Controlled Oxidation and Self-Passivation of Bimetallic Magnetic FeCr and FeMn Aerosol Nanoparticles

Calle Preger,*†‡ Claudiu Bulbucan,* Bengt O. Meuller,‡ Linus Ludvigsson,** Aram Kostanyan,** Matthias Muntwiler,**‡ Knut Deppert,** Rasmus Westerström,*§ and Maria E. Messing†*‡

†NanoLund, ‡Solid State Physics, and §Synchrotron Radiation Research, Lund University, Box 118, 22100 Lund, Sweden
§Physik-Institut, Universität Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland
†Paul Scherrer Institut, 5232, Villigen PSI, Switzerland

Supporting Information

ABSTRACT: Nanoparticle generation by aerosol methods, particularly spark ablation, has high potential for creating new material combinations with tailored magnetic properties. By combining elements into complex alloyed nanoparticles and controlling their size and structure, different magnetic properties can be obtained. In combination with controlled deposition, to ensure nanoparticle separation, it is possible to minimize interparticle interactions and measure the intrinsic magnetic property of the nanoparticles. Most magnetic materials are highly sensitive to oxygen, and it is therefore crucial to both understand and control the oxidation of magnetic nanoparticles. In this study, we have successfully generated oxidized, bimetallic FeCr and FeMn nanoparticles by spark ablation in combination with a compaction step and thoroughly characterized individual particles with aerosol instruments, transmission electron microscopy and synchrotron-based X-ray photoelectron spectroscopy. The generated nanoparticles had an almost identical transition-metal ratio to the electrodes used as seed materials. Further, we demonstrate how the carrier gas can be used to dictate the oxidation and how to alternate between self-passivated and entirely oxidized nanoparticles. We also discuss the complexity of compacting alloyed nanoparticles consisting of elements with different vapor pressures and how this will affect the composition. This knowledge will further the understanding of design and generation of complex alloyed nanoparticles based on transition metals using aerosol methods, especially for the size regime where a compaction step is needed. As a proof of concept, measurements using a magnetometer equipped with a superconducting quantum interference device were performed on samples with different particle coverages. These measurements show that the magnetic properties could be explored for both high and low surface coverages, which open a way for studies where interparticle interactions can be systematically controlled.

INTRODUCTION

Magnetic nanoparticles have shown great potential for applications in various technologies including drug delivery, bioimaging, and as building blocks for future high-performing permanent magnets.1−4 The most common way of producing magnetic nanoparticles today is by multistep chemical methods. However, the main drawbacks with these methods are the risk of chemical impurities, the amount of produced chemical waste, the low flexibility of making quick changes online, and the limitations in mixing different materials governed by material combinations that are miscible on the bulk scale.5 Aerosol generation methods are promising for future generation of magnetic nanoparticles since they are simple, fast, continuous, provide good control of size and composition,6 and offer the possibility to form alloys of material combinations not miscible on the bulk scale.7

High controllability is of utmost importance when generating magnetic nanoparticles since small deviations in size can significantly alter the magnetic coercivity.5,8 Also, the composition of the particles is of high significance since the magnetic properties can be completely transformed by changes in elemental composition or the oxidation state of the particles.9 When studying the intrinsic magnetic properties of nanoparticles, it is crucial to minimize interparticle interactions. This can be achieved with aerosol methods by performing a highly controlled homogeneous deposition of sparsely spaced nanoparticles.10 However, studies on aerosol-generated complex alloys suitable as magnetic nanoparticles are very limited. The particle generation process needs to be further developed, and the understanding behind both alloy formation and oxidation needs to be deepened before the full potential of aerosol generation can be utilized to create magnetic alloy nanoparticles with desired magnetic properties.

In this work, we report the generation of carefully characterized oxidized, bimetallic FeCr and FeMn magnetic nanoparticles produced by the aerosol generation method spark ablation. The particles were generated in the size range of 10−50 nm with an almost identical transition-metal ratio...
to the seed electrodes. We demonstrate and discuss how to control the generation parameters to produce both completely oxidized and self-passivated FeCr and FeMn nanoparticles with tunable size and alternating composition. We further show that the as-produced particles could be deposited to yield a low surface concentration, which is critical for minimizing interparticle interactions during magnetic measurements. Finally, magnetic data from particles of different compositions, structures, and surface concentrations are presented as a proof of concept.

