Experimental Report

Proposal: **5-25-222** **Council:** 10/2012

Title: Formation mechanisms of (metastable) iron nitrides through in situ neutron diffraction of solid-gas-reactions

This proposal is a new proposal

Researh Area: Chemistry

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Samples: iron(II) oxalate
FeCl2

Instrument	Req. Days	All. Days	From	To
D20	3	3	27/05/2013	30/05/2013

Abstract:

In-situ neutron diffraction can provide valuable information on phase formation mechanisms in solid state. We have developed an in-situ neutron diffraction cell, suitable for studies of solid-gas reactions under flowing gas conditions at higher temperatures, for the study of metastable nitride formation. Experiments will be performed under flowing ammonia. Heating will be realized by a laser heating system. The equipment was successfully tested within LTP-5A-1 in cooperation with Dr. Kohlmann (Univ. Saarland, Germany). An interesting system for in-situ measurements is Fe–N, because only partly known intermediate stages are involved in formation of nitride phases. Intermediates are visible through colour changes during the reaction. An exact knowledge on formation mechanisms of such materials will provide a successful approach for a customized synthesis.

Formation mechanisms of (metastable) iron nitrides through *in situ* neutron diffraction of solid-gas-reactions (5-25-222)

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In situ diffraction studies on the Fe–N system using D20´s high-temperature furnace (HTF) instead of the also well established laser heating system have been performed [1]. The resistive furnace was chosen, because on the one hand the absorption of radiation of the laser heating system and heat conduction in light-coloured ionic compounds (*e.g.* $FeCl_2$) is not as good as for dark metal powders resulting within large temperature gradients in the sample and on the other hand additionally a possibility of producing predissociated ammonia (equilibrated at elevated temperatures) exits [2, 3, 4]. For gas flow experiments the HTF is loaded with an silica glass tube closed at one-side [12 x 1 mm] which is connected with ILL's gas supply head towards the gas lines. All measurements carried out at D20 used a wavelength of λ = 186.690(7) pm and a time resolution of 2 min per scan.

In a previous beam time under proposal 5-25-206 the formation of ε-$Fe_3N_{1\pm x}$ and γ-Fe_4N_y from ammonia (high gas flow) and elemental iron was observed. During such experiments formation of ζ-Fe_2N was not detected, yet. In continuation of this previous proposal, now the formation conditions (low gas flow) in ammonia and the thermal decomposition of *ex situ* prepared ζ-Fe_2N in argon were reinvestigated, employing a different thermal treatment compared to those presented in the experimental report 5-25-214. Furthermore, the synthesis conditions of ε-$Fe_3N_{1\pm x}$ from $FeCl_2$ and ammonia as well as of α''-$Fe_{16}N_2$ from γ-Fe_2O_3 and $Fe(C_2O_4)$ x 2 H_2O, respectively, were examined. Additionally, the decomposition behaviour of α''-$Fe_{16}N_2$ was investigated.

The discrimination of the structurally closely related phases ε-Fe_3N_{1+x} and ζ-Fe_2N is difficult in X-ray diffraction, since their iron substructures are almost identical. However, this distinction is easily possible in neutron diffraction, due to considerably different nitrogen substructures. Neutron diffraction experiments show that the sample actually consists of 66(5) wt.% ζ-Fe_2N and 34(5) wt.%

ε-Fe_3N_{1+x} although it appeared single phase in X-ray diffraction. With increasing temperature, the amount of ζ-Fe_2N rises while the amount of ε-Fe_3N_{1+x} diminishes. The maximum value [85(5) wt.% ζ-Fe_2N] is observed at 432 °C. Through further heating to 450 °C and subsequent annealing for 30 min most of the ζ-phase is converted to ε-$Fe_3N_{1.26(8)}$. Between 516 °C and 526 °C single phase ε-$Fe_3N_{1.36(8)}$ is observed. Above 536 °C two ε-phases with different nitrogen content are detected. Between 550 °C and 555 °C a large quantity of nitrogen is released from the nitrogen-rich ε-phase. However, its unit cell is not able to relax so quickly and two different sets of unit cell parameters are gained. Above 570 °C a single ε-phase is observed beside 42(2) wt.% γ'-$Fe_4N_{0.92(2)}$. At 634 °C only γ'-$Fe_4N_{0.907(6)}$ and 31.2(9) wt.% γ-$FeN_{0.085(6)}$ are present. Finally, at 679 °C all nitrogen is released and α-Fe remains. The collected data indicate that below 450 °C the equilibrium state for ζ-Fe_2N/ε-$Fe_3N_{1\pm x}$ is not reached. Additionally, the Fe–N phase diagram has to be revised, taking for γ'-Fe_4N_y an expansion of the homogeneity range towards lower nitrogen contents above 600 °C into account [4].

