Stress state of silver nanoparticles embedded in a silicate glass matrix investigated by HREM and EXAFS spectroscopy

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Abstract. Ag particles of 3.9 and 5.1 nm mean size in silicate glasses were produced by ion exchange and subsequent annealing at 480 and 600 °C. These thermal treatments may induce stresses in matrix and particles in addition to the well known effect of surface atoms because of the thermal expansion mismatch of both materials. Structural characterisation of the particles by high-resolution electron microscopy revealed a size-dependent lattice dilatation quite opposite to the so far observed lattice contraction of similar metal/glass composites. This result, confirmed by X-ray absorption spectroscopy at the Ag K-edge, is discussed in terms of an Ag-Ag bond length increase near the particle surface. The temperature-dependent EXAFS spectra (10-300 K) indicate an increased thermal expansion coefficient of the particles with an increased mean particle size calculated on the basis of an anharmonic Einstein model. With that the bond length increase can be explained. The results can be interpreted by a combination of both the particle size effects and the influence of the surrounding matrix.

PACS. 61.10.-i X-ray diffraction and scattering – 61.16.-d Electron, ion and scanning probe microscopy – 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 61.43.-j Disordered solids

1 Introduction

Nanosized metal particles embedded in an insulating matrix, *e.g.*, silicate glass, have attracted much interest as materials with potential application in optical devices and other fields [1]. Such metal particle/glass matrix composites have been produced by various routes like ion exchange, sol-gel synthesis or ion implantation. The configuration of metal precipitations and their macroscopic properties strongly depend on the preparation conditions, *i.e.* mainly the thermal history, the exploration of which requires detailed knowledge on size, structure and dynamic behaviour of the particles. Structural characterisation down to the atomic scale by high-resolution electron microscopy (HREM) does not only allow determining size, external shape and internal structure of metal particles in nanoparticulate composites. It also allows to evaluate surface/interface effects on the corresponding lattice parameter. X-ray absorption spectroscopy is another strongly structure-sensitive method. From the extended X-ray absorption fine structure (EXAFS) spectra of the corresponding metal atoms the lattice parameter may be determined, even with more accuracy than by HREM.

Furthermore, the Debye or Einstein temperature and thermal expansion coefficient may be inferred from the temperature dependence of the EXAFS characteristics [2,3]. This will result in averaged parameters of atom-atom correlations summed up for particles of all sizes, different from the data determined by HREM for individual particles. The combination of both methods, is advantageous in a more thoroughly characterisation.

The aim of the present work is to determine the lattice parameters of ion-exchanged soda-lime glasses with increased amounts of iron oxide, so-called green glasses. Usually, small particles show reduced lattice parameters in comparison with bulk material due to the influence of surface atoms. This could be confirmed for isolated silver particles [4,5] as well as for silver particles which were formed by precipitation processes in a sodium silicate glass [6,7]. However, there are some experimental investigations that show the opposite behaviour of small particles, *i.e.* a lattice dilatation has been measured. This was explained by interactions with ligands [8], the formation of oxide shells [9] or the lattice mismatch between the particles and surface layers [10]. We will confirm the lattice dilatation of nanoscale silver particles in green glasses by two different experimental methods and discuss the formation of underlying tensile stresses.

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2 Experimental

Commercial sodium silicate glass (Flachglas AG, Weiherhammer) was chosen as dielectric matrix for precipitating Ag particles. The glasses containing (in weight %) 71.9% SiO_2, 13.3% Na_2O and 8.7% CaO as main constituents were additionally doped by 0.865% Fe_2O_3. The portion of Fe^{+2} to the total amount of iron amounts to 26%, *i.e.* there is sufficient reducing agent available to enable Ag precipitation [11]. Ag^+ ions were introduced into the glass matrix well below the glass transformation temperature, T_g, at 330 °C by an ion exchange procedure. The thickness of the glass slides was 0.3 mm. Ag particles of different mean sizes are formed by subsequent annealing at two different temperatures, 480 (168 h) and 600 °C (22 h).

