High Temperature Corrosion of Anchor Systems for Refractory Constructions at Different Atmospheres and Temperatures

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High temperature corrosion decisively influences the durability of anchorage systems in refractory constructions. Various alloying elements, for example nickel and chromium, react differently at distinctive atmospheres; consequently, the proper chemical composition is important for the durability of the construction. Five different materials, which are used as refractories, have been tested and compared with respect to their corrosive properties in reducing, nitriding, carborizing, sulfidizing/oxidizing, and chlorinating media at distinctive temperatures and times of deposition. The metallographic pictures of the withdrawn assays are compared in order to evaluate the stage of corrosion. The materials are finally rated for their suitability in the according medium.
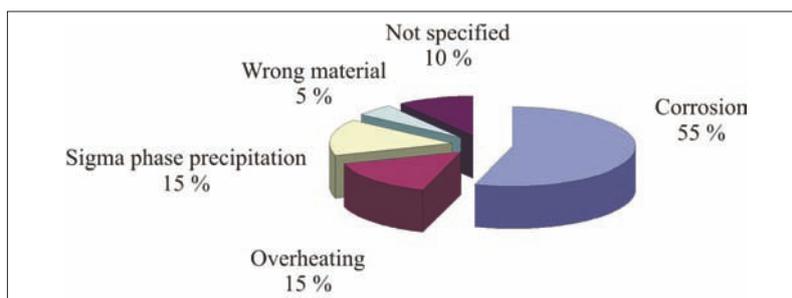
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Fig. 1 Reasons for plant failures [1]

1 Introduction

Highly heat resisting and high-alloyed steels, as well as nickel-based alloys are used for building chemical and metallurgic plants. These materials are used in anchorages and refractory constructions, where high temperatures occur.

Within these areas, the metal components are prone to chemical reactions, since the media are not clear of aggressive elements. In case of failure the refractory breaks out of the construction. A *DGFS* survey asked users of said plants for the reasons of failure (Fig. 1).

Only 20 % of the failures were caused by either too high temperatures or unknown reasons. Almost ¾ of the failures occurred due to corrosion (55 %) or embrittlement (15 %) respectively. Only 5 % of the damages were caused, by selecting the wrong material. This requires an appropriate evaluation of the material reaction within corrosive processes, as well as a more accurate appraisal of the plants by their users. The aim of this research project was hence to characterize the reaction of different high-alloy materials at critical atmospheres, and to guarantee a more efficient use of these materials.

The atmospheres had reducing (H_2), nitriding (N_2), sulfidizing/oxidizing (SO_2), carborizing (CO), and chlorinating (Cl_2) characteristics. The influence of but one atmosphere was considered during each test run.

With respect to the expected reactions at a reducing atmosphere, the selected gas mix-

ture has only an average influence on the material. Stronger effects may be reached in the field.

Nitrides are the reaction products of an alloy at a nitriding atmosphere. The material may embrittle in higher concentrations of nitride and cause a mechanical failure.

Sulfides and oxides are formed simultaneously during corrosion caused by sulfur dioxide. Chromium bears an affinity towards sulfur, which is similar to that towards oxygen; it therefore has good protective characteristics. However, the eutectic Ni/Ni_3N_2 is formed at high nickel concentrations. This eutectic melts at 640 °C and may cause a failure due to local fusing. A similar iron-sulfur eutectic is formed at temperatures slightly below 1000 °C. Silicium may be amalgamated in order to prevent sulfur from penetrating the matrix; like chromium, it contributes to building a protective oxide layer.

Alloys shape carbides and oxides under the influence of CO. During the reaction, oxygen remains in the form of oxides on the surface and shapes a porous layer. The remaining carbon diffuses into the material, where it forms carbide dispositions. Like nitrides, these carbides are unwanted, as they lead to an embrittlement and consequently downgrade the mechanical properties. Chromium-carbides are primarily shaped, which decrease the protective properties of the material. Chromium forms $M_{23}C_6$ carbides; a small amount of carbon hence binds a large

portion of chromium and cannot contribute to the prevention of corrosion.