For the reaction of iron powder with ammonia at a lower gas flow rate [60 sccm vs. 510 sccm] nearly no influence on the formation temperature of γ'-Fe_4N_y is observed [392 °C vs. 387 °C]. In contrast the formation temperature of ε-$Fe_3N_{1\pm x}$ is remarkably increased from 397 °C to 463 °C. However, again only ε- and γ'-phases and no indications of ζ-Fe_2N are observed. *Ex situ* experiments quenching specimens after various annealing temperatures and times revealed the formation of ζ-phase from ε-$Fe_3N_{1\pm x}$ in an Ostwald ripening process with a rather slow reaction rate [1, 4].

For the alternative synthesis route of ε-$Fe_3N_{1\pm x}$, beside direct conversion of iron with ammonia, from $FeCl_2$ and ammonia the involvement of different ammoniates is confirmed through combination of thermal analysis in argon, ammonia and *in situ* neutron diffraction. The occurrence of crystalline $[Fe(NH_3)_6]Cl_2$ and $Fe(NH_3)_2Cl_2$ as well as amorphous $Fe(NH_3)Cl_2$ is observed as it was proposed previously [5]. Additionally, our *in situ* neutron diffraction study reveals the formation of amorphous $FeCl_2$ between 416 °C and 437 °C. A formation of

ε-$Fe_3N_{1\pm x}$ is not observed even after increase of temperature to 500 °C, which we believe is related to hindered removal of NH_4Cl [2, 4].

To investigate the synthesis of metastable α''-$Fe_{16}N_2$ first γ-Fe_2O_3 was tried to reduce in a H_2/N_2 mixture [5 vol.% H_2] between 390 °C and 420 °C, which was not possible due to the too low reduction potential and only formation of Fe_3O_4 is observed. Therefore, the experiment was repeated using pure H_2, hence a special gas mixture device is necessary to dilute the H_2 concentration exhausted from the measurement cell below the explosion limit [4.8 vol.%]. In this experiment a reduction to α-Fe is observed. However, a nitridation of the *in situ* formed iron between 125 °C and 175 C is not observed during 10 h of reaction. We assume this to be related to the very slow reaction rate [*ex situ* observed reaction time are 100 h]. In thermolysis of $Fe(C_2O_4)$ x 2 H_2O at lower temperatures the release of water is observed through the vanishing incoherent scattering contribution. However, even at 475 °C only a small amount of α-Fe is produced [6]. Therefore, a nitridation step was not applied. Instead the decomposition behaviour of an *ex situ* prepared sample of α''-$Fe_{16}N_2$ [93(2) wt.%, balance: Fe] was investigated. The sample was heated with 2.5 $K \cdot min^{-1}$ to 500 °C and afterwards with 5 $K \cdot min^{-1}$ to 675 °C in flowing Ar. Above 213 °C weak reflections representing 1.1(2) wt.% γ'-Fe_4N_y are observed and the amount of α-Fe detected is increased. With increasing temperature more α''-phase is decomposed into γ'-phase without nitrogen loss. Additionally, above 241 °C indirectly the formation of α'-Fe_8N (nitrogen martensite) is observed via a clear increase in *c*/*a* ratio. Above 266 °C α''-$Fe_{16}N_2$ is completely decomposed to 50(2) wt.% α-Fe and 50(2) wt.% γ'-$Fe_4N_{0.88(2)}$. Above 439 °C conversion of γ'-phase to α-Fe occurs and is finished at 578 °C [3].

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[2] R. Juza, *Adv. Inorg. Chem. Radiochem.* **1966**, *9*, 81–131.

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[4] M. Widenmeyer, T. C. Hansen, E. Meißner, R. Niewa, *Z. Anorg. Allg. Chem.* **2013**, in press.

[5] S. Bremm, G. Meyer, *Z. Anorg. Allg. Chem.* **2003**, *629*, 1875.

[6] M. Widenmeyer, Dissertation, Univ. Stuttgart **2014**.