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The Removal of Carbon or Carbon Residues from Ceramic Powders or Greenware with Ammonia

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Abstract

In this paper it is shown that carbon or carbon residue can be removed from ceramic powder, granulate or greenware with NH_3, yielding HCN. Dissociation of NH_3 on the surface of carbon or carbon residue and matrix material occurs simultaneously. If NH_3 is used instead of N_2 in the carbothermal synthesis of nitrides it is necessary to allow for both the dissociation of NH_3 and the formation of HCN.

In diesem Artikel wird gezeigt, daß Kohlenstoff oder Kohlenstoffrückstände mit NH_3 aus Pulver, Granulat oder Grünligen entfernt werden können, wobei HCN gebildet wird. Die Dissoziation von NH_3 an der Oberfläche des Kohlenstoffs oder der Kohlenstoffrückstände und dem Matrixmaterial geschieht gleichzeitig. Wenn NH_3 anstelle von N_2 für die carbothermische Synthese von Nitriden verwendet wird, muß sowohl die Dissoziation von NH_3 als auch die Bildung von HCN berücksichtigt werden.

On montre que l'on peut éliminer le carbone ou les résidus carboniques de poudres, de granulés ou de pièces crues en utilisant NH_3, obtenant ainsi HCN. La dissociation de NH_3 se produit simultanément à la surface du carbone et de la matrice. Si l'on utilise NH_3 au lieu de N_2 lors de la synthèse carbothermique des nitrures, il convient de tenir compte à la fois de la dissociation de NH_3 et de la formation de HCN.

1 Introduction

The removal of carbon or carbon residue from greenware or ceramic powders is well known.[1] The removal of carbon or organic matter by carbon burnout is of great importance in the fabrication of traditional and technical ceramics. In recent years the removal of carbon or carbon residue with gases other than air or oxygen has been studied.[2] It has been discovered that carbon can be removed with ammonia and in this paper features of this reaction are discussed. The reaction of carbon with ammonia dates back to 1741.[3–5] Since 1940 little attention has been paid to this reaction. An important paper on the reaction between carbon and ammonia is from Sherwood *et al.* and dates from 1960,[6] giving the following information that the overall reaction is

$$C + NH_3 = HCN + H_2$$

the reaction proceeds at temperatures higher than 700°C and the dissociation of ammonia is observed simultaneously. Two more recent papers concerning this reaction were found in the literature.[7,8] HCN is not only formed from carbon by reaction with ammonia, but according to Sherwood *et al.* HCN can be formed from the elements (C, N_2 and H_2) as well at temperatures higher than 1400°C.[6] No hydrocarbons are formed in the reaction between carbon and ammonia, but hydrocarbons and ammonia react at elevated temperatures and HCN is formed.[9] These reactions are used or can be used for the synthesis of HCN on a commercial scale, such as the Andrussow, BMA and Shawinigan processes. For the homogeneous dissociation of ammonia temperatures in excess of 2000°C are required. The heterogeneous dissociation of ammonia depends strongly on the reactivity of the surface taking part in the reaction, and occurs at temperatures of 300°C and higher.[9] Ammonia reacts with oxides, converting these into nitrides or oxynitrides.[10–12] In this way Si_2N_2O is produced from silica according to the reaction[10,11]

$$2SiO_2 + 2NH_3 = Si_2N_2O + 3H_2O$$

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So, it can be concluded that carbon or carbon residue can be removed from greenware or ceramic powders with ammonia by the reaction

$$C + NH_3 = HCN + H_2$$

The dissociation of ammonia occurs simultaneously. Oxides may react with ammonia simultaneously as well. No hydrocarbons will be formed. If NH_3 is used for the synthesis of nitrides it is necessary to allow for the dissociation of NH_3. If NH_3 is used for the carbothermal synthesis of nitrides it is necessary to allow for both the dissociation of ammonia and the formation of HCN.

2 State of the Art of the Reaction Between Ammonia and Carbon

The thermodynamics, the kinetics, and the reaction mechanism of the reaction between carbon and ammonia are set out in this section, according to the literature. In the next section experiments are described to verify and extend this knowledge to the removal of carbon with ammonia from SiC and Si_3N_4 powder of greenware.