The spark ablation method is an excellent aerosol method for generating nanoparticles of mixed metals\(^{7,11-15}\) since it is environmentally friendly, scalable, and reasonably cheap.\(^{8}\) Recently, it has been utilized to form ternary amorphous magnetic nanoparticles that exhibit a magnetocaloric effect.\(^{16}\) The method is based on two opposing electrodes that are charged until a spark arises.\(^{13}\) This spark hits the electrodes, and the material is ablated and transported away by a carrier gas flow. Due to the fast quenching of the metallic vapor, nucleation and alloy formation can occur at an early stage enabling formation of nanoalloys consisting of elements that are even immiscible in bulk.\(^{7}\) Small sub-10 nm primary particles are first formed and then transformed into larger agglomerates as they collide.\(^{13,14}\) Agglomeration can be an issue since it is more difficult to control the size and shape of the agglomerates. However, this can be avoided by using a high and controlled carrier gas flow resulting in the formation of non-agglomerated sub-10 nm particles with the drawback that it is difficult to obtain larger monodisperse particles.\(^{17,18}\)

The transition from a superparamagnetic nanoparticle with zero coercivity at room temperature to a single-domain particle with diameter-dependent coercivity occurs between 10 and 100 nm for most materials.\(^{19}\) To study and correlate the magnetic response to the nanoparticle structure and form particles with tunable coercivity, it is crucial to be able to form monodisperse particles within this entire size range. To enable this, a compaction step can be applied to obtain nanoparticles within this size range. In this step, the primary particle consisting agglomerates are heated in the gas flow and compacted into spherical or faceted nanoparticles. Differently sized nanoparticles can be formed, dependent on the initial size of the agglomerates.\(^{20-22}\) Earlier studies have described this compaction step and demonstrated at which temperatures this reshaping step would occur for different single-element nanoparticles of different sizes.\(^{21,23,24}\) Today, little is known on the compaction of alloyed nanoparticles and how the vapor pressure of the individual elements in the alloy affects the final composition of the compacted particles.\(^{25,26}\) This knowledge is necessary to enable production of compact magnetic nanoparticles at sizes where the coercivity is altered.

Apart from controllable size, the purity and composition of the particles are of high importance. Magnetic materials and magnetic nanoparticles typically consist of transition metals or rare-earth metals that are easily oxidized. Nanoparticles are highly sensitive to oxygen, and small traces of oxygen or water can make the entire particle oxidize. It is therefore difficult to avoid oxidation during aerosol generation even though the nanoparticles are generated in a controlled gas environment. However, recently, we have demonstrated that, by adding a small amount of hydrogen to the carrier gas mixture, oxidation can be avoided for several elements during generation.\(^{27}\) The excellent mixing possibilities in combination with controllable size, agglomeration, and purity make spark ablation combined with a compaction step a potential technique for future generation of complex magnetic nanoparticles. However, to reach the full potential of forming new complex magnetic materials, it is vital to first understand and control the alloy formation, compaction, and oxidation of bimetallic systems consisting of transition metals using spark ablation.

The main reason to study iron-based bimetallic nanoparticle systems is motivated by the high abundance of Fe in the earth's crust and its interesting magnetic properties, making them a promising choice for future rare-earth free magnetic materials. Nanoparticle systems consisting of FeCr and FeMn were generated and studied earlier to some extent. There are a few reports on aerosol-generated FeCr nanoparticles and their magnetic properties. However, in these publications, the nanoparticles were generated by an inert gas evaporation method in low pressure, which is more complex and with no obvious control of size distribution, oxidation state, or deposited concentration.\(^{28-31}\) In the case of FeMn nanoparticles, a few studies were performed but only on particles generated by chemical methods.\(^{32,33}\) To our knowledge, FeMn nanoparticles have never been successfully generated by aerosol methods.

In this study, we demonstrate the generation of FeCr and FeMn nanoparticles with an almost identical transition-metal ratio to the seed material. We show that spark ablation is a great method to mix elements, presenting results that indicate the possibilities of tuning the transition-metal ratio in the nanoparticles by varying the composition of the alloyed electrodes. Based on closely examined individual particles, a discussion on the effects of the carrier gas and compaction temperature of bimetallic alloyed nanoparticles is added, which has not been performed earlier. This knowledge is necessary in order to form monodisperse nanoparticles in a wider size range. By comparing these two similar systems, important knowledge regarding what material properties might affect and in some cases limit the composition of alloyed nanoparticles during compaction is also added. Compared to the previous reports on FeCr and FeMn nanoparticles, this study contributes with a more thorough development of the aerosol generation process, as the nanoparticles are intentionally oxidized/nonoxidized and exposed to high temperatures in a complex compaction process and deposited with controlled surface concentration. We demonstrate that it is possible to perform magnetic measurements with a superconducting quantum interference device (SQUID) on sparsely spaced deposited nanoparticles, separated with at least a few particle diameters, which opens a way for studies where interparticle interactions can be systematically studied. High-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS) made it possible to observe significant differences in the composition obtained by carefully tuning the generation parameters. This study also demonstrates, for the first time, the complexity of forming compacted alloyed magnetic nanoparticles at high temperature consisting of elements both sensitive to oxidation and with large differences in vapor pressure.