Chlorine attacking an alloy leads to forming metal chlorides. Especially iron converts rapidly into ferric-(III)-chloride ($FeCl_3$). Nickel-(II)-chlorides ($NiCl_2$) and chromium-(III)-chlorides ($CrCl_3$) are shaped the same way. Since these chlorides bear very low vapour pressures, they considerably start evaporating at very low temperatures (120 °C for $FeCl_3$); the material dissolves and the supporting cross-section is heavily weakened within a short period of time. Chlorine also dissolves the protecting oxide layers, even if the partial pressure of oxygen is low enough in this atmosphere. The material loses alloy elements, which additionally weakens its self protecting properties.

2 Experimental set-up

Four steel grades (1.4828, 1.4845, 1.4862, and 1.4864) and one nickel-based alloy (2.4851) are used within the tests. After being solution-heat-treated, all materials were tested in the form of wires with a diameter of 8 mm.

The initial state of the materials is documented in Fig. 2. A face-centred cubic (austenitic) structure in the core and the external constituted all materials, caused by the high nickel concentration. All pictures show titanium nitrides which formed during the process. Well dispersed carbides can be sporadically found in both areas.

The influence of the gas was checked during each test run. The gas concentrations of sulfur dioxide, carbon monoxide and chlorine were compared to those of stack gas in an incinerator (Tab. 2).
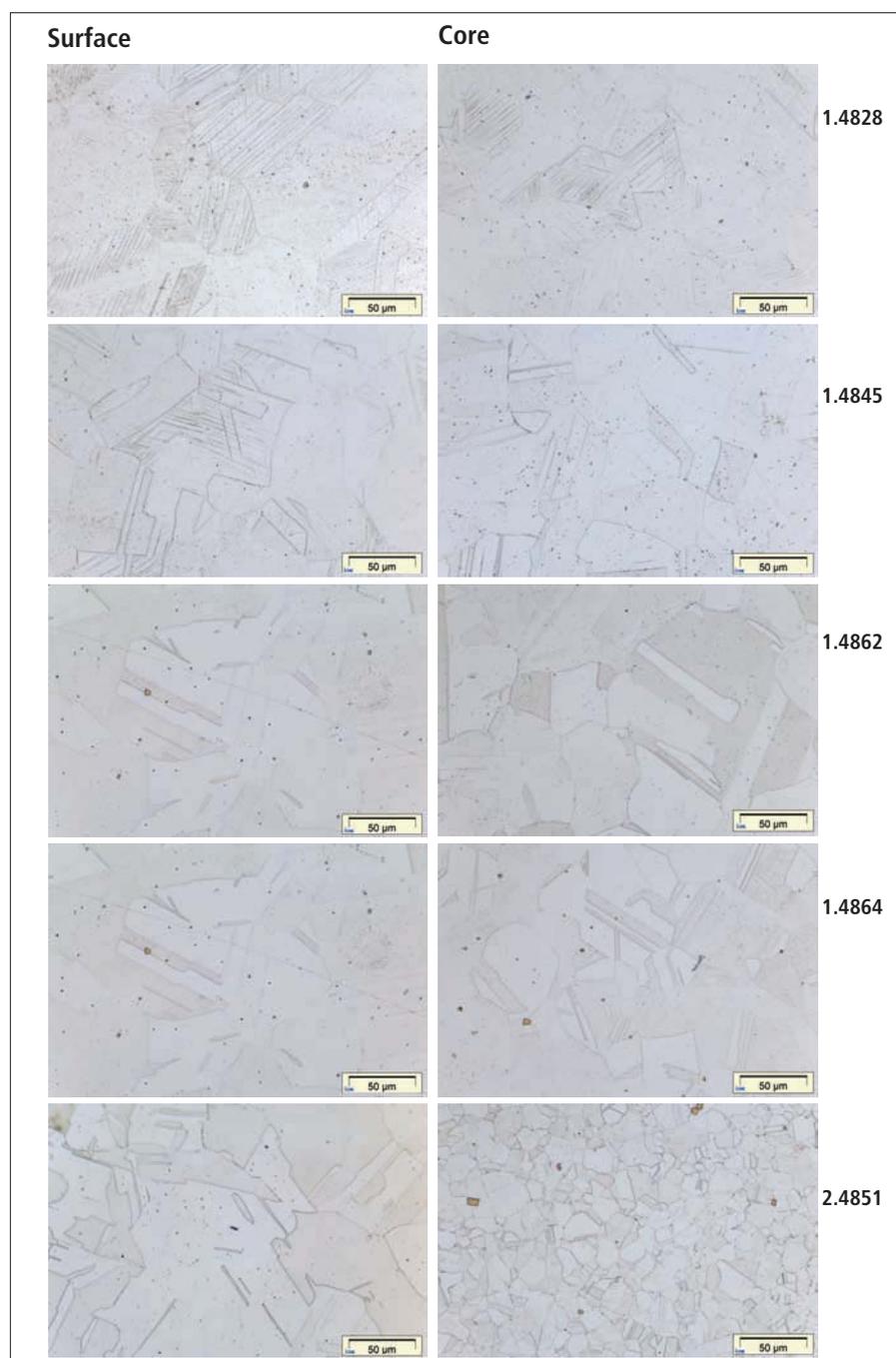
Tab. 1 The chemical compositions of the used materials [mass-%]

