

Effect of Ni on the corrosion behavior of Fe–Al intermetallics in simulated human body fluid

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Received: 18 May 2007 / Revised: 14 August 2007 / Accepted: 18 August 2007 / Published online: 15 September 2007
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Abstract The corrosion behavior of FeAl-type intermetallic alloy in the Hank's solution has been investigated after additions of 1, 3, and 5 at.% Ni with or without thermal annealing at 400 °C for 144 h. Techniques included potentiodynamic polarization curves, linear polarization resistance, and change of the free corrosion potential with time and electrochemical noise in current. Regardless of the heat treatment, additions of Ni increased both the free corrosion potential and the pitting potential values. Additionally, both the corrosion current and the passive current densities were reduced with this element. The alloys which did not suffer from pitting type of corrosion were the heat-treated FeAl base alloy and the one containing 5Ni. Both additions of Ni and thermal annealing improved the adhesion of external protective layer either by avoiding the formation of voids or by lowering the number of precipitates and making them more homogeneously distributed.

Keywords Iron aluminides · Corrosion · Casting · Electrochemical techniques · Human fluid

Introduction

Iron aluminides have been considered good candidates for high-temperature service because of their high oxidation and sulfidation resistance, relatively high strength, and potentially lower costs than many high-temperature structural materials [1, 2]. However, the rather low ductility at room temperature has hindered these aluminides as compared to many other intermetallics [3–6]. FeAl-type intermetallics are widely used for their high-temperature oxidation resistance due to their ability to develop an Al₂O₃ protective layer, which also provides corrosion resistance in molten salts [7, 8]. However, one of the main drawbacks for these aluminides is their poor ductility. Salazar et al. [9] found that by alloying with either Li or Ni results in the improvement of their ductility as measured in their compressive ductility, and this improvement was increased if the specimens were annealed at 400 °C for 120 h. Apart from their high-temperature corrosion resistance, iron aluminide compounds are receiving a considerable attention relative to aqueous corrosion properties such as acidic, basic, chloride, and sulfur compound solutions [10–13]. Among the novel room temperature applications of these materials, can be considered their potential use such as biomaterials, or in applications in a seawater atmosphere [14–17]. Garcia-Alonso, for instance, found that the corrosion rate of Fe₃Al-type intermetallic under three different heat treatments was within the same order of magnitude than that for 316L-type stainless steel in a simulated human body fluid [7], whereas Lopez [8] obtained similar results with another iron-base alloy. Normally, 316L-type stainless steel [18] or Ti-base alloys [19, 20] and with less frequency Ni-base alloys [21, 22] or Al-base alloys [23] have been used for biomedical applications. Thus, the aim of this

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Table 1 Chemical composition of the used electrolyte

	NaCl	CaCl ₂	KCl	Glucose	NaHCO ₃	MgCl ₂ ·6H ₂ O	Na ₂ HPO ₄ ·2H ₂ O	KH ₂ PO ₄	MgSO ₄ ·7H ₂ O
g/l	8	0.14	0.4	1	0.35	1	0.06	0.06	0.06

work is to explore the possible use of FeAl-type intermetallic materials with different additions of Ni and different microstructures as a biomaterial.

Experimental procedure

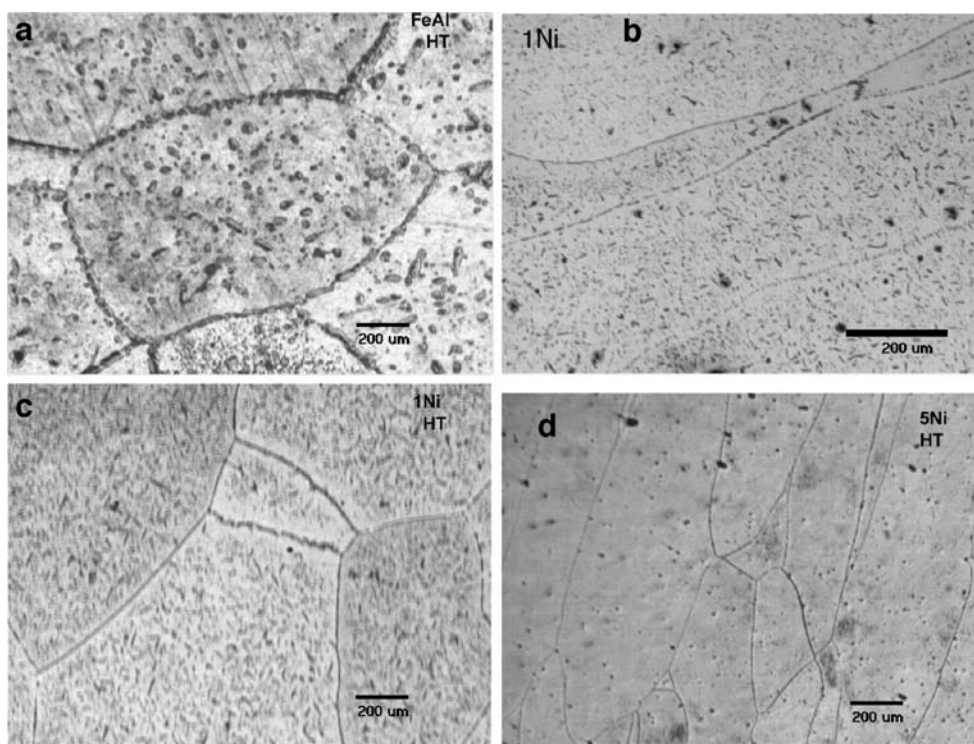
Intermetallic Fe₅₀Al₅₀ alloy was melted in an induction furnace using silicon carbide crucibles. Pure Ni with 1, 3, and 5 at.%, respectively, was added to the AlFe intermetallic compound. All elements were 99.9% of purity. To avoid the specimens machining procedure, the ingots were obtained with ending dimensions according to the E800b ASTM standard. Cylindrical specimen dimensions were 0.5-in. diameter×2-in. length in the test section and 2.5 in. for the final section. The ingots were annealed to minimize the thermal vacancy effects by heat treating them at 400 °C for 144 h under an argon atmosphere. As corrosive agent, the Hank's solution with a chemical composition given in Table 1 was used. This solution simulates the physiological media of the human body. To perform the corrosion tests, specimens of 5×5×3 mm were machined by an electrodischarge machine, encapsulated in epoxy resin and then

