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Pitting corrosion resistance of CA6NM as geothermal turbine blade material in simulated artificial geothermal brine

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Abstract. Fatigue failure of turbine blades originating from pitting corrosion is a critical issue for power plant. Herein, we study the pitting corrosion resistance of cast CA6NM as turbine blade material in simulated geothermal environment with and without CO₂ gas by using cyclic polarization measurement. Three different molybdenum and nitrogen content of CA6NM were used for experiments: (i) CA6NM with a molybdenum content of 1 wt.% and without addition of nitrogen, (ii) CA6NM with a molybdenum content of 2 wt.% and without addition of nitrogen, (iii) CA6NM with a molybdenum content of 2 wt.% and nitrogen content 0.1 wt.%. The measurement reveals CA6NM with molybdenum 2 wt.% and nitrogen 0.1 wt.% is the most resistance to pitting corrosion in simulated artificial geothermal brine with and without CO₂ gas.

1. Introduction

Geothermal energy can contribute a significant portion of electricity to the future energy mix because it has characteristics of low cost, wide distribution, and low pollution [1-2]. However, geothermal steam contains corrosive chemical species that can cause corrosion which can result in high costs associated with maintenance, materials, and loss in production [3]. In some geothermal fields, the geothermal steam contains ammonium chloride (NH₄Cl) and hydrogen chloride (HCl) gas that is generally regarded as originated from the volcanic system. If condensation and/or re-boiling of the steam with HCl and NH₄Cl, risk of localized corrosion arises on blades of the wet section of steam turbine. Nowadays, corrosion mitigation is mainly achieved through steam scrubbing system and chloride abatement with alkaline sodium hydroxide solution. Besides an increase in operating costs, such treatment reduces the fluid temperature leading to relevant loss of power about 0,5 MW on 15 MW turbine. Thus, the use of corrosion resistance turbine material can be a suitable solution [4].

Steam turbine blades are critical components in power plants, which convert the linear motion of high temperature and high-pressure steam flowing down a pressure gradient into a rotary motion of the turbine shaft. The low pressure (LP) turbine blades are designed to extract the final remnant of energy from the passing steam flow. Statistics show that low pressure (LP) turbine blades are generally more susceptible to failure than those of the high pressure (HP) and intermediate pressure because trace amounts of corrosive chemical species present in the steam are easily concentrated in condensed water droplet and accumulate inside gap regions in the phase transition zone due to alternative dry and wet phenomenon [5-6].

Almost 50% of the turbine blades failures are related to fatigue, stress corrosion cracking, and corrosion fatigue [5]. Fatigue failure of turbine blades originating from pitting corrosion can cause catastrophic damage. Fatigue failure of steam turbine blades caused by pitting corrosion occurs



preferentially in low pressure (LP) blades where early condensate develops. Activation of pitting is not expected during standard operational condition because the condensate on the turbine blades is oxygen free. But unexpected occurrences – e.g. leaking of the condenser – may create corrosive environments with critical amounts of corrosives such as chloride. When combined with off-load aeration, corrosion pits can form that can act as stress raisers. If a corrosion pit exceeds a critical size, the increase of the local stresses can initiate a fatigue crack [7]. Therefore, pitting corrosion resistance becomes crucial properties in the material selection of turbine blades to avoid failure.

Material selection guidelines for geothermal turbines mainly recommend the use of stainless steel because of its ability to passivate in a corrosive environment. Cast CA6NM is a low carbon 13%Cr-4%Ni martensitic stainless steel, which is used specifically when applications require a high resistance to fraction, creep, and fatigue[8–10]. This alloy displays improved weldability, strength and corrosion resistance compared to typical martensitic SS such as 410 SS, thereby CA6NM is used as turbine blade material in this experiment. Effect of alloyed elements on pitting corrosion resistance have been investigated and beneficial effect of molybdenum (Mo) has been widely reported [11-12].

Nitrogen (N) is another alloying element that is known to improve the resistance of stainless steels to pitting corrosion. As such, it participates in the empirical pitting resistance equivalent numbers (PREN) equation with a large weight [13].

$$PREN = \%Cr + 3.3 \%Mo + 16 \%N \quad (1)$$

The effect of Mo and N seem to synergistically interact when both of them are present in the stainless steel, but this issue has not been clearly understood yet. The purpose of present work is to elucidate the role of alloyed molybdenum and nitrogen on pitting corrosion resistance of CA6NM in geothermal environment using electrochemical measurement.