It is clear that the reactions of interest for the removal of carbon with ammonia are:

$$C + NH_3 = HCN + H_2 \qquad (1)$$

$$2NH_3 = N_2 + 3H_2 \qquad (2)$$

There is an optimum temperature for the formation of HCN when all other parameters are unchanged.[8] This can be explained in the following way. With increasing temperature the reaction rate of the formation of HCN increases. At very high temperatures the dissociation of ammonia becomes dominant and no ammonia is left for the formation of HCN. Thermodynamic data for the formation of HCN and the dissociation of ammonia is given in Fig. 1. From this figure it can be seen that the dissociation of ammonia is preferred over the formation of HCN from the thermodynamic point of view. Temperatures higher than 1000°C are favoured for the formation of HCN because the change of the Gibbs free energy for the formation of HCN is negative at temperatures higher than 1000°C. According to the thermodynamic principle of 'van het Hoff–Le Chatelier' a high pressure will reduce formation of HCN and dissociation of ammonia. The reaction enthalpy for the formation of HCN according to reaction (1) is 181 kJ/mol at 298 K and 188 kJ/mol at 1000 K and higher. The reaction enthalpy for the dissociation of ammonia according to reaction (2) is 46 kJ/mol at 298 K and 56 kJ/mol at 1000 K. So, both reactions are endothermic.

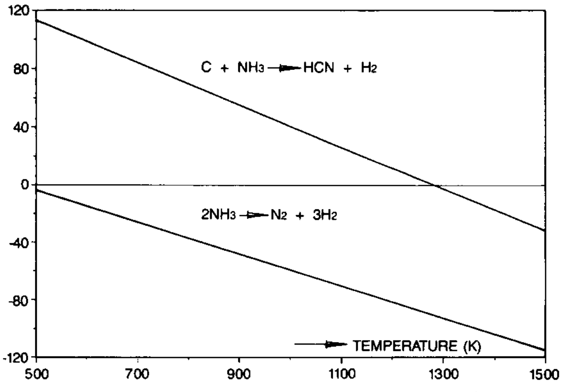

Fig. 1. Change of the Gibbs free energy for the formation of HCN and the dissociation of NH_3 in kJ per mol NH_3.

It is reasonable to assume that the reactivity of carbon for the formation of HCN is similar to the reactivity of carbon for other gasification reactions.[2,13] This means that the reactivity of carbon depends on its temperature history, its specific surface area, impurities and dopes which act as catalytic agents, and interaction of the matrix material. According to Gmelin, Fe and Ca probably do act as catalytic agents.[5] The heterogeneous dissociation of ammonia on carbon is first order in the concentration of ammonia:[6]

$$d[NH_3]/dt = -k_1[NH_3]$$

or

$$[NH_3] = [NH_3]_0 \exp[-k_1 t] \qquad (3)$$

with t as time, $(NH_3)_0$ as initial ammonia concentration and k_1 as reaction rate constant. The rate of the dissociation was not influenced by N_2 or H_2 when the NH_3 content was varied between 20 and 50% and the H_2 and N_2 content was varied between 50 and 80% at temperatures between 840 and 1120°C.[6] The value of the activation energy of the dissociation of ammonia on carbon varies between 88,[6] 147 and 240 kJ/mol.[7] The low value of 88 kJ/mol may have been influenced by gas diffusion limitation of the reaction rate. The influence of high pressures on the rate of dissocation is unknown. The formation of HCN is first order in the concentration of ammonia:[6,7]

$$d[HCN]/dt = k_2[NH_3] \qquad (4)$$

with k_2 as reaction rate constant. The combination of eqns (3) and (4) results in eqn (5) for the formation of HCN:[6]

$$d[HCN]/dt = k_2[NH_3]_0 \exp[-k_1 t] \qquad (5)$$

with t as residence time of the gas in the bed or hot zone. The rate of formation of HCN is not influenced by H_2 or HCN according to this equation. The value of the activation energy of the formation of HCN varies between 160,[6] 185 and 290 kJ/mol.[7] The low value of 160 kJ/mol may be influenced by gas diffusion limitation of the reaction rate.[7] The reaction mechanisms of both reactions (1) and (2) probably consist of an adsorption reaction, a surface reaction and a desorption reaction.[2] The reaction mechanism of the dissociation of ammonia is well known; adsorbed nitrogen atoms/radicals play an important role in the reaction.[9,14]

3 Experimental

Experiments were carried out in a Netzsch STA 429 thermobalance (Netzsch, Selb, FRG) coupled with a mass spectrometer, Balzers QMG 420/112. The mass spectrometer was used to obtain qualitative results. The heated part of the thermobalance was made of alumina of 99·5% purity. The experiments were performed at 1 atm. The gas flow through the balance was 100 ml/min. The partial pressure of both ammonia and helium was 50%. The heating and cooling rates were 40 K/min. Experiments were also carried out in a packed-bed reactor with indirect heating. A sintered SiC tube was used to contain the packed bed. Granules of SiC powder with free carbon were placed on sintered SiC balls with a diameter of 3 mm. The diameter of the bed was 25 mm. Figure 2 shows a schematic illustration of the reactor. The experiments with the packed bed were carried out at atmospheric pressure with 100% ammonia. The gas leaving the reactors was analyzed for hydrogen with a katharometer, MSA Thermatron Analyzer (MSA, Pittsburg, PA).

