Sensitization behaviour of the nitrogen alloyed austenitic stainless steel X8CrMnMoN18-19-2

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Abstract. Austenitic stainless steels have been used in many different industrial branches. Nitrogen alloyed austenite’s with up to 20 wt. % manganese and 0.8 wt. % nitrogen have been available on the market as nickel-free grade for some years. In these steels, the austenitic matrix is stabilized without the addition of nickel, while the corrosive resistance and mechanical properties are significantly improved by addition of Mn and N. As with all stainless steels, the chemical composition and heat treatment have a decisive influence on structure, mechanical properties and corrosion resistance. Solution annealing, quenching and work hardening are applied to combine excellent mechanical properties (Rm from 900 MPa to 2,000 MPa, A5 > 50 %, AV > 350 J) with high corrosion resistance. Solution annealing is applied to eliminate undesired precipitation phases (Cr2N, M23C6 and sigma phase), distribute the alloy elements homogeneously in the austenite and assure the high corrosion resistance. If the distribution of the alloy elements (Cr, Mo and N) is impaired by suboptimal heat treatment, processing or high temperature conditions, the corrosion resistance can be reduced. Precise knowledge of the sensitization behaviour of these high nitrogen alloyed steels is necessary. Therefore, the sensitization behaviour of the nitrogen alloyed austenitic steel X8CrMnMoN18-19-2 (1.4456) was investigated by thermal ageing in the temperature rage of 500 °C to 900 °C for up to 100 h. Thermodynamic calculations were used to predict the formation of different phases. The microstructure of the various sensitization states was evaluated by scanning electron microscopy (SEM) and compared with the corrosion resistance characterized by the electrochemical potentiodynamic reactivation (EPR) test and the KorroPad method. The reduction of corrosion resistance is correlated with the occurrence of M23N nitrides in the microstructure and two sensitization diagrams were created based on the experimental results.

1 Introduction
Besides the widely used chromium-nickel austenitic stainless steels, there are promising alloying concept austenite’s stabilized with manganese and nitrogen. The substitution of Ni with Mn and N ensures the fcc (face-centered cubic) crystal structure, improves the corrosion resistance and the mechanical properties [1]. Nitrogen alloyed austenitic stainless steels with approx. 0.8 wt.% nitrogen offer an exceptional combination of corrosion resistance, strength and toughness [2-5]. In general, a homogeneous distribution of the alloying elements (especially Cr, Mo and N) in the austenitic matrix is of decisive importance for the formation of a stable passive layer and thus the corrosion resistance. The formation of precipitates (Cr2N, M23C6 and sigma phase) by selective ageing at elevated temperatures can be used not only for work-hardening but also for optimizing strength, while processing errors can
cause a significant reduction in corrosion resistance [1, 6-8]. When formed, chromium carbides and chromium nitrides locally reduce the chromium content of the surrounding matrix and decrease the corrosion resistance [6-10]. Despite the known theories on chromium depletion and precipitation formation of these steels, no systematic investigations have been carried out to date on different heat treatment conditions with regard to their specific corrosion resistance. Since the tendency to form chromium nitrides (Cr$_2$N) increases with the nitrogen content, see Figure 1, such characterization is essential for the safe use of these steels.

![Figure 1. Time-temperature-precipitation-diagram (TTT) for various nitrogen-alloyed austenitic stainless steels [11].](image)

The connection between sensitizing heat treatment, phase formation in the microstructure and corrosion resistance is investigated using the example of 1.4456 (X8CrMnMoN18-19-2) in order to enable future use in new technical areas and to initiate new impulses for their processing.

### 2 Material, heat treatment and methods

The nitrogen alloyed austenitic stainless steel 1.4456 (X8CrMnMoN18-19-2) was used for the investigations. The steel was produced by Energietechnik Essen GmbH using pressure electro-slag remelting. The chemical composition of the suited steel is presented in Table 1.

|    | C   | N   | Mn  | Cr  | Mo  | Ni  | Si  | V   | P   | S   |
|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1.4456 | 0.06 | 0.81 | 19.1 | 17.5 | 2.2 | 0.13 | 0.65 | 0.08 | 0.018 | 0.001 |

