The measurement of internal strain in core–shell $\text{Ni}_3\text{Si}(\text{Al})\text{--SiO}_x$ nanoparticles

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Abstract

Internal defects and strain in nanoparticles can influence their properties and therefore measuring these values is relevant. Powder diffraction techniques (neutron and synchrotron) are successfully used to characterize internal strain in the core–shell $\text{Ni}_3\text{Si}(\text{Al})\text{--SiO}_x$ nanoparticles having mean diameters of ~ 80 nm. The nanoparticles, which are strain-free after extraction from the bulk alloys, develop internal strain on heating. Both micro- and macro-strains can be measured from the analysis of Bragg peak shift and broadening. It is identified that differences in thermal expansion coefficient of the metallic core and the amorphous shell of the nanoparticles, as well as partial disordering of the L1_2 ordered core phase, are the main causes of strain evolution. Synchrotron measurements also detected partial crystallization of the amorphous silica shell.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Multifunctional nanostructures are becoming increasingly important for many applications and surface modification of nanoparticles has emerged as an important class of functional nanostructures. Core–shell nanoparticles, where the centre and the surface region of a particle have different structure and/or composition, are being developed. Nanoparticles having an inorganic core and shell are suitable for potential applications in many diverse fields, especially for optical devices, magnetic storage media and in health science [1]. Core–shell nanoparticles with magnetic core capped with an inert biocompatible shell are intensively studied as they are candidates for medical applications like magnetic hyperthermia and targeted drug delivery [2]. Various methods, both physical and chemical, can be used to produce core–shell nanoparticles. Generally, these methods need two steps—first the core particle is produced and then it is covered by the shell material in a second step of the manufacturing process [3–5]. A process to produce nanoparticles of intermetallic phases from simple two-phase metallic alloys has been recently developed by us [6]. In this process, nanosized precipitates

of intermetallic phases are grown in a bulk metallic alloy, and later they are extracted by electrochemical selective phase dissolution (ESPD) of the matrix. When ESPD is applied to binary Ni–Si or ternary Ni–Si–Al alloys for the extraction of Ni_3Si -type precipitates (L1_2 crystal structure), core–shell-type nanoparticles are produced [7]. The shell forms *in situ* during the extraction process through dealloying of the alloy matrix, which in this case is an Ni(Si) solid solution [8]. The shell formation mechanism is described elsewhere [6]. Such core–shell nanoparticles are unique and may be attractive for many useful functional medical applications (see above). The core–shell $\text{Ni}_3\text{Si}(\text{Al})\text{--SiO}_x$ nanoparticles produced by ESPD have been well characterized using small-angle neutron scattering (SANS), x-ray diffraction (XRD) and transmission, and scanning electron microscopy (TEM and SEM) to determine the structure and composition of the core and the shell [7, 9]. In the present work, diffraction with neutron and synchrotron radiation is used to characterize strain inside the particles and after their extraction and after *in situ* heating (to 1000 °C). The stability of the core–shell-type nanoparticles was also studied.

It has been reported that nanoparticles generally exhibit properties that are different from the bulk materials [10, 11]. These differences in nanostructures come mainly due to: (i) their finite size, which give rise to quantum confinement effects and (ii) their large volume fraction of surface atoms. Accurate determination of the atomic scale structure, homogeneous and inhomogeneous strain, structural defects, and geometrical particle parameters, like size and shape, is therefore important for understanding the fundamental mechanisms and processes in nanostructured materials. The atomic scale crystal structure of the nanoparticle gives us information, but structural differences between nanoparticles and the bulk material are not so well understood and are also not easy to resolve. In small dimensions particle diameter becomes comparable with the scale of chemical order fluctuations and therefore crystals, which in bulk form have high order parameters, can become disordered or the crystal structure may be distorted or totally changed [12]. These effects can also affect the physical and chemical properties of nanoparticles. Strain and defect determination in nanoparticles is therefore of relevant interest. Also the stability of nanoparticles may be affected by the internal defects and strain within the particles. When high numbers of defects are introduced in the nanoparticles, they may become unstable and re-crystallize on heating.

Many nanoparticle production methods introduce severe stress in the particles [13, 14]. This stress also alters the properties of particles as compared to the bulk material. However, such property changes may be different than those expected from a simple reduction in size only. In the present study we first show that nanoparticles produced by the ESPD method are generally strain- and defect-free. So the effect of size reduction alone can be studied in extracted particles. However, for composite particles (having a core-shell structure) the situation is more complex, as the core and the shell may behave differently to changes in temperature or pressure. Therefore, monolithic particles (particles without a shell) and composite particles (particles with a shell) may behave very differently.

