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Corrosion behaviours of high Cr–Ni cast steels in the HCl solution

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ABSTRACT

In this study, the effect of composition and heat treatment (aging) on the corrosion resistance of high alloy steels containing 0.4% C, 29% Cr and 4–20% Ni has been investigated. Aging heat treatment was composed of quenching after holding at 1200 °C for 6 h and aging at 750 °C for 18 h. Corrosion tests were performed by suspending the samples of certain sizes into the 10% HCl solutions measuring the weight loss, and also by potentiodynamic polarization measurements in the same solution. The results of the corrosion tests revealed that, corrosion resistance of the aged alloys was increased with increasing Ni content. On the other hand, corrosion resistance of the austenitic matrix alloys was increased upon aging heat treatment while that of ferritic matrix alloy decreased with aging.

1. Introduction

High alloy (high Cr and Ni) steels are widely used in many manufacturing processes in chemical and petrochemical industries. The main advantage of this steel family is the superior corrosion resistance in certain environments. The high corrosion resistance of these steels is due to alloying elements such as Cr, Ni and Mo, but also depends on the microstructure. However, these steels are susceptible to some embrittlement phenomena related to grain growth, sigma-phase formation [1–4].

The improvement in the properties of investigated high alloy steels is directly related to the development of microstructure, which mainly consists of a matrix and carbides and/or intermetallics dispersed in it. Depending on the composition, the matrix can be austenitic, ferritic or martensitic. Chromium, which is a strong carbide forming element stabilizes ferritic matrix. However, Ni stabilizes austenitic matrix and decrease carbide precipitation. Moreover sigma phase is the main types of intermetallics that can appear in the microstructures [5–8]. The increase in the content of the elements Cr, Ni and Mo accelerates the precipitation of σ-phase during exposure to high temperatures (700–1000 °C). This σ-phase formation leads to serious embrittlement. The precipitation of σ-phase is found to be the most rapid and it has the strongest influence on corrosion resistance [9,10].

In the literature about the corrosion and corrosive wear behaviours of stainless steels and/or low alloy Cr–Ni steels in various solutions and there are limited studies on the corrosion behaviours of cast steels containing high Cr and Ni. Additionally, there are only a few studies on the effect of sigma phase on the corrosion behaviours of these steels in HCl solution. In this study the effects of sigma phase in three kinds of high Cr–Ni cast steels on corrosion behaviours were investigated in HCl solution.

In the present work, the corrosion behaviour of high Cr–Ni cast steels with different nickel contents (4–20% Ni) in the HCl solution was studied using potentiodynamic polarization method. The effects of composition and age heat treatment on the corrosion resistance of the alloys were investigated. The effect of sigma-phase precipitation at 750 °C on corrosion behaviour was discussed and optical microstructural examinations and hardness measurements were also performed for evaluation.

2. Materials and methods

Chemical compounds of the investigated alloys, coded as A1, A2 and A3 with respect to their increasing Ni content, are given in Table 1. In the present study, these alloys were tested in the as-cast and heat-treated conditions. Heat treatment consisted of quenching and aging procedures. The alloys held at 1200 °C for 6 h were water quenched and then aged at 750 °C for 18 h.

Characterization of the as-cast and heat-treated alloys was made by metallographic examinations and hardness measurements. The microstructure of the alloys was examined by a Nikon Epiphot 200 model light optical microscope (LOM) after polishing according to standard metallographic procedures and then etching electrolytically with oxalic acid and/or sodium cyanide for 15 s at 1.5 V. Hardness tests were performed on metallographic samples by using Schimadzu microhardness tester with a Vickers pyramid indenter under a normal load of 1 kg.

