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Abstract

In the present work, the structure of core-shell Fe-W-O nanoparticles (NPs) is characterized by various state-of-the-art methods of transmission electron microscopy (TEM). The NPs which exhibit unique physical properties depending on shape and size were provided by the group of Professor Kautek (Faculty of Chemistry, University of Vienna). The NPs with a mean size of 17 nm were generated by laser ablation in ethanol.

Core-shell NPs deposited on amorphous carbon foil show spherical shape of different sizes as concluded from TEM tilting experiments. The NPs are homogeneous or show precipitates. Digital image analysis of TEM micrographs yields a broad size distribution of spherical precipitates in NPs with a mean size of (8.7 ± 5.7) nm. Further analysis reveals the presence of crystalline and amorphous phases: Electron diffraction patterns indicate that the core consists of iron oxide with orthorhombic Fe_2O_3 high-pressure phase and the tilt experiments confirm the amorphous shell.

High-resolution TEM analysis of the cores combined with image simulation agrees with the crystalline orthorhombic structure of Fe_2O_3 .

Analysis of the acquired tilted dark-field electron correlation microscopy (t-DF ECM) time series was conducted in order to observe how amorphous shell regions and atomic dynamics change under the beam. Analysis of the generated time dependent speckle intensity I (t) provides information about the dynamic at a particular location. From two analysed t-DF ECM time series it was concluded that the Fe-W-O particle regions exhibit faster dynamics then the supporting carbon foil. The study, which investigated the influence of acceleration voltage on the resulting dynamics, shows no clear tendency: depending on the way of evaluation the decay time is shorter or longer.

To obtain information about the chemical composition of the sample, high-angle annular dark-field (HAADF) analysis was carried out in conjunction with a simulation based on geometric considerations, which assumes a spherical structure of the coreshell NP. According to intensity profiles a higher intensity factor must be attributed to the core than to the shell of the NP. Therefore, HAADF analysis indicates content of W ($FeWO_3$) in the core when Fe_2O_3 as shell composition is assumed. Based on our analysis, the non-equilibrium orthorhombic Fe_2O_3 phase is stabilized by its nano size and adding W.

Zusammenfassung

In dieser Arbeit wird die Struktur von Fe-W-O-Nanopartikel (NP) mittels verschiedener state-of-the-art Methoden der Transmissions-Elektronenmikroskopie (TEM) untersucht. Nanopartikel weisen einzigartige Eigenschaften auf, welche hauptsächlich von ihrer Form, Größe und Größenverteilung abhängen. Sie wurden in der Gruppe von Professor Kautek (Fakultät für Chemie der Universität Wien) durch Laserablation in Ethanol hergestellt und haben eine mittlere Größe von 17 nm.

NP, die auf einer amorphen Kohlenstofffolie abgeschieden wurden, weisen eine sphärische Form mit unterschiedlichen Größen auf wie aus Kippexperimenten geschlossen werden kann. Die NP sind homogen oder beinhalten Ausscheidungen. Digitale Bildanalysen von TEM Bildern zeigen eine breite Größenverteilung der in den NP vorliegenden sphärischen Ausscheidungen mit einer mittleren Größe von (8.7 ± 5.7) nm. Weitere Analysen zeigen das Vorhandensein von kristallinen und amorphen Phasen: Elektronenbeugung weist auf einen Kern aus Eisenoxid mit orthorhombischer Fe_2O_3 Hochdruck-Phase hin und die Kippexperimente bestätigen die amorphe Hülle.

Die Analyse atomar aufgelöster TEM Bilder der Kerne wurde mit Bildsimulationen kombiniert und steht in Übereinstimmung mit der orthorhombischen Fe_2O_3 Struktur.

Mittels Elektronenkorrelationsmikroskopie wurden Zeitreihen von gekippten Dunkelfeldaufnahmen analysiert, um zu beobachten, wie sich amorphe Schalenbereiche und die atomare Dynamik unter dem Strahl verändern. Die Analyse der erzeugten zeitabhängigen Speckle-Intensität I (t) in einer bestimmten Region liefert Informationen über die Dynamik. Für zwei Zeitreihen wurde festgestellt, dass die Fe-W-O-Partikelregionen eine schnellere Dynamik aufweisen als die Trägerfolie aus amorphem Kohlenstoff. Die Untersuchung des Einflusses der Beschleunigungsspannung auf die resultierende Dynamik zeigt keine klare Tendenz: abhängig von der Art der Auswertung werden kürzere oder längere charakteristische Zeiten gemessen.

Um Informationen über die chemische Zusammensetzung der Probe zu erhalten, wurde eine Analyse mittels high-angle annular dark-field (HAADF) in Verbindung mit einer auf geometrischen Überlegungen basierenden Simulation durchgeführt, die von einer kugelförmigen Struktur der Kern-Schale-NP ausgeht. Den Intensitätsprofilen zufolge muss dem Kern des NP ein höherer Intensitätsfaktor als der Schale zugeschrieben werden. Daher weist die HAADF-Analyse auf einen W-Gehalt ($FeWO_3$) im Kern hin, wenn Fe_2O_3 als Zusammensetzung der Schale angenommen wird. Aufgrund dieser Analyse wird die orthorhombische Fe_2O_3 Nicht-Gleichgewichtsphase durch ihre Nanogröße und den Zusatz von W stabilisiert.

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Acronyms

NPs nanoparticles MRI magnetic resonance imaging **LaSIS** laser ablation synthesis in solutions CA contrast agents fcc face-centred cubic **TEM** transmission electron microscopy **BF** bright-field DF dark-field **SAED** selected area diffraction **HRTEM** high resolution transmission electron microscopy t-DF tilted dark field t-DF ECM tilted dark field electron correlation microscopy HAADF high angle annular dark field ADF annular dark field **STEM** scanning transmission electron microscopy **ECM** electron correlation microscopy BMG bulk metallic glasses **KWW** Kohlrausch-Williams-Watts **FFT** Fast Fourier transform **IFFT** inverse Fast Fourier transform

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1 Introduction

1.1 Laser ablation of colloidal Fe-W-O NPs in ethanol

With the advances in nanoscience and nanotechnology, core-shell nanoparticles (NPs) are a current research area in materials science. Nanomaterials research has evolved as studies focus on manipulating the properties of NPs by controlling their size, shape, and composition. By linking chemical sciences with physical and medical sciences, these materials have found many applications [1, 2, 3, 4] through their specific properties.

Super-paramagnetic iron oxide NPs exhibit properties such as biocompatibility and biodegradability and are used in magnetic resonance imaging (MRI) as an effective contrast agent for cell tracking in vivo [2].

The preparation method has a large effect on the shape and size distribution of NPs. The dual phase tungsten-iron NPs studied in this work are generated conventionally by laser ablation in ethanol, which is considered as a fast and straightforward method for their synthesis [2, 5]. Moreover, the synthesis of NPs by this method can be considered as green method as it does not require the use of toxic or chemical intermediates for their production [6].

Laser ablated NPs have unique physical properties that depend mainly on their shape, size and size distribution, since they have a large surface-to-volume ratio [6].



Figure 1.1: Schematic illustration of laser ablation synthesis in solutions (LASiS).

The term laser ablation in general refers to removal of material from a solid target by an intense laser beam where the temporal width of the laser pulse mainly controls the interaction of the laser beam with the material (Figure 1.1). The Fe-W-O NPs studied in this thesis are generated by ablation in ethanol using a nanosecond laser [2].

When the focused nanosecond laser beam interacts with the target material, there is an increase in the temperature of the irradiated spot, which leads to vaporization of the target material. These vaporized species in the form of atoms and clusters collide with the surrounding molecules, resulting in a laser-induced plasma plume. The plasma plume is confined to a small area by the laser ablation to ensure dispersion of the NPs in the liquid phase [7].

The generation of Fe-W-O core-shell NPs is conducted by laser ablation of the irontungsten oxide ceramic disk, with a solid target in the liquid environment and these particles collected in the form of a colloidal solution. In this way, colloidal alloy NPs are formed. According to reference [2], super-paramagnetic iron oxide and paramagnetic tungsten elements in combination could form an effective dual mode contrast agent (CA) that can find application in ultra high MRI and X-ray computed tomography.

Since the properties of the generated NPs such as shape and size may vary depend-

ing on the type of liquid and laser parameters, amorphous core-shell Fe-W-O NPs were prepared in ethanol by nanosecond laser pulses at a wavelength of 523 nm. Laser-assisted synthesis of NPs also allows manipulation of the size distribution of the generated NPs by adapting the post-irradiation time in colloidal solution or by adjustment of the duration of the ablation time.

Detailed description on the synthesis of the colloidal Fe-W-O in ethanol can be found in literature [2, 6, 5].