For electron microscopy examination thin slices of these glasses were prepared by mechanical grinding and ion beam thinning [12]. The presence of crystalline Ag particles was evidenced and their shape and size characteristics were determined by conventional transmission electron microscopy (TEM) at 100 kV (JEM 100C). The lattice parameter of individual particles was determined from HREM micrographs recorded at optimum defocus settings at 400 kV (JEM 4000EX). The micrographs were evaluated after digital imaging processing in real space as well as after Fourier transformation in reciprocal space. The accuracy of the lattice parameters determined by this method is approximately 0.5%.

EXAFS spectra at the Ag K-edge (25.514 keV) were recorded in the transmission mode at HASYLAB/Hamburg (Germany) using a Si (311) double-crystal monochromator. The X-ray intensities were determined by ionisation chambers. The measurements have been performed in the temperature range from 10 to 300 K using a liquid helium vapour flow cryostat. The parameters characterising the Ag-Ag coordination shells were evaluated by fitting the EXAFS function by means of the UWXAFS program package by means of theoretical amplitude and phase functions calculated by FEFF 7 [13,14]. The data were calculated on the basis of the cumulant expansion technique up to the third-order term to include also anharmonic effects of the atomic vibrations [2,3] resulting from both thermal effects and the interface structure. The procedure of data evaluation is described in detail in [15].

3 Electron microscopy

Because of the low solubility of Ag, metal particles in Ag/Na ion-exchanged glasses are formed upon annealing at temperatures near T_g (550 °C). At such temperatures the mobility of network modifying ions is adequately to achieve reduction by polyvalent ions [11] and aggregation to particles within a certain depth from the glass surface. This process results in nearly spherical, mostly single crystalline particles. Lattice defects like twin boundaries mainly can be attributed to coalescence processes. The particle size sensitively reflects the concentration of nuclei for precipitation and the thermal history, *i.e.* annealing temperature and the duration of thermal treatments, of

the glass. Annealing at 480 °C results in a mean particle size of 3.9 nm whereas for the 600 °C sample a mean size of 5.1 nm is found. For example, the data of annealing at 480 °C are shown in Fig. 1. The non-uniform size of the particles, *i.e.* the observed distribution of sizes of particles, is due to the diffusion of silver ions into the glass matrix, their reduction to neutral silver atoms and the aggregation to clusters and small particles whereby silver species penetrate into the glass. That means, the preparation procedure described here does not allow to achieve a uniform size of particles. However, it is this distribution which allowed to determine the variation of lattice parameter with particle size mentioned below.
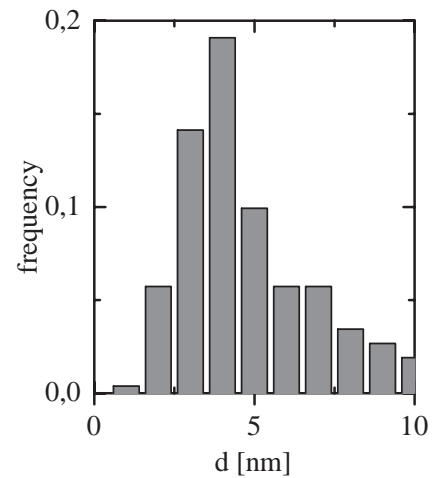

Fig. 1. Size distribution of silver particles as a result of annealing at 480 °C. The data were collected at different penetration depths beneath the glass surface, *i.e.* across the whole sample.

The lattice parameter was calculated for individual Ag particles from the spacing of {111} and {200} lattice plane fringes in digitised HREM images. Fig. 3 demonstrates that with decreasing particle size the corresponding data increasingly exceed the bulk value of silver. This result was not expected since in previous studies on Ag particles embedded in glasses of different composition as well as on isolated particles only size dependent lattice contractions of various amount have been observed [4–7]. It was found, only, for 1 nm silver particles which were prepared by the inert-gas aggregation technique a lattice dilatation of approximately 5% [16]. The dependence of the lattice parameter change Δa on the reciprocal radius can be described using an interface stress f by [17]

$$\Delta a = -\frac{2a\kappa f}{3r} \qquad (1)$$

where a is the bulk lattice parameter and κ the compressibility. The calculated stress values are similar for both sizes of particles with $-(1.5\pm1.0)$ N/m (480 °C, see Fig. 2) and $-(1.4\pm1.0)$ N/m (for 600 °C), respectively.