2. Experimental Details

2.1. Materials

Three types of cast CA6NM with composition as in table 1 were used for the experiments. Cast CA6NM as specimen cut to rectangular coupon and heat treated. All specimen austenized at 1050°C for 3 hours and then tempered at 670°C for 3 hours. After heat treated, CA6NM mounted with resin until the exposed area was 1 cm². The mounted CA6NM abraded with abrasive paper from 120 cw until 1200 cw. Microstructure of all specimen observed using optical microscope. All test material immersed into artificial geothermal brine with or without CO₂ gas during measurement.

Table 1. Materials for experiment.

Samples	C	Mn	Si	P	S	Cr	Ni	Mo	N	Fe
CA6NM1	0.04	0.40	0.35	0.018	0.008	12.83	4.17	1.02	-	Bal
CA6NM2	0.04	0.43	0.55	0.017	0.009	13.02	4.08	1.96	-	Bal
CA6NM3	0.04	0.35	0.35	0.019	0.009	13.07	4.09	2.14	0.11	Bal

2.2. Artificial Geothermal Brine

These experiment were performed using simulated artificial geothermal brine with and without CO₂ gas. To simulate geothermal environment, artificial geothermal brine synthesized from chemicals in table 2. The synthesized artificial geothermal brine contains chloride ions that cause pitting corrosion.

2.3. Measurement Techniques

Pitting corrosion resistance of all samples evaluated using electrochemical measurement. The glass cell used for the experiments contains a three-electrode setup with the test material as the working electrode, a platinum counter electrode, and a saturated calomel electrode (SCE) reference electrode. It has a

volumetric capacity of 500 ml. A scanning electron microscope (SEM, JEOL Model JSM-5400) was employed for the pitting corrosion size and an EDAX attachment was used for qualitative elemental chemical analysis.

The electrochemical measurement was conducted by cyclic polarization techniques at ambient pressure, room temperature, and pH neutral in artificial geothermal brine. Cyclic polarization was applied using Gamry Instruments G750 Series. The polarization experiments were started within 1 h after OCP (Open Circuit Potential) measurement. The measurement of cyclic polarization referred to ASTM G-61. The potential of the sample was swept from the -500mV to +1500mV where a current density limit of 10mA/cm² was applied in the specimen. After reaching current density limit, reverse polarization was started to find susceptibility to pitting corrosion. The forward scan rate was 5mV/s and reverse scan was 2.5 mV/s.

Table 2. Artificial geothermal brine composition[14].

Salt used for synthesis	g/l
NaCl	224.6
NaSO ₄ .10H ₂ O	12.074
MgCl.6H ₂ O	10.620
CaCl ₂ .2H ₂ O	6.452
KCl	0.390
KOH	0.321
NaHCO ₃	0.048