1.2 Phase diagrams for Fe-W and Fe-O

Figure 1.2 shows the Fe-W equilibrium phase diagram [8]. In addition to the austenite γ -Fe and the ferrite α -Fe phases, two intermetallic phases: μ -Fe₇W₆ and λ -Fe₂W are obtained. The solubility of W in α -Fe is very low with 2.8 and 7.8 at.% at 1000 and 1380 °C, respectively.



Figure 1.2: Fe-W phase diagram.

Figure 1.3 shows the Fe-O equilibrium phase diagram [9]. It includes several stable phases: α -Fe or δ -Fe, the face-centered cubic (fcc) austenite γ -Fe, the oxide magnetite Fe_3O_4 in two different structures (monoclinic and fcc), and the rhombohedral oxide hematite Fe_2O_3 . Hematit, however, can undergo a phase transformation into the orthorhombic structure under high pressure [10].



Figure 1.3: Fe-O phase diagram.

1.3 Aims of this work

It is the aim of this work to carry out the structural and chemical characterization of laser-ablated Fe-W-O core-shell NPs.

The experimental measurements will be carried out employing transmission electron microscopy (TEM), using the Philips CM 200 and Titan TEM.

It is planed to conduct a research on the shape and size distribution using electron microscopy imaging modes, such as: bright-field (BF) and dark-field (DF) at different sample tilts. Furthermore, the research of selected area diffraction (SAED) pattern should reveal crystalline or amorphous nature of the NPs.

To investigate the atomic structure of the sample, the high resolution transmission electron microscopy (HRTEM) has to be performed. To confirm the crystal structure, the simulation of the HRTEM image needs to be conducted with the JEMS software.

In order to obtain information about the dynamics of the amorphous regions under the beam is also planed to apply the method of tilted dark-field electron correlation microscopy (t-DF ECM) by taking time series of tilted dark-field (t-DF) images at 80 kV and 200 kV accelerating voltages and fitting the calculated time correlation function. For information on chemical composition of the sample high angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) imaging mode is applied.

2 Experimental methods

2.1 Transmission electron microscopy (TEM)

2.1.1 Diffraction, bright-field (BF) and dark-filed (DF) imaging

Transmission electron microscopy (TEM) is a very useful technique for sample characterization. The information on the internal structure and the chemistry of the sample arises as the electron beam passes trough the sample and interacts with the atoms of the investigated material.

The electron gun emits electrons which are further accelerated to high kinetic energies (typically 80-300 keV) [11]. In conventional or parallel TEM, the combination of condenser lenses forms a parallel illumination on the sample. Electrons interact with the Coulomb potential of the atoms - the closer an electron gets to the nucleus, the stronger this interaction is. Depending on how close an electron passes the nucleus, it can be elastically scattered to smaller or larger scattering angles. The differential cross section describes the scattering of electrons by the nucleus, which is described with the Rutherford model [12, 11]:

$$\frac{d\sigma_R}{d\Omega} = \frac{Z^2 e^4}{16(4\pi\epsilon_0 E_0)^2} \frac{1}{\sin^4\left(\frac{\theta}{2}\right)},\tag{2.1}$$

where Z is the atomic number of the material, e is the charge, ϵ_0 is the dielectric constant, E_0 is the kinetic energy of electrons, and θ is the scattering angle. For small scattering angles, where the screening of the electron cloud and correcting for relativistic effects have to be taken into account, the atomic scattering factor is given by [11]:

$$f(\theta) = \frac{\left(1 + \frac{E_0}{m_0 c^2}\right)}{8\pi^2 a_0} \left(\frac{\lambda}{\sin\frac{\theta}{2}}\right)^2 (Z - f_x),$$
(2.2)

 λ is the electron wavelength (controlled by the beam energy E_0), a_0 is the Bohr radius

of the scattering atom, f_x is the scattering factor, m_0c^2 is the rest energy.

Rutherford elastic scattering shows strong dependence on the atomic number (Z) (Equation 2.1). However, in crystallographic samples and at low angles, the crystallographic orientation effects the image contrast [12].

In crystalline samples with a long range periodic arrangements of atoms, the scattered beams show preferential directions as a result of constructive interference. Constructive interference is present when a momentum transfer $\Delta \mathbf{k} = \mathbf{k} - \mathbf{k}_{o}$ corresponds to the reciprocal lattice vector \mathbf{g} . This is known as the Bragg's condition [11]:

$$\mathbf{k} - \mathbf{k_0} = \mathbf{g},\tag{2.3}$$

and is schematically illustrated in Figure 2.1 .



Figure 2.1: Schematic representation of Bragg's condition. The difference between the scattered \mathbf{k} and the initial \mathbf{k}_o wave vector indicates the direction of the scattering vector.

In a TEM both real space and reciprocal space (diffraction pattern) information is accessible. The objective lens forms the diffraction pattern at the back-focal plane and the real image at the imaging plane (Figure 2.2). Depending on the mode of the TEM, diffraction pattern or image is transferred to the viewing screen. When a thin sample is illuminated with a parallel electron beam, a diffraction pattern is obtained from an entire illuminated area. In order to obtain information from a small specific area of the sample, SAED is conducted by inserting an aperture in a plane comparable with the specimen plane (i.e. image plane of objective lens). SAED is used to reveal the nature of the particle, i.e. whether it is a crystalline or amorphous particle. Unlike crystals, amorphous samples do not exhibit long range ordering of atoms but rather short range or medium range order.



Figure 2.2: Schematic illustration of formation of the diffraction pattern and the real space image at different planes in a TEM.

An important concept in TEM is the formation of contrast because of the transparency of thin samples for electrons. The contrast formation in bright-field TEM relies on amplitude contrast that is based on the intensity distribution of the electrons after the scattering process.

There are two basic ways to form amplitude contrast: mass-thickness contrast and diffraction contrast. The mass-thickness contrast shows a dependence on the atomic number Z of the atoms (Equation 2.1), the density ρ and thickness t; $\rho \cdot t$ is called mass-density. A local change of Z or mass-density affects the amount of scattering. When lattice planes are aligned with the electron beam in Bragg's condition (Equation 2.3), this contributes to the diffraction contrast in the image.



Figure 2.3: Schematic illustration of two imaging modes in TEM: (a) BF mode and (b) DF mode.

Imaging in BF mode and DF mode produce two complementary images. In the case of the BF image the direct beam is selected by the objective aperture and the image is formed in the image plane (Figure 2.3). If the objective aperture selects only scattered or diffracted electrons, a DF image is acquired (Figure 2.3). In the case of the DF image, stronger scattering at a certain sample position gives brighter features in the image [11].

Depending on the size of the objective aperture, one or more diffracted electron beams can be selected to produce the DF image. Therefore, only a small portion of the diffracted electrons are used for imaging. The intensity in DF imaging mode is proportional to the number of diffracted electrons reaching the detector or the viewing screen.

2.1.2 Impact of tilt on TEM images

Depending on the scientific question sample tilt is frequently necessary. This has a different impact on the contrast for crystalline and amorphous samples. The tilt angle of the specimen α is defined with respect to the axis of the goniometer that is perpendicular to the electron beam (optic axis).

Figure 2.4 shows the schematic illustration of dependence of the tilting axis with respect to the optic axis. The tilt angle is defined with respect to the x-direction.



Figure 2.4: Schematic illustration of the dependence of the tilt axis with respect to the incident electron beam.

The orientation of the sample with respect to the electron beam determines the appearance of the diffraction pattern in crystalline samples. If we consider diffraction with some deviation from Bragg condition we write [12]:

$$\Delta \mathbf{k} = \mathbf{g} - \mathbf{s},\tag{2.4}$$

where $\Delta \mathbf{k}$ is adjustable by tilts, \mathbf{g} is reciprocal lattice vector of the crystal and \mathbf{s} is the deviation parameter. This vector \mathbf{s} is a measure of how far we deviate from the exact Bragg condition. Perfect constructive interference is given when the momentum transfer $\Delta \mathbf{k}$ is equal to the reciprocal lattice vector \mathbf{g} . Depending on how the Laue condition is fulfilled, this affects the the intensity of diffracted beams and therefore the diffraction contrast and appearance of features in BF and DF imaging modes.

In the TEM images, the mass-thickness contrast is usually weaker than the diffraction

contrast, unless areas have large differences in the atomic numbers or the diffraction is weak [12].

Depending on the sample material, the diffraction pattern shows diffuse rings for amorphous materials and spots (reflections) for crystalline materials [11]. When examined in TEM with different tilt angles, the orientation of the crystalline structure with respect to the incoming beam is relevant for the contrast, while the contrast in amorphous materials does not change substantially with the tilt angle.

2.1.3 Analysis of the shape of NPs

The projected two-dimensional area of the particles in TEM images provides information about the shape and size of the particles. The particle diameter or length value can be calculated from the projected area using the following equation 2.5 [14]:

$$X_{EQPC} = \sqrt{\frac{4A}{\pi}},\tag{2.5}$$

where A is the projected area of the particle and X_{EQPC} is a diameter of a circle that has the same area as the projection area of the particle.