The phases occurring in thermodynamic equilibrium were calculated based on the chemical composition (Table 1) using the commercial software *ThermoCalc* (database TCFe7). These calculations were used to determine the solution heat treatment temperature (1150 °C) being necessary to dissolve all soluble phases and to select the temperature range for artificial ageing. Temperatures < 800 °C are used to characterize the precipitation dynamics during the simultaneous formation of the three precipitation phases (Cr$_2$N, M$_{23}$C$_6$ and sigma phase). Artificial aging at 900 °C only causes the formation of Cr$_2$N, which means that the influence of M$_{23}$C$_6$ and sigma phase is suppressed. Table 2 summarizes the temperature range for artificial ageing of 1.4456 (X8CrMnMoN18-19-2).
Table 2. Artificial ageing conditions of 1.4456 after solution heat treatment at 1150 °C for 15 min.

| Temperature (°C) | Time (min) | 1 min | 5 min | 10 min | 30 min | 1 h  | 2 h  | 4 h  | 8 h  |
|-----------------|------------|-------|-------|--------|--------|------|------|------|------|
| 900 °C          |            |       |       |        |        |      |      |      |      |
| 800 °C          |            |       |       |        |        |      |      |      |      |
| 700 °C          |            |       |       |        |        |      |      |      |      |
| 600 °C          |            |       |       |        |        |      |      |      |      |
| 500 °C          |            |       |       |        |        |      |      |      |      |

All samples were solution annealed at 1150 °C for 15 min and quenched in water prior to artificial ageing to ensure the dissolution of all precipitation phases and the homogeneous distribution of the alloying elements in the austenite. To characterise the microstructure, grinding, polishing and etching according to Beraha II (35 s) were performed and the microstructure was examined by scanning electron microscopy (SEM). The formation of precipitates as a result of the increasing artificial ageing time was thus detected microscopically and evaluated in relation to the results of the corrosion investigations.

The susceptibility to pitting corrosion of the various ageing conditions was characterized using the KorroPad method [8, 12-13]. The method was originally developed to detect an incompletely formed or unstable passive layer on the austenitic stainless steels X5CrNi18-10 (1.4301). The KorroPad is a water-based agar gel, which contains 3 wt.% agar, 1 mM potassium hexacyanoferrate III (K₃[Fe(CN)₆]) and 0.1 M sodium chloride (NaCl). The agar forms a gel matrix, which holds and immobilizes the electrolyte, while the K₃[Fe(CN)₆] causes the KorroPad to achieve a redox potential of up to +320 mV Ag/AgCl (measured on platinum) and is thus able to polarize the surface of a stainless steel up to 200 mV Ag/AgCl. In addition to the anodic polarization, the NaCl dissolved in the KorroPad also ensures that pitting corrosion is initiated and eventually stabilized.

The KorroPad is used for the detection and evaluation of conditions susceptible to pitting corrosion in stainless steels [13]. Prior to the test, the specimens were wet ground with 180 grit SiC abrasive paper and passivated for 24 h at a relative humidity of more than 95%. This enables the formation of a stable passive layer and ensures the comparability of the individual artificial ageing states. For the subsequent evaluation of the blue indication, the KorroPads were scanned, digitized and visually evaluated. Three typical appearances can be distinguished in the KorroPad test, which allow a comparative evaluation of the pitting corrosion resistance:

- no indication $\rightarrow$ stable passive layer $\rightarrow$ no pitting corrosion
- small indication $\rightarrow$ metastable pitting corrosion $\rightarrow$ low susceptibility to pitting corrosion
- large indication $\rightarrow$ stable pitting corrosion $\rightarrow$ high susceptibility to pitting corrosion

The sensitization behaviour was also investigated by electrochemical potentiodynamic reactivation (EPR test) to detect changes in the passivation and reactivation behaviour [7-8]. For this purpose, the samples were wet ground with 600 SiC abrasive paper to achieve an active state. A potentiostat was immediately anodically polarized wit 2 mV/s from -550 mV Ag/AgCl to +100 mV Ag/AgCl in 0.5 M sulfuric acid with 10 mM potassium thiocyanate as activator. The polarization direction was reversed at +100 mV Ag/AgCl and followed by reverse polarisation back to -550 mV Ag/AgCl with 2 mV/ to reactivate sensitized areas within the microstructure. With the EPR method, the passivation behaviour can be characterised by the maximum passivation current density and the passive layer stability by the maximum reactivation current density. These characteristic values provide information about the average alloy content of the matrix and the existence of chromium-depleted areas. A reactivation current density of more than 0.1 mA/cm² corresponds to sensitized states.
3 Results and discussion

