Article

Corrosion of Stainless Steel by Urea at High Temperature

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Abstract: The corrosion mechanism of stainless steel caused by high temperature decomposition of aqueous urea solution has been investigated. The relationship between aqueous urea solution, its thermal decomposition products and the corrosion mechanism of stainless steel is studied by FTIR spectroscopy, SEM and stereo microscopy. The corroded steel samples, together with deposits, were obtained from the injection of aqueous urea solution on the steel plate at high temperatures. Uniform corrosion underneath the deposits was proposed as the main driver for corrosion of the steel samples. At the crevices, corrosion due to the used geometry and due to high temperature cycling could play an acceleration role as well.

Keywords: stainless steel; urea; biuret; cyanuric acid; ammelide; melamine; uniform corrosion

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1. Introduction

The corrosion of stainless steel by hot urea solution has not been largely studied; on the one hand, this may be due to the limited industrial demand, on the other hand, urea itself is considered as non-corrosive for stainless steel, while some of its decomposition products at high temperature may lead to corrosion [1–3].

Research work on corrosion involving urea mainly belongs to urea production, the fertilizer industry, and selective catalytic reduction (SCR) technology [2,4]. For example, during the manufacturing of urea under high pressure, the most critical intermediate step leading to corrosion is the formation of ammonium carbonate by-product [2,5]. In the fertilizer industry, urea is used as a source of nitrogen in the products, causing some corrosion problems [2,6]. In SCR technology, urea is used as a source of ammonia to reduce the amount of NO_x exhaust gases in automotive systems. The corrosion mechanism in urea-related technology was explained in several ways; one such way was cyclic oxidation caused by thermal cycling [7], and another—external corrosion by road salts [8,9]. Additionally, the effect of acidic condensate with chlorides and active carbon at low temperatures was mentioned [2,10,11]. Besides this, there are studies on melamine, ammonia, nitrogen and g-C₃N₄ (all of them exist during urea decomposition process) reactions with metal oxides, which attract attention as nitrifying and carburization reagents [12–14]. However, more generally, it is concluded that the cracking and fracturing of metal is related to urea decomposition products and intergranular attack [2,4,14–18]. By many scientists, an intergranular corrosion mechanism, sometimes attributed to chromium depletion, and nitride precipitation at grain boundaries, and sometimes without any indication of decrease or increase in the amount of chromium at grain boundaries, was described [4,19,20].

During the desired decomposition of urea at temperatures above 130 °C, some undesired parallel and equilibrium intermediates and by-products in liquid, solid and gaseous

form are produced [21]. From the literature data, more than 23 possible reactions, including urea and its numerous by-products, biuret, cyanuric acid, ammelide, ammeline, melamine and others, exist [22]. In the whole reaction scheme, isocyanic acid has been found to play a major role [22,23]. Nonetheless, it evaporates at 23.5 °C, reactions occurring at temperatures exceeding 133 °C were formulated in the condensed phase [24].

At room temperature, urea is a white crystalline substance. At 133 °C, urea starts to melt and, in the range of 140–180 °C, it gradually decomposes to isocyanic acid (H-NCO (l [23]/g [24])) and ammonia (NH_3 g [23]). Obtained isocyanic acid slowly decomposes with a catalyst into NH_3 and CO_2 . If heating is not very intensive, the highly reactive isocyanic acid may form with undecomposed urea biuret or triuret with ammonia [24]. According to another theory, biuret and triuret are formed from ions NH_4^+ and OCN^- [24,25], a so-called self-recombination of urea.

Some theories about phase transformations of biuret in the range of 190 and 250 °C exist. According to [24], urea and biuret form an eutectic mixture, where biuret has two melting points. At 193 °C, biuret starts to melt and decompose. At around 210 °C, the decomposition slows down, where biuret becomes a solid and, presumably, there is no longer liquid urea present. At this stage, the solid triuret is formed, which then reacts further to form solid deposits of cyanuric acid and ammelide. Triuret is known as a highly unstable substance (stable up to 192 °C, but literature data are insufficient). As seen for triuret, one cannot look at the decomposition of one substance independently. One always has to keep in mind the thermodynamic ensemble consisting of isocyanic acid, urea, biuret and triuret [24]. At 230 °C, the second decomposition step of biuret takes place, where biuret becomes liquid again [22–24].

