



Effects of size reduction on the structure and magnetic properties of core-shell Ni₃Si/silica nanoparticles prepared by electrochemical synthesis



Giancarlo Pigozzi^{a,*}, Debashis Mukherji^b, Yalçın Elerman^c, Pavel Strunz^d, Ralph Gilles^e, Markus Hoelzel^e, Bruno Barbier^f, Patrik Schmutz^a

^aEmpa, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, 8600 Dübendorf, Switzerland

^bInstitut für Werkstoffe, Technical University of Braunschweig, Langer Kamp 8, 38106 Braunschweig, Germany

^cDepartment of Engineering Physics, Faculty of Engineering, Ankara University, 06100 Besevler, Ankara, Turkey

^dNuclear Physics Institute (NPI), 25068 Řež, Czech Republic

^eTechnische Universität München, Forschungs-Neutronenquelle Heinz Maier-Leibnitz (MLZ), 85747 Garching, Germany

^fSteinmann Institut, Poppelsdorfer Schloss, 53115 Bonn, Germany

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ABSTRACT

Nanostructured nickel silicides find application in electronics, high-temperature alloys, electrode materials and catalysis. In this work, the effect of size reduction on the structure and magnetic properties of β_1 -Ni₃Si intermetallic phase nanoparticles is studied. Electrochemical selective phase dissolution (ESPD) was used to produce the β_1 -Ni₃Si nanoparticles of different sizes (from 20 to 215 nm) by extracting β_1 nano-size precipitates from two-phase Ni–Si and Ni–Si–Al precursor alloys. The extracted nanoparticles have a core-shell structure with β_1 -Ni₃Si core and an amorphous silica shell. Particles size and shape are controlled by the composition and thermal treatment of the precursor alloys. Precipitates size is scaled without modifying the ordered L1₂ lattice structure. The bulk β_1 -Ni₃Si is ferromagnetic below 260 K with low saturation magnetization (2 emu/g), while the core-shell Ni₃Si/silica nanoparticles are superparamagnetic at low temperatures (<9–11 K) with low coercivity (<90 Oe) and magnetization >20 emu/g at 5 T. It is suggested that weak particle magnetic moments and low magnetic anisotropy of the L1₂ structure are responsible for these properties. The shell on one hand protects the core from degradation; however the oxidation of the core/shell interface region can influence the magnetic behavior of the nano-powders.

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1. Introduction

Transition metal silicides based on iron, cobalt and nickel constitute an important class of compounds for technological applications. In addition to their use as high-temperature structural materials, metal silicides have been identified as very promising candidates for micro-/nano-electronic devices. Silicides are usually refractory materials with high melting point which possess high strength and high resistance to oxidation and corrosion. They also have narrow bandgap and low electrical resistivity. Transition metal silicides (e.g., NiSi, TiSi₂, CoSi₂) are now widely used in the semiconductor industry and they are very important to complement

metal-oxide semiconductor (CMOS) devices as ohmic contacts, interconnects and gates [1]. In particular, nickel silicides have low electrical resistivity and noble metal-like properties which make these silicides promising candidates for applications as electrode materials [2] as well as in hydro-desulfurization catalysis [3].

Ni₃Si is a L1₂ structured (ordered face centered cubic) intermetallic compound and possesses anomalous yield strength as a function of temperature, and specially, it shows excellent strength and good oxidation resistance at temperatures up to 700 °C [4]. Owing to the unique range of properties, including excellent thermal stability, the metal-rich silicide Ni₃Si has been identified as a promising candidate for several applications (high temperature energy conversion equipment or as gate in nano-electronics devices [5,6]). According to the binary Ni–Si phase diagram, β_1 -Ni₃Si has no congruent melting point but is formed by solid-state (eutectoid and peritectoid) reactions of monoclinic β_2 -Ni₃Si or hexagonal γ -Ni₅Si₂ phases [7]. Synthesis of single phase Ni₃Si alloy is therefore not straightforward. However, different routes are available for the

* Corresponding author. Tel.: +41 58 765 48 27.

