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Corrosion Resistance of High-Alloyed Materials in Artificial Geothermal Brines

Ralph Bäßler, Joana Sobetzki, Helmuth Sarmiento Klapper

BAM – Federal Institute for Materials Research and Testing, D-12200 Berlin/Germany

Ralph.Baessler@BAM.de

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ABSTRACT

The corrosion behavior of different high-alloyed metals including duplex and austenitic stainless steels as well as a nickel alloy have been evaluated in artificial geothermal brines simulating the conditions in the Upper Rhine Graben and the Northern German Basin, some locations with geothermal potential in Germany.

The suitability of X2CrNiMo-22-5, X2CrNiMoCuWN25-7-4, X1CrNiMoCu32-28-7 and NiCr23Mo16Al in these geothermal brines obtained by electrochemical measurements and exposure tests is limited. The nickel alloy NiCr23Mo16Al shows an excellent corrosion resistance against pitting corrosion. Excluding its high cost, it is a very good alternative to be used in the construction of geothermal facilities having highly saline brines. Stainless and duplex steels exhibit a limited corrosion resistance concerning pitting and crevice corrosion.

1. INTRODUCTION

Since geothermal wells are a feasible energy source to replace fossil fuel supply, many technologies have been developed to take advantage of geothermal energy. Nevertheless, service conditions in geothermal facilities are due to the chemical composition of hydrothermal brines and temperatures, in many cases, extreme in terms of corrosion. Therefore, materials selection based on preliminary material qualification is essential to guarantee a secure and reliable operation of the facilities.

Preliminary investigations carried out by the German Research Centre for Geosciences (GFZ) have shown that the geothermal brine of the North German Basin (NGB) having temperatures above 140 °C could be used for production of electric energy (Bäßler et al. 2009). In consequence, GFZ has built a research facility concerning geochemistry, geosciences and corrosion at Groß Schönebeck, a former deep well located in the geothermal area of the NGB. Also for the Upper Rhine Graben (URG) there are facilities designed for production of electric energy (Herzberger et al. 2010).

Nevertheless, until now, corrosion resistance data of possible construction materials in this highly saline brine at service conditions are not available. Currently, a project in Germany deals with the evaluation of long-term corrosion behavior of different metallic materials including low-alloyed steels, austenitic stainless steels, duplex steels and Ni-alloys in different geothermal brines commonly found in Germany including the NGB (Sarmiento Klapper et al. 2011) and the URG.

This paper gives an update on recent experiences from laboratory tests performed on different high-alloyed materials in artificial geothermal brines having the chemical composition of the highly saline brine of NGB and the less aggressive brine of the URG at service conditions.

2. OBJECTIVE

Within a long-term project financed by the German Ministry of Environment, Nature Protection and Reactor Safety a catalogue of suitable materials for applications in German geothermal power plants shall be created based on results and experiences gathered in the laboratory and on-site. Users shall be enabled to have a basis for designing such facilities.

Table 1: Composition of materials obtained by Sparc Emmision Spectrometry

	Content [%]										
	C	Si	Mn	P	S	N	Cr	Mo	Ni	Cu	Fe
X2CrNiMo-22-5 (UNS S31803, 1.4462, F51)	0.03	0.37	1.51	0.022	0.003	0.15	22.64	3.12	5.92	0.18	65.8
X2CrNiMoCuWN25-7-4 (UNS S32760, 1.4501, F55)	0.04	0.26	0.85	0.023	0.002	0.23	25.29	3.73	6.97	0.54	61.1
X1CrNiMoCu32-28-7 (UNS N08031, 1.4562, alloy 31)	0.03	0.06	1.69	0.020	0.006	0.11	27.94	6.28	30.68	1.12	32.8
NiCr23Mo16Al (UNS N06059, 2.4605, alloy 59)	0.02	0.11	0.07	0.007	0.005	-	21.69	13.95	62.8	0.04	0.98

3. EXPERIMENTAL SETUP

3.1. Materials

The corrosion resistance of the duplex steel X2CrNiMo-22-5, the super duplex steel X2CrNiMoCuWN25-7-4, the austenitic stainless steel X1CrNiMoCu32-28-7 and the nickel alloy NiCr23Mo16Al was evaluated by exposure and electrochemical tests in artificial geothermal brines of NGB and URG at 100 °C and 150 °C (1500 kPa). The chemical compositions of the investigated high-alloyed materials are included in .