The Feret diameter can also be used to calculate the particle diameter, which is not actually a diameter, but corresponds to a group of diameters resulting from the distance between two tangents to the opposite pole of the particle in a well-defined direction [14].

2.2 High resolution transmission electron microscopy (HRTEM)

High-resolution transmission electron microscopy (HRTEM) is a method for imaging crystallographic samples at the atomic scale. Image formation in HRTEM is based on phase contrast. The parallel electron beam illuminates the sample as described in a TEM (Figure 2.2).

A plane wave, given by the electron wave function $\Psi_i(\mathbf{r}) = 1$ is transmitted through a thin sample. Here, $\mathbf{r} = (x, y)$ is a two-dimensional vector. When transmitted through

a thin sample only phase of the electron wave is modulated, not the amplitude. For a weak-phase object, this modulation can be expressed as $exp\{-i\phi(\mathbf{r})\} \approx 1 - i\phi(\mathbf{r})$, yielding the exit-plane wave [15]:

$$\Psi_{ep}(\mathbf{r}) = 1 - i\phi(\mathbf{r}) \tag{2.6}$$

Leaving the sample, the exit-plane wave forms a set of diffracted beams, which fulfil Bragg's condition (Equation 2.3), yielding a diffraction pattern in the back-focal plane of the objective lens (Figure 2.2).

The wave function in the back-focal plane is given by [15]:

$$\Psi_{bfp}(\mathbf{r}) = F(\Psi_{ep}(\mathbf{r})) = \Psi_{ep}(\mathbf{q}), \qquad (2.7)$$

where $F(\Psi_{ep}(\mathbf{r}))$ is the Fourier transform of the exit-plane wave, and \mathbf{q} is twodimensional vector in reciprocal space. When the plane is than propagated to the image plane, the wave function is given by [15]:

$$\Psi(\mathbf{r}) = F^{-1}[\Psi_{ep}(\mathbf{q})t(\mathbf{q})], \qquad (2.8)$$

where F^{-1} is the inverse Fourier transform of the product of exit plane wave $\Psi_{ep}(\mathbf{q})$ and the contrast transfer function $t(\mathbf{q})$ containing the microscope imaging characteristics. In real space coordinates, the electron wave function in the image plane is written by the combination of the exit plane wave with the contrast transfer function $t(\mathbf{r})$ [15]:

$$\Psi(\mathbf{r}) = \Psi_{ep}(\mathbf{r}) \otimes t(\mathbf{r}) \tag{2.9}$$

Finally, the intensity in the image plane is given by [15]:

$$I(\mathbf{r}) = |\Psi(\mathbf{r})|^2. \tag{2.10}$$

Considering only the objective lens of a microscope, lens errors influencing the contrast transfer function can be written as [15]:

$$t(\mathbf{q}) = exp - \{\frac{2\pi i}{\lambda}\chi(\mathbf{q})\},\tag{2.11}$$

where λ is the electron wavelength and χ wave aberration function. This wave aberration function is given by [15]:

$$\chi(q) = \frac{1}{2}q^2\lambda^2 C_1 + \frac{1}{4}q^4\lambda^4 C_3, \qquad (2.12)$$

where $q = |\mathbf{q}|$, C_1 is defocus, and C_3 the third-order spherical aberration. By controlling the defocus, C_1 and a given value C_3 , the phase shift is adjusted in such a way that the phase contrast image reflects the structure of the sample.

2.2.1 Simulation of HRTEM images by JEMS Software

The JEMS Software [16] was used to simulate and confirm the assumed crystal structure. The lattice spacings and symmetry in the experimentally acquired HRTEM images are compared with the crystal structures obtained from the Inorganic Material Database (AtomWork) [17]. For the assumed structure, the HRTEM images were simulated in JEMS using the Bloch wave method.

Crystal structure data are based on lattice parameters [10], where the lattice is defined by its space group, atomic coordinates in the unit cell, occupancy, and chemical element. The Wyckoff positions indicate where the atoms are located in a crystal, and are referred to as multiplicity and Wyckoff site symmetry. The space group under consideration contains the symmetry of the structure and is entered in the software by its space group number.

2.3 Electron correlation microscopy (ECM)

Electron correlation microscopy (ECM) is a new method for studying the dynamics of atomic rearrangements using time-resolved coherent electron scattering. This method was originally developed and applied to supercooled metallic glasses to measure their structural dynamics at the nanometer scale [18]. Dynamic heterogeneity is a fundamental characteristic of the dynamic nature of glass transitions, with spatial domains exhibiting widely varying structural relaxation times on the nanoscale [19].

The ECM method offers two different modes: STEM ECM and t-DF, which can provide information about the time and length scales of these dynamic changes [20]. The STEM ECM mode corresponds to the X-ray photon correlation spectroscopy method [21].

In this work, the local dynamics of amorphous Fe-W-O NPs generated by laser ablation in ethanol is investigated with nanometer spatial resolution at room temperature using t-DF ECM to reveal information about the temporal fluctuation of the spatial domains and relaxation phenomena. One major benefit of this method is its spatial resolution.

2.3.1 Spatial heterogeneous dynamics

Understanding the physics behind glass formation is a challenging topic in material science and its active scientific research field. Spatially heterogeneous dynamics, where some regions of the material relax more slowly or more rapidly than others, while structural relaxation typically occurs in clusters rather than uniformly throughout the material, is typically attributed to the dynamic nature of glass transitions. [22]. Crucial for the glass transitions are the length and the time scale of the heterogeneous dynamics. There are a number of theories that explain this complex behaviour, with widely varying views [23, 24, 25, 26, 27].

The process of glass formation is usually described as a change in volume as a function of temperature, as shown in Figure 2.5.



Figure 2.5: Schematic representation of the temperature dependence of the specific volume of liquids, crystals and glass.

Supercooled liquids are formed when the liquid is cooled very rapidly to avoid crystallization in the temperature range below the melting temperature (T_m) , and can be referred to as a quasi-equilibrium state. As a metastable state, it exhibits high atomic mobility and a short relaxation time.

Glasses form as the temperature range approaches the glass transition temperature (T_g) and can be characterized as a non-equilibrium state in which atomic mobility becomes very slow. Most microscopic theories state that the viscosity and relaxation times increase as the temperature drops to T_g and a glass forms, whereby the structural relaxation dynamic (decay time) slowing down [28]. The increased viscosity η means that the forming glass cannot be arranged in the long range order [29]. Bulk metallic glasses (BMG) are non-crystalline metallic alloys that exhibit short-range ordering rather than long-range ordering like crystals.

This dynamical heterogeneity, characteristic of glasses, is most likely determined by the structural heterogeneity due to the β relaxation, where the Kohlrausch-Williams-Watts (KWW) equation can be used to describe the successive degeneracy of spatial heterogeneity during β relaxation [30].

According to the references [31, 32], the β relaxation correlates with the structural heterogeneity of glasses and is the main source of dynamics in glasses. The α relaxation is also related to glass transitions and ceases at the T_g temperature. The difference is that the α relaxation is related to multiple atoms changing their nearest

neighbours, while the β relaxation is related to single atom jumping [33].

2.3.2 Tilted dark-field electron correlation microscopy (t-DF ECM)

Time-resolved coherent scattering of electrons leads to speckle patterns of intensity I(t), where t is time. Each speckle is formed by electron scattering from a particular local structural rearrangement due to constructive interference. Thus, a characteristic time for structural rearrangements can be determined from a time-resolved measurement of speckle intensity [33, 20]. Since the intensity of speckle patterns is linked to local structure and composition, the lifetime of speckle depends on the persistence of a particular pattern.

In this work, we apply ECM to acquire a time series of t-DF micrographs at room temperature, using the time autocorrelation function $g_2(t)$ to analyse the intensity I(t) of a pixel [20]:

$$g_2(t) = \frac{\langle I(t')I(t'+t)\rangle}{(\langle I(t')\rangle)^2},$$
(2.13)

where t' is the time of a frame in the tilted DF time series, t is delay time after t' and $\langle \rangle$ denotes average over all t'.

The resulting time autocorrelation function $g_2(t)$, which exhibits a stretched exponential behaviour, is fitted to the KWW equation in order to obtain the two fitting parameters: the characteristic relaxation time τ , and the stretching exponent β for each pixel in the time series [20]:

$$g_2(t) = 1 + Aexp[-2(\frac{t}{\tau})^{\beta}],$$
 (2.14)

where A is an instrument dependent scaling parameter related to the diffraction intensity variation, t is delay time, τ is relaxation (or decay) time and β is stretching exponent [20]. In addition, both fitting parameters are presented as maps: for the stretching exponent β and the spatial distribution of the relaxation time τ . The mapping of the dynamic changes provides information about the time and length scales of these rearrangements. This is a major advantage of the t-DF ECM method compared to, for example, Xray photon correlation spectroscopy, which does not provide insight into the local spatial dynamics [34]. The t-DF ECM method offers insight into the local dynamical changes, which are spatially resolved at room temperature. Therefore, the speckle intensity at a specific position on the sample can provide information about the dynamics at that specific position.