E-mail addresses: giancarlo.pigozzi@empa.ch (G. Pigozzi), d.mukherji@tu-bs.de (D. Mukherji), Yalcin.Elerman@ankara.edu.tr (Y. Elerman), strunz@ujf.cas.cz (P. Strunz), Ralph.Gilles@frm2.tum.de (R. Gilles), markus.hoelzel@frm2.tum.de (M. Hoelzel), b.barbier@uni-bonn.de (B. Barbier).

synthesis of Ni₃Si nanostructures, for example synthesis of freestanding Ni₃Si nanowires by high temperature chemical reaction in gas has been recently reported [1]. There were also attempts to produce nano-scale Ni₃Si by other routes, e.g. by elemental blending of Ni and Si powders through mechanical alloying [8]. Also, it has been demonstrated in a previous publication by the authors that nanoparticles of Ni₃Si can be produced from two phase Ni–Si alloys by electrochemical selective phase dissolution process [9] and these particles resist to temperatures up to 1000 °C [10].

Nickel/silicon heterostructures and Ni–Si based nanostructured alloys are used in many devices. Nickel silicide phases may be formed at interfaces between nickel and silicon when subjected to heat. In particular, Ni₃Si phase can appear in Ni/Si heterostructures during processes which are, for example, commonly used in electronic applications (e.g., ion-beam mixing and thermal annealing of Ni/Si multilayered films [11] or Ni silicidation of polycrystalline-Si/SiO₂ gates [12]). The physical properties of such systems can be therefore affected by the presence of Ni₃Si.

While many investigations on electronic properties of Ni₃Si nanostructures are found in literature, magnetic properties of Ni₃Si have drawn less attention. Some nickel silicides (Ni₂Si, NiSi, and NiSi₂) have been found to be ferromagnetic at room temperature [13]. However, due to non-continuous changes of the electronic density of Ni silicides with Si content, the behavior of Ni₃Si cannot be directly inferred from properties of other silicides. Few reports on magnetic properties of bulk Ni₃Si are found in literature (see e.g. [14,15]). However, the chemical structure and magnetic behavior of Ni₃Si are of fundamental interest as they can be different at the nano-scale and it is therefore important to characterize them.

In this paper, a fundamental investigation of the size reduction effect for Ni₃Si particles and its influence on their crystal structure, morphology and magnetic properties is presented. It is demonstrated that nanoparticles of the Ni₃Si phase are superparamagnetic at low temperatures, if they can be produced at sizes below ~200 nm. All presented results are obtained from core–shell type Ni₃Si nanoparticles, where the ordered crystalline core is magnetic and the shell is constituted of an amorphous Si-oxide mantel. A shell surrounding the nanoparticles plays an important role in protecting the core from environmental degradation. There is a growing scientific and technological interest in superparamagnetic nanoparticles due to their applications in magnetic resonance imaging, hyperthermia and drug delivery [16]. Capping the particles with an inert biocompatible shell is a necessity and ways how to control shell composition and thickness on the nano-scale are of great general relevance. However, the shell can have an influence on the magnetic properties of the powder and therefore affect the performance in applications. In this work an indication of how the magnetic characteristics of investigated Ni₃Si nano-powders are influenced by the silica shell is also provided and this will be the subject of further investigations.

2. Experimental

2.1. Materials

Ni₃Si nanoparticles of different sizes were prepared by electrochemical selective phase dissolution (ESPD) technique – extracting them from two-phase Ni–Si alloys. In the present work, two Ni–Si-based alloys (one with and the other without ternary element aluminum addition) are investigated (see Table 1). The nanoparticles obtained by extraction of the Ni₃Si precipitates from these alloys are further characterized (details of particles are reported in Table 2). Firstly, nano-sized precipitates of the Ni₃Si-type intermetallic phase are grown to different desired sizes in the solution heat treated two-phase Ni–Si-based alloys by first homogenization at 1100 °C for 48 h and water quenched followed by annealing treatment (ageing) at 600 °C for different times (4–24 h). Afterwards, the alloy is subjected to an electrochemical anodic polarization (selective electro-etching) inducing dissolution of the corrosion susceptible matrix and extraction of the nano-precipitates. This

process was performed by placing a two-phase alloy sample in an electrolytic cell. The cell includes a Pt counter electrode, a Calomel reference electrode (SCE, potential +0.244 V_{SHE}) and a plate-like sample of the alloy as anode (working electrode). Electrochemical experiments were performed using a potentiostat (PGSTAT30 from the company Metrohm-Autolab). As electrolyte, an aqueous solution containing 1% citric acid and 1% ammonium sulfate (pH value 2.5) was used. The ESPD electrochemical processing was performed potentiostatically by holding an extraction voltage between 1.0 and 1.25 V versus SCE at room temperature. The optimal potential giving the highest selectivity between high matrix dissolution rate and nanoparticle production for a given alloy can be first determined by performing electrochemical potentiodynamic polarization scans. After the extraction, the precipitate particles are then collected from the aqueous solution forming the nano-powders described in the present work. Further details of the synthesis were reported in a previous publication [9].

