Experimental Report

05/12/2013

Proposal:	**5-25-214**	**Council:**	4/2012

Title: Formation mechanisms of (metastable) copper, nickel and vanadium nitrides through in-situ neutron diffraction of solid-gas-reactions

This proposal is a new proposal

Researh Area: Chemistry

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Samples:
Vanadium powder
NiBr2
CuF2

Instrument	Req. Days	All. Days	From	To
D20	4	3	03/12/2012	06/12/2012

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. 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). Interesting systems for in-situ measurements are Cu–N, Ni–N and V–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 mechanism of (metastable) copper, nickel and vanadium nitrides through *in situ* neutron diffraction of solid-gas-reactions (5-25-214)

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In situ diffraction studies on metal-nitrogen systems have been performed by using D20´s high-temperature furnace (HTF) instead of the also well established laser heating system [1], because the conduction of heat to light-coloured ionic compounds is not as good as for dark metal powders resulting in large temperature gradients in the sample. For gas flow experiments the HTF is equipped with a one-side closed silica glass tube (12x1 mm) which is connected with ILL's gas supply head towards the gas lines. All measurements carried out at D20 used a wavelength of $\lambda = 186.802(5)$ pm and a time resolution of 2 min per scan.

Due to an unplanned reactor shutdown in early 2012, beam time had to be cancelled and reallocated on short notice. This fact led us to reorganize the order of experiments. The studies concerning the V–N system where executed in the previous measurement time under proposal 5-25-206. In continuation of the previous proposal, now the thermal decomposition of *ex situ* prepared ζ-Fe_2N in argon was investigated.

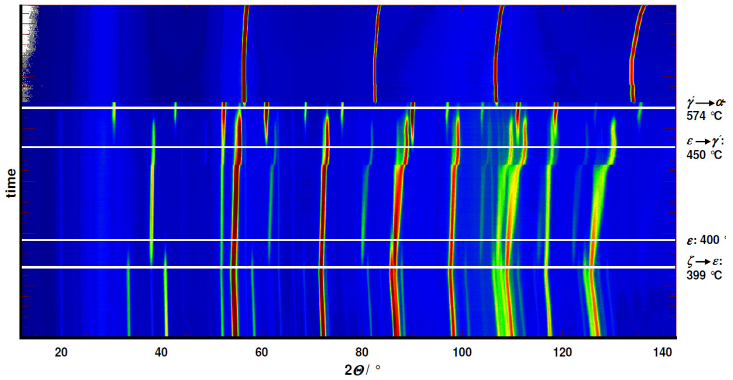

Fig. 1: Temperature dependent neutron diffraction data of the thermal decomposition of ζ-Fe_2N in argon. Intensity is given in false colours.

The differentiation between the structural closely related phases ε-Fe_3N_{1+x} and ζ-Fe_2N is difficult in X-ray diffraction, since the iron substructure is almost identical, however neutron diffraction easily allows to discriminate due to markedly different nitrogen substructures. Neutron diffraction experiment shows that the sample single phase in

X-ray diffraction contains 81(2) % ζ-Fe_2N and 19(1) % ε-Fe_3N_{1+x}. While increasing the temperature to 400 °C ζ-Fe_2N very slowly starts to convert into ε-Fe_3N_{1+x}. At 400 °C the rate of conversion increases considerably, resulting in a 1:1 mixture of ζ-$Fe_2N_{0.948(1)}$ and ε-$Fe_3N_{1.18(5)}$ after 8 min. This transformation to ε-$Fe_3N_{1.22(3)}$ is completed after another 65 min at 400 °C. While ε-$Fe_3N_{1.22(3)}$ slowly starts to release nitrogen during heating to 450 °C the composition changes to ε-$Fe_3N_{0.98(2)}$. Above 450 °C the *in situ* formed ε-phase starts to convert into a nitrogen-poor γ-$Fe_4N_{0.86(9)}$ phase, while on further duration of the reaction the nitrogen content of γ-phase is increased to γ-$Fe_4N_{0.97(1)}$. Continuous heating again increases the conversion rate. Above 540 °C γ-phase slowly starts to release nitrogen to the final composition of $Fe_4N_{0.919(7)}$ at 599 °C and simultaneously residual amounts of ε-phase are decomposed. Additionally, the formation of α-Fe occurs above 569 °C. The transformation of γ-phase into α-Fe is completed at 674 °C [2].