Methods employed in determining defect and strain in particles includes powder diffraction techniques (neutron and x-ray)—which rely on the analysis of Bragg peak broadening [15]. New methods of pair distribution function (PDF) analysis use information from the total scattering powder measurements, which includes Bragg and diffuse scattering, to refine the structure [16, 17]. However, this kind of analysis is suitable when particles are less than 10 nm in diameter. In the present work the mean size of nanoparticles is around 80 nm; therefore conventional width analysis of diffraction peaks is used to estimate average crystallite size and micro-strain.

2. Experimental details

2.1. Nanoparticle synthesis

The synthesis of core-shell nanoparticles was done by an electrochemical selective phase dissolution method (ESPD) developed by us and described elsewhere [7, 18]. In this

Figure 1. SEM image of the etched surface of a heat-treated Ni-13.3Si-2Al alloy showing the nanosized Ni₃Si(Al) precipitates.

process a two-phase metallic alloy containing nanosized precipitates is used to extract the nanoparticles. For the present work, Ni₃Si(Al)-SiO_x core-shell nanoparticles were synthesized starting from a ternary alloy with the composition Ni-13.3Si-2Al (at.%). A small amount of Al is added to the alloy to induce a cubic shape in the precipitates. Al addition controls the coherent lattice misfit between matrix and precipitate phases of the order of 0.1–0.2% which is needed to obtain the cubic-shaped precipitates having sizes in the range of 50–100 nm. The alloy was melted in a vacuum induction furnace and homogenized in the single-phase region at 1100 °C for 48 h. Nanoprecipitates of Ni₃Si(Al) phase were produced in a fine dispersion (~40% volume fraction) by annealing at 600 °C for 24 h and water quenching (figure 1). The precipitate size ranged from 20 to 150 nm, as measured by SANS [9].

The Ni₃Si precipitates were extracted from the alloy by electrochemical dissolution of the matrix phase using an aqueous electrolyte solution containing 1% citric acid and 1% ammonium sulfate (pH value 2.4) and an extraction potential of 1.25 V. The alloy sample was mounted in an electrolytic cell in an aqueous acidic environment and anodic polarized. During polarization performed at a fixed potential, only the Ni-rich matrix was dissolved and a silicon oxide shell formed around the extracted particles as a consequence of dealloying of the Ni(Si) solid-solution matrix. Dealloying of the matrix etches the Ni atoms preferentially from the Ni(Si) solid solution. The released Si atoms oxidize in the aqueous environment and deposit on the extracted precipitate particle surface [7]. As a result, intermetallic Ni₃Si(Al) nanoparticles capped with an SiO_x shell are produced. TEM images of the core-shell particle are shown in figures 2 and 4.

2.2. Powder diffraction measurements

Neutron powder diffraction measurements with *in situ* heating were performed at the structure powder diffractometer (SPODI) in the Heinz Meier-Leibnitz (FRM-II) neutron source at the Technical University of Munich (Germany). SPODI has a detector bank of individual position-sensitive detectors arranged in an arc around the sample holder, and can therefore collect scattered intensity simultaneously over the whole 2 θ

Figure 2. Bright-field TEM images of the core-shell nanoparticles. (A) As synthesized by the ESPD method and before heating. (B) and (C) After *in situ* heating at SPODI. Shell rupture and loss of adhesion are clearly visible as signs of mechanical damage.

range. Since for neutron diffraction the atomic scattering coefficient, the so-called neutron scattering length, does not depend on the scattering angle due to the interaction with the nuclei, higher peak intensities are detected at larger scattering angles in comparison to the case of x-ray diffraction. An advantage of this is that more peaks can be included in the data analysis, thereby increasing the statistical relevance of the results.

A powder sample of the extracted core-shell particles was measured. Only a limited amount of nanopowder (400 mg) was available for measurements by neutron diffraction. The powder was put in a niobium container for heating. Due to the very small amount of the powder sample, special care was taken to align the powder in the neutron beam. A high temperature vacuum furnace, a sample collimator of 20 min and a germanium 551 monochromator providing a neutron wavelength of 0.1549 nm were used for the *in situ* heating measurements. In particular, *in situ* measurements were performed for a total of 10 h on the powder sample at 25, 700 and 1000 °C and again at 25 °C after furnace cooling. Spectra were recorded for scattering angles ranging from 20° to 120° (2 θ). Additionally, a powder diffraction pattern from a standard yttrium oxide powder sample was measured at room temperature to obtain the instrumental resolution function as well.