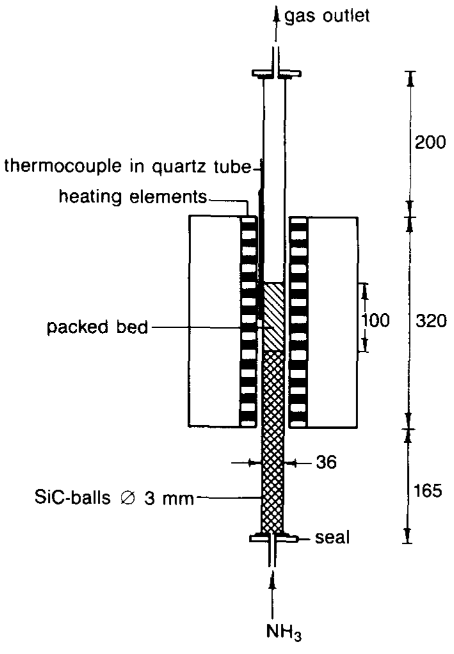

Fig. 2. The packed-bed reactor used to study the removal of C with NH_3 and the dissociation of NH_3. Dimensions in mm.

As raw materials α-Si_3N_4 (UBE SN-E10 UBE Industries Ltd, Tokyo), β-SiC (Superior Graphite HSC-059 Chicago, IL), carbon black (Degussa Printex U, Frankfurt, FRG) and SiC with 9 or 14 wt% free carbon were used. Powders were dry mixed with 5 wt% PEG-200 or distilled water in a mortar. The water or PEG was added as pressing aid. Tablets were pressed with a diameter and a thickness of 5 mm. The density of the tablets made from ceramic powder or the powder mixture was about 1·7 g/ml. The density of the tablets made from carbon black was about 1·0 g/ml.

The SiC with the free carbon was produced from a mixture of silica (aerosil ox 50), carbon black (Printex U) and SiC nuclei (HSC-SiC) by a carbothermal reaction at 1600°C in argon. In the carbothermal reaction 5 wt% nuclei relative to the silica was used. The molar ratio of silica:carbon was 1:3·3 or 1:3·5. The raw materials were wet premixed with a colloid mill and wet mixed in an attritor. The SiC produced in this way will be referred to as 'experimental SiC'.[15]

The oxygen, nitrogen and carbon content of the powders were measured with Strohlein equipment.

4 Results

The mass spectrogram showed that the dissociation of ammonia takes place on the alumina parts in the heated zone of the thermobalance. The dissociation starts at 700°C and increases with increasing temperature. The dissociation of ammonia in the thermobalance was more than 90% at temperatures higher than about 1200°C. The experiments with tablets of carbon black revealed that ammonia indeed reacts fast with carbon. The reaction takes less than 10 min at 1100°C. The reaction starts at 700°C. The mass spectrometer detected no CH_4 as reaction product. It appeared that the main reaction products besides hydrogen and nitrogen were HCN and (a small amount of) CH_3NH_2. Tablets of Si_3N_4 powder were heated in the thermobalance for 10 h at 1120°C. The result is shown in Fig. 3. From this figure it can be seen that over the whole period the weight decreases. Analysis of the oxygen content before and after the experiment revealed a reduction of the oxygen content by 0·5 wt%. This indicates that the oxide or oxynitride layer on the Si_3N_4 particles react with ammonia.