To obtain a reliable time autocorrelation function $g_2(t)$, one must consider the time resolution and the length of the time series of t-DF micrographs. A detailed description of how the length of the time series affects the resulting relaxation time can be found in the literature [35]. However, if the acquired t-DF time series is not long enough, this may cause $g_2(t)$ not to converge to 1. As for the effect of time resolution on $g_2(t)$, the time per frame needs to remain below 0.1 of the structural relaxation time τ [18].

The drift correction is also important for the acquisition and analysis of the time series at room temperature, since artifacts that result from the reduction of the intensity time correlation can occur over time. This causes the reduction of the measured structural relaxation times τ .

The stretching exponent β that is normally used to characterize the relaxation behaviour in amorphous materials usually indicates spatial heterogeneity within the relaxation dynamics [33]. For β relaxation at temperatures in the supercooled domain, the time correlation function decays to one with a stretched exponential behaviour $0 < \beta < 1$.

ECM can be applied in form of t-DF imaging which is obtained by tilting the direct electron beam until the diffracted beam is positioned along the optical axis to pass through the objective aperture. A schematic illustration of implemented ECM using t-DF TEM imaging mode can be seen in Figure 2.6. A parallel beam illuminates the sample. To obtain an t-DF image in the image plane, the objective aperture is used to select speckles in the diffraction pattern, while the rest of the diffraction pattern is blanked out. Only the electrons scattered into those particular speckles contribute to the real-space image and form a spatial map of speckle intensity in a real space [33].



Figure 2.6: Schematic illustration of tilted t-DF ECM.

The time series of speckle patterns showing intensity variations in t-DF TEM images on a very small scale by coherent electron diffraction are recorded and analysed by ECM to obtain the spatial distribution of the structural relaxation time τ , given as τ maps, and the stretching exponent β , represented by β maps.

2.4 High angle annular dark-filed imaging (HAADF)

In scanning transmission electron microscopy (STEM) the convergent electron beam (probe) is scanned across the sample surface instead of illuminating it with the parallel beam as in TEM. The image quality and the resolution of the image depend on the electron probe, therefore optimization of the probe shape is necessary. The probe is formed by the condenser system. A simple schematic STEM configuration is shown in Figure 2.7. Compared to TEM imaging methods, STEM imaging involves capturing images pixel by pixel.

Multiple detectors in the STEM are utilized to acquire common signals by measuring an integrated intensity with different scattering angles that provide different information from the sample.

BF detectors are positioned on the optical axis and collect the direct electron beam

(angles < 10 mrad). Depending on the structure of the sample image contrast is based on the mass-thickness or diffraction contrast.

Detection in STEM instruments is also performed by annular dark-field detectors (ADF), which are arranged in a ring around the optical axis and collect all scattered electrons in defined angular ranges. The ADF detector collect scattered electrons in the angular range between 10 - 50 mrad and these electrons contribute to both Bragg diffraction contrast and chemical contrast (Z-contrast) [11].

Scattered electrons at larger angles (> 50 mrad) are collected by the HAADF detector. In this regime, Bragg diffraction is negligible and the dominant image contrast is the Z-contrast. The origin of the Z-contrast, pure unscreened Rutherford elastic scattering cross section depends on the atomic number Z^2 [36]. The HAADF imaging mode provides information on structural variations down to atomic level.



Figure 2.7: Schematic illustration of STEM.

2.5 Sample preparation

The Fe-W-O NPs for the TEM study were deposited by placing a droplet of the colloidal dispersion on a copper grid coated with a carbon film and then evaporating the solvent in air at room temperature. The deposition of the NPs was done about 4 years after production by LASIS.

2.6 Equipment

For structural characterization of the NPs two different electron microscopes were used: (i) Philips CM 200 TEM with a LaB_6 cathode, equipped with GATAN Orius CCD camera and N EDAX EDS system; (ii) FEI Titan 80-300 (S)TEM with mono-chromator, Cs image corrector (CEOS) and Gatan 2k Ultrascan 1000 camera. Details of the settings are given in the corresponding paragraphs of the experimental results.



Figure 2.8: Photograph of Philips CM 200 (photograph courtesy of Semir Tulic)



Figure 2.9: Photograph of FEI Titan 80-300 kV S (TEM) (photograph courtesy of Prof. Christian Rentenberger).

3 Experimental results and discussion

3.1 TEM analysis of Fe-W-O core-shell NPs by BF and DF imaging modes

3.1.1 Structural characterization of the Fe-W-O NPs

The structural characterization of the core-shell Fe-W-O NPs was carried out using different TEM state-of-the art methods.

To get an overview of the structure of the sample under investigation, BF images of the sample region of interest were first acquired. Figure 3.1 shows BF, DF and the SAED pattern images, of the same area containing core-shell structures deposited on amorphous carbon foil.

The majority of NPs show a characteristic circular shape of different sizes. Based on tilting experiments (see below) the 3-dimensional spherical nature of the NPs could be identified. Previous measurements yield a mean size of the NPs of about 17 nm [2].

The BF image in Figure 3.1a shows core-shell Fe-W-O NPs next to thin amorphous layers (called matrix). It reveals significant characteristic intensity differences in the NPs:

(i) an intensity gradient between edge and centres and

(ii) dark areas in form of cores and bright shells.

Assuming an amorphous structure of the NPs the intensity variation can be interpreted based on the mass-density thickness contrast: thicker and/or higher mass density area (e.g. the larger atomic Z) appears darker in the BF image. Therefore, intensity variation between edge and center of the NPs originates by their thickness variation due to their spherical shape, whereas the significant dark core areas seem to be caused by a different mass density.



Figure 3.1: (a) BF TEM image of core-shell Fe-W-O NPs (b) SAED with marked positions of objective (contrast) aperture A1 and A2, (c) and (d) DF TEM images of core-shell Fe-W-O NPs correspond to the marked positions in (b), respectively.

SAED in Figure 3.1b shows diffuse rings due to the presence of the amorphous phase and some weak bright spots due to the presence of the crystalline phase. These bright spots (encircled and numbered) indicate crystalline phases distributed over the amorphous sample area. The interplanar spacing d of the lattice planes corresponding to the spots are given. In diffraction mode, the central beam is blocked during acquisition with the camera.

In contrast to the BF TEM imaging mode, where transmitted electrons contribute to image formation, in the DF TEM imaging mode diffracted electrons at small angles contribute to image formation (Figure 2.3). The DF images shown in Figures 3.1c and 3.1d correspond to the A1 and A2 objective aperture positions, respectively. Whereas the objective aperture A1 is placed on the reflection 1 in the diffraction pattern, which is characterized by the atomic distance d and is related to the Fe_2O_3 [121] of the orthorhombic system, the objective aperture A2 is placed on the reflection 2 corresponding to the Fe_2O_3 [002] of the orthorhombic system.

In the DF TEM images NPs show core-shell structures and the strong variation between core and shells can be seen, where the core is lighter and the shell is darker. It appears that the shell is amorphous and the core is composed of crystalline phases randomly distributed. The same sample area was imaged under BF and DF conditions by choosing different positions in reciprocal space, resulting in complementary images.

In the Table 1 the crystallographic data and phase identifiers from the selected area diffraction pattern which is identified with the Inorganic Material Database (Atom-Work) [17, 10] are summarized. The experimental error is due to the uncertainty of 1 pixel = $0,007 \ nm^{-1}$.

In literature, Fe-W-O NPs produced by laser ablation in ethanol are reported as coreshell NPs with both amorphous core and shell [2]. In our study we clearly identify also the presence of crystalline cores embedded in amorphous shell. This different results of the same sample material could be caused by some variability of the NPs or an instability of the amorphous core phase over time.

Space Group Number	62	62	62	62	62	62	
Personal Symbol	$^{\rm oP20}$	oP20	oP20	oP20	oP20	$^{\mathrm{oP20}}$	
Miller Indices	[121]	[002]	[311]	[321]	[123]	[242]	
Crystal System	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	
Lattice distance [nm]	0.237	0.229	0.152	0.141	0.134	0.119	
Materail	Fe_2O_3	Fe_2O_3	Fe_2O_3	Fe_2O_3	Fe_2O_3	Fe_2O_3	

l. Crystallographic data and	
Ps generated in ethanol	
1: Selected area diffraction pattern results of Fe-W-O core-shell NPs	identifiers obtained from Inorganic Material Database (AtomWork).
Table	phase

3.1.2 Series of the tilted BF TEM images

In order to gain 3-dimensional information on the shape of the NPs and their precipitates (cores), the shape and the position of the dark volumes as a function of particle tilt were analysed.