There are also some theories about the decomposition of cyanuric acid. Thus, solid cyanuric acid may transfer directly into the gaseous phase during evaporation [24] or gaseous cyanic acid [23].

The remaining solid substances, ammelide, ammeline, and melamine, gradually decompose by numerous reactions at higher temperatures, around 360–400 °C [24]. For example, melamine forms during heating the following products: melam, melem, melon and graphitic carbon nitride $\text{g-C}_3\text{N}_4$ [12].

The overall reaction scheme (Figure 1) is much simpler than described, but it is necessary to note that the reaction sequence is not completely understood yet.

Figure 1. Scheme of aqueous urea decomposition under heating [22–24].

In this study, we investigate which step(s) of the urea decomposition process plays a role in the corrosion of stainless steel. For this purpose, we analyse all corresponding decomposition products, which exist in the solid, liquid and gaseous state and correlate with temperature and pH value at which they may lead to uniform corrosion. To test the chemical composition of solid deposits, we use the spectroscopic method FTIR (Fourier-transform infrared spectroscopy). While for corroded steel samples, we do a visual microscopic examination of the attacked area by SEM (scanning electron microscopy). Additionally, the presence of precipitates on grain boundaries is investigated to verify the origin of intergranular corrosion by nitridation or carburization.

2. Materials and Methods

2.1. Materials

The corrosion experiment was conducted with a sample made of the highly alloyed ferritic grade 1.4509. The microstructure is purely ferritic with a fine grain size between 10 and 30 μm . The chemical composition is shown in Table 1.

Table 1. Chemical composition of steel sample. All data in mass percentage.

EN	AISI	Fe	C	Si	Mn	Cr	Ni	Mo	Nb	Ti	P	S
1.4509	441	Bal.	0.017	1.0	1.0	17.990	0.233	0.075	0.391	0.115	0.040	0.015

2.2. Corrosion Testing

The corroded steel sample, together with deposits, was obtained from an experimental test bench where the injection of aqueous urea solution (32.5% urea and 67.5% deionized water, AdBlue, AVIA AG, München, Germany) on the steel plate at high temperatures for different times took place. The test track and sample are shown in Figure 2. The gas (air) mass flow and temperature together with solution injection rate and frequency can be varied. As can be seen in the scheme, the solution injector is located right in front of the sample. The area with a sample is covered with a high-temperature resistant glass window to allow for the visual observation of the experiment.

Figure 2. Schematic illustration: 1—test track, 2—test sample, 3—injection system, 4—monitoring window, 5—mass flow direction.

In Figure 3, on the left side a graphical representation of the test cycle is shown. The duration of one cycle is one hour. After estimation, a total test time of 100 h (meaning 100 cycles) was specified for the corrosion experiment. In Figure 3, on the right side the test specimen during the experiment is shown. In the red highlighted area, a sample surface during the high temperature phase (600 $^{\circ}\text{C}$) is shown. Afterwards, the temperature and mass flow of injected urea solution is changed, where the formation and decomposition of urea-related deposits take place (orange marked image). On both images, one may see a sign of former electrolyte flow (visible in grey colour). The difference between the images, is a formed deposit shown inside the dashed green circle. Due to cyclic loading, a more harmful corrosive effect was found when compared to isothermal tests [4].

Figure 3. Graphic representation of the test cycle for the corrosion experiment.

For the understanding of the relationship between the chemical composition of deposits and heating temperature, a set of six experiments on isothermal heating of injected aqueous urea solution was performed. For this purpose, each experiment was carried out at a strongly defined temperature of the airflow in the chamber. Besides the temperature of the airflow, the temperature of the steel sample was measured by installed thermocouples, both temperatures are listed in Table 2. For understanding the chemical composition of the product (s) related to corrosion of stainless steel, the cyclic heating of injected urea solution was performed (sample C, Table 2). Throughout the text, all deposit samples are labelled with the short names, given in Table 2. For example, in the sample index, I-110, the letter I means isothermal heating, the number 110 means the temperature of the deposit collected during heating at 200 °C air flow in the closed chamber.

Table 2. Summary of deposit samples.

