Experimental Report

08/03/2013

Proposal:	**5-25-206**	**Council:**	10/2011
Title:	Formation mechanism of (metastable) iron nitrides through in-situ neutron diffraction of solid-gas-reactions		

This proposal is a new proposal

Research Area: Chemistry

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Samples:
Iron powder (alpha)
zeta-Fe2N
alpha"-Fe16N2

Instrument	Req. Days	All. Days	From	To
D20	4	3	02/11/2012	05/11/2012

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 or argon. 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 and the nitride phases therein due to its importance in different industrial processes, i.e., steel hardening. A comprehensive knowledge on the formation mechanisms of such materials will provide a successful approach for a customized synthesis.

Formation mechanism of (metastable) iron nitrides through *in situ* neutron diffraction of solid-gas-reactions (5-25-206)

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In situ diffraction studies on metal-nitrogen systems have been performed by using a newly developed gas flow cell made from silica glass and a continuous 2x40 W laser heating system. A part of equipment development was realized during LTP-5A-1 [1]. All measurements executed at D20 used a wavelength of λ = 186.764(4) pm and a radial oscillating collimator as well as a time resolution of 2 min per scan.

The *ex situ* synthesis of ζ-Fe_2N from iron powder in flowing ammonia is well known from literature as well as the fact that this reaction is very sensitive towards temperature and gas flow rate [2, 3]. Therefore, the expected formation of ζ-Fe_2N could not be observed, instead γ'-Fe_4N and ε-Fe_3N_{1+x} were formed. For those phases complete Rietveld refinements were carried out between 397 °C and 607 °C. Fig. 1 depicts the progression of the reaction [1].

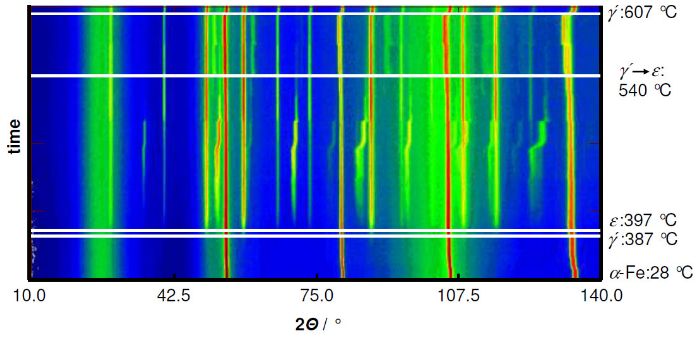

Fig. 1: Temperature dependent neutron diffraction data of the reaction of iron powder with ammonia. The formation of γ'-Fe_4N_{1-y} and ε-Fe_3N_{1+x} is visible. Intensity is given in false colours on a logarithmic scale [1].

Above 387 °C γ'-Fe_4N forms. With increasing temperature at 397 °C ε-$Fe_3N_{1.15(8)}$ appears. Further heating decreases the amount of elemental iron, which reacts to nitride phases and concomitant in a slight increase of the nitrogen content of the ε-phase. Above 497 °C the *in situ* formed ε-phase slowly starts to release nitrogen and simultaneously the nitrogen content of the γ'-Fe_4N phase is increased. This allows the assumption that most of the nitrogen released by the ε-phase is taken up by the γ'-phase. This transformation is completed above 527 °C and the diffraction patterns only show γ-$Fe_4N_{0.943(5)}$ and some residues of unreacted iron. The decomposition of the ε-phase is accompanied by a remarkable shrinking of the unit cell from a = 477.5(1) pm, c = 443.0(2) pm to a = 472.2(1) pm and c = 441.8(2) pm [1]. A similar behaviour was earlier observed by *Leineweber et al.* for an ε-$Fe_3N_{1.22}$ sample heated in vacuum at temperatures above 477 °C [4]. The decomposition of ζ-Fe_2N could not be observed so far, due to the lack of formation of this phase during the experiment. Information on the decomposition of ζ-Fe_2N is expected from an experiment using *ex situ* prepared ζ-Fe_2N.

It is well known from studies carried out by, *e.g. Kikkawa et al.* that a successful synthesis of α''-$Fe_{16}N_2$ is strongly correlated with the particle size because a small size of about 100 nm for the iron particles is needed [5]. These particles form in our optimised synthesis route *in situ*, starting from nanosized Fe_2O_3 (avg. particle size 25 nm) by reduction in flowing hydrogen at 390 °C. The *in situ* synthesis of such particles could not be achieved during the experiment, due to technical reasons concerning the used sealings, therefore for safety reasons a further proceeding of the reaction was not executed. A promising approach to overcome this obstacle in future experiments is the usage of a sapphire single crystal cell similar to this developed during LTP-5A-1 [6], but in an adapted design for gas flow experiments. Instead a part of the investigation of the V–N system was preferentially carried out. The observed reaction of vanadium powder in flowing ammonia (510 sccm) mainly produced δ-VN_{1-x} and to a minor fraction β-V_2N_{1-y} (s. Fig. 2). The temperature was raised stepwise within 4.5 h to additionally allow an observation of a potential formation of $V_{16}N_{1.5}$. The formation of $V_{16}N_{1.5}$ could not be observed during the *in situ* neutron diffraction experiment, due a scattering length close to zero of vanadium and the small fraction of phase, but in an afterwards executed *ex situ* X-ray diffraction experiment the existence of $V_{16}N_{1.5}$ in the sample was confirmed.

Above 602 °C the strongest reflections of δ-VN appear and at 652 °C reflections of β-V_2N were observed [1]. Additionally, an *ex situ* prepared sample of $V_{16}N_{1.5}$ contained in a standard vanadium cylinder was measured. A full Rietveld analysis was not possible regarding to the above mentioned low scattering power of this compound, but we were able to carry out the determination of the unit cell parameters based on a structure model from literature [7].

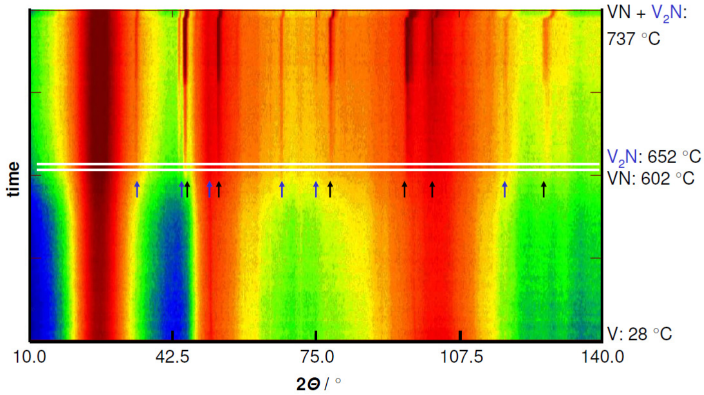

Fig. 2: Temperature dependent neutron diffraction data of the reaction of vanadium powder with ammonia. The formation of δ-VN_{1-x} (black arrows) and β-V_2N_{1-y} (blue arrows) is visible. Intensity given in false colours [1].

Due to unplanned reactor shutdown, beam time had to be cancelled and reallocated on short notice. This fact led us to shift the *in situ* experiments concerning the formation and decomposition of α''-$Fe_{16}N_2$ as well as the decomposition of ζ-Fe_2N to the next beam time.

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