X-ray synchrotron powder diffraction measurements were performed on the BW5 beamline at HASYLAB in DESY, Hamburg (Germany) with synchrotron energy 77 keV equal to a wavelength of 0.0161 nm, on a 2D position-sensitive detector with exposure times between 1 and 60 s per frame. The powder sample was mounted in an amorphous quartz capillary which contributed no peaks to the performed diffractogram. The quartz capillary was measured separately and showed no contribution to any Bragg peak. The high resolution and the low noise of the synchrotron measurement allowed detecting very weak additional reflections in the spectrum, which arose in the nanopowder after heat treatment during the *in situ* measurement at SPODI.

3. Results

Nanoprecipitates of Ni₃Si(Al) ordered L1₂ phase in an Ni–13.3Si–2Al (at. %) alloy are seen in figure 1. These precipitates

Table 1. Summary of data of Ni₃Si(Al) nanoparticle core obtained after Rietveld fitting and peak broadening analysis.

Temperature (°C)	<i>a</i> (nm) ^a	ϵ_L (%) ^b	$\langle D_V \rangle$ (nm) ^c	Micro-strain (%) ^d
25 (before)	0.351 523	0.00	58.5	0.00
700	0.355 206	1.04	51.6	0.11
1000	0.357 191	1.61	46.0	0.16
25 (after)	0.351 311	−0.06	51.6	0.14

^a Temperature-dependent lattice parameter.

^b Lattice thermal expansion (equation (2)).

^c Crystallite size.

^d Non-homogeneous micro-strain.

were extracted using ESPD to obtain nanoparticles. The extracted nanoparticles have a two-phase structure with a crystalline Ni₃Si(Al) core and an amorphous oxidized silicon (SiO_x) shell (figure 2(A)). Previous measurements by small-angle neutron scattering demonstrated that the powder consists of two nanoparticle populations with mean core sizes of 80 and 200 nm with shell thicknesses of 5 and 15 nm, respectively, the first one being predominant [9].

Typical diffractograms obtained from the powder sample at different temperatures are shown in figure 3(A). The powder diffraction patterns show all peaks of the L1₂ structure corresponding to the nanoparticle core (indexed) and additional peaks (marked with arrows) from the Nb container used to hold the powder sample. The measured diffraction patterns could be fitted to the two phases L1₂ Ni₃Si and A2 Nb using the Rietveld method and the FullProf software [19]. The results of the lattice parameter values are reported in table 1.

A peak broadening analysis was performed to estimate the crystallite size and micro-strain in the nanoparticle core. Peak breadths were calculated by fitting a Gaussian function to the peaks and taking the contribution from the instrumental resolution function (also assumed to be of Gaussian shape) into account. The instrumental broadening was obtained from measurement of yttrium oxide powder (cubic with space group *Ia* $\bar{3}$) used as a reference standard. Only the fundamental peaks of the L1₂ structure were used for an estimate of the crystallite size and the micro-strain in the nanoparticles. Including the very weak L1₂ superstructure peaks introduced large errors in the fit, and was therefore avoided. By considering only the fundamental peaks, the values obtained are to be considered

Figure 3. (A) Neutron diffraction patterns from the powder sample measured at different temperatures. Arrows indicate the position of reflections from the niobium container and reflections from the $L1_2$ core phase are indexed. (B) Plot of the Gaussian full width at half-maximum (FWHM) of the main lattice peaks as a function of 2θ calculated from the diffraction peaks of the $Ni_3Si(Al)$ phase in the measured diffractograms. The data marked by a dotted circle (i.e. the (222) peak at 1000 °C) was not used in the analysis (see text).

as the strain and size of an equivalent face centred cubic (fcc) lattice containing the $L1_2$ structure of the Ni_3Si phase. Since the $L1_2$ structure is only an ordered form of the fcc lattice, there is no significant difference by this consideration. The values obtained allow a realistic analysis of the distortion and deformation in the lattice and also of the size of the coherent crystallites. Figure 3(B) shows a plot of the Gaussian full width at half-maximum (FWHM- Γ) of the main diffraction peaks as a function of 2θ angle. The plot includes data from the $Ni_3Si(Al)$ phase measured at RT and high temperatures and also from the standard yttrium oxide powder. A comparison with the standard sample clearly shows that heat treatment of the nanoparticles resulted in a general peak broadening.