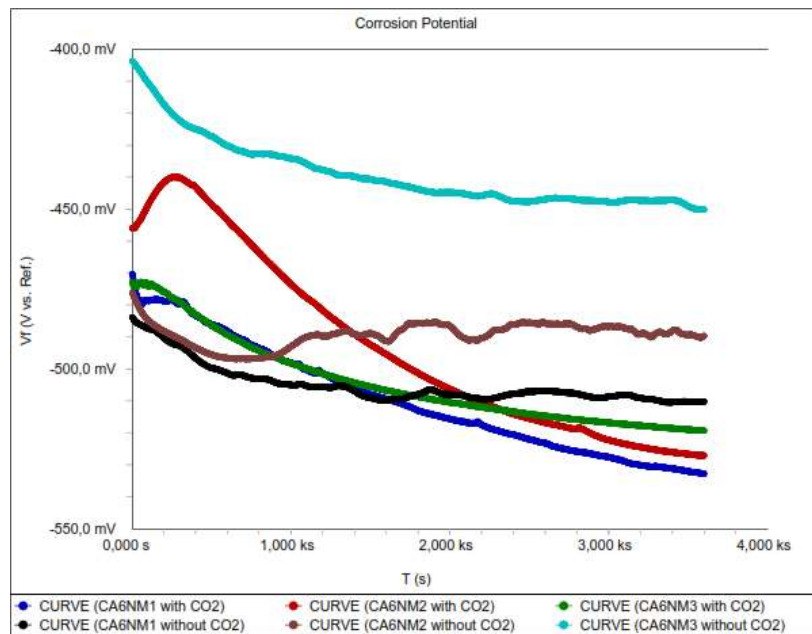
3. Result and Discussion

3.1. Open Circuit Potential Analysis

Open circuit potential (E_{oc}), also referred to as the free corrosion potential (E_{corr}) is a measure of a tendency of the investigated, i.e. working electrode to dissolve (lose electrons) and undergo oxidation. It is measured versus a stable reference electrode, when no potential or current is being applied to the electrochemical cell[15]. OCP is the mixed electrode potential in the given corrosion environment. The evolution of the OCP for the test materials in artificial geothermal brine with and without CO₂ gas is given in figure 1. Based on figure 1, the OCP increases with increase in molybdenum content and existence of nitrogen. Table 3 showed the maximum and minimum electrode potential and OCP value of test materials after 1 hours immersion in artificial geothermal brine with and without CO₂ gas. The highest OCP value is CA6NM alloy with the highest molybdenum and nitrogen content. From these results, it can be concluded that molybdenum and nitrogen content give effect on the reactivity of CA6NM alloys. The higher the molybdenum and nitrogen content, the less reactive and more noble of CA6NM alloy and vice versa. From figure 1, CA6NM immersed in artificial geothermal brine without CO₂ gas have more positive value of OCP than CA6NM immersed in artificial geothermal brine with CO₂ gas. This happens because artificial geothermal brine with CO₂ gas is more aggressive environment.

Table 3. Maximum and minimum electrode potential and open circuit potential value for 1h.

Samples	V _{max} (mV vs SCE)	V _{min} (mV vs SCE)	OCP (mV vs SCE)
CA6NM1 with CO ₂ gas	-470.3	-532.8	-532.7
CA6NM2 with CO ₂ gas	-439.9	-527.1	-527.1
CA6NM3 with CO ₂ gas	-472.7	-519.3	-519.3
CA6NM1 without CO ₂ gas	-483.8	-510.5	-510.2
CA6NM2 without CO ₂ gas	-476.2	-496.9	-489.6
CA6NM3 without CO ₂ gas	-403.7	-450.1	-450.1

**Figure 1.** Open circuit potential measurement in artificial geothermal brine with and without CO₂ gas.

3.2. Cyclic Polarization Analysis

Figure 2 and figure 3 depict the cyclic polarization curves of all specimen obtained in the artificial geothermal brine with and without CO₂ gas, respectively. The parameters determined from the cyclic polarization of all test materials, such as pitting potential (E_{pit}), protection potential (E_{prot}), and corrosion potential (E_{corr}) were presented in table 4. Based on table 4, all test material immersed in artificial geothermal brine with CO₂ gas have higher protection potential value than pitting potential. If the protection potential value is more positive (anodic) than the pitting potential, there will be no tendency to pit [16]. From table 4, CA6NM materials immersed in artificial geothermal brine without CO₂ gas have higher pitting potential value than protection potential. It means, CA6NM immersed in artificial geothermal brine without CO₂ was susceptible to pitting corrosion [17]. However, in figure 3, only small hysteresis loop is found in all CA6NM immersed in the artificial geothermal brine without CO₂ gas. This indicates that CA6NM can quickly repassivation of the attacked local sites [15].

The pitting potential of different molybdenum and nitrogen content of CA6NM follow the sequence: CA6NM1 < CA6NM2 < CA6NM3. The lower E_{pit} value indicates more chances of easily breakdown of passive film and early start of pitting corrosion [18]. CA6NM immersed in artificial geothermal brine with CO₂ gas have lower E_{pit} value than CA6NM immersed in artificial geothermal brine without CO₂ gas. This proves OCP measurement that artificial geothermal brine with CO₂ gas is a more aggressive

environment. Nevertheless, E_{prot} value of CA6NM in artificial geothermal brine with CO_2 gas higher than CA6NM in artificial geothermal brine without CO_2 gas. This result shows that CA6NM has ability to protect its passive film in artificial geothermal brine with CO_2 , so pitting corrosion does not occur.