**EXPERIMENTAL SECTION**

Nanoparticles were generated by spark ablation,\(^{14,15}\) and the generation setup can be seen in the Supporting Information. The electrodes were rod-shaped with diameters of 7.5 and 10 mm, and the compositions were Fe\(_{80}\)Mn\(_{20}\) and stainless steel grade 430 (Fe\(_{80.4}\)Cr\(_{17}\)/Mn/Si/C/S/P), respectively, both of
which were acquired from Goodfellow. The stainless steel grade 430 had an Fe-to-Cr relation of Fe$_{82.5}$Cr$_{17.5}$. The carrier gases used was nitrogen and a gas mixture of nitrogen with 5% hydrogen. Also, argon and a gas mixture of argon with 5% hydrogen were used in this study, and all four gases had a purity of 99.9999% with single ppm levels of oxygen and water. The carrier gas was set to 1.68 lpm and controlled with mass flow controllers, and the pressure in the system was set to 1015 mbar and kept constant to minimize impurities. The aerosol was first generated in the electrode chamber and started by flowing through a Ni$^{63}$ bipolar diffusion charger to obtain a known charge distribution. The particles then passed through a tandem differential mobility analyzer (DMA) setup with one TSI Model 3081 DMA and one in house built Vienna-type DMA. In between the two DMAs, the particles passed through a Lenten LTF tube furnace with a heating zone of 180 mm. The particle concentration was measured with a TSI Electrometer Model 3068B, and the particles were deposited onto Si wafers with a custom built electrostatic precipitator similar to the one developed by Dixkens and Fissan, after the deposition the particles were stored and transferred in ambient conditions.

The deposited nanoparticles were characterized by a JEOL 3000F transmission electron microscope (TEM) for high-resolution electron microscope (HRTEM). Compositional analysis was performed with energy-dispersive X-ray spectroscopy (XEDS) in scanning transmission electron microscopy (STEM) mode where compositional analysis from individual particles was obtained. The X-ray photoelectron spectroscopy (XPS) measurements were performed at the PEARL beamline at the Swiss Light Source. For the XPS measurements, the generated nanoparticles were deposited on a Au-coated Si wafer. The compaction scans were performed by setting the first DMA to 40 nm and scanning the second DMA to determine the peak position of the size distribution. The temperatures were varied from room temperature to 1250 °C and changed in steps of 100 °C until 600 °C and from 600 °C and up in steps of 50 °C with some exceptions. For the magnetic measurements, the nanoparticles were deposited onto a quartz sample holder, and the measurements were performed using a Quantum Design MPMS3 vibrating sample magnetometer.

### RESULTS AND DISCUSSION

Monodisperse nanoparticles with diameters between 10 and 50 nm were successfully generated from two different sets of alloyed electrodes (Fe$_{82.5}$Cr$_{17.5}$ and Fe$_{85}$Mn$_{15}$, see Experimental Section for the exact composition) in four different carrier gas mixtures (argon and nitrogen with and without additional 5% hydrogen). The elemental compositions of the FeCr- and FeMn-alloyed nanoparticles were thoroughly characterized with energy-dispersive X-ray spectroscopy (XEDS) in scanning transmission electron microscopy (STEM) mode to obtain the average composition and internal differences of individual particles. The nanoparticles had an almost identical transition-metal ratio to the electrodes for all carrier gases and for differently sized particles, indicating great mixing of the elements (see Table 1). The values in the table are solely based on the relation between the two transition metals and do not describe the complete composition such as the amount of oxygen or other impurities. It should also be noted that the measured compositions are for the entire particle and internal differences within each particle were, in these measurements, not considered.

