

Temperature dependence of thermal expansion coefficient of silver nanoparticles and of bulk material determined by EXAFS

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The thermal expansion behaviour of silver fcc has been described by an anharmonic Einstein model using EXAFS data in the temperature range between 10 and 300 K. The linear expansion coefficient of a bulk silver foil agrees well with X-ray diffraction data. In the case of silver particles embedded in a silicate glass matrix, this parameter shows an increase for particles of 3.2 nm in size by 70% whereas samples with an average size of particles of 5.1 nm show no changes compared with bulk fcc. The increase for small particles reflects the size effect as well as the influence of the surrounding matrix of glass. The results reveal a substantial influence of the distribution of particle sizes on the expansion coefficient.

Keywords: EXAFS, silver lattice, thermal expansion

1. Introduction

Usually, small particles in the nanometer size range show a specific behaviour in comparison with bulk material. The increased number of surface atoms causes changes in the electronic and atomic structure of particles which are associated with changes of particular macroscopic properties. Here, the thermal expansion coefficient is of specific interest because this parameter determines the stress state of a composite that was produced at elevated temperatures. The evaluation of EXAFS (extended X-ray absorption fine structure) data of small particles, usually, yields a reduced coordination number, a dilatation or a contraction of the lattice structure and an increased Debye-Waller factor as well as an increased static disorder (for a review see Iwasawa, 1996). Recent Temperature-dependent EXAFS experiments demonstrated that the calculation of higher cumulants allows determining the Debye temperature and the thermal expansion coefficient of materials (Rabus, 1991; Yokoyama et al., 1989 and 1996; Wenzel et al., 1990; Frenkel and Rehr, 1993; Tröger et al., 1994) in addition.

In the present work, silver particles embedded in a silicate glass matrix will be considered which were prepared by various thermal treatments near the glass transformation temperature. First experiments indicated an increase of thermal expansion parameter by 20% for 2.5 nm particles, however, the size of particles showed a large distribution (Dubiel et al., 2000). Therefore, this distribution should be narrowed in order to clarify the real size dependence. The results will be discussed in comparison with first data of thermal expansion of isolated Ag particles that demonstrated a large increase compared with bulk material (Yokoyama et al., 1989).

2. Experimental

Soda-lime glasses (Flachglas AG, Germany) containing (in weight %) 71.87% SiO₂, 13.30% Na₂O and 8.69% CaO as main components and 0.865% Fe₂O₃ as reducing agent were used as the insulating glass matrix to incorporate silver particles. The silver ions were introduced into the glass matrix by immersing the glasses into

a mixed nitrate melt (0.05% AgNO₃/99.95% NaNO₃) at 330°C for 330 hours. This extended exchange period and the reduced thickness of glasses of 0.16 mm should realise a more homogeneous distribution of silver species. The subsequent annealing at 600°C (22 hours) yields a mean particle size of 5.1 nm, whereas a twofold treatment at 410 (73 hours) and 480°C (187 hours), respectively, gives particles of 3.2 nm in size. The sizes of particles as well as their distribution have been determined by electron microscopy. The result for the twofold annealing (410 and 480°C) is represented in Fig. 1 and 2 in comparison with previous experiments. The data show a narrow distribution of spherical particles in the range between 1.8 and 6.0 nm. Especially, the formation of larger particles than 6 nm which show a similar behaviour as the bulk material could be excluded.

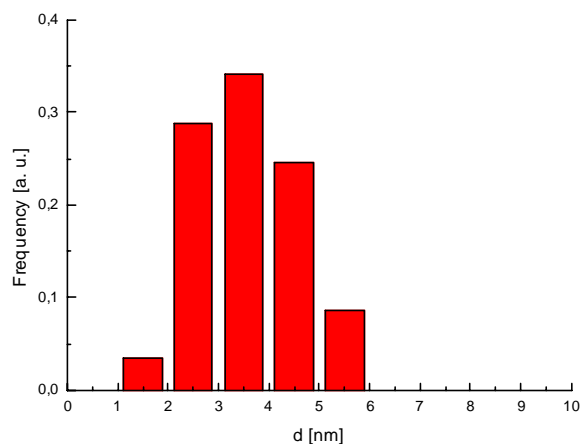


Figure 1

Size distribution of silver particles as a result of the ion exchange (330°C) and a twofold thermal treatment at 410 and 480°C. The mean size of particles is 3.2 nm.

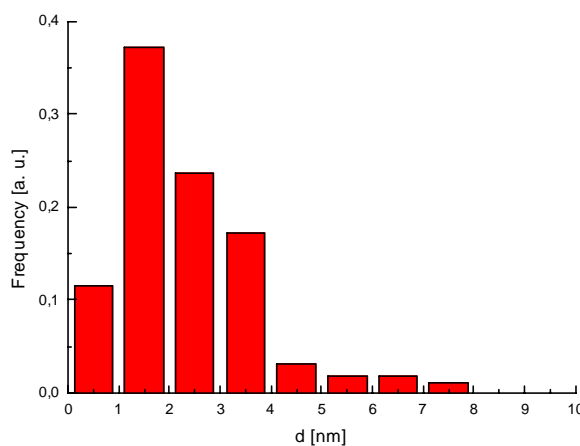


Figure 2

Size distribution of silver particles as a result of the ion exchange (330°C) and a single thermal treatment at 480°C. The mean size of particles is 2.5 nm.