In cyclic polarization curves the probability of localized corrosion is related to the difference between the protection potential, E_{prot} , and corrosion potentials, E_{corr} , thus the higher the difference the lower the probability of pitting corrosion [19]. Overall, the experimental results obtained on CA6NM with varying content of molybdenum and nitrogen immersed in artificial geothermal brine showed that in absence of nitrogen and lower molybdenum content the pitting corrosion activity on the CA6NM surface strongly increases leading to low pitting potentials as observed in table 4. However, the addition of molybdenum and nitrogen content to the alloys, once corrosion was initiated, leads to a repassivation of this activity. Thus the results of electrochemical measurements suggested that molybdenum and nitrogen are able to reduce pit initiation. The results of the electrochemical measurements for predicting pitting corrosion resistance of CA6NM in artificial geothermal brine are certified and confirmed by the results of the calculations of PREN value listed on table 5. The higher the PREN value, the more resistant the pitting corrosion.

To study the synergistic interaction between Mo and N the pitting potential direct increase, ΔE_{pit} , which appeared as a result of the addition of Mo or both is listed on table 5. In this sense, ΔE_{pit} , represents individual effects of only Mo being added to the alloy, that is, $\Delta E_{\text{pit, Mo}} = E_{\text{pit CA6NM2}} - E_{\text{pit CA6NM1}}$ (1).

In the sameway, the synergistic effect should be related to the concomitant presence of Mo and N, expressed by

$$\Delta E_{\text{pit, Mo and N}} = E_{\text{pit CA6NM3}} - E_{\text{pit CA6NM1}} \quad (2)$$

Results of the calculation of the pitting potential direct increase clearly shows that the combined effect of Mo and N represented by equation (2) is largely beyond the sum of Mo individual effects (equation (2)). Hence the existence of a synergetic positive effect of Mo and N on the pitting potential values is confirmed for CA6NM. This experiment result is in good agreement with Carole Loable, et.al experiment result [13].

Table 4. Parameters from cyclic polarization.

Samples	E_{pit} (mV vs SCE)	E_{prot} (mV vs SCE)	E_{corr} (mV vs SCE)
CA6NM1 with CO_2 gas	-548.2	-335.9	-528.7
CA6NM2 with CO_2 gas	-462.7	-265.4	-528.1
CA6NM3 with CO_2 gas	-454.2	-256.9	-439.2
CA6NM1 without CO_2 gas	-435.1	-462.5	-530.5
CA6NM2 without CO_2 gas	-311.0	-331.0	-486.2
CA6NM3 without CO_2 gas	-258.8	-308.1	-463.9

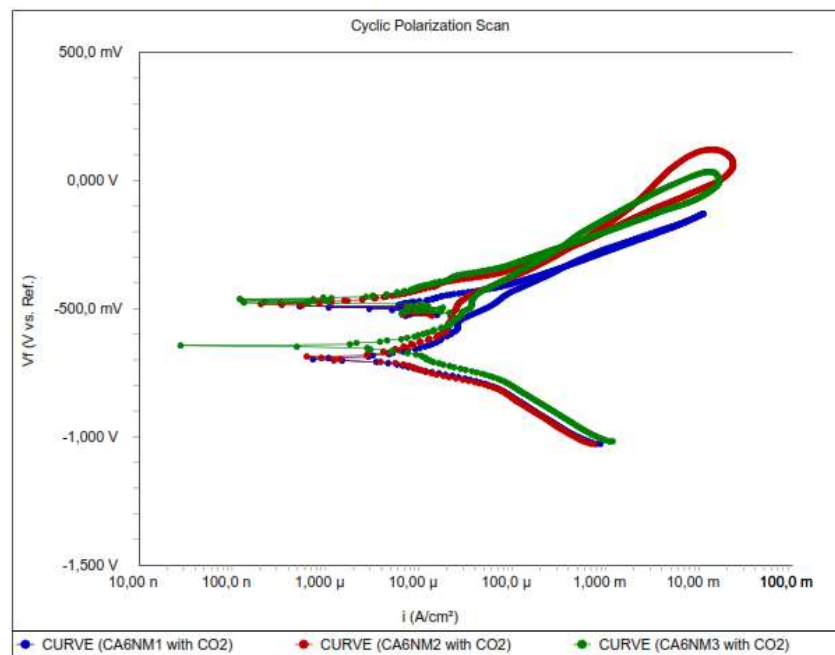


Figure 2. Cyclic polarization curve CA6NM in artificial geothermal brine with CO₂ gas.

