Segregation in metastable Fe-Cu nanoparticles

Yelsukova A, Li Zi-An, Acet M, Spasova M and Farle M
Experimentalphysik (AG-Farle) & CENIDE, Universität Duisburg-Essen, D-47048 Duisburg, Germany
E-mail: anna.elsukova@uni-due.de

Abstract.
Fe-Cu nanoparticles have been prepared by sputtering and subsequent in-flight sintering. Particles deposited onto amorphous carbon are examined by electron diffraction, energy dispersive x-ray line-scans and electron energy loss spectroscopy using high resolution transmission electron microscopy. The results show that non-sintered particles form a metastable Fe-Cu alloy, whereas the sintered particles undergo a spinoidal decomposition leading to an iron-rich core and a Cu-rich shell. The investigations are carried out on particles of various sizes ranging from 5-50 nm. Within this size range, the sintered particles show similar compositional properties.

1. Introduction
Elements that are immiscible in the solid state under thermodynamic equilibrium conditions can be forced to alloy into metastable random solid solutions by using methods such as rapid quenching from the liquid or vapor phases to the solid state, mechanical alloying, and ion-implantation. Non-equilibrium properties of metastable iron alloys prepared under such conditions have been extensively studied in relation to both metallurgical and magnetic properties, whereby Fe-Cu has been studied in particular detail [1, 2]. When rapidly quenched, Fe-Cu alloys form random solid solutions with FCC or BCC structures; occasionally accompanied by tetragonal distortions. Their structural and magnetic properties in the metastable state conform in general to the scheme of the valence electron concentration-dependence (e/a) of the average magnetic moment (Slater-Pauling behaviour).

At elevated temperatures (T > 700 K), metastable Fe-Cu decomposes. In the case when the metastable alloy is in the form of a particle at nanoscale dimensions, Cu can segregate to the surface on annealing giving rise to a core-shell structure. Wang et al. have shown that it is possible to take advantage of segregation in metastable Fe and Co-based alloy-particles by a single-process in-flight annealing of sputter-produced nanoparticles to generate core-shell structures [3, 4]. Here we show by energy dispersive x-ray (EDX) line-scan analysis and electron energy loss spectroscopy (EELS) on as-prepared-primary (primary) and in-flight-annealed (sintered) particles the nature of segregation in Fe-Cu nanoparticles.

2. Experimental
Particles were prepared by DC-sputtering Cu-patched Fe-targets in a liquid nitrogen cooled chamber. Helium gas at 50 sccm was introduced into the chamber along with Ar sputtering gas flowing also at 50 sccm. Helium serves as a thermal heat-sink thereby facilitating the coalescence
of the plasma into particles. The primary particles were further guided with the Ar/He carrier gas through a sintering furnace at 1000 °C prior to depositing on amorphous carbon films held at about −150 °C. Details of the setup are given elsewhere [5].

The particles are polydisperse with sizes ranging from about 10-150 nm giving the advantage of examining the segregation properties of the particles in a broad size-range. Structural and compositional characterizations were conducted on a field-emission Tecnai F20 TEM/scanning TEM (STEM) SuperTwin microscope (operating at 200 kV), including EDX with energy resolution of 134 eV and EELS with energy resolution of about 1 eV. The line scan measurements were carried out in STEM mode with an electron nanoprobe of about 1 nm.

3. Results and Discussion
Images of the primary and sintered particles and their corresponding electron diffraction patterns obtained over a region of about 16 μm in diameter are shown in Fig. 1. The primary particles with sizes ranging from 5 up to about 50 nm appear to be either separated or grouped, whereas the sintered particles are in the form of aggregates. Isolated particles of various sizes can also be found. The average Fe-compositions of the primary and sintered particles are 64 at% and 62 at%, respectively. The diffraction patterns of the primary and sintered particles are give in the lower panels of Fig. 1. The results of the analysis of the diffraction patterns are collected in Tab. 1 and Tab. 2.