The immersion tests were carried out by suspending the square shaped samples (20 mm × 15 mm × 4 mm) in a still solution of 10 wt.% HCl in deionized water exposed to atmospheric air. The amount of the solution in the beaker was estimated by taking the surface area of the specimens as 0.3 ml/mm^2 into account. Evaluation of the corrosion was determined by measuring weight loss for 165 h. For measurement of the weight loss, the surfaces of the samples were ground with 1200 mesh

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SiC abrasive paper prior to the tests. After the test, these samples were well cleaned with distilled water and were weighed by an electronic balance having a resolution of ±0.1 mg. The normalized weight loss values of the investigated alloys were calculated in the unit of g/mm^2 by dividing the weight loss of the each sample by their initial total surface area.

For the potentiodynamic polarization measurement tests, machined samples (10 mm in length and 15 mm in diameter) were mounted on copper rod using epoxy resin for electrical connection, and open surfaces of all samples were polished with up to 1200 grit SiC emery paper. The electrochemical tests were carried out at room temperature using a Gamry model PC4/300 mA potentiostat/galvanostat controlled by a computer with DC 105 Corrosion analysis software. The electrochemical cell consisted of three electrodes: a working electrode, a reference electrode (a saturated calomel electrode, SCE) and a counter electrode (a carbon rod). During the electrochemical corrosion test, the electrode potential was scanned at a scan rate of 1000 mV/min from −1500 mV towards anodic potential. Experiments were performed at room temperature in a glass cell containing 10% HCl solution. Each data point for both immersion and potentiodynamic polarization tests represents the average of three different measurements.

Finally, the cross-sections of the samples were examined with a LOM after employing the conventional metallographic preparation procedure in order to examine corrosion penetration through the thickness.

Table 1
Chemical compounds of the investigated alloys.

Alloys	C %	Ni %	Cr %	Si %	Mn %	Mo %	V %	Cu %	W %
A1	0.33	4.65	27.45	1.21	0.74	0.15	0.06	0.12	0.06
A2	0.36	12.37	24.63	1.08	0.73	0.17	0.06	0.14	0.08
A3	0.38	19.75	24.54	0.92	0.68	0.15	0.05	0.13	0.09

Table 2
Hardness of the as-cast and aged alloys.

Alloys	As-cast	Aged
A1	275 ± 12	290 ± 8
A2	221 ± 11	272 ± 12
A3	210 ± 10	260 ± 9

3. Results and discussion

The microstructures of the as-cast and aged alloys are shown in Fig. 1. In general, microstructures consisted of a matrix (light regions) and carbides (dark regions). Carbides, which appeared in globular (cored) morphologies, are $Cr_{23}C_6$ type. Steels containing more than 21 wt.% Cr generally have ferritic microstructure at room temperature if the ratio of Cr_{eq}/Ni_{eq} is higher than 1.8. Austenite persists to room temperature at extended concentrations of Ni. High alloy steels, whose Cr_{eq}/Ni_{eq} ratio is less than 1.3, solidify fully austenitic and remain austenitic at room temperature