	Fe	Ni	Cr	C	Si	Mn	P	S
1.4828	Rest	11,0 –13,0	19,0 – 21,0	≤ 0,20	1,50 –2,50	≤ 2,00	≤ 0,045	≤ 0,015
1.4845[1] (Alloy 310H)	Rest	19,0 – 22,0	24,0 – 26,0	≤ 0,10	≤ 0,75	≤ 2,00	≤ 0,045	≤ 0,015
1.4862	Rest	35,0 – 39,0	17,0 – 19,0	≤ 0,10	1,50 –2,50	0,80 –1,50	≤ 0,030	≤ 0,030
1.4864	Rest	33,0 – 37,0	15,0 – 17,0	≤ 0,15	1,00 –2,00	≤ 2,00	≤ 0,045	≤ 0,015
2.4851	≤ 18,0	Rest	21,0 – 25,0	0,03 – 0,10	≤ 0,50	≤ 1,00	≤ 0,020	≤ 0,020

[1] The steel grade 1.4845 has been used in the modified version Alloy 310H; its silicon concentration of Si < 0,75 differs from specification DIN EN 10027-2

Tab. 2 Gas compositions and their effects

Gas composition	Effect
6 vol.-% H_2, rest Ar	reducing
95 vol.-% N_2, 5 Vol.-% H_2	nitriding
2500 ppmv SO_2, rest Ar	sulphidizing / oxidizing
1600 ppmv CO, rest Ar	carborizing
1000 ppmv Cl_2, rest Ar	chlorinating

Fig. 2 The initial state of the tested materials under the optical microscope; grinded and etched, 500x
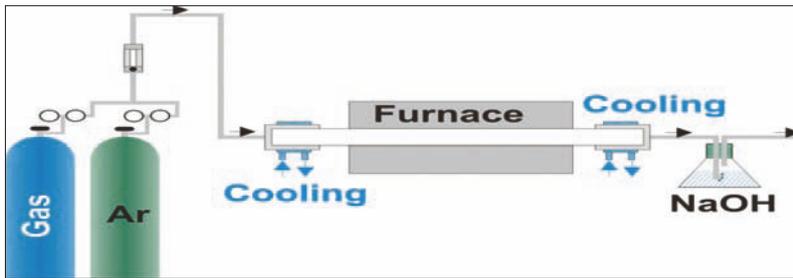
Fig. 3 Experimental set-up for the annealing tests in reactive atmospheres

The tests took place in two different furnaces; one was equipped with a steel tube for the less aggres-sive media, the other one with a fused glass tube for the sulfidizing and chlorinating atmospheres. Fig. 3 represents the experiment set-up. The assays are placed in the centre of the furnace through which inert gas (argon) passes during the heat-up phase. Once the set temperature is reached, the reactive gas composition streams through the furnace with a volume flow of 8 liters/h. The flow is regulated by an area flow meter. The reactive components (SO_2 or Cl_2) are elutriated with an alkaline dissolution. The system cools down, and the furnace is rinsed with argon.

The alloys were intercalated for 10, 50, and 200 h. The process of the chemical reactions was checked at 400 °C, 700 °C, and 1000 °C respectively. The atmosphere was free of oxygen and water.