X-ray absorption measurements were carried out in transmission mode using a Si (311) double crystal monochromator. The Ag K-edge (25514 eV) data were collected at the positron storage ring DORIS III at beam line X1 (RÖMO II) of HASYLAB

in Hamburg, Germany, in the temperature range between 10 to 300 K using a liquid helium vapour flow cryostat for the Ag foil as well as for all glasses.

UWXAFS 3.0 program package (Zabinsky et al., 1995) was used for evaluation of EXAFS parameters. The normalised spectra, $\chi(k)$, were weighted by k^2 and Fourier transformed using a Hanning window function. The parameters were fitted in real space between 1.5 and 4.05 Å at 10 K for each sample on the basis of theoretical amplitude and phase functions by FEFF7. Anharmonicity effects of radial distribution of bond lengths were considered by third-order and fourth-order cumulants, C_3 and C_4 , respectively. The anharmonicity parameters, C_3 and C_4 , obtained by the ratio method were used as starting points of fitting procedure and variations were only allowed in small ranges. Further details of data evaluation are described in a previous article (Dubiel et al., 2000). The linear expansion coefficient of both silver foil and nanoscale silver particles in glass was calculated by means of the anharmonic Einstein model and thermodynamic perturbation theory (Rabus, 1991; Frenkel & Rehr, 1993). That gives:

$$\alpha = \frac{c_3}{rT\sigma^2} \frac{3z(1+z)\ln(1/z)}{(1-z)(1+10z+z^2)}$$

with $z = \exp(-\Theta_E/T)$, where $\Theta_E = \frac{\hbar\omega}{k_B}$ and

$$\sigma^2 = \frac{\hbar}{2\mu\omega} \frac{(1+z)}{(1-z)}$$

4. Results of data evaluation

The temperature-dependent spectra of Ag foil and of the glasses containing silver particles were evaluated in the whole range of temperature between 10 and 300 K. The Ag-Ag coordination number for the first shell of bulk material has been fixed to 12. Besides the Ag-Ag environment of all silver species the data of glasses showed a contribution of Ag-O correlations (between 2.1 and 2.2 Å) caused by isolated silver ions which will not be discussed here. The result of fit procedure is parameters r , σ^2 and C_3 calculated for the first Ag-Ag sphere. The accuracy of parameters is $\Delta r = 0.003\text{Å}$, $\Delta\sigma^2 = 0.001\text{Å}^2$ and $\Delta C_3 = 2 \times 10^{-5}\text{Å}^3$, respectively. For example, the bond length, r , for Ag foil and the glasses containing Ag particles of 3.2 and 5.1 nm in size, respectively, are represented in Fig. 3.

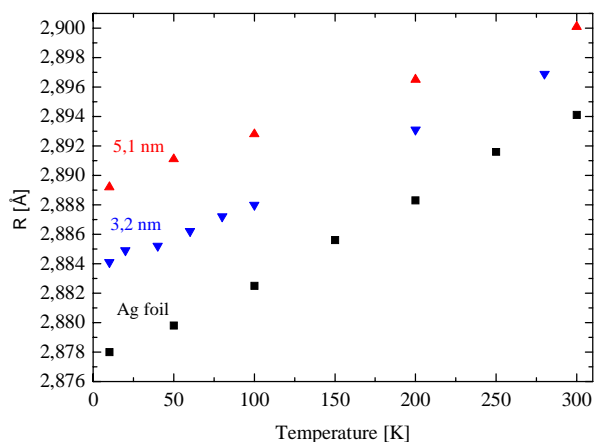


Figure 3
Ag-Ag bond length of the first coordination sphere as a function of the temperature.

The Fourier transforms of one glassy sample are shown in Fig. 4. The Ag-Ag distances of the silver particles exceed the distances of silver foil within the whole temperature range. That means, it was found a dilatation of fcc structure of silver particles that are formed within a glass matrix at elevated temperatures. This effect will be discussed later. The Debye-Waller factors, σ^2 , of the particles of 5.1 nm in size are similar to that of silver foil. There is only a small decrease of the Einstein temperature calculated by a fit of temperature-dependent Debye-Waller factor to 160 K compared with 165 K of silver foil. However, the mean square displacement values of smaller particles of 3.2 nm in size are larger. The fit by the equation mentioned above yields a further decrease of the Einstein parameter to 158 K and an increase of the static Debye-Waller factor by $0.21 \times 10^{-4}\text{nm}^2$. This data describe the increased number of silver atoms at the surface of the particles as a result of the small size. Here, these atoms are incorporated into the interface between the nanoscale particle and the surrounding glass matrix. The calculated parameters are comparable with the results of particles of comparable sizes of 2.5 and 6 nm (Dubiel et al., 2000).