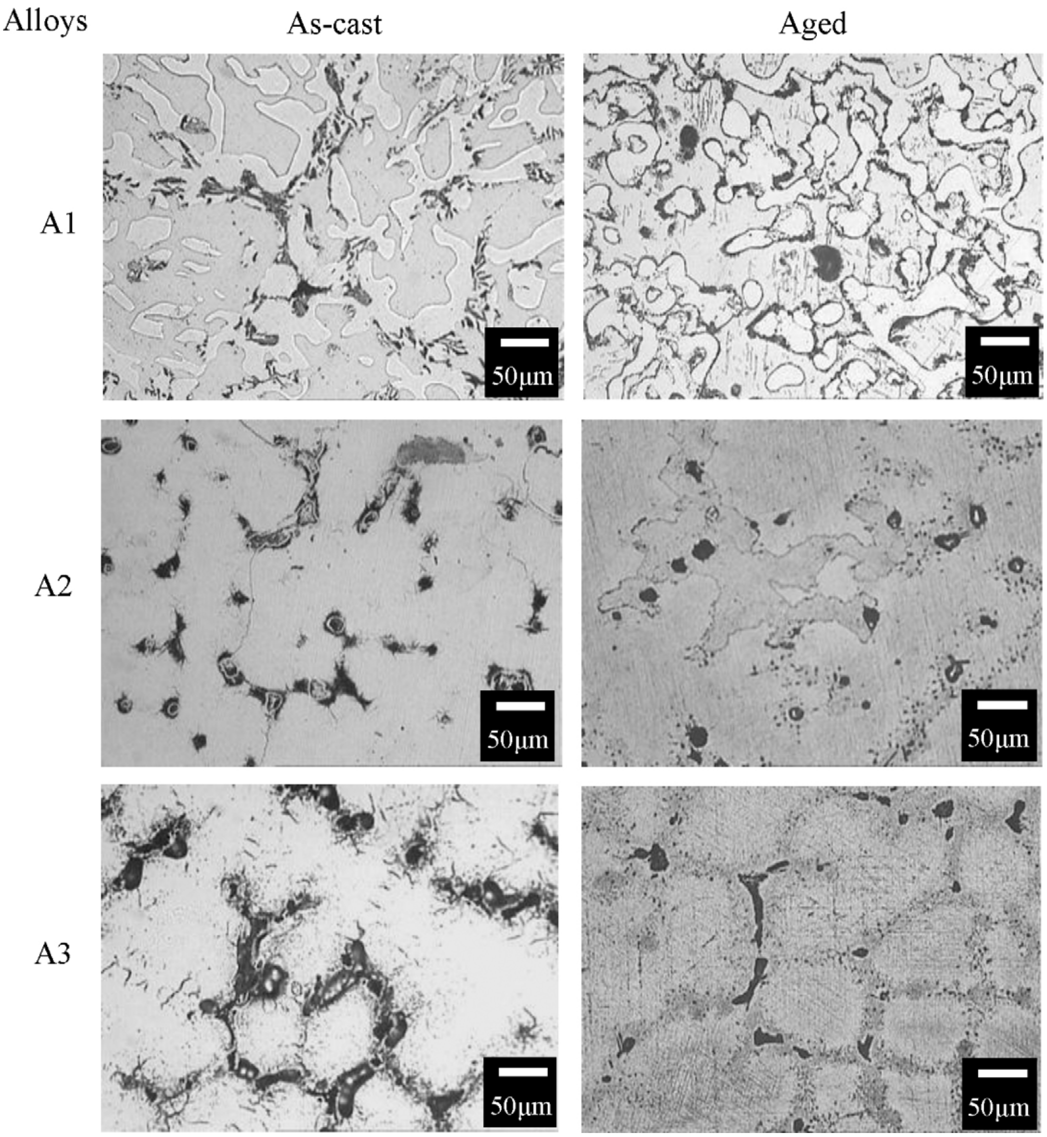

Fig. 1. Oxalic acid etched microstructures of the as-cast and aged alloys.