Afterwards pictures were taken by means of an optical microscope (LOM), as well as – for some tests – by a microprobe at the *Institute for Electronic Microscopy* (GFE) of University RWTH Aachen. The
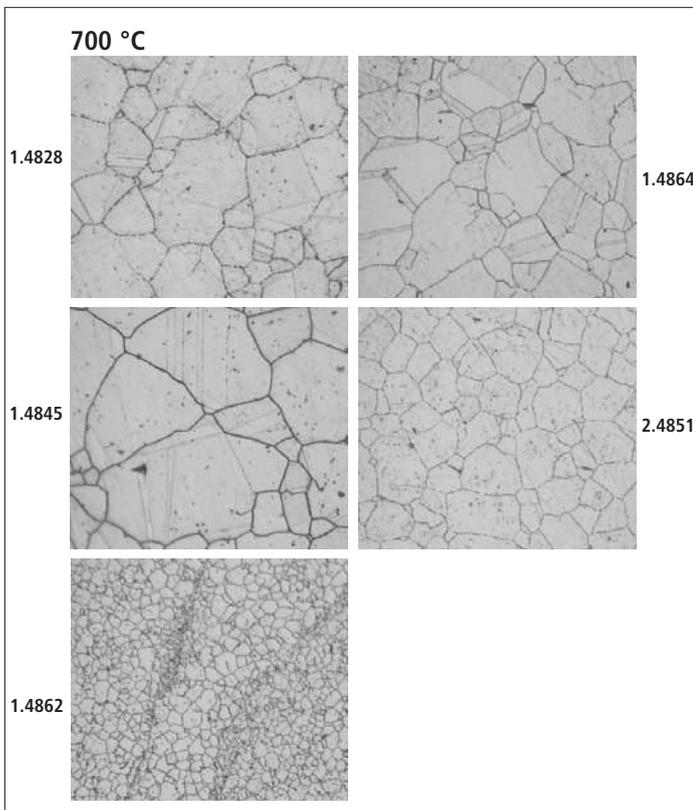

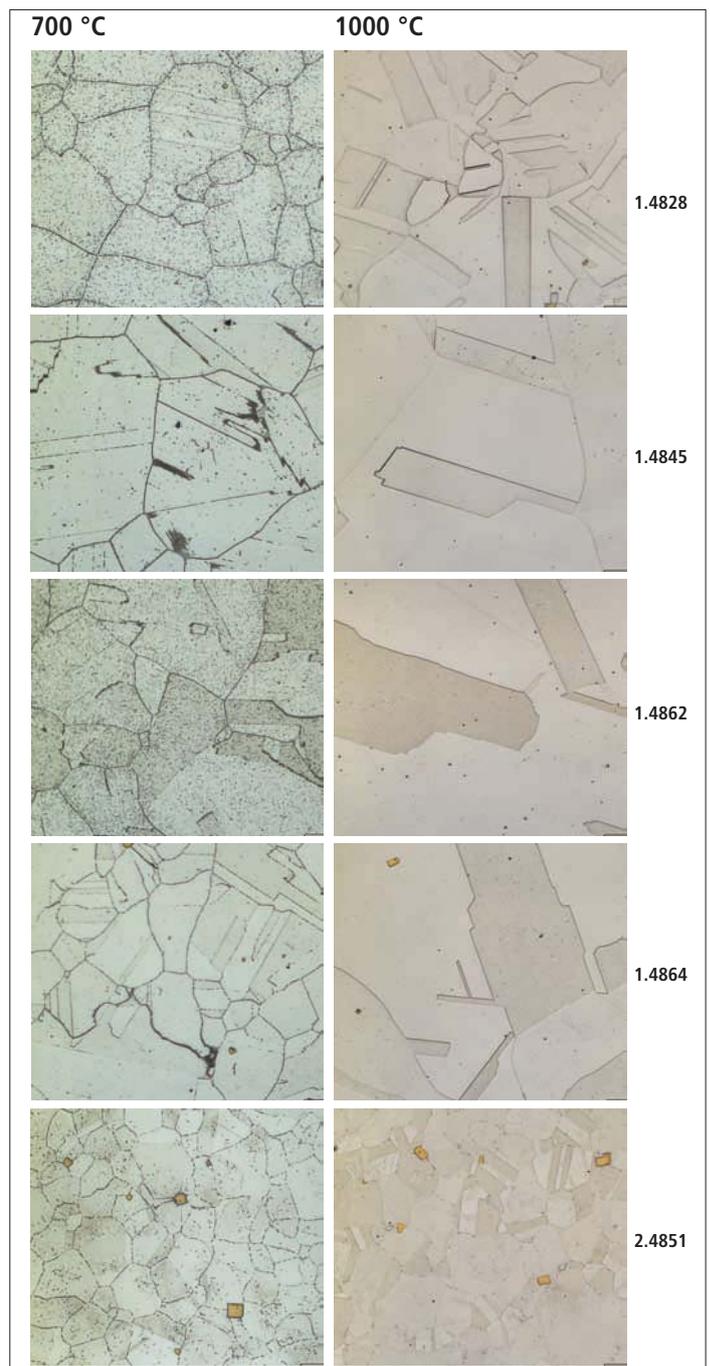**Fig. 4 Results at a reducing atmosphere for 100 h, LOM, 500x**