Sample Index	T _{sample} , °C	T _{air} , °C	Test Duration
I-110	110	200	10 min
I-181	181	250	10 min
I-208	208	300	10 min
I-258	258	350	10 min
I-301	301	375	10 min
I-322	322	400	10 min
C	cyclic heating	cyclic heating	100 h

2.3. Characterization Methods

The cross-section morphology of the corroded sample was analysed by scanning electron microscopy (SEM/EVO MA 25, Carl Zeiss SMT, Oberkochen, Germany) coupled with energy dispersive X-ray spectrometry (EDX/X-ACT10, Oxford Instruments NanoAnalysis, Bucks, UK). The EDX point analysis was performed with the interaction volume of 1 µm. After the experiment, two steel parts were cleaned from deposits and carefully separated from each other. Before cross-section analysis, the corroded specimen of defined geometry was cut out of the baseplate along the dashed line shown in Figure 4b. A polished cross-section was prepared and investigated in the direction shown with arrows in Figure 4b. An ion slicer (IM4000+, Hitachi High-Technologies Europe GmbH, Krefeld, Germany) was used for the final polishing of samples before SEM analysis (visible on a specimen in Figure 5a).

Figure 4. Macro- and microscopic images of corroded specimen after 100 h, 1.4509 grade (cleaned from deposits). (a) macroscopic image, (b) microscopic image.

Figure 5. SEM image of corroded specimen after 100 h, 1.4509 grade ((a–d,f) (SE detector), (e) (BS detector): different magnification).

The chemical composition of deposits and reference materials was characterized with an FTIR spectrometer (Bruker VERTEX 70, Billerica, MA, USA) equipped with a Diamond ATR (attenuated total reflection) unit. The prepared specimens were measured in the

transmission mode in the wavelength range $4000\text{--}400\text{ cm}^{-1}$, resolution: 0.4 cm^{-1} . Urea, biuret, cyanuric acid, ammeline, ammeline and melamine were used as reference materials.

The structure of the deposits was examined by stereomicroscope (Olympus SZX12, Vienna, Austria).

3. Results

3.1. Characterization of Corroded Specimen 1.4509 Grade 100 h

After 100 h of cyclic heating and injection of aqueous urea solution on the steel plate, the material shows a differently coloured, oxidized surface. The material loss is localized in the crevice where two design parts were in contact (Figure 4a,b). There are also areas between two design parts, where no material loss was found, probably due to a narrower crevice between them.

The cross-section morphology of the attacked zone is shown in detail in Figure 5. In Figure 5a, the yellow dashed line shows the boundary of the sample surface, which was prepared by argon ion for the SEM investigation, and the white dashed line shows the sample area selected for the detailed SEM analysis under higher magnification. SEM images taken with the SE-detector show attack along grain boundaries as well as uniformly. In some case, the grains are almost completely exposed. The chemical element analysis of the grain boundaries' area near the occurred cracking was investigated by EDX-technique (area of analysis is shown by black dashed line in Figure 5d). Neither signs of nitrogen nor any precipitation of chromium-rich phases at the grain boundaries were observed. In contrast, numerous large precipitates visible not just on the grain boundaries, but also in the grains, were identified by EDX-technique as primary precipitates $\text{Ti}(\text{C}, \text{N})$ and $\text{Nb}(\text{C}, \text{N})$ originating from the steel manufacturing process. Besides the intergranular cracking, the exposed grains indicate a dissolving type of attack, which is typical for uniform corrosion.

3.2. Deposit Analysis

The identification of obtained deposits was done using the FTIR technique. FTIR spectra were recorded with emphasis on primary and secondary amide, primary amine and triazine absorption bands (Figures 6–10).

Figure 6. FTIR spectra of deposit I-110 and I-181 obtained at $T_{\text{air}} = 200\text{ }^{\circ}\text{C}$ ($T_{\text{sample}} = 110\text{ }^{\circ}\text{C}$) and $T_{\text{air}} = 250$ ($T_{\text{sample}} = 181\text{ }^{\circ}\text{C}$), correspondingly.