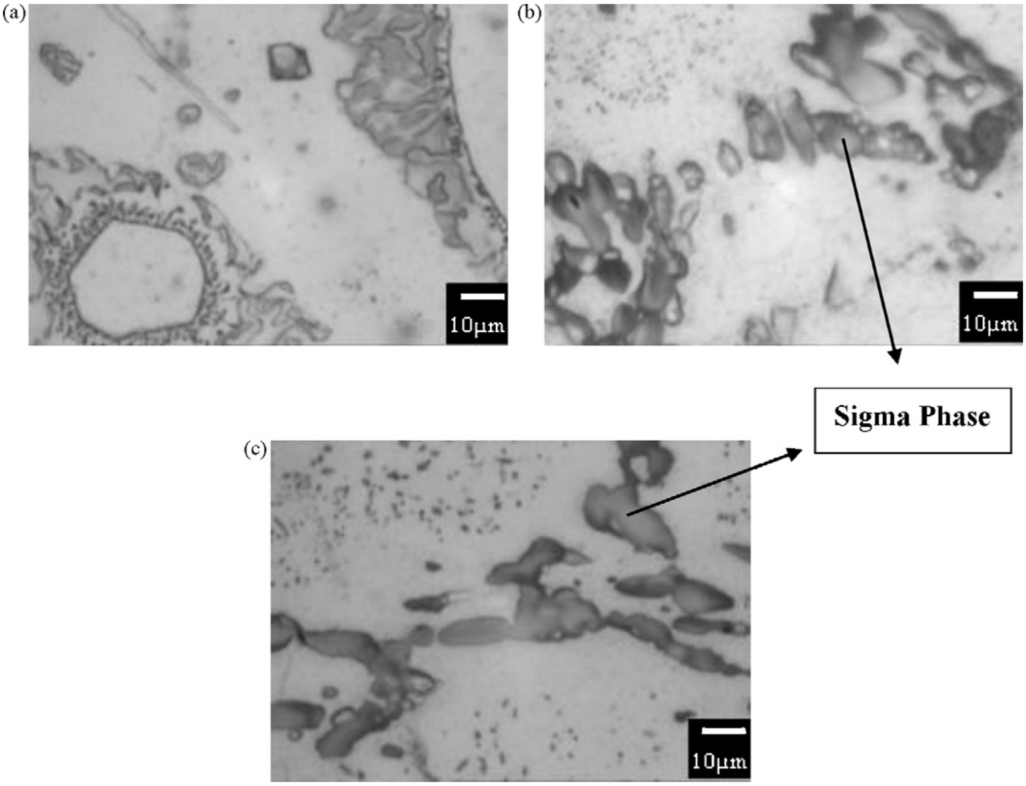

Fig. 2. Sodium cyanide etched microstructures of the aged alloys (a) A1, (b) A2 and (c) A3, showing sigma-phase precipitation.

[5,11–13]. Both in the as-cast and in the heat-treated conditions (Fig. 1), the matrix of the low Ni containing alloy A1 was fully ferrite. The matrixes of alloys A2 and A3 remained austenitic at room temperature because of their relatively high Ni contents.

In our literature study [1,4], it is expected that the sigma phase will occur in microstructure with aging heat treatment in these alloys. However, it is stated that sigma phase cannot be seen due to etching in oxalic acid, but it can be seen if it is etched in sodium cyanide solution. Therefore, optic microscope images were determined by etching aged alloys in sodium cyanide solution (Fig. 2). In this way, sigma phase was observed in alloys A2 and A3.

The result of hardness measurements conducted on the as-cast and heat-treated alloys is presented in Table 2. In the as-cast and heat-treated conditions, the hardness of the alloys decreased with increasing Ni content. This can be attributed to the stabilization of austenitic matrix. Since the austenite has greater capacity of carbon dissolution than ferrite, Ni addition reduces carbide precipitations in the matrix. In a given composition, the hardness increased due to precipitation of sigma phase, during the applied heat treatment [8,14,15]. The improvement in hardness after heat treatment is evident for austenitic matrix alloys, A2 and A3.

According to the results of immersion corrosion, the change in weight loss values of investigated alloys depending on the experiment period is shown in Fig. 3. With increase of the experiment period both in the as-cast and aged alloys, the weight loss increased too. The least corrosion in the as-cast condition was obtained from alloy A1. With aging heat treatment, while corrosion of A1 alloy severely increased, aging was observed to have a positive effect on corrosion in alloys A2 and A3.

The change of weight loss values of investigated alloys occurred after 165 h with regard to Ni content is given in Fig. 4. As it can be seen in this figure, while there occurred a severe increase in the weight loss of alloy A1 with aging heat treatment, only a little amount of decrease was observed in the other alloys. However, exacerbation of corrosive environment brought these values closer to each other.