In principle, the state of the crystal lattice of metal particles embedded in a glass matrix is influenced, besides the particle size, by the strength of interaction
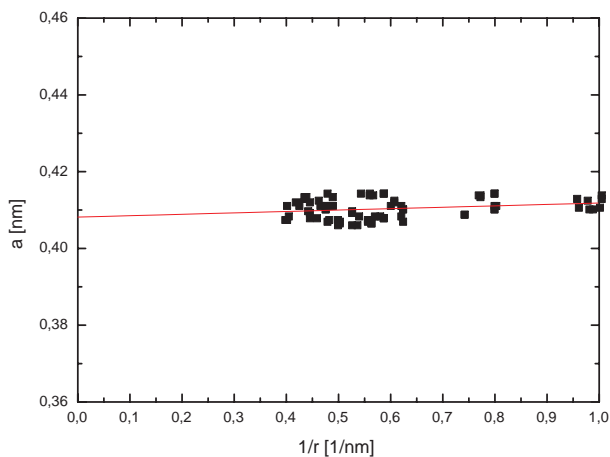
Fig. 2. Lattice parameter of individual particles which are formed at 480 °C calculated from the spacing of such fringes in dependence on the reciprocal particle radius.

(adhesion work) across the metal/glass interface. Obviously, for the glasses under investigation this interaction is strong enough to reduce the influence of the cohesion energy of the embedded metal particles. One possible explanation of the observed effect is an Ag-Ag bond length increase mainly in a surface near region of the particles. This should result in a net lattice dilatation being directly related to the portion of surface atoms and therefore also to the reciprocal of the particle size.

4 EXAFS spectroscopy

The Fourier transformed EXAFS oscillations, *i.e.* the modulations of the X-ray absorption coefficient above the absorption edge of an atom by its nearest neighbours, demonstrate the crystalline structure of silver particles in addition to HREM images (see Fig. 3). The evaluation of such EXAFS spectra enables to calculate the Ag-Ag distance R ($R = a/\sqrt{2}$) with high accuracy by fitting procedures simultaneously with the coordination number and the Debye-Waller factor of the corresponding coordination shell. Fig. 4 shows the results of Ag particles compared with Ag foil as reference material. These distances are averaged over all Ag-Ag correlations of silver particles within the sample. Over whole the range (10-300 K) investigated the EXAFS data confirm the lattice dilatation as it was determined by HREM for room temperature (see Tab. 1 and Fig. 4). The accuracy of the data is given in Table 1. Moreover, this can be judged by comparison of lattice parameter of bulk silver (0.4086 nm at 300 K) with reference parameters determined by both methods. For a precise discussion of lattice parameters of Ag foil there are to consider two additional facts. The value of HREM has been extrapolated from the size-dependence for infinite large sizes what could be influenced by an overall stress state of the sample. The EXAFS data may be slightly increased (approximately 0.0004 nm) due to the specific vibrational disorder in fcc lattices [15].

Table 1. Lattice parameter in [nm] of Ag/glass samples by fit of the 300 K EXAFS spectra for particles of 3.9 and 5.1 nm mean size compared with HREM data determined at 300 K for the corresponding particles.