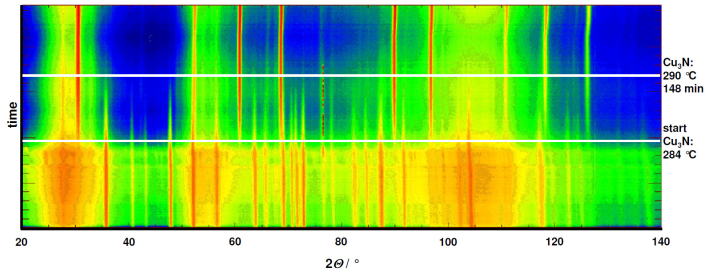

Fig. 2: Temperature dependent neutron diffraction data of the reaction of CuF_2 with flowing ammonia. Intensity is given in false colours on a logarithmic scale.

The synthesis of Cu_3N typically starts from colourless CuF_2 powder, which is reacted with flowing ammonia at 280 °C for several hours [3]. By contact of CuF_2 with ammonia immediately a reaction starts and a dark blue coloured, voluminous, but crystalline product is formed. We believe that the *in situ* formed compound is an ammoniate of CuF_2, because the background of the measurements is obviously increased, due to the large incoherent scattering of the hydrogen atoms of the ammonia ligands. A structural refinement was not successful yet. Above 284 °C the formation of Cu_3N starts. Afterwards the temperature was increased to 290 °C and kept there for 260 min. After 148 min single phase Cu_3N is observed with a composition of $Cu_3N_{0.97(2)}$. Additionally, the thermal expansion of the unit cell was determined to be $a = a_0 + 0.002T$ in the temperature range between 290 °C and 64 °C.

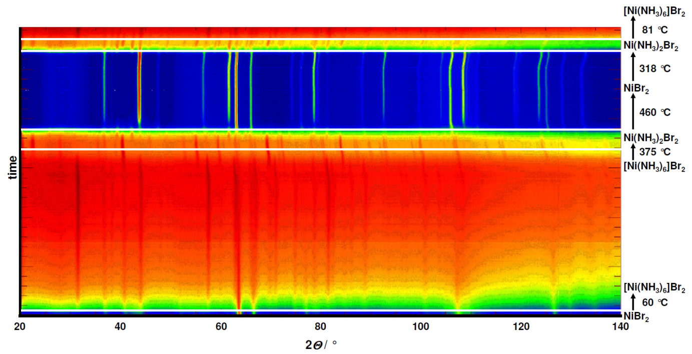

Fig. 3: Temperature dependent neutron diffraction data of the reaction of $NiBr_2$ with flowing ammonia. Intensity is given in false colours.

A possible synthesis route to Ni_3N starts from $NiBr_2$ powder, which is reacted with flowing ammonia at 420 °C for 4 h [4]. In analogy to CuF_2 by contact between $NiBr_2$ and ammonia immediately a strongly exothermic reaction producing $[Ni(NH_3)_6]Br_2$ starts and the temperature is increased to 60 °C. Above 375 °C $[Ni(NH_3)_6]Br_2$ transforms into β-$Ni(NH_3)_2Br_2$ through release of 4 molecules of ammonia. This transformation temperature is considerably increased compared with thermal decomposition in argon (162 °C) in *ex situ* DTA experiments. During further temperature increase to 460 °C remaining ammonia is released and $NiBr_2$ is formed in accordance to *Juza et al.* [4]. However, in contrast to our *ex situ* observed results no Ni_3N was produced in the further progress of the reaction, instead the crystallization of $NiBr_2$ was observed. Upon cooling, below 318 °C β-$Ni(NH_3)_2Br_2$ is formed again. Further cooling below 81 °C results in the formation of $[Ni(NH_3)_6]Br_2$.

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[1] M. Widenmeyer, R. Niewa, T. C. Hansen, H. Kohlmann, *Z. Anorg. Allg. Chem.* **2013**, *639*, 285.

[2] M. Widenmeyer, T. C. Hansen, E. Meißner, R. Niewa, *Z. Anorg. Allg. Chem.* 2013, submitted.

[3] R. Juza, H. Hahn, *Z. Anorg. Allg. Chem.* **1938**, *239*, 282.

[4] R. Juza, W. Sachße, *Z. Anorg. Allg. Chem.* **1943**, *251*, 201.