Figure 7. FTIR spectra of deposits I-181, I-208 and I-258 obtained at $T_{\text{air}} = 250\text{ }^{\circ}\text{C}$ ($T_{\text{sample}} = 181\text{ }^{\circ}\text{C}$), $T_{\text{air}} = 300\text{ }^{\circ}\text{C}$ ($T_{\text{sample}} = 208\text{ }^{\circ}\text{C}$) and $T_{\text{air}} = 350\text{ }^{\circ}\text{C}$ ($T_{\text{sample}} = 258\text{ }^{\circ}\text{C}$), respectively.

Figure 8. FTIR spectra of deposits I-301 and I-322 obtained at $T_{\text{air}} = 375\text{ }^{\circ}\text{C}$ ($T_{\text{sample}} = 301\text{ }^{\circ}\text{C}$) and $T_{\text{air}} = 400\text{ }^{\circ}\text{C}$ ($T_{\text{sample}} = 322\text{ }^{\circ}\text{C}$) correspondingly.

Figure 9. FTIR spectra of deposit C obtained after 100 h cyclic heating and urea injection.

Figure 10. FTIR spectra of reference materials.

3.2.1. Ten-Minute Isothermal Heating of Injected Aqueous Urea Solution Comparison of FTIR Spectra of Deposits I-110 and I-181

The FTIR spectrum of deposit I-110 shows a group of strong signals in the higher wavenumber region $3440\text{--}3200\text{ cm}^{-1}$ assigned to the N-H stretching band (Figure 6). The detected strong peak with shoulders at 1664 and 1588 cm^{-1} belongs to the C=O stretch vibration and NH_2 band; the last one was also found at 785 and 713 cm^{-1} . The observed strong peak at 1454 cm^{-1} and weak peak at 1057 cm^{-1} are responsible for the anti-symmetrical stretch C-N band, while a signal of medium intensity at 1153 could originate from the N-C-N band. Thus, all signals presented on spectrum I-110 belong to

characteristic groups of urea product, and this spectrum corresponds closely to that of the reference pure urea material (Figure 10).

Besides all signals presented in sample I-110, the spectrum I-181 contains some new signals that correspond to the reference pure biuret material. For example, two observed bands of medium intensity at 1731 and 1327 cm^{-1} correspondingly belong to C=O and C–N bands of secondary amides. Small peaks at 945, 785 and 713 cm^{-1} could be assigned to the NH_2 band. Hence, the composition of sample I-181 consists of urea and biuret as the main constituents.

Comparison of FTIR Spectra of Deposits I-208 and I-258

Spectra I-208 and I-258 in Figure 7 look relatively similar, but their comparison with spectrum I-181 revealed some differences. Firstly, a signal at 3254 cm^{-1} (N–H band) of deposit I-181 is not present in samples I-208 and I-258; instead, the new signal at 3175 cm^{-1} appeared nearby (N–H or C=O band). This is explained by the transformation of urea towards biuret and cyanuric acid, which is why sample I-181 contains the signal from urea, while samples I-208 and I-258 contain the signal from biuret and cyanuric acid. Secondly, the weak signal appears at 1778 cm^{-1} (C=O band) in spectrum I-258. Thirdly, the signal at 1587 cm^{-1} (NH_2 band) of sample I-181 has changed its shape when looking at samples I-208 and I-258, which both have two clear signals at 1615 cm^{-1} (C=O band) and 1556 cm^{-1} (NH_2 band), indicative for the formation of biuret and ammelide, respectively. Besides this, the weak absorbance band found at 1360 cm^{-1} in sample I-258, is probably responsible for the ammelide product.

Comparison of FTIR Spectra of Deposits I-301 and I-322

The FTIR spectrum of deposit I-301 in Figure 8 shows the strong absorbance at higher wavenumbers 3448, 3320 and 3184 cm^{-1} to be indicative for N–H vibration. The strong absorbance bands in the fingerprint region at 1778, 1732 and 1667 cm^{-1} originate from the C=O band. Two overlapped signals of strong intensity detected at 1593 and 1563 cm^{-1} and two medium signals at 763 and 699 cm^{-1} can be attributed to the NH_2 band. Five strong signals in the region 1456–1061 cm^{-1} are assigned to the C–N band. After the comparison of deposit I-301 with spectra from reference materials (Figure 10), a clear presence of biuret, ammelide and cyanuric acid in the sample can be observed. The spectrum, however, contained many overlapping signals, suggesting a lower content of biuret in comparison to ammelide and cyanuric acid.