Series of BF TEM images of the investigated sample were acquired from the same sample area by tilting the sample in the range of - 50° to 50° with 5° steps (Figure 3.2). Figure shows representative BF TEM images taken at different tilts of an area consisting of small particles and one large particle. The latter shows bright and dark contrast at several positions. The tilt axis is indicated approximately.

The small spherical volumes labelled 1, 2, and 3, at the large NP change their position as the function of tilt angle. By tilting the sample in the range between -50 ° and +50 ° it can be seen that these circular regions are contained within the particle and therefore are considered as precipitates of different phases within the surrounding matrix. The particle 4 is outside the large NP and also changes position with the tilt angle. It overlaps with the large NP at tilt position +50 °.

The contrast in the BF images of the precipitates inside the particles was not greatly affected by tilting the sample. This indicates some amorphous nature of the precipitates. However, some significant variation in contrast can be seen in precipitate 1 and particle 4 during tilting. Therefore, some of the precipitates and particles comprise crystalline regions.

It should be noted that crystalline regions with the same composition as the amorphous phase can show darker or brighter contrast with respect to the amorphous phase. Assuming an orientation that fulfils the Bragg condition the crystalline precipitate becomes dark in BF images, whereas in orientations far away from the Bragg condition they look brighter then the amorphous surrounding.


(a) -50° tilt angle



(b) 0° tilt angle





Figure 3.2: BF TEM images of core-shell Fe-W-O NPs acquired at different tilting angles. The tilt axis is indicated approximately.



Figure 3.3: Variation of the distance between spherical areas (Figure 3.2) as a function of the tilting angle in range between - 50° and 50°. (a) Distance between 1 and 2, (b) distance between 1 and 3, and (c) distance between 1 and 4. Data points (black) are fitted by curves (red) according the Equations 3.1 and 3.2.

Figure 3.3 shows the plot of the distance of the dark and bright spherical precipitates within the observed NPs as a function of tilt angle.

The behaviour of the distance variation depends on the relative height and the position of the precipitates under consideration. In order to find the projected positions in the images taken at different tilts digital image processing was applied. The procedure is described in detail in the Digital Image Processing section (Section 3.1.5).



Figure 3.4: Schematic geometry representation of the spherical areas.

A schematic representation of the geometry of the considered precipitates is shown in Figure 3.4. The distance of the considered precipitates changes according to the equations:

$$d_2 = \sqrt{d_{\parallel}^2 + d_{\perp}^2} \tag{3.1}$$

$$d_{\perp} = d_1 \cdot \sin(\alpha + \varphi), for \ \alpha = \frac{\pi}{2} \quad d_{\perp} = d_1 \cdot \cos \varphi$$
 (3.2)

The projected length parallel to the rotation axis d_{\parallel} does not change with tilting angle φ , while the measured projected distance d_2 depends on the height difference based on d_1 and the angles α and φ . α represents the angle between the tilt value for which $d_{\perp} = 0(\varphi = -\alpha)$ and the untilted case ($\varphi=0$). The distances shown in Figure 3.3 have been plotted according to the Equations 3.1 and 3.2. The analysis yields that particle 4 and precipitate 1 are on similar height (i.e. alpha close to 90 °), whereas precipitates 1, 2, and 3 are at different heights. The values of the fit parameters used for Figure 3.3 are given in Table 2.

$d_1 \; [nm]$	α [°]
31	0
11	50
33	85
	d ₁ [nm] 31 11 33

Table 2: The values of the fit from Figure 3.3.

3.1.3 Shape of the dark precipitates in the NPs

The shape of the generated core-shell NPs is roughly circular at different tilt angles and circular area of the observed dark precipitates 1 and 2 is independent of the tilt angle (Figure 3.5). Only a few exceptions appeared in the image, which could be due to the fact that the precipitates are partially crystalline and thus affected by the tilt of the sample. Therefore, we can conclude that the 3-dimensional shape of the particles are spheres containing spherical precipitates.



Figure 3.5: Areas of the precipitates 1 and 2 within the NP given in Figure 3.2 as a function of tilt angle.

3.1.4 Size distribution of the dark precipitates in the NPs

To determine the size of the dark precipitates in the NPs, the BF TEM image shown in Figure 3.1a is used. Digital image processing in the Fiji software [37] was performed to obtain the quantities used for further analysis. The procedure is described in detail in the Digital Image Processing section (Section 3.1.5).

The equation 2.5 is applied to calculate the EQPC diameter of the dark precipitates. The histogram of the plotted EQPC diameter of the dark precipitates is shown in Figure 3.6. The histogram shows a broad size distribution from 3.9 nm to 24.8 nm for the diameters of the dark precipitates with an average size of (8.7 ± 5.7) nm, using the log-normal function to fit the experimental data.



Figure 3.6: Histogram of size distribution of the dark precipitates in NPs (Figure 3.1a) given by EQPC diameter.



Figure 3.7: Histogram of size distribution of the dark precipitates of core-shell NPs (Figure 3.1a) given by (a) maximum Feret diameter and (b) minimum Feret diameter.

The particle diameter can also be expressed by the Feret diameter. By definition, the maximum Feret diameter is always larger than the diameter of EQPC and corresponds to an average core-shell W-Fe-O NP size of (9.9 ± 5.9) nm. In contrast, the minimum Feret diameter is always smaller than the diameter of EQPC and is (8.2 ± 5.4) nm. The size distribution of minimum and maximum Feret diameters is illustrated in Figure 3.7. The results are summarized in Table 3.

Curve Fitting (Log-normal)	Median [nm]	Mean [nm]	Standard Deviation
EQPC diameter	$7,9\pm0,5$	$8,7\pm0,5$	5,6
Feret min diameter	$7,3\pm0,5$	$8,2\pm0,5$	$5,\!5$
Feret max diameter	$9,3\pm0,5$	$9,9\pm0,5$	5,9

Table 3: EQPC diameter, minimum and maximum Feret diameters of the dark precipitates in the NPs.

3.1.5 Digital image processing by Fiji Software (ImageJ)

Digital image processing methods were performed using Fiji software (ImageJ) [37]. The following steps were applied for the analysis shown in Figures 3.8 and 3.9:

- The scale was adjusted so that 2688 pixels correspond to 75 nm;
- A median filter (4 pixels) was applied to reduce noise in the image;
- The local contrast is enhanced resulting the images 3.8a and 3.9a;

- The drawing tool was used to encircle the areas of interest and then erased; The deleted areas were used as particles for further analysis, applying tresholding segmentation to obtain binary images as shown in Figures 3.8 (b) and 3.9b.;

- After the particle analysis was set, a list of quantities used for the further analysis was displayed in the results window.

Figure 3.8 shows described steps of digital image processing using Fiji software applied to BF TEM image 3.2 to determine the distance between the spherical regions inside the NP. The spherical regions are labeled 1 and 3. It should be noted that the same procedure is applied to determine the distances between spherical regions 1 and 2, and 1 and 4, which are marked in the corresponding BF image. The obtained quantities are used for further analysis to calculate the distance between the precipitates as a function of the tilting angle.



Figure 3.8: (a) BF TEM image and (b) corresponding processed image using Fiji Software.

Figure 3.9 shows the steps of digital image processing using Fiji software applied to the BF TEM image acquired at a tilt angle of 0° (Figure 3.1a) to determine the diameter of the dark precipitates and the minimum and maximum Feret diameters.



Figure 3.9: (a) BF TEM image and (b) corresponding processed image using Fiji Software.

3.1.6 Experimental details

BF, DF and diffraction imaging of the core-shell NP were performed at an accelerating voltage of 200 kV using a Philips CM 200 TEM with a LaB_6 filament shown in Figure 2.8. The images and selected area diffraction pattern were recorded with a GATAN Orius CCD camera. For BF and DF imaging an aperture of 20 µm in size was used. The SAED patterns were taken from a circular area with a diameter of 300 nm.

3.2 HRTEM analysis of Fe-W-O core-shell NPs

The structural analysis of TEM images of the core-shell Fe-W-O NPs revels presence of crystalline and amorphous phases, assuming the cores consist of iron oxide with orthorhombic Fe_2O_3 phase.

As an additional analysis method of the crystalline core, HRTEM imaging was applied. In this case the distances between the lattice fringes visible in the HRTEM images and the corresponding angles were analysed and used to simulate and assign the corresponding crystalline phase.

The procedure was as follows: the analysed HRTEM images were first compared with the lattice parameters and X-ray diffraction data for the considered phases from the Inorganic Materials Database (AtomWork) [17]. Then, the simulation of the Fe_2O_3 structure was performed using the JEMS software [16]. Finally, the observed patterns of the acquired HRTEM images were compared with the simulated patterns of the assumed crystal structure and crystal orientation.

3.2.1 Analysis of the acquired HRTEM images

The evaluated HRTEM image of the core-shell Fe-W-O NP is shown in Figure 3.10 (a) and displays a spherical core-shell particle. The contrast of the core is significantly darker compared to the shell and the surrounding matrix.