Results of experiments with the packed-bed reactor with tablets of experimental SiC powder with 9 or 14 wt% free carbon are given in Tables 1

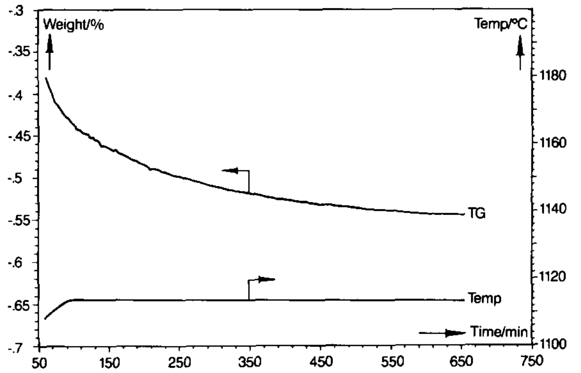

Fig. 3. TGA of Si_3N_4 from UBE in a gas flow of 40% NH_3 and 60% N_2 at 1 atm and 1120°C.

and 2. Experiments were also performed with an empty reactor. It appeared that NH_3 dissociates on the surface of the SiC balls and the SiC tube. The results as given in Table 1 were corrected for the dissociation of NH_3 in an empty reactor. The volume percentage ammonia entering the bed was taken as:

$$\%NH_3 = (1-x)/(1+x).100\% \tag{6}$$

with x as the conversion of ammonia in an empty reactor. The residence time of the gas in the bed was calculated. Corrections were taken into account for heating up the gas, the porosity of the bed and the volume increase of the gas due to reactions. The gas flow rate increases due to an increase in temperature from room temperature to reaction temperature. This gas flow rate is calculated according to eqn (7):

$$V_0 = F/(\pi R^2) \tag{7a}$$

$$V_R = V_0 T_R/293 \tag{7b}$$

Table 1. Dissociation of ammonia in a packed-bed reactor with a bed height of 50 mm packed with SiC with 14 wt% free carbon at 1 bar

Temperature (°C)	*Gas flow*[a] *(ml/s)*	*NH_3 cracked (%)*[b]
790	5	83
790	15	48
790	30	30
890	5	100
890	15	68
890	30	42
980	5	98
980	15	71
980	30	49
1 090	5	100
1 090	15	100
1 090	30	83
1 200	5	100
1 200	15	100
1 200	30	85

[a] At 293 K.
[b] After 4 h.

Table 2. Removal of carbon with ammonia in a packed-bed reactor packed with SiC with 36 wt% carbon (9 wt% free carbon) at 1080°C and 1 bar

Gas flow[a] *(ml/s)*	*Bed height (mm)*	*NH_3 cracked (%)*	*Time (h)*	*C content*[b] *(wt%)*	*N content*[b] *(wt%)*
15	50	85	2	31·4	0·1
15	50	85–70	3	30·1	0·7
15[c]	50	63	2	31·5	0·1
30	100	76–66	3	30·7	0·9
30	100	78–62	6	29·7	0·2

[a] At 293 K.
[b] After reaction.
[c] Broken tablets.
The first value of the percentage ammonia cracked is related to the beginning and the second value to the end of the experiment.

with F as volume flow of the gas, R the radius of the bed, V_0 the gas flow rate at room temperature, T_R the reaction temperature in kelvin and V_R the gas flow rate at reaction temperature. Due to the 40% vol. porosity of the bed, the gas flow rate in the bed is 2·5 times the gas flow rate in an empty reactor:

$$V_p = 2{\cdot}5\,V_R \tag{8}$$

With V_p as the gas flow rate corrected for the porosity of the bed. Due to the reaction of ammonia, one molecule of NH_3 forms two molecules of gaseous products (reactions (1) and (2)). Thus, the gas flow rate is increased by the reactions. The correction of the gas flow for the reaction of ammonia is taken as:

$$V_{real} = V_p(1 + 0{\cdot}5x) \quad \text{for } x < 0{\cdot}9 \tag{9a}$$

$$V_{real} = V_p(1 + x) \quad \text{for } x > 0{\cdot}9 \tag{9b}$$

The corrected results from Table 1 and the calculated residence time were used to calculate a reaction rate constant for the dissociation of NH_3. The reaction rate constant, k, is calculated according to eqn (10):

$$\ln(N_{out}/N_{in}) = -kt \tag{10}$$

with t as residence time of the gas in the bed, N_{out} the concentration of ammonia in the gas leaving the bed and N_{in} the concentration of ammonia entering the bed. N_{out} was derived from the hydrogen concentration in the gas leaving the reactor with the packed bed as measured with the katharometer. N_{in} was derived from the hydrogen concentration in the gas leaving the empty reactor as measured with the katharometer. Equation (10) is derived from eqn (3). It appeared that a large excess of ammonia had to be used in the experiments. Relatively little ammonia reacts with carbon; therefore it was assumed that all hydrogen, as measured with the katharometer,