Corrosion tests at 100 °C should simulate conditions in the technical facilities e.g. heat exchanger above ground. On the other hand, tests at 150 °C consider downhole conditions. Since the natural geothermal brines become unstable at normal pressure, they cannot be used for laboratory investigations at atmospheric conditions. Therefore, two artificial brines based on the chemical analysis of aquifer brines in Groß Schönebeck (NGB) and Bruchsal (URG) carried out by GFZ were used for the investigations. The chemical compositions are presented in table 2.

The pH of the NGB-brine was 5.6 and 6 for URG-brine. The redox potential considering oxygen-free conditions was 200 mV_{SHE}. For the measurements at 150 °C, the oxygen concentration in the brines was adjusted to very low values by purging the solution with argon for 10 min prior to the start of the measurements. The pressure of 1500 kPa was further achieved by using argon.

3.2. Setup

Exposure tests were carried out according to DIN 50905/4 (DIN 1987) with gravimetric determination of time dependent corrosion at 100 °C. The specimen size for exposure tests was 50 x 15 x 3 mm (length x width x thickness). Three specimens of each material were exposed for 24 weeks. Each specimen had a 5 mm hole for fixation using a polytetrafluoroethylene (PTFE)-cord (see figure 1, left).

Figure 1: Specimen design for exposure, SCC, crevice corrosion and electrochemical tests

In order to prevent interaction between the different materials and their corrosion products all materials were tested separately using a glass vessel. The specimens were completely immersed in the brine. The threshold for suitability was set to be a corrosion rate of 0.3 mm/year. This corresponds to a wall thickness reduction of 6 mm by uniform corrosion during 20 years of service.

Beside the determination of weight loss, susceptibility to stress corrosion cracking (SCC) and localized corrosion phenomena were investigated as well. It has been distinguished between pitting and shallow pit corrosion in order to use the right criteria for suitability evaluation. If pitting would occur, the material is not suitable. In case of shallow pitting the depth of the shallow pit during exposure was extrapolated to one year resulting in the corrosion rate. Specimens were evaluated by optical microscopy.

Table 2: Composition of investigated brines

	Content [g/L]										
	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	K^+	Na^+	NH_4^+	Fe^{2+}	Pb^{2+}	Sr^{2+}	SiO_2
NDB	166	0.05	56.5	0.5	3.1	38.7	0.2	-	0.2	1.55	-
URG	102	1.5	10.9	1.9	3.7	47.9	-	0.25	-	0.5	0.15

Figure 3: Materials after 6 months exposure in artificial URG-brine at different temperatures; from left to right: X2CrNiMo-22-5, X2CrNiMoCuWN25-7-4, X1CrNiMoCu32-28-7 and NiCr23Mo16Al

The susceptibility to localized corrosion of the materials in the artificial geothermal brines was additionally investigated by determination of open circuit potential (OCP), cyclic potentiodynamic polarization and potentiostatic measurements. A typical 3-electrode configuration including a saturated Ag/AgCl reference electrode and a graphite-counter-electrode were used for the electrochemical measurements at 100 °C.

Investigations at 150 °C were carried out within an autoclave using a special saturated Ag/AgCl reference electrode and a Ti-oxide covered titanium mesh as a counter electrode. The temperature in the autoclave was adjusted by an external hotplate and constantly monitored by a thermocouple. The autoclave was additionally located in a sand bath in order to avoid electrical interferences between heater and measurement device. The specimen size for electrochemical tests was 20 x 15 x 3 mm, resulting in 8 cm² surface (figure 1, right). All specimens were ground to grit 320 in order to have comparable surface conditions.