It has been proposed in literature [14–18] that because Ni increases the stability of oxide film on surface in Fe–Cr–Ni alloys, it improves corrosion resistance of the alloy. The case in point was significantly seen in aged alloys in this study. It is known that $Cr_{23}C_6$ precipitation in microstructure of stainless steel reduces the amount of free Cr dissolving in matrix and thus the corrosion resistance decreases. On the other hand, it is claimed that corrosion resistance improves due to the precipitation of the sigma phase behaving as less cathode compared to carbide and nitride in microstructure [8,16]. In fact, obtaining higher corrosion resistance with aging in alloys A2 and A3 having austenitic matrix can be based on the precipitation of sigma phase in microstructure. Because the sigma phase did not occur with aging in microstructure in alloy Al, these alloys presented less corrosion resistance than in as-cast condition. The reason of this can be based on chromium carbide precipitation causing the matrix to lack Cr during aging heat treatment.

The potentiodynamic polarisation behaviours for the as-cast and aged alloys in 10% HCl solution are given in Fig. 5a and b, respectively. Fig. 5 shows potentiodynamic polarisation curves as a function of Ni content indicating that increasing Ni addition improves corrosion resistance. While aging heat treatment of A2 and A3 alloys has slightly reduced I_{corr} value, in the aged A1 alloy, the I_{corr} value significantly has increased. Aging heat treatment of A2 and A3 alloys has not caused a significant change in E_{corr} value. However in the aged A1 alloy E_{corr} value has decreased. The change of current concentration values (I_{corr}) obtained from these curves depending on Ni content of the alloys is shown in Fig. 6. As it is seen in Fig. 6, with an increase in the Ni content both in the as-cast condition and in aged samples, current concentration decreases. The more the current concentration decreases, the more corrosion resistance increases. Therefore, these results coincide with the

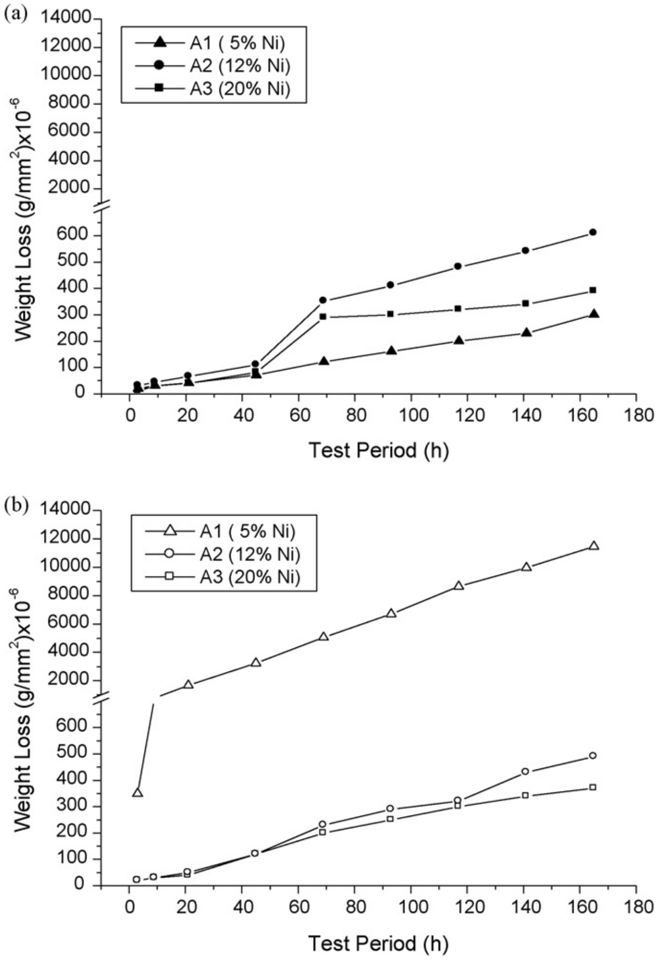

Fig. 3. Weight loss of the investigated alloys with respect to test period (a) as-cast and (b) aged.

results of weight loss. While the current concentration of alloy A1 increases with aging heat treatment, it tends to decrease in alloys A2 and A3 although it is not apparent.