Further observations with TEM revealed structural differences between particles produced in a carrier gas with and without hydrogen (see Figure 1). The different gases had some effect on the spark behavior. Additional hydrogen caused a minor increase in the discharge voltage, and a major reduction in the discharge voltage was observed when argon was used instead of nitrogen, as was reported earlier. However, whether the particles were generated in argon or nitrogen did not have a noticeable effect on the size, shape, or transition-metal ratio. We can therefore rule out that the differences in particle structures are due to the spark characteristics; hence, the main focus will be on the differences between particles produced with and without additional hydrogen in the carrier gas. For both the FeCr- and FeMn-generated nanoparticles, a core−shell structure with a crystalline core and a thin amorphous shell was observed when generated in a hydrogen-containing carrier gas. In contrast, the particles generated without additional hydrogen consisted of a crystalline structure with no amorphous region and with distinct facets. The FFT of the FeCr particles revealed a crystalline core with a lattice parameter close to bcc Fe for particles generated in a hydrogen-containing carrier gas (see Figure 1a) and a spinel structure with lattice parameters similar to Fe$_3$O$_4$ for the particles generated without hydrogen (see Figure 1c).

To complement the FFT and XEDS, XPS measurements were performed on the FeCr-alloyed nanoparticles. Core−shell nanoparticles generated in a hydrogen-containing carrier gas and single-crystal nanoparticles generated without hydrogen were studied to obtain higher qualitative information regarding the differences between the two systems. The Fe 2p$_{3/2}$ spectra recorded from the core−shell particles in Figure 1b display a resolved elemental Fe(0) bulk component at a binding energy of 707 eV. The broad peak at higher binding energies (710 eV) can be attributed to nonresolved components of Fe(II) and Fe(III). The intensity of the elemental Fe(0) peak increased with respect to the oxidized component as the photon energy was increased from 1000 to 1300 eV, indicating that the Fe(0) signal originates from deeper inside the particles while the oxidized Fe is located closer to the surface. The Cr 2p$_{3/2}$ spectra exhibit a broad peak at a binding energy corresponding to Cr(II) with no detectable signal from elemental Cr(0) (see the Supporting Information). These results indicate that the core−shell nanoparticles are made up of an Fe(0)-rich core and an amorphous FeCr oxidized shell.

### Table 1. Relation between the Two Transition Metals in Individual Nanoparticles of Different Sizes Measured with XEDS in STEM Mode

| electrode/nanoparticle composition | mean Fe (at %) | standard deviation (at %) |
|-----------------------------------|---------------|---------------------------|
| FeCr electrode                     | 82.5          | 2                         |
| compacted FeCr nanoparticles       | 80            | 2                         |
| generated without hydrogen         |               |                           |
| compacted FeCr nanoparticles       | 84            | 2                         |
| generated with hydrogen            |               |                           |
| FeMn electrode                     | 85            | 3                         |
| compacted FeMn nanoparticles       | 86            | 3                         |
| generated without hydrogen         |               |                           |
| compacted FeMn nanoparticles       | 85            | 3                         |
| generated with hydrogen            |               |                           |
was expected since it was shown that addition of hydrogen to the amount of oxygen in the core was significantly lower (see Figure 1c) than 3.5 nm. Observations of the same sample of core−shell nanoparticles more than 1 year after the first TEM analysis revealed that the passivation layer did not change significantly. In order for this self-passivation to occur, the nanoparticles first need to form a stable and significantly large core upon oxidization. The thickness of this passivation layer is not dependent on the core size, and for smaller nanoparticles, a larger fraction of its unoxidized content will therefore be consumed during oxidization. The core of a 6 nm self-passivated particle will only contribute to 3.7% of the total volume of the entire particle, if assuming that a 2 nm thick layer surrounds a perfect spherical particle. This can be compared with the core of a 15 and 30 nm self-passivated particle that will comprise 40 and 65% of the total volume. The primary particles in the agglomerates are typically sub-10 nm, and a substantial amount of the metallic content in these agglomerates will therefore be consumed during oxidization.

The additional hydrogen in the carrier gas clearly had an effect on the oxidization of the particles as they are formed. This was expected since it was shown that addition of hydrogen benefits the formation of unoxidized nanoparticles. The particles formed with additional hydrogen appeared to be self-passivated, while the particles produced without hydrogen appeared entirely oxidized. Comprehensive research was earlier performed on the oxidation and self-passivation of pure Fe nanoparticles produced in chemical solutions as well as with aerosol-based methods. The oxidation of these particles was reported to be driven by the Cabrera−Mott model of low-temperature oxidization. For such oxidation, a 2 nm thin passivation layer will form almost instantly. The continuing growth to reach a 3 and 4 nm layer for pure Fe in ambient conditions is much slower and would take 40 weeks and 600 years, respectively. For Fe nanoparticles, this self-passivated oxidation layer will consist of a mixture of Fe₃O₄ and y-Fe₂O₃.