The FWHM curve from the $Ni_3Si(Al)$ phase at 25 °C before heating (figure 3(B)) is uniformly translated vertically with respect to the curve of yttrium oxide over the complete 2θ range, i.e. the intrinsic peak width shows no dependence on the scattering angle. This indicates the presence of only size broadening for the extracted nanoparticle and no broadening due to micro-strain. Therefore, it may be concluded that defect-and strain-free nanoparticles are generally produced by extraction using the ESPD method. A high resolution TEM image of a lattice-resolved core-shell nanoparticle is shown in figure 4, which also shows the core lattice to be undistorted. It may be noted that the coherent crystallite size (table 1), which is obtained from peak broadening analysis (Scherrer formula), has no direct correlation to the mean particle size [15]. The coherent crystallite size value can be smaller or in maximum equal to the mean particle size, depending on the sample. Further, this value is also a volume-weighted average of the contribution from the two particle populations present in the measured powder sample. A comparison between different crystallite size values obtained at different temperatures is made.

From the smooth variation of curve $\Gamma(2\theta)$ with the reflection order angle (figure 3(B)), it can be concluded that the strain and size parameters are isotropic, i.e. they follow the same curve irrespective of the reflection order. This indicates that the coherent crystallite shape is close to spherical. In the data at 1000 °C, the value of Γ for the (222) peak is outside the average trend of data at lower scattering angles. As this

Figure 4. (B) High resolution electron microscopic image of a single core-shell nanoparticle. (A) Magnified image showing the lattice resolved image of the particle core. The shell has an amorphous structure.

particular peak has very low intensity at 1000 °C, an accurate fitting is difficult. Therefore, this value having a larger error is not included in our analysis.

The FWHM curves at 700, 1000 and 25 °C after heating (figure 3(B)) show a vertical shift and also a change in the slope, i.e. a dependence of the intrinsic width from the scattering angle is observed, which indicates the coexistence of both size and strain broadening. Good separation of strain and size effects is possible using the Williamson-Hall plot, since theoretically the width of the size-broadened profile does not vary with 2θ angle, while the strain-broadened profile depends on 2θ . The average crystallite size that contributes to peak broadening represents the length over which the crystal scatters x-rays coherently and is a volume-weighted average value. The strain value that can be calculated by the broadening analysis is a volume-weighted strain value averaged in all directions which includes contributions from all the sources of strain. A Williamson-Hall plot from the measured data is shown in figure 5(A).

Figure 5. (A) Williamson-Hall plot of the full width at half-maximum of diffraction peaks of powder measured at the different temperatures. Temperature dependence of (B) micro-strain and (C) crystallite size in the nanoparticle core.

Assuming that the size and strain broadened profiles are Gaussian, the variation of the square of the full width at half-maximum of a peak with its Bragg position is described by the following equation:

$$\Delta \Gamma^2 \cos^2(\theta) = \frac{\lambda^2}{\langle D_V \rangle^2} + 16\epsilon^2 \sin^2(\theta) \quad (1)$$

where θ is the half scattering angle (Bragg peak position), Γ_{obs} the Gaussian FWHM as measured, Γ_{instr} the Gaussian FWHM of the instrumental profile (radians), $(\Delta \Gamma)^2 = \Gamma_{\text{obs}}^2 - \Gamma_{\text{instr}}^2$, λ the neutron wavelength (nm), $\langle D_V \rangle$ the average volume-weighted crystallite size (nm) and ϵ the average crystallite micro-strain (dimensionless). The formula expresses the sum of the squares of two contributions. The first term on the right-hand side is the Scherrer formula and the second term comes

Figure 6. Synchrotron powder diffraction pattern showing peak positions of different silicon oxide phases: tridymite (t), alpha quartz (a) and cristobalite (c) marked by arrows and indicated with the letters a, c or t to denote the corresponding phases. The reflections from $\text{Ni}_3\text{Si}(\text{Al})$ core are indexed.

from the formula that describes the typical $\tan^2(\theta)$ dependence of the strain from the peak width [15].