Fig. 5 Results at a nitriding atmosphere for 200 h at 700 °C and 1000 °C respectively; LOM, 500x
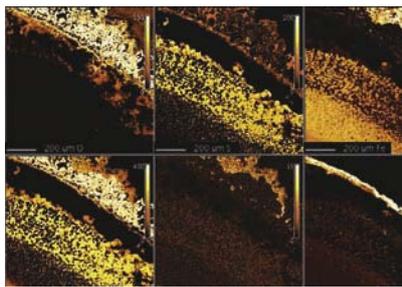
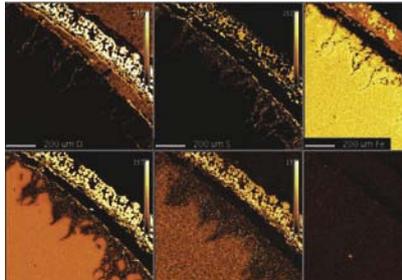**Fig. 6** Material 2.4851, 200 h, 1000 °C, SO_2, microprobe
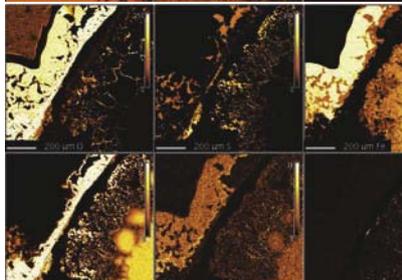

Fig. 7 Material 1.4864, 200 h, 1000 °C, SO_2, microprobe

Fig. 8 Material 1.4862, 200 h, 1000 °C, SO_2, microprobe
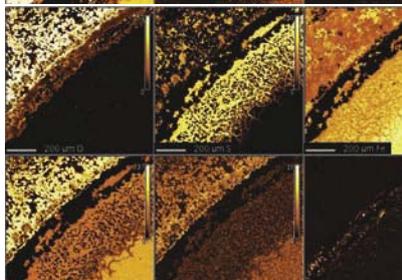

Fig. 9 Material 1.4845, 200 h, 1000 °C, SO_2, microprobe
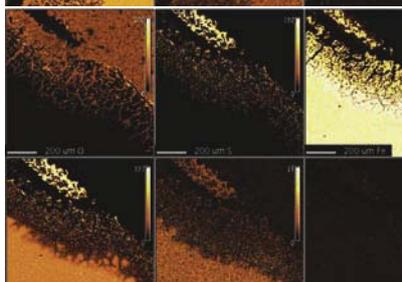

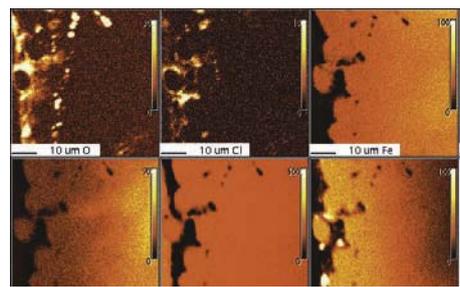**Fig. 10** Material 1.4828, 200 h, 1000 °C, SO_2, microprobe

Fig. 11 Material 2.4851, 200 h, 1000 °C, Cl_2, microprobe
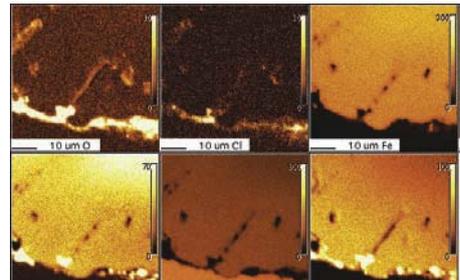