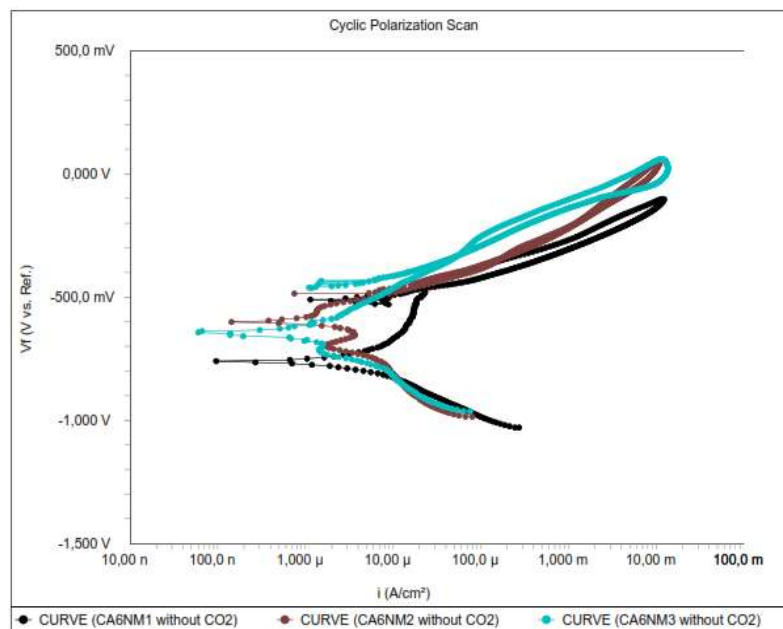


Figure 3. Cyclic polarization curve CA6NM in artificial geothermal brine without CO₂ gas.

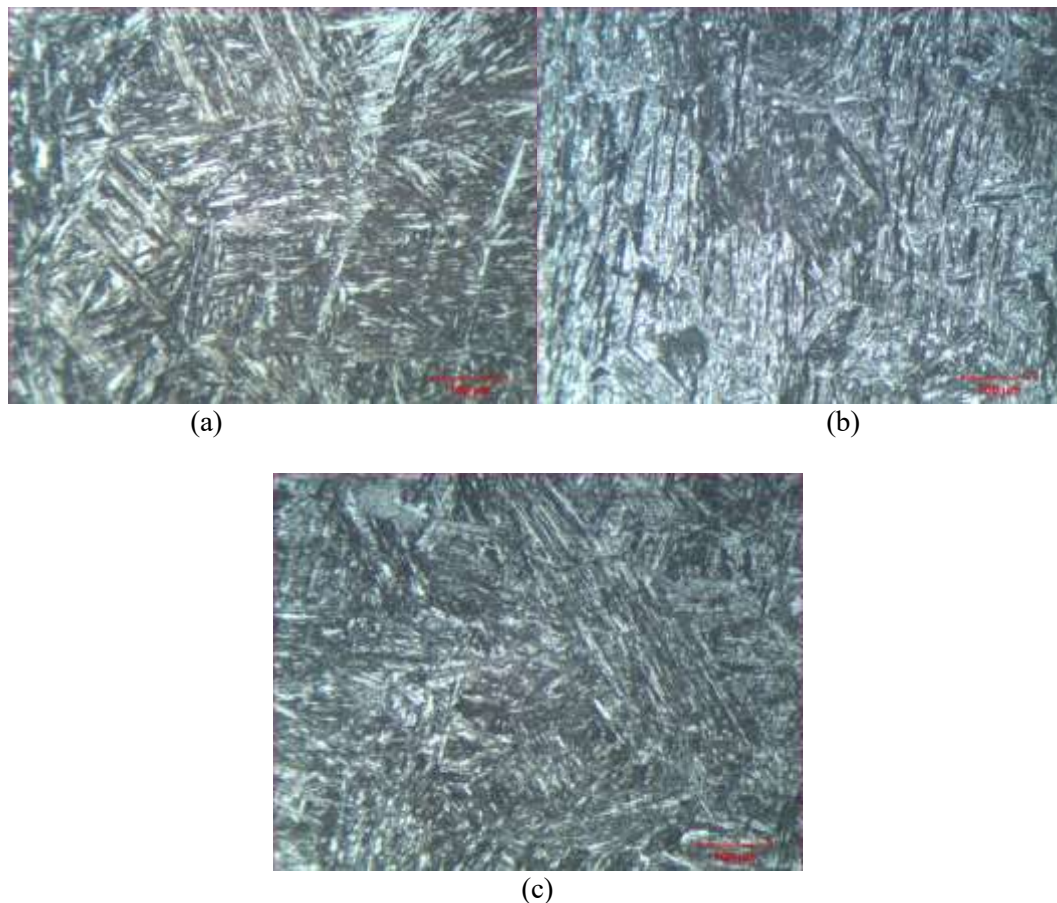
Table 5. PREN value of CA6NM.