Optic microscope images obtained from the section after test of alloy A1 subjected to corrosion tests in 10% HCl solution are given in Fig. 7. As it can be seen here, corrosion exacerbated significantly with aging heat treatment because extensive cracks which started on the surface and penetrated inside

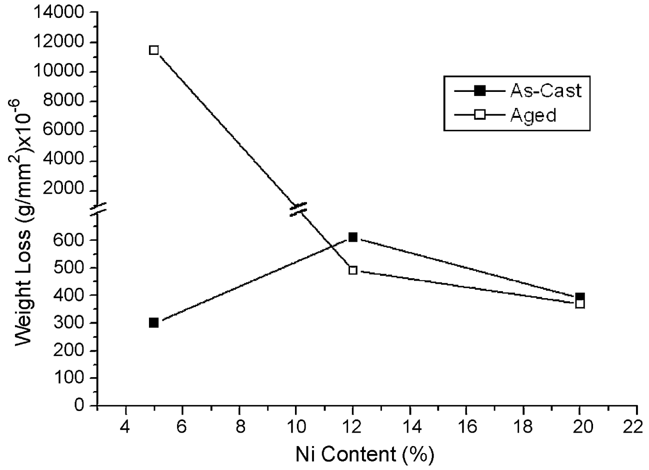

Fig. 4. Weight loss of the as-cast and aged alloys with respect to Ni content (%).

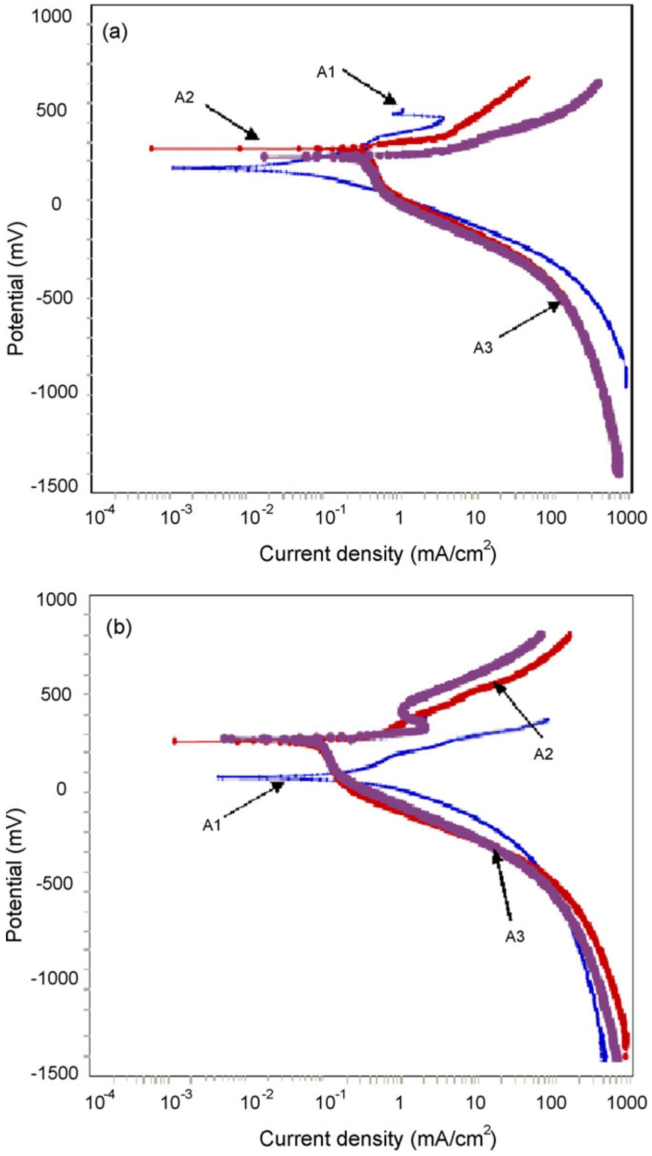

Fig. 5. Potentiodynamic polarisation curves for investigated alloys, (a) as-cast and (b) aged.