The calculated crystallite size and strain values are reported in table 1 and their dependence on temperature is plotted in figures 5(B) and (C). Both parameters show hysteresis with heating and cooling. The micro-strain increases monotonically from 0% at 25 °C before heating, to 0.11% at 700 °C, 0.16% at 1000 °C and finally to a value of 0.14% on cooling to RT (at 25 °C after heating). The crystallite size has an initial value of 58.5 nm at 25 °C, it decreases slightly to 51.6 nm at 700 °C and some more to 46.0 nm at 1000 °C. A final size of 51.6 nm is found at 25 °C after furnace cooling. So there is an actual decrease in the crystallite size at RT after the heating cycle with respect to the initial value.

In addition to the *in situ* heating neutron measurement, a synchrotron powder diffraction measurement was done on the same powder after the neutron experiment. The high resolution of the synchrotron measurement allowed resolving very weak extra reflections which arise in the diffraction pattern after the heating and cooling cycle. The resulting diffractogram (see figure 6) shows reflections from the Ni_3Si phase and additional phases. The measured peak positions are compared to different silicon dioxide phases (marked in figure 6): cristobalite, tridymite and alpha quartz. A perfect match with only one of the phases is not found: however, it may be concluded that all these three phases coexist in the shell volume after the *in situ* heating cycle. It is clear that the original amorphous SiO_x shell partially crystallizes to SiO_2 crystals on heating to 1000 °C.

4. Discussion

In general, we can distinguish between two types of strain in the Ni_3Si nanoparticle core. The first is a *uniform macro-strain*, which is represented by a uniform compression or expansion of the crystal lattice of all the particles. The second is a *non-uniform micro-strain* which varies from grain to grain and even inside single particles. The first is manifested on heating at 700 and 1000 °C and almost vanishes when the

powder is cooled down to 25 °C after heating. This strain is due to thermal expansion combined with thermal stress and is therefore reversible. On the other hand, on nanoparticles, which are originally strain-free at room temperature before heating, the second type of strain arises during heating and cooling.

In the core-shell nanoparticles having an intermetallic core and a ceramic shell, the uniform macro-strain is generated by the thermo-mechanical stress due to the difference in the thermal expansion coefficients of the core and the shell material. The non-uniform micro-strain, instead, originates from crystal defects, which eventually produce local lattice distortions. While the uniform macro-strain produces a homogeneous shift of the Bragg peak positions in the powder diffraction patterns, non-uniform micro-strain fields generate a broadening of the diffraction peaks. The broadening has a smooth variation with reflection order. We can therefore reasonably assume that the micro-strain in the Ni₃Si(Al) core is isotropic.

The core of the nanoparticles is initially strain-free, as reported in figures 3(B) and 4, even though the nanoprecipitates in the bulk alloy (figure 1) are non-uniformly strained as a consequence of coherency strain due to the lattice mismatch between the matrix and the precipitate phase. On extraction, the matrix around the nanoprecipitate is dissolved and the misfit constraint is thereby released, leading to a strain-free nanoparticle core. The SiO_x shell which forms over the nanoparticle core after the precipitate surface is freed from the matrix is amorphous and therefore imposes no constraint on the crystal lattice of the nanoparticle core [7]. Non-uniform micro-strain arises again in the core only during heating and cooling of the composite nanoparticles.

4.1. Uniform macro-strain due to different thermal expansion of the core and the shell

The lattice thermal expansion ε_L is calculated for each temperature T with respect to the lattice parameter measured at 25 °C (before heating) by using the equation

$$\varepsilon_L(T) = \frac{a_T - a_{25^\circ\text{C}}}{a_{25^\circ\text{C}}}. \quad (2)$$

This value is to be considered as an effective expansion of the core phase capped with a shell and it must be clear that it is not a direct measurement of the thermal expansion coefficient of the Ni₃Si(Al) phase. We consider a model of the core-shell nanoparticle in order to explain this further. A single composite particle can be modelled as a metal sphere, representing the core, which is capped with a uniformly thick layer of a ceramic material, representing the shell (figure 7). In general, thermal expansion in ceramic materials is less than in (inter-) metallic materials. Typical values for bulk SiO₂ (amorphous) and Ni₃Si are $0.5 \times 10^{-6} \text{ K}^{-1}$ and $14 \times 10^{-6} \text{ K}^{-1}$, respectively [20]. Therefore, thermal expansion on heating will be different for the two parts of the particle. In general, if we make the assumption that the coefficient of thermal expansion of the ceramic shell is negligible at a given temperature T compared to the metallic core, then when the composite particle is heated,