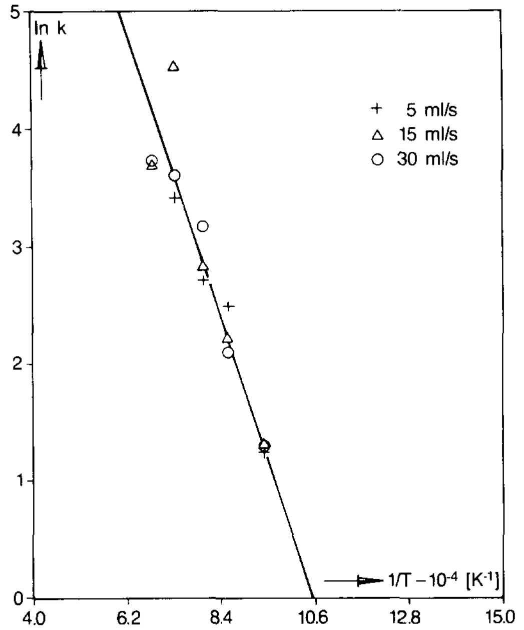

Fig. 4. Arrhenius plot for the dissociation of ammonia in a bed packed with tablets of SiC powder with 14 wt% free carbon. The height of the bed is 50 mm and the diameter of the bed is 25 mm. The height and the diameter of the tablets are both 5 mm.

originates from the dissociation reaction. This reaction rate constant, k, is given as a function of the temperature in an Arrhenius plot (Fig. 4). From this figure the activation energy was calculated. The activation energy of the dissociation of NH_3 appeared to be 100 kJ/mol. In Table 1 the results obtained for the dissociation of ammonia are given. From Table 1 it is seen that the dissociation of NH_3 increases with temperature and residence time of the gas in the bed.

In Table 2 the results obtained for the removal of carbon with ammonia are given. From Table 2 it is seen that it takes approximately three hours to remove the carbon. When the residence time of the gas in the bed is constant, but the height of the bed is varied, the results for the removal of carbon are constant. For the removal of carbon 5 kg of ammonia per kg SiC is used if about 10 wt% free (pure) carbon is present in the mixture of SiC and C. It appears that the dissociation of ammonia decreases with time. If broken tablets are used less ammonia dissociates. The dissociation of ammonia decreases when both the height of the bed and the gas flow are linearly increased.

The gasification of carbon is described by eqn (11):

$$\ln(C_{begin}/C_{end}) = k_g t \qquad (11)$$

with C_{begin} the concentration of free C at the beginning of the gasification, C_{end} the concentration of free C at the end of the gasification, k_g the reaction rate constant and t the gasification time. By substitution in eqn (11) of data obtained from Table 2, for instance $C_{begin}/C_{end} = 10$ and $t = 10\,800$ s, a value of $2{\cdot}1 \times 10^{-4}\,s^{-1}$ is found for k_g at 1080°C and 1 bar.

5 Discussion

The calculated activation energy of the dissociation of NH_3 of 100 kJ/mol may be influenced by (Knudsen) gas diffusion. This indicates that the value of 100 kJ/mol is a minimum value. The observation that the dissociation of NH_3 is reduced with time can be explained by the removal of carbon, which decreases the surface area available for the dissociation, or by passivation of the surface of SiC. The observation that the dissociation of ammonia decreases when both the bed height and the residence time of the gas in the bed are linearly increased is probably due to less dissociation on the reactor wall and the SiC balls, because the residence time of the gas in the reactor is reduced. It seems likely that the reduced dissociation of ammonia on broken tablets is due to the influence of (Knudsen) gas diffusion on the reaction when whole tablets are used. Due to severe dissociation of ammonia, a large excess of NH_3 has to be used for the removal of carbon. This circumstance, together with the formation of HCN, which is a poison, will probably limit the application of carbon removal with ammonia on an industrial scale. The high nitrogen content in some of the samples after carbon removal is most likely due to the adsorption of nitrogen on the last traces of free carbon. This is indicated by the last experiment as given in Table 2. Here the sample contains neither free carbon nor nitrogen after removal of carbon. The estimated value for the gasification rate constant of pure carbon with NH_3 at 1 bar and 1080°C of $2{\cdot}1 \times 10^{-4}\,s^{-1}$ is of the same order as the gasification rate constant with steam.[13]

6 Conclusion

Carbon can be removed with ammonia, with formation of HCN. Dissociation of NH_3 occurs simultaneously on both the surface of carbon and the matrix material. This will limit the application of the removal of carbon with ammonia. For some materials, for instance AlN, this method may be of interest because the material is improved, due to the conversion of traces of oxides to (oxy)nitrides.

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