The core−shell particles in this study generated in a hydrogen-containing carrier gas showed a similar behavior to the self-passivated Fe nanoparticles. The generated core−shell nanoparticles also had a thin amorphous shell that never exceeded 3.5 nm regardless of the core size. Observations of the primary particles in the agglomerates are typically sub-10 nm, and a substantial amount of the metallic content in these agglomerates will therefore be consumed during oxidization.
exposed to an oxygen-rich atmosphere without additional hydrogen present, as in the case of the particles formed in a hydrogen-containing carrier gas when the particles are deposited and transferred into ambient air. The hydrogen in the gas mixture prevents the alloyed agglomerates from oxidizing both during generation and compaction.

As noted in Table 1, the FeMn particles had a similar transition-metal ratio to the electrodes both for the entirely oxidized and the core−shell particles. However, in contrast to the FeCr alloyed particles, the internal structure of the core−shell FeMn nanoparticles was not homogeneous, and the composition of the particles was also sensitive to the tube furnace temperature during compaction (see Figure 2). When the furnace temperature was 900 °C, the deposited agglomerates were not fully compacted, and primary particles could be observed (Figure 2a). At 950 °C, all particles appeared fully compacted; however, about half of the measured particles consisted of only pure Fe without any Mn present. When increasing the temperature to 1100 °C, no Mn was detected; instead, all particles were self-passivated Fe nano-

particles (Figure 2d). The optimal temperature to form FeMn particles was found to be 925 °C where all the measured particles were fully compacted but also had the same Fe-to-Mn ratio as the electrodes.

The loss of Mn above 925 °C could be explained by the onset of evaporation of Mn. Pure Mn has a significantly higher vapor pressure than Fe and Cr and therefore starts to evaporate earlier than the other elements at high temperatures. Figure 3a−d displays the compaction behavior of the FeCr and FeMn alloys together with their pure metals in the two different carrier gases. The first slope in the electrical mobility diameter that can be seen in all graphs occurs when the particles are reshaped from agglomerates to compacted particles. A second slope, observed in Figure 3d for the FeMn and Mn systems when generated with additional hydrogen, indicates initiation of evaporation. This evaporation could only be observed for particles produced in a hydrogen-containing carrier gas where no oxidation occurred upon compaction. Also, no other studied material systems started to evaporate at the observed temperatures (see Figure 3a−c). We can therefore see a clear

Figure 3. Compaction scans performed in (a,b) nitrogen as the carrier gas without additional hydrogen and (c,d) with hydrogen-containing nitrogen. (a,b) The low amounts of Cr and Mn in the alloy did not affect the compaction temperature substantially when the carrier gas was pure nitrogen. (d) Noticeable is the evaporation that occurs for Mn and FeMn in a carrier gas with additional hydrogen where the FeMn particles start to evaporate at roughly 900 °C and the pure Mn starts at 1000 °C. The dashed lines in the figure are added as a guide for the eye.

Figure 4. Starting from the left, data from FeCr oxide, FeCr core−shell, FeMn oxide, and FeMn core−shell. Top panel: SEM images displaying the particle concentration of each sample with scale bar indicating 1 μm. Center panel: temperature dependence of the magnetic moments recorded at a rate of 3 K/min with an applied magnetic field of 10 mT. Bottom panel: magnetization curves recorded at 2 K for the four systems.

Figure 3. Compaction scans performed in (a,b) nitrogen as the carrier gas without additional hydrogen and (c,d) with hydrogen-containing nitrogen. (a,b) The low amounts of Cr and Mn in the alloy did not affect the compaction temperature substantially when the carrier gas was pure nitrogen. (d) Noticeable is the evaporation that occurs for Mn and FeMn in a carrier gas with additional hydrogen where the FeMn particles start to evaporate at roughly 900 °C and the pure Mn starts at 1000 °C. The dashed lines in the figure are added as a guide for the eye.

Figure 4. Starting from the left, data from FeCr oxide, FeCr core−shell, FeMn oxide, and FeMn core−shell. Top panel: SEM images displaying the particle concentration of each sample with scale bar indicating 1 μm. Center panel: temperature dependence of the magnetic moments recorded at a rate of 3 K/min with an applied magnetic field of 10 mT. Bottom panel: magnetization curves recorded at 2 K for the four systems.
effect on the carrier gas, especially when the system included Mn. Surprisingly, the FeMn alloy started to evaporate at lower temperatures than pure Mn, and the difference between the two compositions was roughly 100 °C.

