CHEMISTRY OF MATERIALS

ADDITION/CORRECTION

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Correction to The Ternary Nitrides $GaFe_3N$ and $AlFe_3N$: Improved Synthesis and Magnetic Properties

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Not too long ago, we published a two-step ammonolysis reaction which combines a high-temperature sintering step and a low-temperature nitriding reaction to yield a number of ternary magnetic nitrides of the general formula MFe_3N.[1] In the course of these investigations, we came across much older studies in which Al-substituted derivatives of γ'-Fe_4N had already been mentioned.[2] Indeed, the use of the two-step ammonolysis reaction then made us claim the existence of the compound $AlFe_3N$ in this very journal.[3] According to our report, ferromagnetic $AlFe_3N$ was synthesized in almost phase-pure form, and the Rietveld refinement of $AlFe_3N$ based on Cu Kα_1 radiation (λ = 1.54056 Å) resulted in a lattice parameter of a = 3.7967(3) Å with a statistical occupation of Fe and Al (ratio 3:1) in space group $Fm\bar{3}m$. At T = 546(20) °C both XRPD and magnetic measurements indicated the decomposition of $AlFe_3N$ into an iron–aluminum alloy. SQUID magnetometry further showed its specific saturation magnetization to be 144(2) A m^2 kg^{-1} at 5 T, about 30% smaller than for γ'-Fe_4N, and the coercive field of $AlFe_3N$ was given as ten times smaller than for γ'-Fe_4N. Together with the 0.25(2) T large magnetic remanence of $AlFe_3N$, we classified the material to be a soft ferromagnet.

Very unfortunately, these findings are invalid in their entirety. We have reinvestigated various samples of "$AlFe_3N$" by means of scanning-electron microscopy and elemental mapping, as depicted in Figure 1. These data clearly evidence that the material dubbed as "$AlFe_3N$" consists of an intimate solid mixture of γ'-Fe_4N and *amorphous* aluminum oxide, Al_2O_3. Because of the amorphous character of the latter, it was totally invisible in the XRPD study.[3] We have also crystallographically reinvestigated these samples but by using the harder Mo Kα_1 radiation (λ = 0.70932 Å) which suppresses the fluorescence and increases the overall quality of the diffraction data. While the amorphous Al_2O_3 contribution is still invisible from the Rietveld plot (Figure 2), the refined lattice parameter of "$AlFe_3N$" (a = 3.8026(1) Å) is clearly identified as the one of γ'-Fe_4N (a = 3.8009(6) Å).[4] Fortunately enough, the new XRPD pattern *does show* the extremely weak low-angle reflections (100) and (110) which appear in space group $Pm\bar{3}m$. Also, by use of the higher-quality (i.e., proper intensities) data, an aluminum occupancy on Wyckoff position 1a and/or 3c can be excluded. With respect to the mentioned side phase in ref 3, one reflection at 20° (Figure 2) still cannot be attributed to any known compound.

The magnetic data of "$AlFe_3N$", in particular the magnetic saturation moment, help to semiquantitatively characterize the solid mixture. The saturation moment of "$AlFe_3N$" equals 5.35 μ_B.[3] Since γ'-Fe_4N has a saturation moment of 8.86 μ_B, the composition appears to consist of ca. 78 mass % γ'-Fe_4N and 22 mass % of Al_2O_3. As said before, a third component is also present.

The described reaction is easily interpreted as an alumothermal procedure. The mixture of Al and Fe_2O_3 ignites at 1200 °C, and because of the high oxygen affinity of aluminum, Al_2O_3 releases a large lattice energy. Fe_2O_3 is then reduced to Fe, followed by a nitridation using the NH_3/H_2 stream to yield γ'-Fe_4N. Al_2O_3 cannot be reduced within the hydrogen stream under the present conditions. Summarizing, $AlFe_3N$ was not

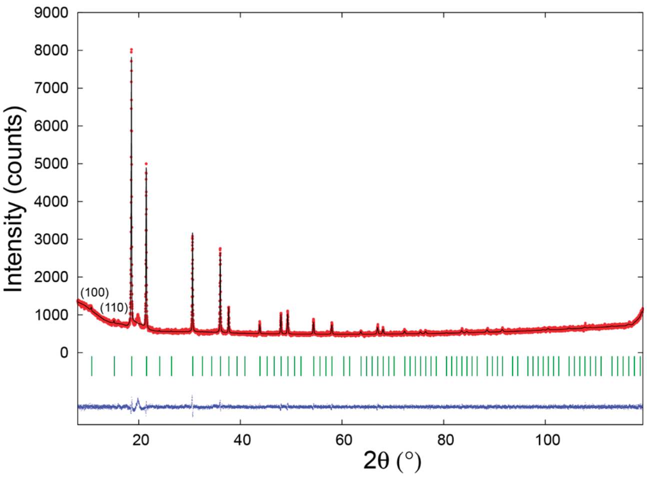

Figure 2. X-ray diffraction pattern and Rietveld refinement (R_{Bragg} = 0.061) of "$AlFe_3N$" on the basis of Mo Kα_1 radiation using the structural model of γ'-Fe_4N and space group $Pm\bar{3}m$. The lattice parameter arrives at a = 3.8026(1) Å.

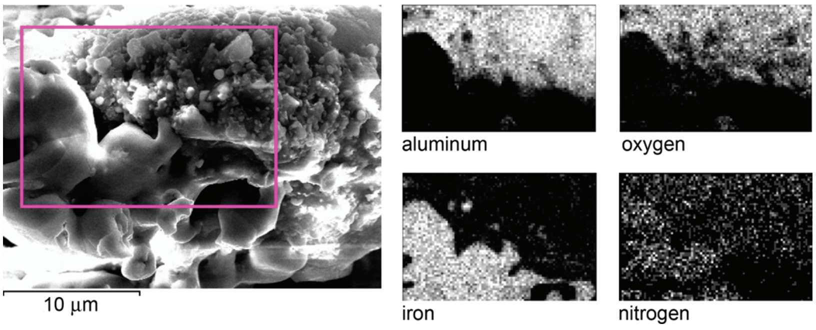

Figure 1. Scanning-electron microscopy analysis of "$AlFe_3N$" (left) and elemental mapping (right). "$AlFe_3N$" consists of a solid mixture of γ'-Fe_4N and amorphous Al_2O_3.

synthesized as claimed. It is not clear whether $AlFe_3N$ can at all be made by a (high-temperature) reaction. Nonetheless, the investigations by Bronger and Klemm[5] suggest that a coupled reduction of Al_2O_3 including a noble metal, e.g., Pt, might lead to *quaternary* nitrides of the general type $Al_xM_{1-x}Fe_3N$.

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