Cyclic potentiodynamic measurements were carried out after 336 hours of exposure. During this time (14 days) the OCP was monitored. Polarization was started from OCP in anodic direction using 0.2 mV/s. After reaching a current density of 0.1 mA/cm² or a potential of 1.2 V vs. OCP the polarization was switched in cathodic direction in order to evaluate the repassivation behavior. In addition, the susceptibility to crevice corrosion was electrochemically determined by means of potentiostatic measurements. Crevice conditions were simulated using a rubber crevice shown in figure 1 (3rd). All electrochemical measurements were carried out using a Gamry REF600 potentiostat.

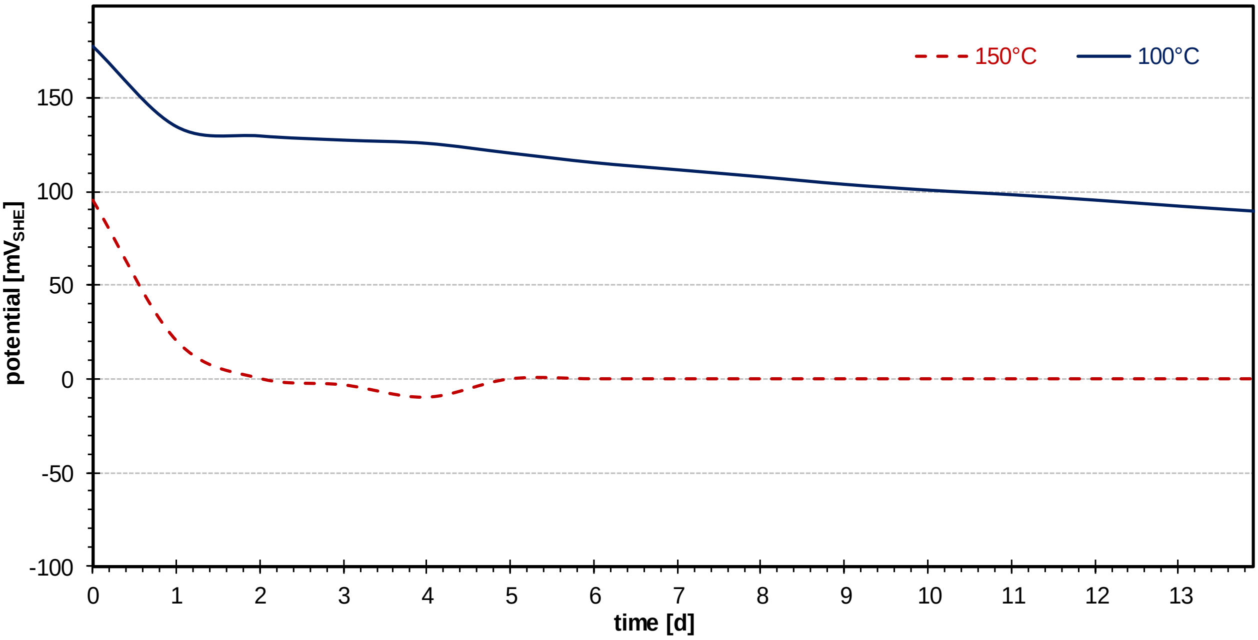

Figure 2: Open circuit potential of X2CrNiMoCuWN25-7-4 in artificial URG-brine at different temperatures

