Ultrastructure of Core-Shell Nanoparticles by High-Resolution Electron Microscopy

Debashis Mukherji¹ and Giancarlo Pigozzi²

1. Institute for Materials, Technical University Braunschweig, Braunschweig, Germany
2. Laboratory for Nanometallurgy, ETH Zurich, Zurich, Switzerland

ABSTRACT

Core-shell nanoparticles of Ni₃Si-type intermetallic phase were produced by extracting precipitates from two-phase Ni-Si alloys using an electrochemical phase separation technique. The method can be controlled to produce nanoparticles with or without a shell. The extracted nanoparticles were characterized by TEM, EDS and electron powder diffraction. It was found that the nanoparticle core maintains the size, shape, and crystal structure of precipitates that existed in the bulk alloys prior to their extraction. An amorphous SiO₂ shell formed around the precipitates during the extraction process. It is suggested that the shell forms as a result of de-alloying of the Ni-Si solid solution matrix.

KEYWORDS

Transmission electron microscopy, high-resolution electron microscopy, electron diffraction, imaging plate, energy-dispersive X-ray spectroscopy, core-shell nanoparticles

INTRODUCTION

Nanostructured materials, and in particular nanoparticles, have attracted much attention recently as they are finding increasing applications in chemistry, biomedicine, electronics, and materials engineering. Multifunctional nanosystems are gaining importance, and nanoparticles formed as core-shell type structures by surface modifications of nanoparticles have emerged as an important class of functional nanomaterial.

Recently, we reported a novel method for producing nanoparticles of intermetallic compounds from two phase metallic alloys [1,2]. In this process nanosized precipitates (with a wide size range - typically from a few to several hundred nanometres) were extracted from metallic alloys by selectively dissolving the matrix phase in which the precipitates were embedded. An electrochemical selective phase dissolution (ESPD) process was adopted and the phase selection was achieved through suitable choice of electrolyte and process control [2]. The technique is versatile and can also be applied to produce nanoparticles with a core-shell structure in a single step. Particles with an intermetallic phase core (e.g. Ni₃Si) capped with an inorganic shell of controlled thickness have been produced. Electron microscopes, both transmission and scanning electron microscopes (TEM and SEM), are invaluable tools for characterising such particles. In this article some of the results of our microscopic investigations are presented.

MATERIALS AND METHODS

Ni₃Si-type and Ni₃Al-type nanoparticles (10 to 500 nm in size) extracted from ternary and multicomponent Ni-base alloys were characterised by various techniques including TEM and SEM. An FEI Tecnai F30 field-emission TEM was used for high-resolution imaging and a Philips CM 30 microscope fitted with a LaB₆ cathode was used for the electron powder diffraction and energy-dispersive X-ray spectroscopy (EDS). Both microscopes were operated at 300 kV. Additionally, nanoparticles were imaged in a Leo 1530 FEG SEM.

Debye-Scherrer ring patterns from the powder samples were recorded on an imaging plate (IP) from Fuji Films. Imaging plates provide a high-definition image recording on a large usable area and have definite advantages over conventional recording media for quantitative diffraction analysis and therefore were chosen instead of film or CCD. As the intensities recorded on the IP varied linearly over a wide dynamic range (six orders of magnitude), it allowed recording of very low intensities along with the high intensity peaks. Thereby, the weak peaks from, for example, superlattice reflections or diffuse amorphous peaks could be well resolved in the presence of the high intensity Bragg peaks. Also the Q-range of the spectrum was extended and a larger number of Debye-Scherrer rings could be recorded at camera lengths of 900 mm and 1650 mm. The IP images were digitized by scanning in a Ditabis Micron readout device at

Figure 1:

Electron microscopic images of a typical two-phase single crystal alloy Ni-11.6 Al-2.4 Ta-3.5 W-6.0 Cr-1.3 Mo (at.%). (a) Darkfield TEM image showing precipitates of Ni₃Al-type γ phase with L1₂ crystal structure in two different sizes: large cuboidal shaped (~450 nm cube edge length) and small spherical shaped (~50 nm diameter), which are embedded in a Ni-rich solid solution matrix. (b) SEM image of the precipitates after they are extracted from the alloy by dissolving the matrix by the ESPD process.
Nanoparticle sample preparation
For TEM imaging the powder samples of nanoparticles were dispersed in ethylene after extraction from the metallic alloy and deposited on a holey carbon foil supported on a copper grid. In order to obtain cluster free dispersion, only a small amount of nanoparticles in the fluid media were subjected to ultrasonic vibration for a few minutes. In this way isolated particles could be obtained for TEM imaging. In contrast, an even dispersion of the powder sample with a high density of nanoparticles was necessary for the electron diffraction analysis. This required a different sample preparation method. The best powder diffraction samples were achieved by dispersing a large number of nanoparticles in ethylene followed by ultrasonic agitation for several hours before depositing the particles on the holey carbon foil. This ensured a homogeneous distribution of a monolayer of particles as a thin film on the foil.