Figure 2 shows the results of the thermodynamic equilibrium calculations with the *ThermoCalc* software. The calculations show that solution annealing at 1150 °C can dissolve all soluble phases (Cr$_2$N, sigma phase, M$_{23}$C$_6$ and M$_6$C) in the austenite and thus achieve a homogeneous initial state after water quenching. In the further course of the investigations, these calculations also serve as a basis for explaining changes in corrosion resistance during artificial ageing.

![Figure 2. Results of thermodynamic calculations with *ThermoCalc* for the stainless steel 1.4456 (X8CrMnMoN18-19-2).](image)

At artificial ageing temperatures < 800 °C all important precipitation phases (Cr$_2$N, M$_{23}$C$_6$ and sigma phase) can precipitate within the austenitic matrix. The calculations also show that at 900 °C only chromium nitrides are formed in the austenitic matrix. A comparison of the results at 700 °C and 900 °C makes it possible to evaluate the influence of Cr$_2$N on corrosion resistance. Figure 3 shows SEM images of three selected artificial ageing states at 700 °C. With increasing artificial ageing time, a clear occupation of the grain boundaries with small precipitates can be seen. Only after 5 min at 700 °C no precipitates are present in the austenitic matrix.

![Figure 3. SEM images of the microstructure as a function of the artificial ageing time at 700 °C: a) 5 min, b) 2 h and d) 8 h.](image)

Based on the thermodynamic calculations, the precipitates at the grain boundaries can be M$_{23}$C$_6$, Cr$_2$N or the sigma phase. The phases and phase fractions are too small for a local chemical analysis by energy dispersive X-ray radiation (EDX) or a phase analysis by X-ray diffraction. An exact identification would therefore only be possible by transmission electron microscopy (TEM). Whether the precipitates at the grain boundaries already have a detrimental effect on the pitting corrosion
resistance was subsequently investigated using the KorroPad test. The corresponding appearances after the KorroPad test are shown in Figure 4.

![Figure 4. KorroPad test of the 1.4456 as a function of artificial ageing at 700 °C: a) 5 min, b) 10 min, c) 30 min, d) 1 h, e) 2 h, f) 4 h.](image)

It can be clearly seen that even very short artificial ageing times of only 10 min at 700 °C cause increased susceptibility to pitting corrosion. The number of stable pitting corrosion indications tends to increase with the ageing period. The susceptibility to pitting corrosion correlates with the first occurrence of precipitation at 10 min. The further decrease in pitting corrosion resistance can be explained by the pronounced precipitation at the grain boundaries. The results of the EPR test are shown in Figure 5 using selected current density potential curves.

![Figure 5. EPR curves of 1.4456 after solution heat treatment and artificial ageing at 700 °C.](image)

An increasing reactivation loop is visible in the EPR curves with increasing ageing time at 700 °C. This proves that the precipitations at the grain boundaries lead to chromium depletion, which also explains the decreasing pitting corrosion resistance in the KorroPad test. The passivation current density remains constant because the average alloy content in the matrix hardly changes with increasing precipitation. The ability to form the passivation layer is therefore only affected locally at the grain boundaries. In correlation with the microstructural images in Figure 3, there is a direct correlation between the increasing phase content of the precipitates and the increasing chromium depletion. Artificial ageing of this nitrogen alloyed stainless steel destabilizes the passive layer.

Comparing the results of ageing at 700 °C and 900 °C is intended to clarify whether chromium nitrides are causing the reduction in corrosion resistance, since only chromium nitrides are formed at 900 °C, see Figure 2). The results of artificial ageing at 900 °C are presented in the following figures. Figure 6 shows the microstructure after artificial ageing at 900 °C. Cr$_2$N precipitation can already be observed after 30 minutes of artificial ageing at the grain boundaries. The phase content of these lamellar nitrides increases with the ageing time. In comparison to the ageing at 700 °C, large parts of the microstructure show perlite-like precipitation of Cr$_2$N within whole grains.
Figure 6. Microstructure of 1.4456 as a function of the artificial ageing time at 900 °C:
  a) 30 min, b) 1 h and c) 8 h.