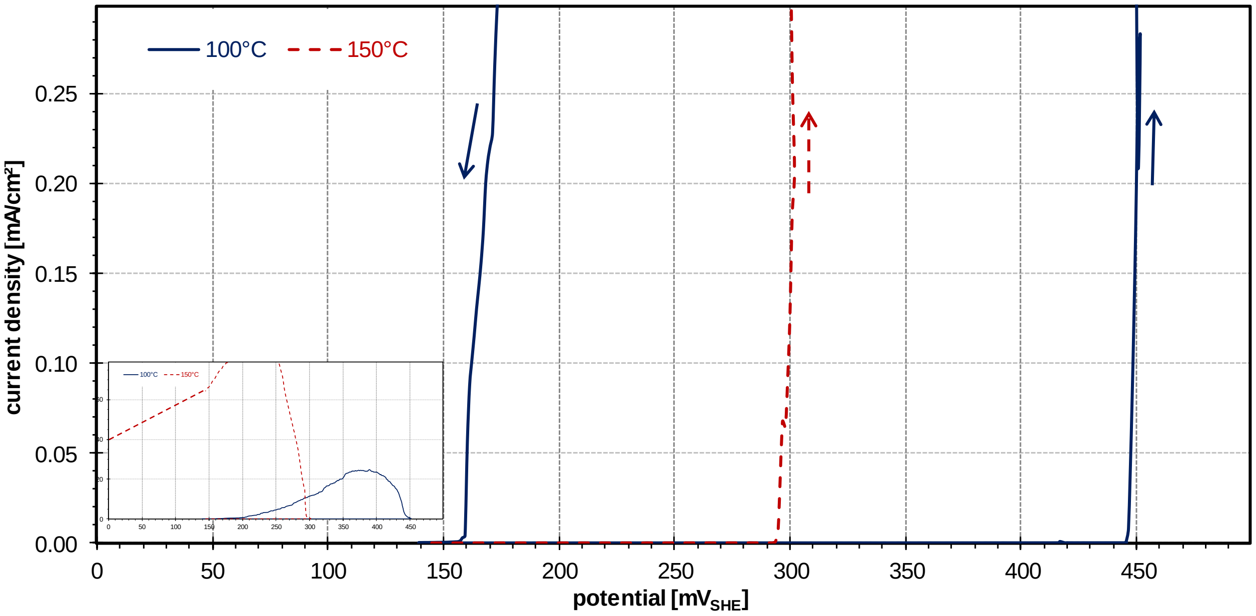

Figure 4: Cyclic polarization curves of X2CrNiMoCuWN25-7-4 in artificial URG-brine at different temperatures

4. RESULTS

4.1. Exposure tests

All evaluated materials showed after 24 weeks corrosion rates lower than the threshold value specified previously at 0.3 mm/year. All four materials exhibit a remarkable corrosion resistance to corrosion. No evidences of SCC-susceptibility have been found.

Specimens of the materials X2CrNiMo-22-5 and X2CrNiMoCuWN25-7-4 showed nevertheless some signs of crevice corrosion in the area of fixation by PTFE-cord in both solutions, and X1CrNiMoCu32-28-7 just in NGB (Sarmiento Klapper et al. 2011) but not in URG (figure 3). Therefore, specific electrochemical tests regarding susceptibility to crevice corrosion were carried out. According to the results of the exposure test the nickel alloy NiCr23Mo16Al could be considered as suitable at 100 °C and 150 °C.

4.2. Electrochemical Tests

All measured values are summarized in tables 3 and 4. Some of the NGB-results have been described previously (Sarmiento Klapper et al. 2011). In the following text selected test results in URG-brine are described in more details.

The open circuit potential of super duplex steel X2CrNiMoCuWN25-7-4 in the artificial brine of URG at 100 °C stabilizes after 8 to 10 days resulting in values around 100 mV$_{SHE}$ after 14 days. Increasing the temperature to 150 °C leads to more negative OCP around 0 mV$_{SHE}$ (figure 2).

The critical pitting potential (CPP) and the repassivation behavior of the materials were determined by means of cyclic potentiodynamic measurements. In figure 4 the polarization curves of X2CrNiMoCuWN25-7-4 in the artificial brine of URG are presented. Despite of slight fluctuations within the current, the CPP of X2CrNiMoCuWN25-7-4 at 100 °C varies between 350 and 450 mVSHE. In addition, X2CrNiMoCuWN25-7-4 exhibits a repassivation potential (REP) more positive than its OCP, being between 150 and 250 mV$_{SHE}$.