Lattice fringes are visible in the core of the NP as shown in zoomed Figure 3.10 (b), indicating the presence of nanocrystals located in the core within the amorphous shell of the sample. It should be pointed out that this surrounding amorphous shell decreases the signal to noise ratio of the crystalline core considerably since in projection amorphous and crystalline phases overlap.

The HRTEM images were analysed using their Fast Fourier Transform (FFT) by selecting the region of interest to investigate the presence of periodicity in the images. The images are analysed in the Digital Micrograph Software. The procedure is described in detail in the HRTEM analysis by Digital Micrograph Software section (Section 3.2.2).



Figure 3.10: (a) HRTEM image of spherical core-shell NP and (b) lattice fringes of the acquired nanocrystals. The inset shows the crystalline phase at higher magnification.

The FFT in Figure 3.11 shows the reflections for the HRTEM image shown in Figure 3.10. Measured inverse lattice spacings d⁻¹ and the characteristic angles between the reflections were used for further analysis and comparison. Here, the lattice spacings for the reflections labelled A, B, C, and D in the evaluated FFT image are compared with the literature values of the lattice parameters from the AtomWork according to Reference [10].



Figure 3.11: FFT of the HRTEM image shown in Figure 3.10.

Table 4 lists the lattice spacings labelled as A, B, C and D in the inverse FFT (IFFT) shown in Figure 3.12. These spacings obtained from the intensity profile agree with literature values. The error value for the measured lattice distance is 0,018 nm and corresponds to the value of one pixel. As can be seen from the FFT and IFFT images of the analysed HRTEM image, the measured angles between reflections A and B, and between C and D are 90° which is consistent with the values reported in the literature for the given orthorhombic structure. The corresponding perpendicular lattice planes are marked in the Figure 3.11.

Reflections FFT	d spacing FFT	d spacing AtomWork	Assumed reflections
А	$0,255\pm0,018nm$	0,2485	(200)
В	$0,223\pm0,018nm$	0,2295	(002)
С	$0,169\pm0,018nm$	0,1683	(202)
D	$0,169\pm0,018nm$	0,1683	(202)

Table 4: Lattice spacings d corresponding to the reflections shown in Figure 3.11.

According to the experimental data of the observed HRTEM images, the structure is consistent with the orthorhombic Fe_2O_3 structure with Pearson symbol oP20 and Pnma space group No 62 from AtomWork [10]. The experimental HRTEM images were also compared with the following structures from AtomWork [17]: $Fe_{2.67}O_4$ structure with Pearson symbol cF56 and Fd-3m space group No 227 Fe_2O_3 structure with Pearson symbol hR30 and R-3c space group No 167 Fe_2O_3 structure with Pearson symbol tP160 and $p4_12_12$ space group No 92 $W_{0.75}O_{0.25}$ structure with Pearson symbol cP8 and Pm-3n space group No 223, but did not match with any of these mentioned structures.

3.2.2 HRTEM analysis by Digital Micrograph Software

The analysis of the HRTEM images was performed using the Digital Micrograph Software from the Gatan company [38]. The script for the Digital Micrograph: Wiener filter was used to enhance the atomic structure in the image (inset in Figure 3.10b). The database of Digital Micrograph scripts is hosted and maintained by FELMI, Graz University of Technology, Austria.

To reduce the influence of the amorphous shell and the matrix on the FFT the core of the NP was selected (Figure 3.10). The obtained FFT image can be seen in Figure 3.11. The individual inverse lattice spacings d labelled in the evaluated FFT image and their characteristic angles were measured with respect to the central spot by the drawing tool provided by the Digital Micrograph. The center of the FFT image is defined as central spot.

The intensity profile for reflection A yields (Figure 3.13) real space lattice spacing for that reflection. The same procedure was used for other reflections. The lattice fringes in the inverse FFT (Figure 3.12) were obtained by selecting all visible reflections with a filtering mask in the corresponding FFT. Planes oriented perpendicular to each other are marked.



Figure 3.12: IFFT of the image shown in Figure 3.10. The lattice planes corresponding to reflections A, B, C and D shown in Figure 3.11 are indicated.



Figure 3.13: The intensity profile for reflection A.

3.2.3 Simulation of HRTEM images by JEMS Software

The JEMS Software was used to simulate the HRTEM images of the crystal phase using the crystal structure data from the Inorganic Materials Database (AtomWork) [10]. The simulation was performed in order to confirm the crystal structure shown in the analysed HRTEM images.

The observed patterns of the acquired HRTEM images are compared with the one simulated of the Fe_2O_3 crystal structure in the [010] crystal orientation.

Parameters for the simulation were set consistent with the FEI Titan electron microscope and are shown in Table 5.

Acc. $[kV]$	Cc [mm]	Cs [mm]	$\Delta E \; [eV]$
200	2	0.01	0.80

Table 5: Microscope parameters used for the simulation by JEMS softare.

The cell parameters and atom coordinates of the Fe_2O_3 crystal structure with the space group Pnma (No. 62) are listed in the Tables 6 and 7, respectively. The data are provided by the AtomWork database [10].

Structure	Cell parameters
Fe_2O_3	$a = 0.487nm; b = 0.668nm; c = 0.459nm; \alpha = \beta = \gamma = 90^{\circ}$

Table 6: Cell parameters of the Fe_2O_3 crystal structure (Structural type: GdFeO₃; Pearson symbol: oP20; Space group: Pnma, No:62) obtained from Inorganic Material Database (AtomWork) [10].

~					7
Occupancy	1.0	1.0	1.0	1.0	
x y z	0.43716, 1/4, 0.01556	0,0,0	0.1984, 0.0506, 0.3043	0.5328,1/4,0.6005	
Site Symmetry	.m.	-1	1	.m.	
Wyckoff	C	а	q	C	
Multiplicity	4	4	8	4	
Atom	Fe	Fe	0	0	
Structure	Fe_2O_3				

Table 7: Crystal structure data for Fe_2O_3 obtained from Inorganic Material Database (Atom Work) [10].

The simulated HRTEM maps were generated for Fe_2O_3 crystals for a [010] zone axis direction.

The HRTEM maps shown in Figure 3.14 are composed of individual images with different defocus (horizontal direction) and sample thickness (vertical direction) and are created by changing defocus in the range of 5 to 75 nm and sample thickness from 5 to 9.5 nm. Defocus steps of 5 nm and thickens steps of 0.5 nm were used for simulation.



Figure 3.14: Simulated HRTEM maps for Fe_2O_3 crystals for a [010] zone axis.

Based on the spherical shape of the precipitates a maximum thickness of about 8 nm is established. The simulated HRTEM image shown in Figure 3.15 agrees closest with the experimentally acquired HRTEM image when the defocus is 20 nm. It also shows the positions of the atoms as overlay. Therefore, under this imaging conditions Fe atoms are imaged as bright spots. Following the performed JEMS simulation, the Fe_2O_3 crystal structure for a [010] zone axis direction can be confirmed for the observed experimental HRTEM image.



Figure 3.15: Simulation of the Fe_2O_3 structure: defocus 20 nm, thickness 8 nm. The position of Fe atoms are indicated gray, the position of O atoms blue.

3.2.4 Experimental details

HRTEM imaging was performed on the FEI Titan 80-300 TEM using a Scottky field emission gun. The accelerating voltage of 200 kV was used for imaging. For HRTEM the condenser aperture 1 and 2 were set to: 2 000 μm and 150 μm , respectively, and the lens 3 was off in free control mode. Before imaging the corrector was tuned.

3.3 Time series of Fe-W-O core-shell NPs by t-DF ECM

The structural and HRTEM analysis of the Fe-W-O NPs shows the presence of crystalline phases and amorphous phases in the core-shell NPs. t-DF ECM was used to observe how amorphous regions change under the beam, and to evaluate the dynamics under the beam.

Amorphous materials generate speckle intensity, while crystalline materials generate high intensity if the Bragg condition is fulfilled. The high intensity feature was used for drift correction in series of images. Time-dependent coherent electron scattering produces speckle patterns with intensity I (t). The utilized method shows how this intensity changes with time.

Analysis of speckle intensity of time series of images at a particular location of the sample provides information about the spatially heterogeneous dynamics of amorphous structures caused by their structural heterogeneity and composition.

3.3.1 Analysis of the acquired t-DF ECM images

Two time series of t-DF images of 450 micrographs were acquired over a period of 575 s at room temperature applying 80 and 200 kV accelerating voltage and are shown in Figure 3.16. From these two series the time correlation function (Equation 2.13) for each pixel was calculated as described in section 3.3.3 by using Fiji script written by Stefan Noisterning.

In the first step three identical regions, each 50 pixels in size, were selected for the analysis of the core-shell Fe-W-O NPs (green) and the amorphous carbon background regions (red).



Figure 3.16: t-DF ECM micrographs of two time series recorded at room temperature with (a) 80 and (b) 200 kV accelerating voltage.