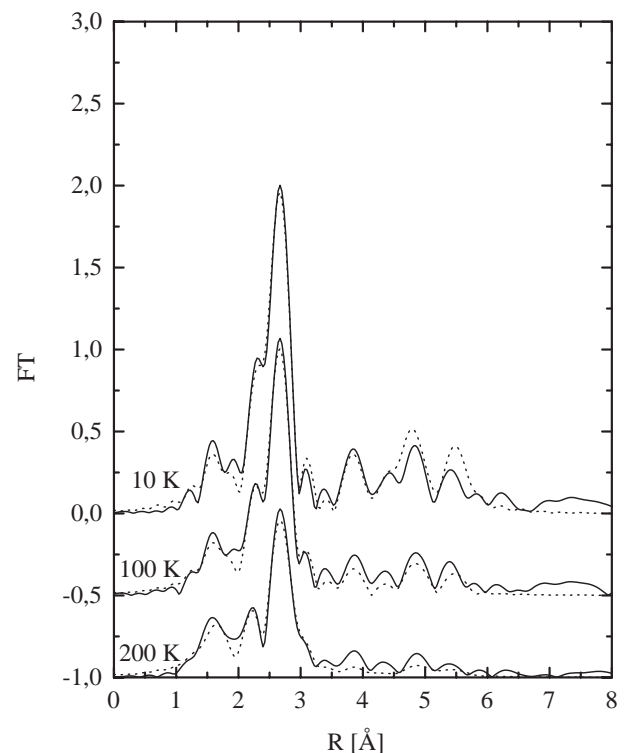| Ag foil	480 °C sample	600 °C sample
EXAFS:		
0.4093 ± 0.0004	0.4100 ± 0.0005	0.4101 ± 0.0004
HREM:		
0.4080 ± 0.0008	0.4107 ± 0.0010	0.4101 ± 0.0006

Fig. 3. Fourier transforms of EXAFS oscillations measured at different temperatures and the corresponding fitted curves (dashed lines) using UWXAFS program package for Ag particles of 3.9 nm size embedded in glass.

By assuming an anharmonic Einstein model [3] the dynamic behaviour of the particles is evaluated from the temperature dependence of the EXAFS spectra. Accordingly, the mean-square relative displacement and the anharmonicity parameter were calculated. With that the low-temperature thermal expansion coefficient of small Ag particles could be calculated [15]. The fitted parameters indicate an increased expansion coefficient for decreased particle sizes. Whereas for larger particles (5.1 nm) the expansion coefficient is similar to that of bulk material an increase of 25% could be calculated for the mean particle size of 3.9 nm in the temperature range between 100 and 300 K. This tendency was already expected for non-embedded clusters [2]. Thus the dilatation of lattice
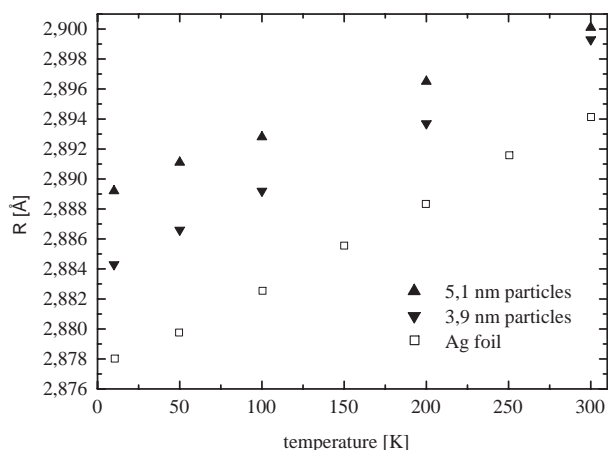
Fig. 4. Ag-Ag distances calculated from EXAFS of silver foil and of the two glasses which were measured in the temperature range 10-300 K.

parameters can be explained as a consequence of the thermal expansion mismatch of the particles and the glass matrix that occurs during the cooling procedure down to room temperature after the formation of silver particles at elevated temperatures. The stronger dilatation of 5.1 nm particles is caused by the starting temperature for cooling procedure. In any case, the thermal expansion coefficient of the silver particles is twofold of the parameter of glass matrix at least.

5 Conclusions

Structural characteristics of Ag nanoparticles embedded in silicate glass have been investigated by a combination of HREM and EXAFS spectroscopy. Different from previously studied systems we now concentrated on achieving rather small particles and high number density by choosing appropriately glass composition, ion exchange conditions and annealing treatment. The observed lattice dilation for very small particle sizes is found to be related to a size-dependent increase of the corresponding expansion coefficient. This tensile stress state has been generated during cooling procedure to room temperature under the assumption of an adhesion between nanoscale particle

and the surrounding matrix. Efforts are in progress now to investigate the structural basis for interactions across the interface as well as to consider the influence of such interface effects on the optical properties of these materials.

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