When increasing the temperature to 150 °C, the CPP of X2CrNiMoCuWN25-7-4 shifts slightly in cathodic direction. The CPP is now between 300 and 350 mVSHE, and the repassivation potential could not be determined due to its shift to values far more cathodic than the OCP. Once pitting has been initiated it will not have the chance to repassivate. The super duplex steel X2CrNiMoCuWN25-7-4 is, in con-

Table 3: Electrochemical parameters of the high-alloyed materials in NGB-brine

Material	OCP [mV$_{SHE}$] 100 °C	OCP [mV$_{SHE}$] 150 °C	CPP [mV$_{SHE}$] 100 °C	CPP [mV$_{SHE}$] 150 °C	CCP [mV$_{SHE}$] 100 °C	REP [mV$_{SHE}$] 100 °C	REP [mV$_{SHE}$] 150 °C
X2CrNiMoCuWN25-7-4	75 - 125	-50	280 - 330	25 - 50	150	≤ OCP	< OCP
X1CrNiMoCu32-28-7	170 - 180	120 - 150	550 - 580	425 - 450	275	330 - 380	< OCP
NiCr23Mo16Al	90 - 160	125 - 300	> 900	500 - 590	325	≅ CPP	420 - 450

Table 4: Electrochemical parameters of the high-alloyed materials in URG-brine

Material	OCP [mV_{SHE}] 100 °C	OCP [mV_{SHE}] 150 °C	CPP [mV_{SHE}] 100 °C	CPP [mV_{SHE}] 150 °C	CCP [mV_{SHE}] 100 °C	REP [mV_{SHE}] 100 °C	REP [mV_{SHE}] 150 °C
X2CrNiMo-22-5	-10 - 140	-20 - 100	225 - 230	160	200	170	< OCP
X2CrNiMoCuWN25-7-4	80 - 160	40 - 100	325 - 350	300	275	230	< OCP
X1CrNiMoCu32-28-7	50 - 180	80 - 100	600 - 630	440	500	600	290
NiCr23Mo16Al	20 - 260	250 - 360	700 - 900	780	600	≅ CPP	≅ CPP

sequence, not suitable in URG-brine at 150 °C too.

The duplex steel X2CrNiMo-22-5 exhibits, in general, a similar performance as the super duplex steel in the URG-brine, so it is not acceptable for this medium either. It needs to be concluded that this fits to the results in the NGB-brine as well, where X2CrNiMo-22-5 has not been tested, but the X2CrNiMoCuWN25-7-4 has.

The higher alloyed materials exhibit a different behavior.

Tables 3 and 4 summarize the electrochemical parameters obtained from the OCP and the potentiodynamic measurements carried out on the different high-alloyed materials at both temperatures.

Cyclic polarization measurements at the Ni-alloy at 100 °C in NGB brine show high critical potentials. Therefore, this alloy exhibits a very good corrosion resistance, because the critical and the repassivation potentials are already within the transpassive area and much more anodic than its free corrosion potential. So, occurrence of corrosion is very unlikely. If the material is exposed to certain high potentials (within potentiostatic polarization tests) it is still much higher than the free corrosion potential. Crevice corrosion has been observed always before pitting (Sarmiento Klapper et al. 2011). The critical crevice corrosion potentials (CCP) are certainly more cathodic than critical pitting corrosion potentials (CPP) but still much more positive than the free corrosion potentials (OCP). This means that crevice corrosion is not to be expected in this brine.

Concerning susceptibility to crevice corrosion, as mentioned above, during exposure tests, crevice corrosion was found in the area in contact with the PTFE-cord of the specimens of the steels X2CrNiMoCuWN25-7-4 and X1CrNiMoCu32-28-7. A preliminary study (Bäßler et al. 2009) has shown that undefined metal/polymer-crevices are in fact more critical than metal/metal-crevices especially for austenitic stainless steels. For this reason, potentiostatic measurements using the special rubber crevice set-up shown in figure 1 (3rd) were carried out at 100 °C.