Samples	PREN
CA6NM1	16.3
CA6NM2	19.6
CA6NM3	21.2

3.3. Microstructure Analysis

Figure 4(a)-4(c) were microstructure photos using optical microscope of CA6NM1, CA6NM2, and CA6NM3, respectively that austenitized at 1050°C for 3 hours and tempered at 670°C for 3 hours. The result showed all samples have same microstructure that consists most of lath martensite, small portion of ferrite and austenite.

After conducting cyclic polarization measurement, all samples were characterized using scanning electron microscope (SEM) to observe pitting size. Figure 5(a)-5(c) show the SEM images of CA6NM1, CA6NM2, and CA6NM3, respectively in artificial geothermal brine without CO₂ gas. Based on figure 5, pitting corrosion exist in test materials immersed in artificial geothermal brine without CO₂ gas at different diameter size of pit. The smallest pit size is CA6NM3 which has an average pit diameter of 3µm. To prove that pitting corrosion exist was carried by using EDAX analysis. Figure 6 shows EDAX result in pit area and not corroded area of CA6NM1. The presence of O element in pit area proves that there is product corrosion in pit area, so it is true that the pit is pitting corrosion.

**Figure 4.** Microstructure of (a)CA6NM1, (b)CA6NM2, (c)CA6NM3.

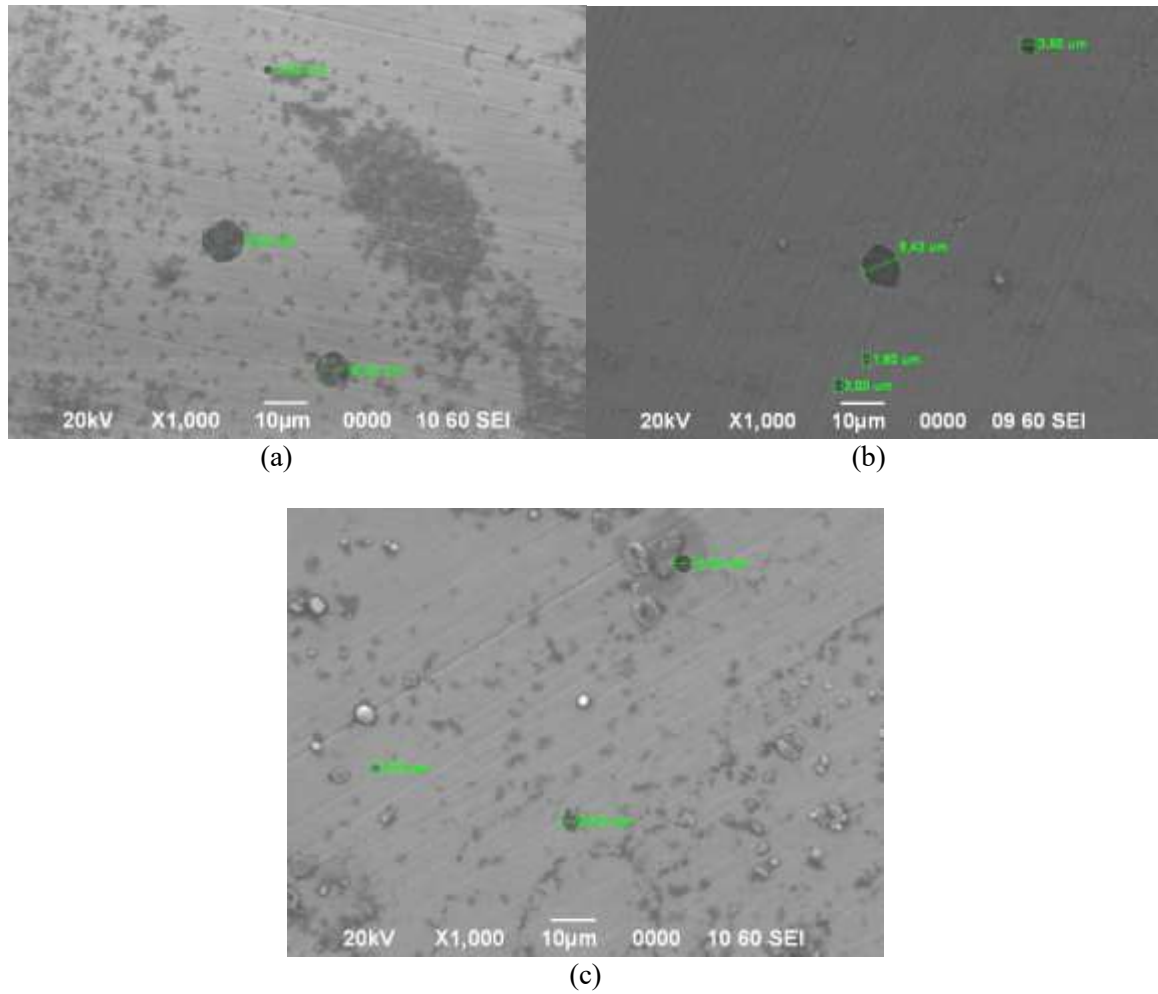


Figure 5. SEM micrograph of (a) CA6NM1, (b) CA6NM2, (c) CA6NM3 after conducting cyclic polarization in artificial geothermal brine without CO₂ gas.

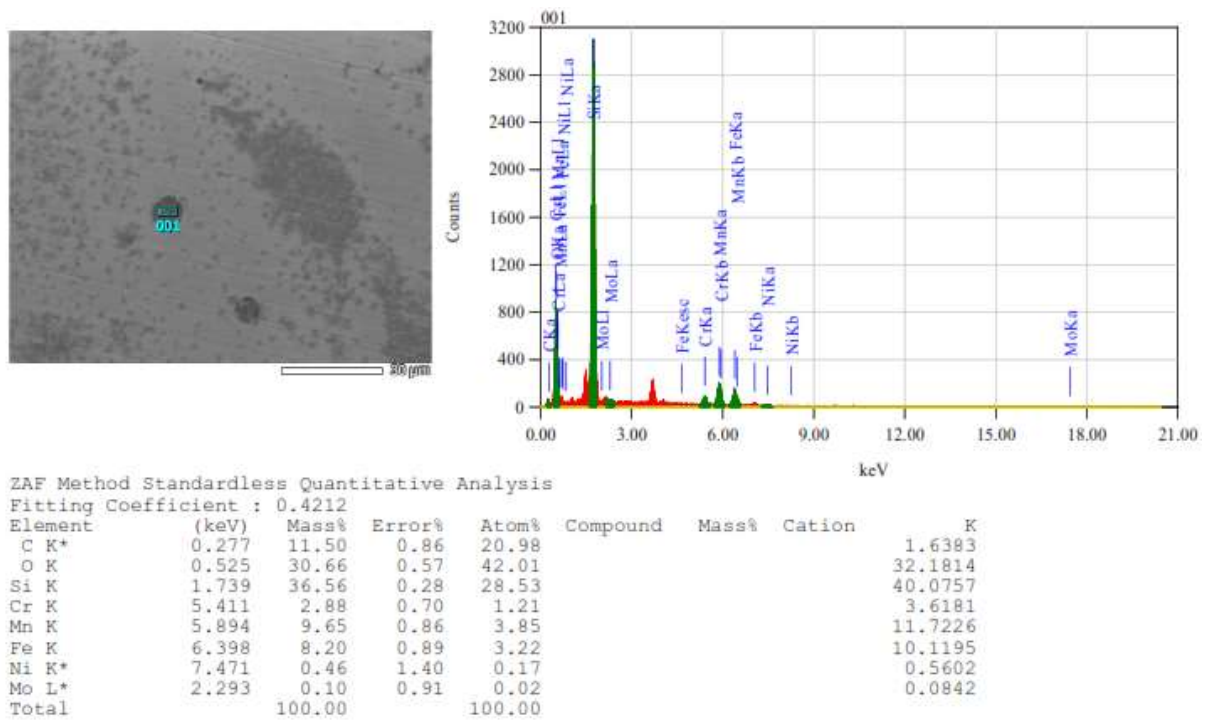


Figure 6. EDAX analysis in pit area of CA6NM1.