The evaporation at low temperatures for the FeMn alloy compared to pure Mn could be explained by the internal structure of the FeMn nanoparticles. XEDS line scans and mapping revealed an almost complete phase separation of Fe and Mn in the self-passivated core–shell FeMn nanoparticles at 925 °C (see Figure 2e–g). Since the particles analyzed by TEM have been exposed to air and oxidized, it is difficult to determine the exact shape and composition as they pass through the furnace. However, as argued in the earlier paragraphs, the passivated shell has to form after the compaction when the particles are exposed to an oxygen-rich atmosphere without additional hydrogen present, as in the case when the particles are transferred in ambient air. Consequently, the particles will consist of the pure metal components as they pass through the tube furnace. The Fe-rich region in Figure 2e appeared large enough to self-passivate, but the opposing Mn-rich side appeared to be too small and was instead entirely oxidized when exposed to oxygen. The phase separation of the two metals must therefore take place in the furnace as the particles are compacted. From the TEM images, it appears that the nanoparticles form Janus particles with a smaller Mn-rich particle adhered to the larger Fe particle and the smaller Mn-rich region can then be seen as an individual small particle with large surface curvature. Nanda et al. demonstrated that the evaporation of nanoparticles is governed by the Kelvin equation and that the onset temperature of evaporation for PbS nanoparticles was shifted 100 °C when decreasing the diameter of the particle from 20 to 10 nm; a similar shift can therefore be expected for the Mn particles. This could explain why the FeMn alloy with a smaller Mn particle starts to evaporate at lower temperatures than both the pure Fe and the pure Mn particles.

Magnetic measurements obtained using a SQUID from the four studied particle systems are shown in Figure 4. Given the size of the nanoparticles with a crystalline oxide, and the core–shell nanoparticles with a smallest 10 nm Fe(0)-rich core all particles in the four systems are expected to be single-domain. The measurements were performed on samples with different particle concentrations as displayed in the top panel of Figure 4. The central panel in Figure 4 displays the magnetic moment dependence on temperature for the four samples. After cooling from room temperature down to 2 K in zero field, the magnetic moment was measured by applying a small field of 10 mT while warming up to 400 K, a protocol known as zero-field cooled (ZFC) warming. After reaching 400 K, the sample was cooled down again using the field cooling protocol (FC) with the same applied field. All four samples exhibit irreversibility between the ZFC and FC curves. The difference between the two curves is a consequence of cooling the samples in zero field and thus starting the experiment with no preferential orientation of the magnetization vector of the individual nanoparticles. As the measurements start, the small applied magnetic field and the low thermal energies were not sufficient for the systems to reach an equilibrium magnetization under the given conditions and thus resulted in a lower magnetization for the ZFC curves. For noninteracting particles, the irreversibility in the FC and ZFC curves is related to the magnetic anisotropy of the individual nanoparticles. If the interparticle interactions are non-neglectable, the anisotropy properties of the individual nanoparticles are modified and can lead to collective behavior such as superspin-glass behavior or superferromagnetism, which substantially changes the magnetic response of the systems.

The bottom panel in Figure 4 shows magnetization curves recorded from the four samples. At 2 K, the systems exhibit hysteresis, and the coercive fields are given in the Supporting Information. Hysteresis is also observed at room temperature with significantly smaller coercive fields, indicating that the systems are not superparamagnetic, but this can also be seen in the Supporting Information. It is interesting to note that the 2 K hysteresis curve from the entirely oxidized FeCr system is open in the whole field range of +/− 7 T. Such behavior was reported for NiFe₂O₄ particles where the irreversibility in the magnetization curves was attributed to a ferrimagnetically coupled core with a spin-glass-like surface layer. A detailed magnetic study of the presented nanoparticle systems is outside the scope of this article and will be published elsewhere. Nevertheless, the presented data demonstrate the feasibility of studying the magnetic properties of both sparsely spaced aerosol-generated nanoparticles, separated with at least a few particle diameters, and particles that are situated mainly in clusters. These results open a way for studies where interparticle interactions may not only be minimized but also be systematically turned on by varying the particle concentration.

**CONCLUSIONS**

To conclude, in this study, we have successfully formed bimetallic alloyed nanoparticles consisting of an almost identical transition-metal ratio to the electrodes used as seed materials in the size range of 10–50 nm. We demonstrate how tuning of the carrier gas can be used to deliberately alter between entirely oxidized and self-passivated nanoparticles. We also discuss and demonstrate for the first time the complexity of compacting alloyed agglomerates consisting of elements that have substantially different vapor pressures. This is highly relevant when the compaction temperature for the alloy is close to the temperature where the elements start to evaporate, and it becomes even more important if the elements are phase-separated within the particle. This phenomenon could not only limit which material combinations are possible to generate particle sizes above 10 nm by spark ablation but also be applied to fine tune the composition of a multielement alloy or to remove impurities.