In the case of the super duplex steel X2CrNiMoCuWN25-7-4, the critical crevice potential (CCP), located at 150 mVSHE, was very close to its OCP (125 mVSHE). In some experiments performed on X2CrNiMoCuWN25-7-4 at 175 mVSHE, pitting and crevice corrosion took place simultaneously.

Austenitic steel X1CrNiMoCu32-28-7 was susceptible to crevice corrosion as well, but its susceptibility was considerably lower than for X2CrNiMoCuWN25-7-4. A CCP of 275 mVSHE was determined for X1CrNiMoCu32-28-7 being relatively close to its OCP (180 mVSHE).

For nickel alloy NiCr23Mo16Al its CCP at 325 mVSHE was clearly more anodic than for X1CrNiMoCu32-28-7. Because of the significant difference between OCP and CCP of UNS N06059 in NGB-brine at 100 °C its susceptibility to crevice corrosion is negligible. So, only the nickel alloy NiCr23Mo16Al was found to be not susceptible to crevice corrosion in the artificial brine of NGB at service conditions.

The duplex steel X2CrNiMo-22-5 shows limited corrosion and repassivation properties at both temperatures. The CPP at 100 °C is certainly more anodic than the OCP, but decreases with increasing the temperature to 150 °C and comes close to the OCP. That means there is not much effort necessary (e.g. fluctuation within the service conditions) in order to initiate corrosion of this material. The repassivation potentials are within or behind the OCP. So, once corrosion has started a repassivation is very unlikely at 100 °C and can almost be excluded at 150 °C. However, there is no difference between start of crevice corrosion and pitting. Both critical potentials are close to OCP.

For super duplex X2CrNiMoCuWN25-7-4 it looks slightly better. It has the possibility to repassivate at 100 °C, because the REP is some more mV away from OCP. Also the CCP is a bit more anodic than OCP. At 150 °C it behaves similar to the duplex steel as mentioned previously.

A much better resistance exhibits the superaustenite X1CrNiMoCu32-28-7. CPP and REP are close together and relatively far away from OCP at 100 °C. This means, there is a big effort necessary in order to initiate the corrosion. Then a very quick repassivation occurs. Crevice corrosion occurs before pitting. CPP and REP shift to more cathodic values, but are still more anodic than OCP. Therefore a good corrosion resistance can be concluded.

As already in NGB-brine, the nickel alloy NiCr23Mo16Al is the most resistant material. Again the CPP and REP are within the transpassive area at 100 °C, far away from OCP. Still there is a quick repassivation possible. Also critical crevice and pitting corrosion potentials achieved by long-term tests are far more anodic than OCP. Due to temperature increase CPP and REP certainly shift in cathodic direction, but only slightly. Here also a quick repassivation is possible.

Within the URG-brine only the nickel alloy and the superaustenite provide a sufficient corrosion resistance, whereas the duplex and the super duplex steel just show a certain resistance up to 100 °C.

CONCLUSION

According to the experimental results obtained in 2 different artificial geothermal brines in the laboratory, the duplex steel X2CrNiMo-22-5 and the super duplex steel X2CrNiMoCuWN25-7-4 are not suitable for geothermal applications in brines having compositions comparable to NGB and URG, due to their critical susceptibility to localized corrosion in form of pitting and crevice corrosion at service conditions.

Austenitic steel X1CrNiMoCu32-28-7 is suitable in URG brine. In NGB brine it seems to be suitable at 100 °C, but its susceptibility to crevice corrosion limits its applicability.

The nickel alloy NiCr23Mo16Al is suitable and represents a safe option to be used in geothermal facilities working with highly saline brines of the NGB and URG up to 150 °C.

Publication of results achieved so far should provide a basis which might lead to create a catalogue for materials suitable for diverse applications in geothermal power plants.

OUTLOOK

The project is still running, comparing the results achieved in static conditions to flowing brines and at the real plant in Groß Schönebeck/Germany (NGB).

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