As seen in Tab. 1, the positions of the rings indicate diffraction from planes associated with the bcc and fcc structures. Diffraction from the {111} planes of the fcc structure and the {110} planes from the bcc structures lead to intensities at almost the same position. The structure
Table 2. Sintered particle electron diffraction analysis.

| Rings | BCC Fe       | Cu$_2$O      |
|       | ($a = 0.289$ nm) | ($a = 0.426$ nm) |
|       | plane | $d$ (nm) | plane | $d$ (nm) |
|-------|-------|----------|-------|----------|
| 1     | 0.251 | (111)   | 0.246 |
| 2     | 0.208 | (100)   | 0.202 | (200)   | 0.213 |
| 3     | 0.181 | (211)   | 0.176 |
| 4     | 0.147 | (200)   | 0.143 | (220)   | 0.150 |
| 5     | 0.131 | (310)   | 0.134 |
| 6     | 0.120 | (211)   | 0.117 | (222)   | 0.123 |
| 7     | 0.111 | (400)   | 0.106 |
| 8     | 0.104 | (220)   | 0.101 |

of the primary particles is essentially mixed fcc and bcc. However, the presence of a thin oxide layer on the surface cannot be excluded due to passivation. In the case of sintered particles, the pattern can be better matched to be combined bcc and Cu$_2$O. These become more evident below when we discuss the EDX line-scans and the EELS data.

Figure 2. Line-scans of primary and secondary particles. Upper part: TEM images of primary and sintered Fu-Cu nanoparticles. The white dashed line shows the path of the electron beam during the line-scan. Lower part: Local composition determined by EDX and intensity of characteristic x-rays over the position along the scan.

Elemental distribution within the particles was probed by EDX line-scans. Fig. 2 shows the line-scans for representative primary ($\sim 30$ nm) and sintered ($\sim 50$ nm) particles. The dashed line across the images are the paths along which the line-scans shown below the images are taken. The intensities of the Cu-K and Fe-K edge characteristic x-rays and the local composition are plotted as a function of position. For the primary particle, the intensities from the Fe and the Cu edges begin to increase with increasing distance at the edge of the particle ($5$ nm scan-point) and merge and vanish at the $35$ nm point. The corresponding local Fe composition determined by EDX shows oscillations around an average composition of about $64$ at% Fe, which is the average composition of the ensemble of primary particles. The uncertainty in the composition is given with error bars, which have a size of about the symbols themselves. At this composition, Fe-Cu is in a mixed fcc and bcc state [1]. This is in agreement with the results of the diffraction measurements given in Tab. 1.

For the sintered particle, the intensity associated with Cu begins to increase at a position before an increase in the intensity associated with Fe is observed, and the similar is seen at the exit of the line-scan. This indicates that segregation by sintering leads to the formation of a Cu-rich shell, leaving the core behind as Fe-rich. Indeed, the corresponding average local Fe-composition in the core region of the particle shows $71$ at% in contrast to the average Fe-
concentration of the sintered samples of 62 at% as mentioned above. At 71 at% Fe, Fe-Cu is well within the region of the bcc state, and [1], in accordance with the electron diffraction results given above. The Cu-rich shell oxidises as Cu$_2$O at ambient atmosphere as evidenced above in Fig. 1 and Tab. 2.

Another prominent character of the position dependence of the local composition is that it is oscillatory, whereby the oscillations are stronger in the case of the sintered particle. Moreover, these oscillations follow those that are seen in the line-scan intensity. The fact that the oscillations strengthen when the particles are sintered indicates that these oscillation can be related to spinoidal decomposition. Spinoidal decomposition is known to occur in metastable Fe-Cu alloys [6].

![Figure 3. EELS studies on primary and secondary particles of various sizes. The core of the particles are essentially metallic Cu and Fe.](image)

The results of EELS studies for primary and sintered particles of various sizes are shown in Fig. 3. The L-edge spectra for Cu are found to be of essentially metallic character for both primary and sintered particles when spectra of metallic Cu and those of various Cu-oxides are compared [7]. This is also the case for the Fe L2 and L3-edges. The area ratio of the L3 to L2 peaks for metallic Fe is expected to be 3.8 ± 3 for metallic Fe according to the method given by Colliex et al. [8]. This is the case also here, where the ratio is estimated to be about 3.66. The metallic nature of the cores of the particles are independent of size of the particles investigated in this study. Since EELS probes the volume of the particle and the contribution to the EELS signal from the volume is more significant than that from the surface for the sizes investigated, any EELS contribution from surface oxides are essentially insignificant.

4. Conclusion
We have prepared Fe-Cu nanoparticles in as-prepared and sintered states. Sintering causes segregation of the metastable Fe-Cu nanoparticle alloy leading to an Fe-rich core and a Cu-rich shell. We describe qualitatively the elemental distribution of the species within the particle and demonstrate the spinoidal decomposition nature of the segregation process.

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