Figure 7. Schematic representation of strain formation in the composite nanoparticle due to differential thermal expansion of the core and the shell. It is assumed that the shell expansion is negligible and the shell is infinitely hard. Then at a given temperature T , the core outer boundary is constrained in the surface S_T , while in a free state (particles without a shell) it would have expanded to reach S_{free} . This constraint gives rise to a uniform strain inside the core lattice.

a hydrostatic stress proportional to the temperature will be introduced in the particle core. Under the constraint of the non-expanding shell, the metallic core which tries to expand cannot freely expand and its outer boundary is constrained in a surface S_T , while in the case of a naked particle (without a shell) after heating, it would have expanded to reach the surface S_{free} (see figure 7). This confinement gives rise to a homogeneous thermo-mechanical strain in the metallic core lattice given by

$$\varepsilon_{\text{TM}}(T) = \Delta\alpha\Delta T \quad (3)$$

where $\Delta\alpha$ is the difference in the thermal expansion coefficient between the core and the shell and $\Delta T = T - T_{25^\circ\text{C}}$ is the temperature increase. The situation in the composite particles is somewhat different to what is found in the literature for other systems like thin films deposited on a substrate or bimetallic beams [21]. In planar surfaces the thermal strain field has an anisotropic distribution. The strain in the present core-shell nanoparticles is instead isotropic. In the near-spherical particles the developed strain field had no preference for any particular crystallographic direction. Since the shell uniformly covers the core and exerts a hydrostatic pressure in all directions on the nearly spherical particles, the strain is rather uniform.

Following this model, the total homogeneous thermal strain of the nanoparticle core, ε_{TM} , is a measure of the actual expansion of the core lattice, ε_L , under the constraint of the shell (the shell actually expands to a smaller extent than the core). Therefore, we can equate equations (2) and (3) and the difference between the coefficient of thermal expansion of core and shell, $\Delta\alpha$, is then found by fitting the curve of ε_L versus ΔT . The calculated value of $\Delta\alpha$ is $(1.64 \pm 0.8) \times 10^{-6} \text{ K}^{-1}$, which indicates that fused silica (amorphous silicon dioxide) and its crystalline polymorphs have coefficients of thermal expansion much smaller than that of the Ni₃Si(Al) phase.

Deviation from this model is possible due to the fact that particles are not perfectly spherical. Moreover, in the real case the shell is fragile and breaks at some point (figures 2(B) and (C)), thereby releasing part of the stress accumulated in the core.

Figure 8. Intensity ratio of superstructure reflections (100), (110), (210) and (211) with respect to the (111) reflection as measured for the $\text{Ni}_3\text{Si(Al)}$ phase core of the nanoparticles. The relative intensity is decreased during the heat treatment and is not recovered after cooling, indicating a reduced degree of order in the L1_2 structure.

4.2. Non-uniform micro-strain due to chemical disorder

The thermal treatment has shown many effects on the nanoparticles. In the first place, the initial crystallite size has not been fully recovered after the cooling (figure 5(C)) but decreased from 58.5 to 51.6 nm in diameter, compared to the original core size. In particular, the volume-weighted average crystallite size decreased by 6–7 nm at 700 °C and by 8–9 nm at 1000 °C from the size measured at 25 °C before heating. The measured average crystallite size of ~56 nm is, however, much smaller than the actual particle core diameter determined by SANS, e.g. 80 and 200 nm for the two populations (see section 2). The core-shell nanoparticles in TEM images (e.g. figure 2(A)) confirm the size of the core-shell nanoparticles measured by SANS. Further, although in TEM images the extracted nanoparticles appear as single crystals (figures 2(A) and 4), one would expect the scattering coherency to be broken locally resulting in the smaller crystallite size. This is actually measured in the present study.

Moreover, an average micro-strain of 0.14% developed in the particle core during heating and cooling and the particle core did not completely relax on cooling to room temperature. A careful analysis of the superstructure peaks shows that their relative integrated intensity is also affected by heating. The integrated intensity decreases with increasing temperature (figure 8) and is only partially restored after cooling to room temperature. The ratio of the integrated intensity of superstructure peaks to that of a fundamental peak is a direct measure of the degree of order in the core lattice [15]. Firstly, the presence of superstructure reflections at high temperature indicates that the initial L1_2 order of the core structure is maintained even at high temperatures. However, the decay in their integrated intensity indicates that the degree of ordering is decreased. Complete disordering did not occur and no deviation from the cubic crystal lattice was observed.