Finally, we have, as a proof of concept, shown the possibilities to measure the magnetic properties of different systems deposited with different and highly controlled surface concentrations. This allows for a high control of interparticle interactions that is needed to systematically study both the intrinsic and cluster behavior of magnetic nanoparticles. The combination of this highly controlled deposition with the possibility to produce complex alloy nanoparticles at sizes relevant for tuning of magnetic properties truly demonstrates the strengths of spark ablation for production of novel magnetic materials.

**ASSOCIATED CONTENT**

## Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b01678.

XPS measurement of Cr 2p₃/₂, oxygen estimation with XEDS, coercivity field measurements at 2 and 300 K,
hysteresis curves at room temperature, and setup of the nanoparticle generation (PDF)

■ AUTHOR INFORMATION

Corresponding Authors
*E-mail: calle.preger@ftf.lth.se (C.P.).
*E-mail: maria.messing@ftf.lth.se (M.E.M.).

ORCID
Calle Preger: 0000-0003-2333-6773
Matthias Muntwiler: 0000-0002-6626-3977

Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was performed with financial support from NanoLund and Myfab as well as the Swedish Research Council (Grant No. 2013-05280 and Grant No. 2015-00455) and Sklodowska Curie Actions co-founding project INCA NanoLund and Myfab as well as the Swedish Research Council (Grant No. 2013-05280 and Grant No. 2015-00455). The SQUID was founded by Swiss National Science Foundation SNF grant 206021_150784.

REFERENCES

(1) Frey, N. A.; Feng, S.; Cheng, K.; Sun, S. Magnetic Nanoparticles: Synthesis, Functionalization, and Applications in Biomaging and Magnetic Energy Storage. Chem. Rev. 2009, 38, 2532.

(2) Gupta, A. K.; Gupta, M. Synthesis and Surface Engineering of Iron Oxide Nanoparticles for Biomedical Applications. Biomaterials 2005, 26, 3995–4021.

(3) Arruebo, M.; Fernández-pacecho, R.; Ibarra, M. R.; Santamaría, J. Magnetic Nanoparticles for Drug Delivery. Nano Today 2007, 2, 22–32.

(4) Balamurugan, B.; Sellmyer, D. J.; Hadjipanayis, G. C.; Skomski, R. Prospects for Nanoparticle-Based Permanent Magnets. Scr. Mater. 2012, 67, 542–547.

(5) Kruis, F. E.; Fissan, H.; Peled, A. Synthesis of Nanoparticles in the Gas Phase for Electronic, Optical and Magnetic Applications—A Review. J. Aerosol Sci. 1998, 29, 511–535.

(6) Feng, J.; Guo, X.; Ramlawa, N.; Pfeiffer, T. V.; Geutjens, R.; Basak, S.; Nirschl, H.; Biskos, G.; Zandbergen, H. W.; Schmidt-Ott, A. Green Manufacturing of Metallic Nanoparticles: A Facile and Universal Approach to Scaling Up. J. Mater. Chem. A 2016, 4, 11222–11227.

(7) Tabrizi, N. S.; Xu, Q.; Van Der Pers, N. M.; Schmidt-Ott, A. Generation of Mixed Metallic Nanoparticles from Immiscible Metals by Spark Discharge. J. Nanopart. Res. 2010, 12, 247–259.

(8) Kolhatkar, A. G.; Jamison, A. C.; Litvinov, D.; Willson, R. C.; Feng, J.; Biskos, G.; Zandbergen, H. W.; Schmidt-Ott, A. Green Manufacturing of Metallic Nanoparticles: A Facile and Universal Approach to Scaling Up. J. Mater. Chem. A 2016, 4, 11222–11227.

(9) Tabrizi, N. S.; Xu, Q.; Van Der Pers, N. M.; Schmidt-Ott, A. Generation of Mixed Metallic Nanoparticles from Immiscible Metals by Spark Discharge. J. Nanopart. Res. 2010, 12, 247–259.

(10) Dickens, J.; Fissan, H. Development of an Electrostatic Precipitator for Off-Line Particle Analysis. Aerosol Sci. Technol. 1999, 30, 438–453.

(11) Byeon, J. H.; Park, J. H.; Hwang, J. Spark Generation of Monometallic and Bimetallc Aerosol Nanoparticles. J. Aerosol Sci. 2008, 39, 888–896.