Figures 3.17 and 3.18 show examples of the normalized, resampled time autocorrelation functions $(g_2(t) - 1)/A$ extracted from selected background and particle regions of the t-DF ECM time series (Figure 3.16) recorded at 80 and 200 kV accelerating voltage, respectively.

The time correlation function calculated for each pixel was averaged over identical selected regions. The resulting data points show the typical stretched exponential decay type and were fitted to the KWW function (2.14) choosing the logarithmic time scale. The structural relaxation process in glasses is usually described by the KWW function to calculate the fitting parameters: the relaxation time τ and the stretching exponent β of the selected regions shown in Figure 3.16 [39].

Figures 3.17 and 3.18 show that the time correlation function converges well to zero for longer delay times and the faster processes with shorter decay times are represented by the more stretched exponential decay.



Figure 3.17: The normalized time autocorrelation function $g_2(t)$ extracted from the selected (a) background and (b) particle regions of the t-DF ECM time series obtained at 80 kV fitted with KWW function.



Figure 3.18: The normalized time autocorrelation function $g_2(t)$ extracted from the selected (a) background and (b) particle regions of the t-DF ECM time series obtained at 200 kV fitted with KWW function.

The values of the individual KWW fitting parameters to normalized $(g_2(t) - 1)/A$ function for background b_i and particle regions p_i are given in Tables 8 and 9, respectively. The particle regions show for both accelerating voltages shorter decay times compared to the carbon foil, but the trend of the decay times with increasing accelerating voltages is different for the particle and the foil.

Accelerating voltage 80 kV	$ au~[\mathrm{s}]$	β
b_1	$98,67\pm1,44$	$0,73\pm0,01$
b_2	$87,78\pm1,54$	$0,69\pm0,02$
b_3	$111, 41 \pm 11, 81$	$0,70\pm0,02$
p_1	$9,83\pm0,8$	$0,36\pm0,01$
p_2	$13,53\pm1,64$	$0,30\pm0,01$
p_3	$5,42\pm0,49$	$0,37\pm0,01$

Table 8: KWW fitting parameters to $(g_2(t) - 1)/A$ for background b_i and particle regions p_i shown in Figure 3.17.

Accelerating voltage 200 kV	$ au \; [\mathrm{s}]$	eta
b_1	$61,63\pm0,89$	$0,68\pm0,01$
b_2	$68,78\pm1,35$	$0,64\pm0,02$
b_3	$80, 16\pm1, 57$	$0,74\pm0,02$
p_1	$20,87\pm1,03$	$0,43\pm0,01$
p_2	$21,36\pm0,82$	$0,48\pm0,01$
p_3	$19,78\pm1,20$	$0,36\pm0,01$

Table 9: KWW fitting parameters to $(g_2(t) - 1)/A$ for background b_i and particle regions p_i shown in Figure 3.18.



Figure 3.19: Spatial maps of structural relaxation time τ in seconds (a) and stretching exponent β obtained from time series recorded at 80 kV accelerating voltage.

The spatial distribution of structural relaxation times shown as τ maps (a) and stretching exponents as β maps (b), calculated from $g_2(t)$ for each pixel from time series recorded at 80 kV and 200 kV accelerating voltages, are shown in Figures 3.19 and 3.20, respectively. The KWW fits similar to Figures 3.17 and 3.18 give spatial maps that provide visual evidence of spatially heterogeneous dynamics. The maps in the color code, where τ is shown in seconds, show regions with different times. The mapping provides insight into the local structure of the sample and its low-temperature dynamics, providing spatial and temporal information on the heterogeneous dynamics of these rearrangements.



Figure 3.20: Spatial maps of structural relaxation time τ in seconds (a) and stretching exponent β obtained from time series recorded at 200 kV accelerating voltage.

Figures 3.21 and 3.22 show the histogram of the decay times of the FeW core-shell particle and the carbon foil for time series at 80 kV accelerating voltage, denoted as p_3 and b_3 in Figure 3.16.



Figure 3.21: Structural relaxation time in the FeW (p_3) and carbon foil b_3) of the time series recorded at 80 kV.

Again, it can be concluded that the FeW particle regions exhibit faster dynamics than the carbon background regions, for both time series recorded with different accelerating voltages. Both relaxation times and stretching exponents β of the particle regions are clearly different from those of the background regions, as can be seen from the values estimated from the normal fits to the histogram of the spatial maps of the structural relaxation times (Figure 3.21).

The analysis reveals a broad distribution of decay times and can be described by the Gaussian distribution. The decay times of the FeW particle regions are about four times shorter than those of the carbon background regions, with the normal fit yielding τ_{mean} around (20.16±3.41) s for the faster dynamic regions and (95.56±1.97) s for the slower dynamic regions. For particle regions, the relative distribution of frequencies shows a narrow decay time distribution, while a wide peak around 100 s is seen for background regions.



Figure 3.22: Stretching exponent beta in the FeW (p_3) and carbon coated background regions (b_3) of the time series recorded at 80 kV.

The stretching exponent β (Figure 3.22) ranges less then 1 and correlates with the with decay times: the regions with the longer decay times τ have higher β . The exponent β less than 1 indicates a stretched exponential decay and can be related to multiple relaxation processes typical of metallic glasses. For particle regions, the β exponent tends to shift to smaller values, with small values of the stretching exponent also implying heterogeneous dynamics [33].

Figures 3.23 and 3.24 show the results for the values of τ_{mean} and β_{mean} resulting from the normal fits to the histogram of the spatial maps of the structural relaxation times and the stretching exponent β . Two accelerating voltages were used to investigate the influence of the beam on the resulting atomic dynamics. It is found that the dynamics at room temperature is slower or faster depending on the accelerating voltage applied. According to reference [40], two factors that affect the result of the decay times are the influence of the electron beam during the measurement and the total observation time. It is shown in literature that the time series that have longer observation times result in higher decay times [40]. Since both time series were recorded with the same total observation time of 575 s, this can be excluded as one of the factors affecting the different result of the decay times.



Figure 3.23: The structural relaxation time corresponding to spatial map shown in Figure 3.19.

The peak value of the decay time for time series recorded at 80 kV accelerating voltage is (25.20 ± 1.05) s for the particle region whereas the second peak related to the carbon background is hidden due to the broad distribution. The time series recorded at 200 kV accelerating voltage exhibits two maxima, with two main characteristic times (14.83 ± 1.32) s and (117.83 ± 1.67) s of FeW particle and background regions, respectively. Based on the decay time distribution, the higher applied accelerating voltage of 200 kV leads to faster dynamics with a narrow decay time distribution for the particle region, while the carbon foil seems to become slightly less beam sensitive (compare Figure 3.21).



Figure 3.24: The stretching exponent β . corresponding to spatial map shown in Figure 3.20.

Figure 3.24 shows the histograms of β stretching exponents and their fits from the 3.19b and 3.20b spatial maps for time series at 80 and 200 kV accelerating voltage, respectively. β ranges from 0 to 1 and is shifted to smaller values for time series recorded at lower accelerating voltage. For 80 kV accelerating voltage, the mean value of β is (0.37±0.007) and for 200 kV two peaks are observed. $\beta < 1$ corresponds to very local relaxation of mobile atoms and can be described as "rattling in the cage" [41].

3.3.2 Experimental details

Method of t-DF ECM was carried out at FEI Titan 80-300 TEM (Figure 2.9). Condenser aperture 1 and 2 were set to: 2 000 μm and 150 μm , respectively, and the lens 3 was off in free control mode. The objective aperture was set to 20 μm .

The t-DF TEM series of the core-shell FeW NPs were obtained by tilting the electron beam in such a way that the diffracted electron beam is positioned on the optical axis (Figure 2.6).

Two time series were taken at two different accelerating voltages of 80 and 200 kV, where the objective aperture on axis of 20 μ m blocks most of the pattern and a speckle was selected at a given **k** to produce a real space image of only the scattered electrons, resulting in a speckle intensity map (Figure 3.16).

The long-range ordered regions appear as bright patches with high intensity in the t-DF micrographs and produce a sharp diffraction feature that is used as an alignment feature of the analysed time series.

The two time series of 450 t-DF micrographs were acquired with an exposure time of 1 s using the Ultrascan 1000 camera and a binning of 4 (512×512) pixels.

3.3.3 Analysis of t-DF ECM images by Digital Micrograph Software and Fiji Software (ImageJ)

The acquisition of data is conducted in Digital Micrograph Software using TEM recorder in fast mode in order to increase time resolution. It allows to take consecutive images that are stored in the memory. After recording and storing the alignment of the image stack is conducted by image alignment in Digital Micrograph software. Sample drift correction is an important step in data processing since it can lead to artefacts in the evaluated data, such as reducing the measured τ values [40]. By aligning the time series images, this method offers the possibility to measure slow dynamics [18].