RESULTS AND DISCUSSION
Morphology of nanoparticles
A darkfield TEM image of a typical two-phase alloy (in this case a single crystal Ni-superalloy) is shown in Figure 1a. The bright precipitates of Ni3Al-type γ with an L12 crystal structure were found in two different sizes - large cuboidal shaped (~450 nm cube edge length) and small spherical shaped (~50 nm). They were embedded in a Ni-solid solution matrix. The precipitates are seen in the SEM image (Figure 1b) after they were extracted from the alloy on dissolving the matrix by the ESPD process. A comparison of the two images shows that both the large and the small particles are completely and cleanly separated from the alloy by the selective removal of the matrix solid solution. It has been demonstrated that nanoparticles as small as 10 nm diameter can be isolated by this method (2).

Further, the ESPD process parameters can be controlled and nanoparticles with or without a shell can be produced. Figure 2 shows TEM images of isolated nanoparticles which were either homogeneous (Figure 2a) or had a core-shell (Figure 2b) structure. In Figure 2a nanoparticles with 50 to 100 nm size are seen. Each particle shows different grey colours as they are differently oriented in the electron beam. However, each particle has a uniform contrast within them, which indicates a homogeneous structure. The darker colour of the particle on the top left (Figure 2a) implies that it was oriented along a low-index zone axis direction in the electron beam and was strongly diffraction. The micrograph in Figure 2b, on the other hand, shows that the region near to the particle surface has a different contrast than its core, indicating that a shell has formed around the particle. The particles are about the same size as in Figure 2a and the shell around them is of very uniform thickness (~10 nm). Contrast variation experiments by small angle neutron scattering (SANS) on Ni3Si-type nanoparticles dispersed in a mixture of H2O/D2O also confirmed the existence of a core-shell structure of the nanoparticles (4).

High-resolution electron microscopy
When a nanoparticle was precisely oriented in the electron beam with the help of a double tilt goniometer stage in TEM and imaged with 300 kV, a high resolution lattice-resolved image of the nanoparticle could be obtained. A single isolated Ni3Si nanoparticle (~20 nm diameter) oriented in the [001] direction is seen in Figure 3a. The diffraction image (Figure 3b) shows that the particle is a single crystal with a high degree of ordering. The lattice structure is defect free and extends right up to the surface atomic layer in the particle. It further shows that the structure is very uniform and there is no distortion in the lattice, even near the free surface. Figure 4a shows a high resolution image of a typical Ni3Si(Al)-type core-shell nanoparticle. The magnified image in Figure 4b shows that the particle core and the shell have completely different structures. The core, where the atomic columns of the L12 lattice are resolved, is crystalline (here oriented along the [110] beam direction). The interface between the core and the shell is very sharp, within a few Å, and the outer boundary of the shell is also very smooth. The shell is clearly not crystalline and shows a contrast typical of an amorphous phase. The Ni3Si-type particles with sizes ranging from less than 20 nm to more than 150 nm and a uniform shell thickness of 10-15 nm were typical.

Structural studies by electron diffraction
The crystallographic structure of the core and the shell of the nanoparticles were investigated further by electron powder diffraction (also by neutron and X-ray diffraction (XRD), but mainly the results from the electron diffraction are presented here). There are a few critical aspects which influence the quality of the Debye-Scherrer ring pattern (Figure 5a).
and the resolution of the powder profile analysis. First of all, a precise centring of the ring pattern is important for a proper azimuthal averaging of intensities in the ring pattern. For analysis, we used a graphical aid in the form of a help circle, as a guide for centring. The bright Debye-Scherrer rings in the pattern were matched with the guide circle, whose centre then provided the pattern centre. For precise measurement of lattice parameters the camera length of the microscope was calibrated with standard gold powder (\(a_{\text{Au}} = 0.40786\) nm).

A second critical point relates to the unevenness of particle distribution on the sample grid. This leads to a very high background signal, especially at small scattering angles, where the background intensity is strongly affected by the extending tail of the main transmitted beam. Larger particles (>80 nm) pose other problems. For example, even when a relatively large selected-area diffraction (SAD) aperture was used, only a limited number of nanoparticles were illuminated by the beam and this causes the diffraction pattern to be spotty (discontinuous rings). In addition, large particles give rise to multiple scattering, affecting the relative intensities of the diffraction peaks. Due to this the kinematical scattering condition is not truly applicable for data analysis. There is considerable discussion in the contemporary literature on dynamical scattering in electron diffraction (see e.g. [5]) which takes into account multiple scattering, but most of these treatments were applied to single crystals. Only a few earlier studies (see e.g. [6]) deal with the simulation of electron scattering intensities from large powder samples, however, they do not take account of dynamical scattering effects. Calculations for powder diffraction are very complicated as the dynamical effects will critically depend on the orientation of individual particles in the powder samples and the thickness of each particle in their particular orientation. It is, however, known that dynamical effects do not alter the peak positions but change only the modulus of the scattering factor. This could be a serious obstacle for refining unknown crystal structures. In the present study, however, this is not the case, as we measure lattice constants of known intermetallic compounds (e.g. Ni3Si or Ni3Al with L12 structure). On the other hand, inelastic scattering of electrons by the powder sample was not critical for the measurements. There is also good evidence [7] that inelasticity does not generally influence the refinement of electron powder data.