Table 1 not only reports the composition of the alloys NS1 and NS2 (referred to as precursor alloys in this work) from which the nanoparticles are extracted, but it also includes the detail of the heat treatments. Different ageing times were applied on the two alloys with the purpose of producing different sizes of nano-precipitates. A third alloy (NS3) was also prepared to characterize the bulk properties of the Ni₃Si phase. Instead of the stoichiometric 25 at.% Si, the composition of NS3 was chosen as Ni–22.5Si (at.%) in order to avoid formation of unwanted γ -Ni₅Si₂ phase richer in Si. This alloy was annealed differently than the precursor alloys (heat treatment details in Table 1). Table 2 shows details about the investigated nano-powder samples (composition, size); with reference to the precursor alloys they are extracted from. In both cases, the extracted nanoparticles have a core–shell structure. Although two different alloy compositions are used (different Al and Si amounts), this variation has no consequences on the crystal structure of the Ni₃Si precipitate phase which maintains the L₁₂ structure.

2.2. Characterization methods

2.2.1. Structure

Both the precursor alloys and the nano-powders were characterized by diffraction methods. X-ray diffraction (XRD) measurements were made on a high resolution Siemens D 5000 powder diffractometer with a focusing graphite monochromator in front of the scintillation counter, set up in the Bragg–Brentano geometry [18]. Measurements were done on solid samples with Cu K α radiation (doublet: $\lambda_{21} = 1.54056$ Å, $\lambda_{22} = 1.54439$ Å) in the angular range 2 θ –130° and a 2 θ step of 0.02°. Neutron powder diffraction (ND) measurements were performed at the high-resolution-Powder Diffractometer (SPODI) [19,20] in the Heinz-Meier-Leibnitz neutron source (MLZ) at the Technical University of Munich. The powder samples were placed in a niobium container and special care was taken to align the powder in the neutron beam. A Ge 551 monochromator with 0.1549 nm neutron wavelength (λ) was used for these measurements. Morphology and composition of the bulk alloys and nanoparticles were investigated in a FEI Nova Nano-SEM 230 Scanning electron microscope (SEM) equipped with Oxford X-Max Energy Dispersive X-ray (EDX) system and a Jeol JEM 2200FS transmission electron microscope (TEM), operating at 200 kV. The TEM was equipped with a field emission source, an Omega[®] energy filter and EDX detector. Small-Angle Neutron Scattering (SANS) measurements were carried out using the SANS-II instrument at the spallation neutron source (SINQ), at the Paul Scherrer Institute (Villigen, Switzerland) [21]. Scattering data were collected at several geometries by varying the sample-detector distance from 1.2 m to 6 m at two neutron wavelengths (λ) of 6.3 Å and 10.5 Å. The full covered range of scattering vector magnitude (Q) was 1.5×10^{-3} Å⁻¹–0.13 Å⁻¹. To further characterize the core–shell structure of the Ni₃Si nanoparticles, contrast variation measurements were also performed by SANS [22]. The very different neutron scattering lengths of hydrogen and deuterium are exploited in this SANS experiment. This technique has also been applied in the past to characterize core–shell structures [17,23,24]. The nanoparticles were dispersed either in D₂O or in H₂O or in ethanol (in which the particles are usually stored) and eventually in different mixtures of D₂O and ethanol. The measured raw SANS data were corrected for background scattering from the particular solvent or mixture of solvents and converted to an absolute scale using the SASFit software [25]. The particle size distribution (PSD) is obtained by fitting the scattering profile data with the theoretical scattering profile of a distribution of spherical particles having a core–shell structure. The distributions of core diameter and shell thickness are varied in the model in order to match the experimental results (see Ref. [17] for more details on SANS data reduction).

2.2.2. Magnetic properties

Direct Current (DC) magnetic field measurements of the temperature-dependent and field-dependent magnetization were carried out at the Ankara University. The temperature range between 5 and 300 K was investigated with a Physical Properties Measurement System (PPMS) and Magnetic Properties Measurement System (MPMS) from Quantum Design. In PPMS, the DC measurements were made in zero field cooled (ZFC) and field cooled (FC) sequences with cooling/heating rate of 2.5 K/s. The room temperature magnetic measurements were performed using the Vibrating Sample Magnetometer-VSM (EV9 from MicroSense) with cooling/heating sequences in 5 K steps. The magnetization of the powder samples were first measured in the ZFC mode, whereby the samples were first cooled from 350 K to 5 K

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