For calculating the time correlation the Fiji script written by Stefan Noistering was used. The script checks the change in intensity between successive images in a stack and calculates the time correlation function $g_2(t)$ (Equation 2.13) for each pixel of the aligned image stack. The range of the delay time is set by defining the minimum (1) and maximum slice number (200), and using correct time step between image slices of the stack. As a result, a stack of 200 images is obtained with a delay time between images of 1.28 s. Image 1 shows the $g_2(t)$ value for each pixel with a delay time of 1.28 s, image 200 shows $g_2(t)$ for a delay time of 256 s, since the total acquisition time of 450 micrographs was 575 s. The resulting $g_2(t)$ present as z-axis profile along the stack follows the stretched exponential decay and is fitted with KWW to calculate the fitting parameters: the relaxation time τ and the stretching parameter β . For the selected regions fitting of $g_2(t)$ was done in qti programme. For fitting per pixel Fiji script written by Stefan Noisternig was used.

3.4 Structural characterisation of Fe-W-O NPs by HAADF STEM imaging mode

To get information on chemical composition of the investigated sample further structural characterisation was carried out using HAADF STEM imaging mode. By collecting scattered electrons at high angles, the contrast formation in HAADF images strongly depends on approximatively Z^2 (Equation 3.3) [11].

$$I \cong a \cdot Z^2 \tag{3.3}$$

where I is intensity, a is constant and Z is atomic number of element that caused scattering of electrons.

Therefore, assuming that that the core and the shell are spherical, the elemental information within NP can be obtained from the HAADF images by analysing the intensity contrast between the core and shell.

In order to obtain information about the HAADF intensities and to approximate the Z values of the core and the shell, the simulation was performed considering the geometry and the background of the NPs. Figure 3.25 shows the geometric representation of the homogeneous sphere with radius r. Here x is the coordinate from the center of the sphere and -z to +z is the projected atomic column depth, which is proportional to the HAADF intensity values obtained along the direction of the electron beam [42].



Figure 3.25: Schematic geometry representation of the sphere with the radius r.

The intensity profile of the homogeneous sphere can be easily calculated and compared with the real intensity profile using the equation 3.4.

$$I = I_0 \cdot 2 \cdot \sqrt{r^2 - x^2} \tag{3.4}$$

where r is the radius of the homogeneous sphere, x is the coordinate from the center of the sphere, 2 represents the two halves of the sphere, and I_0 is the characteristic intensity factor containing the information about the composition.

Simulating the intensity profile of a core inside the shell, first the intensity based on the shell has to be removed at the position of the core before the intensity of a core has to be added. The background intensity of the supporting foil can be added by the constant value.



Figure 3.26: Schematic geometry representation of the core and shell used for the simulation.

3.4.1 HAADF analysis

The intensity contrast in the HAADF images is investigated by creating intensity profiles in the regions of interest to distinguish the core from the shell. The obtained line and radial intensity profiles were analysed individually.

HAADF STEM images of the investigated sample are shown in Figure 3.27, including: (a) line intensity profile and (b) radial intensity profile. Figures show core-shell NPs lying on an amorphous carbon supporting foil. As it can be observed, the core of NP shows evidently higher intensity compared to the shell and the core is well distinguishable from the shell. This difference in intensity contrast can also be clearly seen in the intensity profiles in Figure 3.28.



Figure 3.27: HAADF STEM images of core-shell NPs, including: (a) line intensity profile and (b) radial intensity profile.

Figure 3.28 displays the intensity profiles labelled in Figure 3.27, where (a) is the line profile through the center of the NPs and (b) the radial intensity profile of core-shell NP. The obtained intensity profiles show a circular shape due to the spherical shape of the observed NPs. It can be observed that the intensity is highest in the central part of the NP, since the depth of the projected atomic columns impacts the intensity observed in HAADF images. HAADF STEM images with representative line profiles



Figure 3.28: The intensity profiles of the HAADF STEM images labelled in Figure 3.3 (a) line intensity profile and (b) radial intensity profile.

for Au/Ag core-shell NPs confirms this observation [42]. Moreover, chemical species and microscope parameters have impact on intensity signal in HAADF STEM images [36].

To analyze the contrast differences within the NPs in more detail, a simulation was performed based on the particle geometry and is shown as fitted curve to the data points in Figure 3.28. From the plot, it can be seen that the smaller particle (red) shows contrast according to the shape and lower intensity compared to larger NP. The larger particle show contrast differences within the NP, with the core (blue) showing significantly higher intensity compared to the shell (green). The intensity factors according to Equation 3.4 are given in Figure 3.28 and Table 10.

However, as the contrast in HAADF images is proportional to approximately Z^2 , the observed high intensity differences indicate large differences between atomic numbers, with the atomic numbers for the observed core-shell NPs being as follows: Z(W) = 74, Z(Fe) = 26, and Z(O) = 8.

Intensity factors	I_1^*	I_1	I_2	I_2 / I_1
Line	95	108	275	2.55
Radial		108	270	2.50

Table 10: Intensity factors of the simulated intensity profiles shown in Figure 3.28.

According to the simulated intensities using the Equation 3.4 of core and shell the intensity factor of the core is about 2.5 times higher than that of the shell (see Table 10). The result is similar for the line profile and the radial profile. The ratio of the intensity factor of the core and the shell I_2/I_1 can be related to Z_2^2/Z_1^2 .

Assuming Fe_2O_3 as shell composition results in a mean $\overline{Z_1}^2 = 15.2$, after replacing Fe by W, $FeWO_3$ results in $\overline{Z_2}^2 = 24.8$. The ratio $Z_2^2/Z_1^2 = 2.6$ is similar to that of the intensity factors I_2/I_1 given in Table 10 and indicates content of W in the core. For confirmation of this result energy-dispersive X-ray spectroscopy line scans would be essential. Binary FeW core-shell NP produced by physical vapour deposition show also a core consisting W [5].

3.4.2 Experimental details

The structural characterization of the investigated sample was performed by applying HAADF STEM imaging mode, performed at FET Titan 80-300 TEM (Figure 2.9). For the imaging the high voltage of the microscope was set to 200 kV.

Initially, the TEM mode was used to find the region of interest of the studied sample. When switching to STEM mode to illuminate the sample, the camera length, spot size, and condenser aperture were adjusted. The spot size of the electron beam affects the lateral resolution in STEM imaging mode [11]. The size of the condenser aperture also affects the resolution of STEM images by reducing aberrations.

To obtain STEM images with higher quality and resolution, the alignment of the Ronchigram was performed. The Ronchigram is basically a shadow image created from the amorphous regions of the sample, whereby focus, defocus, and condenser astigmatism affect the shape and symmetry of the Ronchigram.

3.4.3 Analysis of HAADF STEM images by Fiji Software and Qti plot

To relate the Z contrast in the HAADF STEM images with the atomic numbers in the NP for the observed sample the intensity profiles were analysed in Fiji software. Line intensity profile through the center of the NP and radial profile of the core-shell NP for the same sample area were performed (Figure 3.27). Qti plot was used for the plotting of the experimental data and for the simulation of intensity profiles using Equation 3.4

4 Conclusions

Conventional TEM analysis confirms the spherical morphology of the NPs and precipitates. Analysed Fe-W-O core-shell NPs generated in ethanol show the presence of crystalline and amorphous phases, where the shell is amorphous and the core precipitates are frequently crystalline with the Fe_2O_3 structure based on electron diffraction patterns. Geometry between precipitates is determined by tilting experiment of series of the tilted bright-field images and comparing measured distances with geometric models. The size distribution shows a mean size of precipitates of 8.7 nm.

HRTEM analysis of the cores of the acquired HRTEM images of core-shell NPs combined with image simulations using the JEMS software agrees with the presence of the orthorhombic Fe_2O_3 high-pressure crystal structure for a [010] zone axis direction.

Two time series of t-DF ECM images at 80 kV and 200 kV accelerating voltage revealed local atomic dynamics of the amorphous shell induced by the electron beam. Both the supporting carbon foil and the NP show variation of dynamics on nanometer scale. In difference to carbon foil, FeW core-shell particle regions show shorter decay times (higher dynamics). The investigation of the dynamics as function of the accelerating voltage shows no clear trend and depends on the way of evaluation, e.g. the decay time of the amorphous particle shell increases with increasing accelerating voltage when g_2 -averaging over small regions is done (Tables 8 and 9) whereas the histogram of decay times shifts to smaller values when a pixelated evaluation is carried out (Figure 3.23).

For HAADF-STEM, the line intensity profile of the intensity variation within the particle is fitted with a model based on the geometry that assumes a spherically symmetric structure of the NP to obtain intensity factors for the core and shell of the NP. The ratio of the intensity factors indicates content of W in the core. Therefore, based on the TEM analysis the formation of $FeWO_3$ preciptates with the high-pressure orthorhombic Fe_2O_3 structure during LASiS seems reasonable when Fe_2O_3 as shell composition is assumed. This non-equilibrium orthorhombic phase seems stabilized within the nanoparticles by its nano size and the W content.

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