Fig. 12 Material 1.4864, 200 h, 1000 °C, Cl_2, microprobe
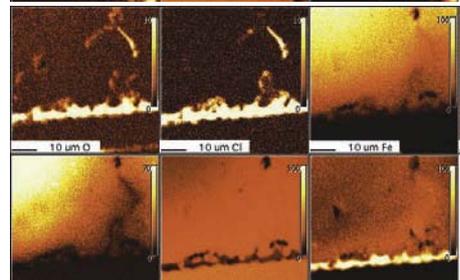

Fig. 13 Material 1.4862, 200 h, 1000 °C, Cl_2, microprobe
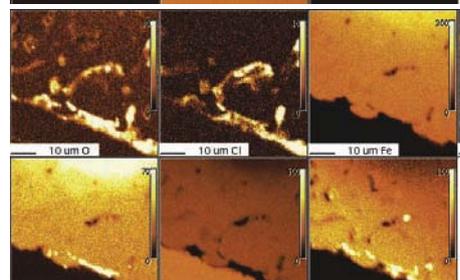

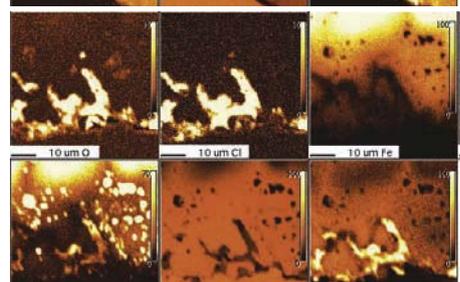**Fig. 14** Material 1.4845, 200 h, 1000 °C, Cl_2, microprobe

Fig. 15 Material 1.4828, 200 h, 1000 °C, Cl_2, microprobe

distribution of the elements gives evidence of the composition of the corrosion layers.

The criteria for evaluating the materials were:

- penetration depth of the corrosion products into the material
- thickness of the corrosion layer
- mitigation of elements.

3 Results
3.1 Reducing atmosphere

Carbides shaped primarily at a reducing atmosphere. Clefts that might have been caused by hydrogen did not occur. The depositions were caused by the carbon which already existed in the material.

Thus, only the pictures for a temperature of 700 °C are shown (Fig. 4).

3.2 Nitriding atmosphere

Mostly carbides formed at this atmosphere. Nitrides did not shape. There is a clear difference between the two temperatures (Fig 5); at 700 °C chromium carbides ($Cr_{23}C_6$) shape which become thermodynamically unstable at a temperature above 900 °C, and dissolve. This causes a grain coarsening at 1000 °C. This is true

Tab. 3 Evaluation of the material in a SO$_2$ atmosphere

Alloy	Temperature 700 °C	Temperature 1000 °C
1.4828	slightly restricted advisable	restricted advisable
1.4845	restricted advisable	restricted advisable
1.4862	advisable	restricted advisable
1.4864	slightly restricted advisable	advisable
2.4851	not advisable	restricted advisable

Tab. 4 Evaluation of the material in a Cl$_2$ atmosphere

Alloy	Temperature 700 °C	Temperature 1000 °C
1.4828	not advisable	not advisable
1.4845	restricted advisable	restricted advisable
1.4862	slightly restricted advisable	slightly restricted advisable
1.4864	slightly restricted advisable	slightly restricted advisable
2.4851	slightly restricted advisable	slightly restricted advisable

of all materials, as they bear a high chromium concentration. Only a sufficient amount of chromium can lead to shaping a verifiable portion of carbides. All results are due to material inherent phenomenon.

3.3 Sulfidizing / oxidizing atmosphere

The corrosion products are clearly visible at the boundary in the microprobe pictures, taken after the deposition in SO$_2$.

Fig. 6 shows the distribution of oxygen, sulfur, iron, silicium, chromium, manganese, aluminium, and nickel (top left to down right). As the tests take place in an atmosphere free of oxygen, the products diverge into an oxide layer (outside, top right), and a sulfur layer (inside). The mechanism of sulfur regeneration is clearly visible; this is due to the low partial pressure of oxygen in the inner material. Sulfides shape, as sulfur remains the only reaction partner of the alloy elements.