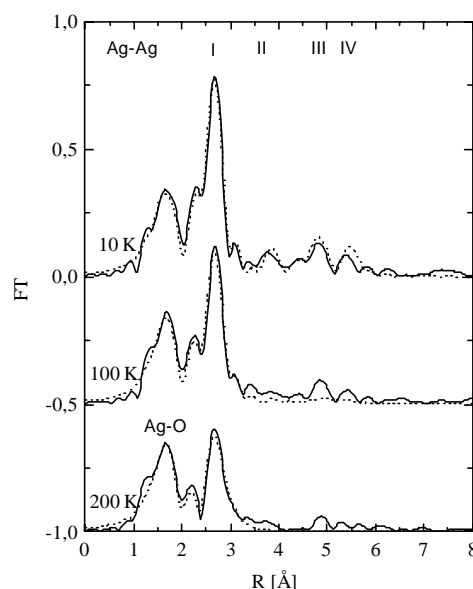


Figure 4

Fourier transforms of EXAFS data of particles of 3.2 nm measured at different temperatures together with the fitted curves (dashed lines).

5. Third cumulant and thermal expansion

The Einstein temperature, the Debye-Waller factor and the third cumulant has been used to calculate the thermal expansion coefficient. The fit procedure showed that C_4 could be neglected in each case. The third cumulant of Ag foil at 10 K has assumed to be zero as a reference value. The accuracy of the thermal expansion parameter could be estimated to be $0.3 \times 10^{-3}\text{K}^{-1}$. The data are represented in Figure 5. The estimated parameters of Ag foil agree within the accuracy of results with known data of Ag fcc lattices (Touloukian et al., 1975) over the whole temperature range. Especially, the temperature dependence reflects very well the X-ray diffraction data. With that it can be assumed that the EXAFS spectroscopy allows determining the expansion parameters of small particles in the same way.

In Fig. 5 is shown that larger particles as the particles with a size of 5.1 nm indicate no changes compared with bulk material (see also Dubiel et al., 2000). For decreased particle sizes, however, a distinct increase of the expansion parameter was found. Here, for

an average size of particles of 3.2 nm an increase by 70% could be calculated in the temperature range between 100 and 300°C. This is a significant change with respect to particles of 2.5 nm in size in the previous work (Dubiel et al., 2000) even though the particle size is larger in the present work. That can be explained by the distribution of sizes of particles only (see Fig. 1 and 2). The drastically increased proportion of surface atoms for larger particles (> 6 nm) in Fig. 2 causes a less pronounced increase of the expansion parameter. Thus, it is to expect that a further narrowing of distribution of sizes of particles as in the present state yields a further increase of expansion parameter. Nevertheless, the data should not reach the values of isolated Ag particles of 1.3 in nm in size which showed an increase of the thermal expansion coefficient by 6.5 times compared with bulk silver (Yokoyama et al., 1989). That can be estimated from the proportion of surface atoms of small particles in dependence from their size. This effect is due to the influence of the glass matrix for ion-exchanged silicate glasses that are considered here. The interaction of the particles and the disordered glass structure, e. g. by bonds across the particle-glass-interface, reduces the effect of surface atoms of isolated particles.

On the basis of expansion coefficient the dilatation of lattice parameters of small particles can be discussed. Because the particles were formed at increased temperatures, 480 and 600°C, there is a tensile stress produced by the cooling to room temperature as a result of the less expansion parameter of the silicate glass, e. g. $8 \times 10^{-6} \text{ K}^{-1}$ at room temperature. This effect depends on the strength of adhesion between particle and glass. Fig. 3 shows a more pronounced increase of lattice parameter for particles of 5.1 nm in size than for sizes of 3.2 nm that is due to the drastic influence of starting temperature for cooling, i. e. 600°C in the case of particle sizes of 5.1 nm and 480°C for particles of 3.2 nm. Consequently, this EXAFS investigations should allow to describe in detail changes of bond lengths and with that the stress state of composite materials on the basis of a thermal expansion mismatch.

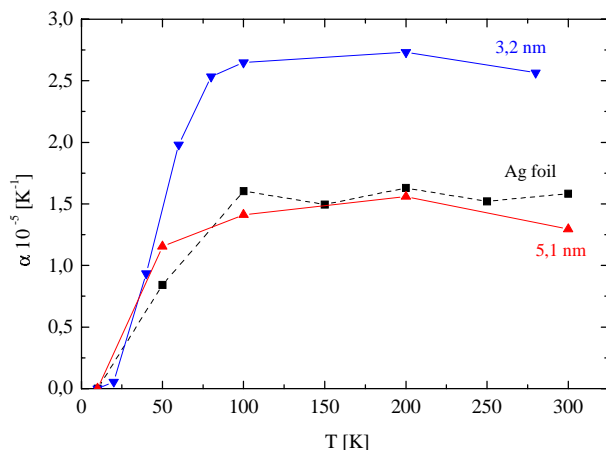


Figure 5
Thermal expansion coefficient of Ag foil and of silver particles in dependence on the temperature.

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