The FTIR spectrum of deposit I-322 in Figure 8 looks similar to sample I-301, but a slight difference was still observed. The high wavenumber region 3500–3100 cm^{-1} results in minor differences in signal shape. Additionally, the fingerprint region at 1732–1333 cm^{-1} shows that sample I-301 has better separated, straight signals in comparison to overlapped signals of sample I-322. Additionally, unlike sample I-322, the deposit I-301 contains a signal at 830 cm^{-1} (cyanuric acid). Thus, the comparison of both samples, shows that sample I-301 contains more cyanuric acid by-product than deposit I-322.

3.2.2. One Hundred Hours Cyclic Heating and Injected Aqueous Urea Solution (Deposit Sample C)

The FTIR spectrum in Figure 9 shows a group of sharp strong overlapped signals in the region 1720–1644 cm^{-1} belonging to C=O stretching band. Two strong signals observed at 1455 and 1415 cm^{-1} are assigned to ring str band from triazine. Another strong sharp signal at 1179 cm^{-1} originated from a symmetric N–C–N stretching band. The signal with a shoulder detected at 773 cm^{-1} could belong to N–H or C=O band. The analysis of the spectrum revealed that deposit C contains mostly cyanuric acid and ammelide in its composition.

4. Discussion

Two types of experiments were performed in this research work. The main experiment was cyclic heating of a stainless steel sample under continued injection of aqueous urea

solution. One hundred cycles (1 cycle lasted one hour) in total were performed. During this experiment corrosive attack and deposits were obtained. The deposits were collected for identification of chemical composition by help of FTIR analysis. According to this analysis, the deposit obtained after 100h experiment mainly consists of cyanuric acid and ammelide products, the sample resembles a white powder with beige colour inclusions (Figure 9).

To understand the urea-decomposition reactions happening during different temperatures within one heating cycle, six short isothermal experiments were performed in addition to the main 100 h corrosion experiment. The IR results of 10 min heating experiment ($T_{\text{air}} = 200\text{ }^{\circ}\text{C}$), at which the collected deposit had a temperature of $110\text{ }^{\circ}\text{C}$, showed that the product consists of urea, this is in agreement with the colourless gel state of the sample I-110 (Table 3). At higher heating temperature ($T_{\text{air}} = 250\text{ }^{\circ}\text{C}$; $T_{\text{sample}} = 181\text{ }^{\circ}\text{C}$), the collected deposit I-181 has slightly changed its aggregate state to solidified gel and its colour became denser white (Table 3), which can be explained by the beginning of the urea decomposition process ($T_{\text{urea dec.}} = 133\text{ }^{\circ}\text{C}$ [22,26,27]) and formation of biuret product ($T_{\text{biuret form.}} = 150\text{ }^{\circ}\text{C}$ [22,27]). Sample I-208 obtained at $208\text{ }^{\circ}\text{C}$ ($T_{\text{air}} = 300\text{ }^{\circ}\text{C}$) as a white powder (Table 3) consisted mostly of biuret with a small amount of urea and cyanuric acid. At this stage, no liquid urea was present in the sample ($T_{\text{urea instable}} = 210\text{ }^{\circ}\text{C}$ [24]) and biuret reached its first decomposition step ($T_{\text{biuret 1st dec.}} = 193\text{ }^{\circ}\text{C}$ [22,24,27]), which is explained by the appearance of cyanuric acid. Sample I-258, heated at $T_{\text{air}} = 350\text{ }^{\circ}\text{C}$, has a milky colour and crystallized form (Table 3), which can happen when biuret has passed the second decomposition step ($T_{\text{biuret 2nd dec.}} = 230\text{ }^{\circ}\text{C}$ [24]) from solid into the liquid phase. The IR analysis confirmed this and showed the presence of thermally stable at this temperature ammelide ($T_{\text{ammelide form.}} = 250\text{ }^{\circ}\text{C}$ [22,27], $T_{\text{ammelide dec.}} = 360\text{--}410\text{ }^{\circ}\text{C}$ [22,24,26,27]) as the main product with a sign of ammeline ($T_{\text{ammeline form.}} = 250\text{ }^{\circ}\text{C}$ [22,27], $T_{\text{ammeline dec.}} = 360\text{--}430\text{ }^{\circ}\text{C}$ [22,24,27]). Deposit I-301, collected at $301\text{ }^{\circ}\text{C}$ ($T_{\text{air}} = 375\text{ }^{\circ}\text{C}$), was the first sample of beige colour (powder-crystalline) (Table 3), which is confirmed by the detection of cyanuric acid (it has a characteristic beige colour) besides ammelide. The last sample, I-322, from the isothermal set obtained at $T_{\text{sample}} = 322\text{ }^{\circ}\text{C}$ ($T_{\text{air}} = 400\text{ }^{\circ}\text{C}$), has a milkier colour than the beige sample I-301 (Table 3) because the cyanuric acid was decomposed until gaseous products ($T_{\text{cyanuric acid dec.}} = 320\text{--}330\text{ }^{\circ}\text{C}$ [22,27]) and ammelide could be directly obtained from biuret or cyanuric acid. Thus, sample I-322 consists of ammelide and contains less cyanuric acid in comparison to sample I-301.