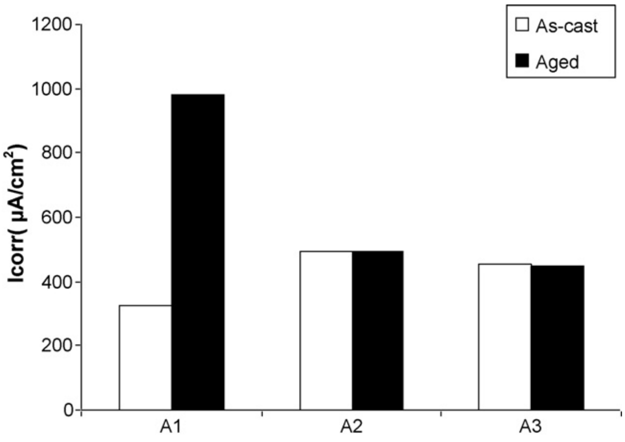

Fig. 6. The change of current concentration values (I_{corr}) obtained from the polarization curves of the investigated alloys.

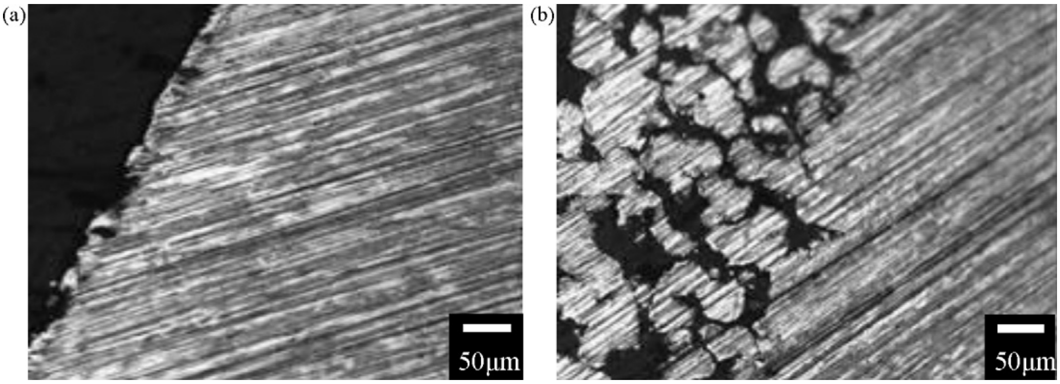

Fig. 7. Optic microscope images obtained from the section after test of alloy A1 subjected to corrosion tests, (a) as-cast and (b) aged.

are observed in cross-section image after test of aged alloy A1.

4. Conclusions

The effects of the composition and age heat treatment on the corrosion behaviours of high Cr–Ni cast steels have been investigated. Following conclusions can be drawn from the experimental works.

- Three high Cr–Ni cast alloys having various nickels content is studied. The alloy containing 5% nickel is composed of ferritic microstructure, while the alloys containing 12 and 20% nickel have austenitic microstructure at room temperature. The observations indicate that the microstructures of the alloys are strongly depended on nickel ratio in the microstructures. On the other hand, all the alloys have chromium rich $Cr_{23}C_6$ type carbides in the microstructures. Besides, sigma (σ) phase is occurred in the microstructures of the alloys containing 12 and 20% nickel after aging.
- Nickel ratio in the alloys has an effect on hardness values, which decrease with increasing nickel content. However, aging heat treatment contributes to hardness increase due to sigma (σ) phase formation in the austenitic matrix of the alloys.
- The results of corrosion tests in 10% HCl solution show that the solution used in the tests is very aggressive. Weigh loss values of as-cast alloys are not strongly influenced by nickel contents compared with aged alloys. However, weight loss values of the alloys exposed age heat treatment decrease with increasing of nickel content. Corrosion resistances are improved by increasing nickel contents in the microstructure.
- Potentiodynamic polarization tests preformed in 10% HCl solution exhibit that current concentration increases in the alloy coded A1 after aging, however, it presented very close values to one another in alloys A2 and A3 both in the as-cast and aged conditions.

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