The measured powder diffraction patterns were analyzed using the FullProf software [8] applying the Rietveld refinement technique ([9]). The presence of crystalline core and amorphous shell was revealed in the powder electron diffraction pattern (Figure 5). The measured spectrum (red curve in Figure 5b) is a superposition of contributions from two different structures: (i) the sharp peaks (green curve) matching the L12 structure of the crystalline core of the Ni3Si(Al) nanoparticles; and (ii) the broad diffuse peaks (blue curve) corresponding to a modulated intensity due to coherent scattering from an amorphous phase, is attributed to the particle shell. The positions of the broad peaks, determined from the electron powder diffraction data, are listed in Table 1 and compared to the XRD results (from the same powder sample) [2]. The first broad peak at \(Q = 1.7\ \text{Å}^{-1}\) seen in the XRD pattern, is, however, not observed in the electron diffraction pattern because at very low angles the electron powder pattern is strongly affected by the very high background resulting from the tail of the primary beam. The lattice parameter of the Ni3Si(Al) particle core determined by electron (0.3513(3) nm) and X-ray diffraction (0.35094(3) nm) agree very well. This attests to the quality of the electron diffraction measurement and the data analysis method adopted.

**Composition of core and shell by EDS**

The composition of the core and the shell was measured by energy dispersive X-ray spectroscopy in the TEM.

Typical EDS results are shown in Figure 6a. In Figure 6b, the brightfield TEM image of a single core-shell nanoparticle of Ni3Si(Al) with three contamination marks (one in the core and two in the shell region) is seen. These marks indicate the actual position where the beam was focused on the specimen to obtain the EDS spectra. Measurement from the nar-
row shell (~15 nm thick) was possible. However, as the particle core is covered by shell all over, measurement in the core region always included a small volume of the shell material. This contribution from the shell could not be separately estimated and in the present analysis it was ignored, considering that the shell volume involved is extremely small. All the measured spectra show presence of Cu and C peaks. However, since the powder was placed on a carbon foil on top of a copper grid, this is a contribution from the sample environment and not from the Ni₃Si(Al) particles. Therefore, for quantitative evaluation of core and shell compositions, Cu and C peaks were not considered. The spectrum from the core (blue) of Ni₃Si(Al) nanoparticles shows the presence of O, Ni, Si and Al, while that from the shell (red) contains only Si and O peaks (Figure 6a). The shell thickness is narrow, so there was always the possibility that the beam may touch the core during a measurement in the shell. However, this is easily detected from the contamination spots (e.g. see the contamination spot marked by golden yellow dotted circle in Figure 6b) and the corresponding spectra (golden yellow colour curve in Figure 6a) where the Ni peak is readily detected. Such unsuccessful measurements were rejected. The absence of Ni and Al in the shell is an indication that the oxide shell forms upon de-alloying of the Ni(Si,Al) matrix solid solution after the depletion of Ni and Al from the matrix.

Other evidence [2] also supports this view. The measurement of the core composition independent of the shell was, however, not possible because the shell covers the particles completely. Oxygen peaks were detected in spectra from both core and shell; but it is not a priori clear if oxygen was actually present in the core also. Considering the ESPD process used for extraction of nanoparticles from the bulk alloys and knowing that the particle core was not affected by electrolysis [2], it is more likely that oxygen was present only in the shell. In that case, Ni, Al, and Si are the only elements in the particle core, same as in the precipitates in the bulk alloy. Considering this, the results of quantitative analysis (in at.%) shows that the shell of the Ni₃Si(Al) nanoparticles contains 85% O and 15% Si and its core contains 67.7% Ni, 29% Si and 3.3% Al. The measured Si content is higher than in Ni₃Si β phase (22.5 to 24.5 at. % Si [10]). The excess of Si is quite likely a contribution from the shell volume (Si rich) measured along with the core.

**CONCLUSIONS**

Electron microscopy complemented with EDS analysis is a versatile and invaluable tool for the study of fine structures including nanoparticles. With the example of Ni₃Si(Al)-SiOₓ core-shell nanoparticles we demonstrated its usefulness in characterizing the complex structure and composition of the core shell of particles in the size range of 20 to 450 nm. However, care is needed in sample preparation and analysis. Different measurement methods also demand particular care.

**REFERENCES**


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