell layer of the starting particles. In other words, about half the volume of the SiO2 layer moved to fill the pores. By comparing with images of the starting nanoparticles (Fig. 2), it is found that the shape of the core particles is maintained, which strongly suggests that the creep deformation of the shell layer governs the entire densification. The magnetization curve of the nanocomposite indicated a decrease in saturation magnetization from 77.8 to 58.1 emu/g because of the net reduction in the amount of magnetic material compared with monolithic nano-Fe3O4 ceramics, whereas an increase in coercive force from 118 to 141 Oe was also observed, indicating decoupling of the interaction between the core crystals by the SiO2 layer.

IV. Conclusion

Nanostructuring of bulk oxides is of interest in the present work. Specifically, we focused on an architecture based on core–shell nanoparticles; this architecture allows the modification in the interface phase while retaining the dimensions of the core phase. However, prevention of core-grain growth and phase mixing was a challenge. Such issues are connected with the high-temperature process required for densification; thus, a significant reduction in the process temperature is essential. Here, we have reported the feasibility of low temperature densification via creep deformation of SiO2 glass. Although the process temperature was below the glass transition temperature, obvious densification was measured when an external pressure higher than 300 MPa was applied to 30-nm-sized SiO2 particles. This densification was reasonably explained by a model based on power law creep deformation. Analysis based on the model revealed that external pressures of 1.8 and 1.2 GPa are required to reach high density at 300°C and 500°C, respectively. Following this computational analysis, we demonstrated densification of core–shell nanoparticles (consisting of 30-nm diameter Fe3O4 cores surrounded homogeneously by a 2-nm SiO2 layer). The final densities reached corresponded well with those predicted by the original analysis. The microstructure showed homogeneously distributed SiO2 phase between Fe3O4 nanograins. Furthermore, no core-grain growth or phase mixing was observed. Thus, we believe our demonstration paves a new way to design and control the nanostructure of bulk oxide materials.

Acknowledgments

YK is grateful to Dr. K. Takagi of AIST for his help with the setup of the high-pressure apparatus and also to Ms. R. Suzuki of AIST for her support with TEM observations. This study was supported by New Energy and Industrial Technology Development Organization (NEDO) project of “Research and development of alternative new permanent magnetic materials to Nd–Fe–B magnets”.

References

30