The susceptibility to pitting corrosion was also investigated with the KorroPad test in dependence on the time of artificial ageing at 900 °C, see Figure 7. Despite the formation of Cr2N precipitates at 900 °C, no reduction in pitting corrosion resistance can be detected by the KorroPad method. The strong decrease in pitting resistance at 700 °C is therefore not primarily due to the formation of Cr2N. However, this does not mean that the chromium nitrides do not have a damaging effect on the corrosion resistance in more severe test conditions.

Figure 7. KorroPad test on 1.4456 as a function of artificial ageing at 900 °C:
  a) 5 min, b) 10 min, c) 30 min, d) 1 h, e) 2 h, f) 4 h.

The results of the EPR test regarding sensitization did not show any reactivation due to artificial ageing at 900 °C, see Figure 8. Despite the high content of chromium bond in the nitrides and their lamellar morphology, there is no detectable chromium depletion.

Figure 8. EPR curves of 1.4456 after solution heat treatment and artificial ageing at 900 °C.
At 8 h artificial ageing time, only a slight increase in the passivation current density is visible, which can be explained by the chromium bond in the Cr₂N phase. In the context of processing these steels and the hardening effect of the chromium nitrides, artificial ageing at 900 °C offers interesting application potential with regard to corrosion resistance.

Finally, the results of all artificial ageing conditions were used to specify the sensitization behaviour of the nitrogen alloyed steel 1.4456 on the basis of the KorroPad method and the EPR test, see Figure 9. It is noticeable that artificial ageing at 500 °C and 600 °C does not cause stable pitting corrosion. This can be attributed to too short ageing times or too low diffusion rates at these low temperatures. Artificial ageing at 700 °C and 800 °C proves detrimental to the corrosion resistance due to the fact that stable pitting corrosion sets in after only 10 min and 40 min, respectively. The EPR process also shows chromium depletion only in this temperature range. The KorroPad test is therefore much more sensitive in detecting silently corrosion-prone conditions. Artificial ageing at 900 °C, on the other hand, is not as critical as 700 °C and 800 °C since only metastable indications occur even after 8 hours of artificial ageing.

Figure 9. Sensitization diagrams of the nitrogen alloyed austenitic stainless steel 1.4456 (X8CrMnMoN18-19-2) based on the results of: a) the KorroPad method and b) the EPR test.

4 Conclusions
The sensitization behaviour of the nitrogen-alloyed austenitic, stainless steel X8CrMnMoN18-19-2 was investigated as a function of the artificial ageing treatment. The EPR (electrochemical potentiodynamic reactivation) test and the KorroPad method were used to demonstrate the effect of precipitation at different temperatures. The KorroPad method was more sensitive to the precipitation-related reduction of corrosion resistance compared to the EPR method, so that a susceptibility to corrosion was detectable at shorter artificial ageing times. Using the EPR test, significant chromium depletion (Iₖ ≥ 0.1 mA/cm²) could only be detected for five conditions in the temperature range of 700 °C and 800 °C. The general trend visible in the results of the KorroPad method was confirmed with the results of the EPR test. No sensitization was detected at 500 °C and 600 °C due to the low diffusion rate and the limited ageing times.

No increased susceptibility to corrosion could be detected at 900 °C as well. This is quite remarkable, since chromium nitrides precipitate at the grain boundaries and growth within the austenitic grains. However, this does not impair the corrosion resistance. This may lead to the assumption that the susceptibility at 700 °C and 800 °C was not caused by chromium nitrides and the formation of chromium carbides may be the decisive effect. The reason why the chromium-rich nitrides (approx. 80 wt.% chromium) do not cause chromium depletion is still to be clarified. One possibility is that the diffusion of chromium at 900 °C is faster than the consumption of chromium by the formation of chromium nitrides. Another possibility is that molybdenum is not incorporated into chromium nitrides. This means
that molybdenum compensates the local depletion of chromium to such an extent that no detectable susceptibility to corrosion occurs.

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