All materials corroded in this atmosphere. The nickel-based alloy is mostly affected due to the forming of eutectics. Sulfur dioxide has a higher diffusion coefficient; through this and through the occurrence of melt it can pene-trate faster and in larger portions into the material during the liquid phase. Figs. 6 – 10 show the materials after a time of deposition for 200 h at a temperature of 1000 °C. The pictures are principally equal to those taken at 700 °C.

As mentioned in Chapter 1, the penetration depth, the corrosion products and the mitigation of ele-ments are used for evaluation purposes. Protecting oxide and sulfide layers are shaped on the sample surface, caused by the relatively high contents of silicium and chromium. The concentration of these elements is high enough to guarantee a sufficiently chemical durability at high temperatures.

However, the fraction of nickel within the iron-based alloys is low enough to minimize the appearance of the low melting Ni-Ni$_3$S$_2$ eutectic. Meanwhile, the nickel-based alloy is strongly corroded, because nickel sul-fide is formed during the corrosion attack. The oxide layer can almost not adhere to the very soft to liquid underground; the ongoing corrosion forces sulfur into the core and keeps mobilizing it, which rapidly damages the material. The damage is intensified by a diffusion velocity, which is several times higher in melt phase than in solid state. At a temperature of 400 °C the results were insignificant.

3.4 Carburizing atmosphere

The fraction of carbides increased at a carburizing atmosphere. As nickel diminishes the solubility of carbon within the metallic matrix, chromium forms protecting oxide scales. On this account materials with an appropriate concentration of chromium and nickel are less prone to corrosion in such media. The least alloyed steels are most prone

to carburizing and therefore to embrittlement.

3.5 Chlorinating atmosphere

Of all tested atmospheres the chlorine containing gas mixtures are the most aggressive ones. For protecting purposes, the material has to enclosed by an intact oxide layer and sufficient alloy elements. Consequently, the higher alloyed steels show the smallest corrosion (Tab. 4). The tests at 400 °C did not bear significant results.

4 Conclusions

Five materials were exposed to five distinctive atmospheres and temperatures of 400 °C, 700 °C, and 1000 °C.

In a reducing and nitriding atmosphere, the assays did not show any changes due to external influences. Hydrogen did not embrittle the material; the deposition of nitride neither occurred in a re-ducing, nitriding atmosphere at temperatures of 700 °C and 1000 °C respectively. A high splitting energy is necessary to change molecular nitride into nuclear one, which is responsible for the formation of a small content of nitrides.

A significantly more aggressive medium with respect to nitriding reactions would be ammoniak; here, stronger corrosion phenomena would probably be observable.

In a sulfidizing atmosphere, high proportions of nickel tend to form eutectics, which are unwanted. The tests give evidence of this. Instead of nickel, chromium forms strong compounds with both oxygen and sulfur, and also shapes closed layers; it is hence an appropriate protecting element. The nickel-based alloy 2.4851 received the worst results. A thick corrosion layer shaped, as well as the eutectic Ni/Ni$_3$S$_2$.

A high nickel concentration is useful in a carbonizing atmosphere, since it reduces the solubility of carbon in the metal matrix. As soon as a gas atmosphere becomes reducing and no further oxygen exists, a high chromium concentration may lead to a stronger forming of chromium carbides. Under oxidizing circumstances a chromium oxide layer may function as a diffusion barrier and may thus minimize a carbonizing of the matrix.

The concentration of iron should be as small as possible in a chlorinating atmosphere, since the iron chlorides begin evaporating at temperatures above 100 °C. On the contrary, nickel chlorides and chro-mium chlo-

rides sublime at much higher temperatures. Consequently, the materials – from nickel-based alloys to the least alloyed iron-based alloys – can best survive in a chlorine gas flow. The durability of a material with respect to high temperature corrosion significantly depends on the atmosphere in which it is tested. Long-run tests have to verify these results in the future.

References

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[2] Bürgel, R.: Handbuch Hochtemperaturwerkstofftechnik – Grundlagen, Werkstoffbeanspruchungen, Hochtemperatur-legierungen und -beschichtungen, 3. Auflage. Verlag Friedr. Vieweg & Sohn, Wiesbaden, 2006, S. 324