Metallographic analysis of the stainless steel sample corroded during 100 h of cyclic heating and injection of aqueous urea solution revealed a mixed type of corrosion. Intergranular corrosion favoured at the crevice area could not be confirmed due to the absence of chromium depletion or enrichment and any nitride or carbide precipitates. Partially and completely exposed grains could indicate a dissolving character of attack typical for uniform corrosion. It could be assumed that urea-related products were likely to accumulate at the crevice supported by its cavity, where several chemical reactions could be responsible for the dissolution of the oxide layer and base metal. Thus, uniform corrosion underneath the deposits is assumed to be the main cause of the attack. Generally, to obtain uniform corrosion at these temperatures, two types of conditions are required, a low pH value and the presence of an electrolyte. After reviewing all chemical transitions happening during urea decomposition in the heating cycle, the liquid phase of biuret ($T_{\text{biuret 2nd dec.}} = 230\text{ }^{\circ}\text{C}$ [24]) and constant humidity were found to play a role of the electrolyte necessary for uniform corrosion. The regular injection of aqueous urea solution and release of water molecule during most of the chemical transitions are assumed to be the source of high constant humidity in the experiment. The dissolved cyanuric acid deposit ($\text{pH} = 3.8$) and/or gaseous isocyanic acid ($\text{pH} = 3.7$) may continuously decrease the pH value in the cavity. The cyanuric acid is one of the main products of the deposit mixture obtained after 100 h cycle experiment; the cyanic acid is consumed and released during one pathway of urea thermal decomposition.

Besides uniform corrosion, found here on a large scale, a certain preferential attack along grain boundaries was observed. On the one side, it could be a notice of not confirmed

intergranular corrosion. Although the inspection of grain boundaries for the presence of nitrides and carbides under high resolution did not reveal any precipitates, this hypothesis is not fully excluded yet. There are some studies, where g-C₃N₄, NH₃, N₂ and melamine are used as nitrifying and carburization reagents to convert metal oxides into nitride and carbide nanoparticles at high temperatures [12,13]. On the other hand, the regular attack, which may be associated with some cracking, could be the result of cyclic heating and cooling.

Table 3. Characterisation of deposit samples from the isothermal experiment.

Sample Index	T _{sample} , °C	T _{air} , °C	FTIR Results		Deposit Image
			Main Product	Minor Product	
I-110	110	200	urea
I-181	181	250	urea, biuret
I-208	208	300	biuret	Urea, cyanuric acid
I-258	258	350	ammelide	urea, biuret, cyanuric acid, ammeline
I-301	301	375	cyanuric acid, ammelide	melamine, ammeline
I-322	322	400	cyanuric acid, ammelide	biuret

5. Conclusions

After 100 h cyclic heating and injection of aqueous urea solution on the 1.4509 stainless steel, a uniform attack with some intergranular morphology was obtained. The grain boundary precipitates were either not present or extremely small. FTIR revealed the cyanuric acid as one of the main corrosive constituents. The temperatures with maximum

damage were found, where a liquid phase of biuret did present, which were around 193 °C (first decomposition step) and 230 °C (second decomposition step).

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