(12) Tabrizi, N. S.; Ullmann, M.; Vons, V. A.; Lafont, U.; Schmidt-Ott, A. Generation of Nanoparticles by Spark Discharge. J. Nanopart. Res. 2009, 11, 315–332.
(33) Sun, S.; Zeng, H.; Robinson, D. B.; Raoux, S.; Rice, P. M.; Wang, S. X.; Li, G. Monodisperse MFe\textsubscript{2}O\textsubscript{4} (M = Fe, Co, Mn) Nanoparticles. J. Am. Chem. Soc. 2004, 126, 273–279.

(34) Wiedensohler, A. An Approximation of the Bipolar Charge Distribution for Particles in the Submicron Size Range. J. Aerosol Sci. 1988, 19, 387–389.

(35) Knutson, E. O.; Whitby, K. T. Aerosol Classification by Electric Mobility: Apparatus, Theory, and Applications. J. Aerosol Sci. 1975, 6, 443–451.

(36) Muntwiler, M.; Zhang, J.; Stania, R.; Matsui, F.; Oberta, P.; Flechsig, U.; Patthey, L.; Quitmann, C.; Glatzel, T.; Widmer, R.; et al. Surface Science at the PEARL Beamline of the Swiss Light Source. J. Synchrotron Radiat. 2017, 24, 354–366.

(37) Biesinger, M. C.; Payne, B. P.; Grosvenor, A. P.; Lau, L. W. M.; Gerson, A. R.; Smart, R. S. C. Resolving Surface Chemical States in XPS Analysis of First Row Transition Metals, Oxides and Hydroxides: Cr, Mn, Fe, Co and Ni. Appl. Surf. Sci. 2011, 257, 2717–2730.

(38) Mills, P.; Sullivan, J. L. A Study of the Core Level Electrons in Iron and Its Three Oxides by Means of X-Ray Photoelectron Spectroscopy. J. Phys. D: Appl. Phys. 1983, 16, 723–732.

(39) Lee, D.; Lee, K.; Kim, D. S.; Lee, J. K.; Park, S. J.; Choi, M. Hydrogen-Assisted Spark Discharge Generation of Highly Crystalline and Surface-Passivated Silicon Nanoparticles. J. Aerosol Sci. 2017, 114, 139–145.

(40) Yao, Y.; Hu, Y.; Scott, R. W. J. Watching Iron Nanoparticles Rust: An in Situ x-Ray Absorption Spectroscopic Study. J. Phys. Chem. C 2014, 118, 22317–22324.

(41) Linderoth, S.; Morup, S.; Bentzon, M. D. Oxidation of Nanometer-Sized Iron Particles. J. Mater. Sci. 1995, 30, 3142–3148.

(42) Wang, C. M.; Baer, D. R.; Thomas, L. E.; Amonette, J. E.; Antony, J.; Qiang, Y.; Duscher, G. Void Formation during Early Stages of Passivation: Initial Oxidation of Iron Nanoparticles at Room Temperature. J. Appl. Phys. 2005, 98, No. 094308.

(43) Wang, C.; Dierdorff, S.; Baer, D. R.; Amonette, J. E.; Engelhard, M. H.; Antony, J.; Qiang, Y. Morphology and Electronic Structure of the Oxide Shell on the Surface of Iron Nanoparticles. J. Am. Chem. Soc. 2009, 131, 8824–8832.

(44) Shafranovsky, E. A.; Petrov, Y. I. Aerosol Fe Nanoparticles with the Passivating Oxide Shell. J. Nanopart. Res. 2004, 6, 71–90.

(45) Cabrera, N.; Mott, N. F. Theory of the Oxidation of Metals. Rep. Prog. Phys. 1949, 12, 163–184.

(46) Ermoline, A.; Dreizin, E. L. Equations for the Cabrera-Mott Kinetics of Oxidation for Spherical Nanoparticles. Chem. Phys. Lett. 2011, 505, 47–50.

(47) Zhdanov, V. P.; Kasemo, B. Cabrera-Mott Kinetics of Oxidation of Nm-Sized Metal Particles. Chem. Phys. Lett. 2008, 452, 285–288.

(48) Leslie-Pelecky, D. L.; Rieke, R. D. Magnetic Properties of Nanostructured Materials. Chem. Mater. 1996, 8, 1770–1783.

(49) Kodama, R. H.; Berkowitz, A. E.; McNiff, E. J., Jr.; Foner, S. Surface Spin Disorder in NiFe 2 O 4 Nanoparticles. Phys. Rev. Lett. 1996, 77, 394.