Figure 9(A) shows a drawing of the (001) lattice plane in a Ni_3Si crystal with L1_2 ordering. In figure 9(B) a slightly off-stoichiometric composition is shown. Although the average superstructure L1_2 is maintained, locally the order is broken. It is typical of multi-component off-stoichiometric ordered phases that disordered regions (marked 1 in figure 9(B)) appears locally within an ordered structure (marked 2 in figure 9(B)) by nucleation and growth of small islands of defects or excess atoms and form crystallite domains [22]. The presence of disordered domains reduces the coherency length of scattered neutrons and induces a broadening of Bragg peaks; from this the crystallite size is measured. Thereby the coordination environment of atoms is modified (Si–Si, Si–Ni and Ni–Ni atom couples have different bond lengths). The domains present a modified cubic unit cell size and different stiffness modules locally, and non-uniform micro-strain is generated in the particle core. This process gives rise to an inhomogeneous strain field inside the core of the composite nanoparticles, whose magnitude is proportional to the temperature. The higher the temperature is, the larger is the average micro-strain. The experimental observations can be described well by the simple structural model.

Figure 9. (Left) (001) planar section of the Ni_3Si lattice with L1_2 crystal structure fully ordered. (Right) Same section of a similar crystal containing Ni and Si atoms in proportion off stoichiometry. Regions marked 1 represent domains with chemical disorder, regions marked 2 represent domains in nearly complete chemical order.

4.3. Transformation of the shell

Due to the high resolution of the synchrotron measurements, weak diffraction peaks originating from the very small volume of the crystallized shell could be detected (figure 6). These extra peaks could not be resolved in neutron diffraction, but were also observed in electron powder diffraction in a separate *ex situ* heating study [7]. The extra peaks confirmed that the amorphous shell is subject to partial crystallization on heating to 1000 °C. The shell to core volume in the powder sample is around 50% and the shell has a density three times smaller. The shell contains elements (Si and O) on average lighter than the core (containing Ni, Si and Al atoms) and therefore scattering x-rays much less. After heating most of the shell volume still remains amorphous. Therefore, the effective volume fraction of the crystalline silicon dioxide phases is very small and difficult to detect in general. Further, when amorphous SiO_x crystallizes different crystalline phases, e.g. quartz, cristobalite or tridymite, can form. From the present measurement it was not possible to clearly identify which phase crystallized in the shell, and it is apparent that all three polymorphs of SiO₂ are detected.

Alpha quartz, tridymite and cristobalite are polymorphs of quartz which are commonly found in volcanic rocks. The crystallization temperature ranges from 870 to 1470 °C for tridymite and below 870 °C for alpha quartz and they are therefore expected to form also in the shell of the nanoparticles upon heating up to 1000 °C. However, cristobalite, which crystallizes above 1470 °C in volcanic rocks, was also found in the shell [23]. This is an indication that the crystallization temperature of cristobalite is reduced when the size of the material is reduced to the nanoscale.

Crystallization of molten rocks upon cooling is different from the process of formation of crystalline quartz polymorphs in the solid phase upon heating from amorphous silicon dioxide, which is also a common phenomenon (see, e.g., [24]) and was observed in the present work. In the molten rocks the crystallization is favoured by the presence of other alloying elements and it occurs from a melt. In the core-shell nanoparticles no other elements are present with silicon and oxygen in the shell and the process occurs in a solid phase. Moreover in this case thermo-mechanical stress may also have an effect of reducing the crystallization yield. This explains why only partial crystallization of the shell was observed.

5. Conclusions

We measured non-uniform micro-strain in core-shell nanoparticles and followed its evolution during heating and cooling by *in situ* neutron powder diffraction. The results show that the nanoparticle fabrication method (electrochemical selective phase dissolution—ESPD) produces stress-free and generally defect-free nanoparticles of complex composition. On heating, differential thermal expansion of the core and the shell material induces strain in the particle core. Further non-uniform micro-strain is developed on heating due to partial disordering in the L1₂ ordered lattice in the particle core. The amorphous shell partially crystallizes on heating to 1000 °C. As a consequence of the differential thermal expansion of the core and

the shell materials, the shell occasionally ruptured. Neutron and synchrotron scattering are powerful tools for characterizing strain and size of core-shell nanoparticles in the size range of 100 nm. Even the very small amount of the powder sample (only 400 mg) was adequate to extract meaningful results.

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