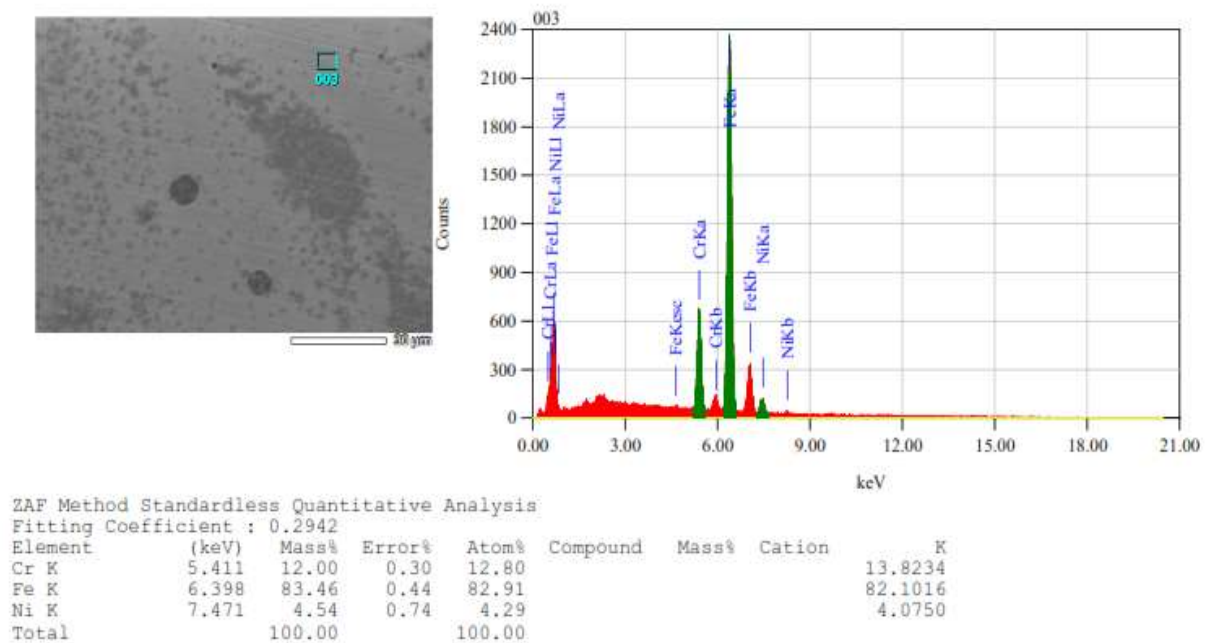


Figure 7. EDAX analysis in not corroded area of CA6NM1.

4. Conclusion

The following conclusions can be drawn from the results of the present work with regard to the performance of CA6NM stainless steel material at different content of Molybdenum and Nitrogen in the artificial geothermal brine with and without CO₂ gas. CA6NM in artificial geothermal brine without CO₂ gas have susceptibility to pitting corrosion while CA6NM in artificial geothermal brine with CO₂ gas have no tendency to pit even though the environment is more aggressive. CA6NM have ability to lead repassivation when pitting corrosion initiated so CA6NM resistant to pitting corrosion. This resistance to pitting increases with increasing Mo content in the alloy. Pitting corrosion resistance of CA6NM in artificial geothermal brine was significantly intensified when added both Mo and N as we clearly showed that the combined effect of Mo and N is largely beyond the sum of their individual effects in artificial geothermal brine. Pitting corrosion considerably in the presence of O element in pit area as product corrosion. Average diameter of pit decreases with increasing Mo and N content in CA6NM. Therefore, Mo and N content give positive effect in the pitting corrosion resistance of CA6NM in artificial geothermal brine.

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