polished with diamond paste to a 0.1-μm finish. Electrochemical experiments were performed using an ACM Instruments potentiostat controlled by a personal computer. Potentiodynamic polarization curves were obtained by varying the applied potential from −500 mV with respect to the free corrosion potential, E_{corr} , up to +600 mV at a rate of 1 mV/s. Before the experiments, the E_{corr} value was measured for approximately 30 min, until it was stable. All the potentials were measured using a Saturated Calomel Electrode as reference electrode. The counter electrode was graphite. Corrosion rates were calculated in terms of the corrosion current, I_{corr} , by using linear polarization resistance curves, which was done by polarizing the specimen from +10 to −10 mV, with respect to E_{corr} , at a scan rate of 1 mV/s, a standard scanning rate for this kind of experiments, to get the polarization resistance, R_p . Using the Stearn–Geary [22] equation, the I_{corr} value was calculated as follows:

$$I_{\text{corr}} = \frac{b_a b_c}{2.3(b_a + b_c)} \cdot \frac{1}{R_p} \quad (1)$$

where b_a and b_c are the anodic and cathodic slopes obtained from the polarization curves. The susceptibility to pitting

Fig. 1 SEM micrograph of **a** heat-treated FeAl, **b** FeAl+1Ni, **c** heat-treated FeAl+1Ni, and **d** heat-treated FeAl+5Ni alloys



corrosion was evaluated by using electrochemical noise (ECN) readings in current. For the ECN measurements, a zero resistance ammeter from ACM Instruments was used, controlled using a desk top computer. Time records consisted of blocks of 1,024 readings, taken at 1-s intervals, using two identical electrodes arrangement. After the experiments, the specimens were cleaned to be observed in the scanning electronic microscope (SEM).

Results and discussion

Microstructures

Figure 1 shows the effect of Ni contents and heat treatment on the FeAl-type intermetallic microstructures. As we can see, the presence of a big amount of precipitates is evident in most of the specimens. In these type of FeAl-base alloys, these precipitates have been reported to be Fe₃AlC, inside the grains, and Al₂O₃, present at the grain boundaries together with the FeAl matrix [9]. The size and distribution of these precipitates change with the chemical composition or heat treatment, but in essence, they are the same particles. An exception is found with the heat-treated alloy containing 5Ni, where an appreciable reduction in these precipitates is observed. The presence of these precipitates affects the corrosion behavior of the material, as micro-electrochemical cells are established between the precipitates and the matrix, acting either as local cathodes or anodes, or acting as discontinuities in the passive film, therefore inducing local type of corrosion.

Corrosion tests

Figures 2 and 3 show the effect of Ni contents and heat treatment on the polarization curves for FeAl-type inter-

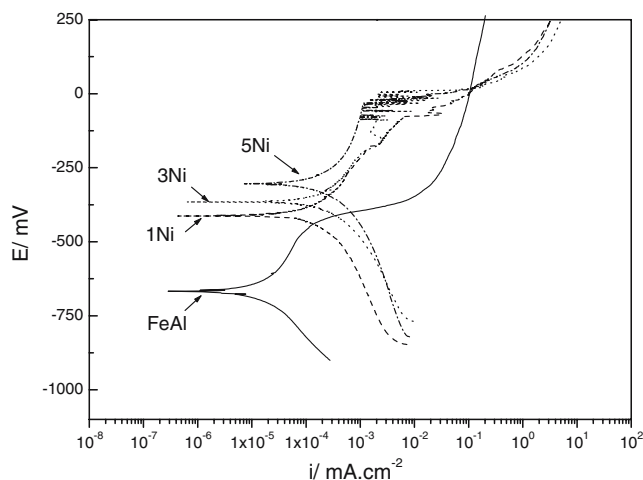


Fig. 2 Effect of Ni content on the polarization curves of FeAl intermetallic alloys

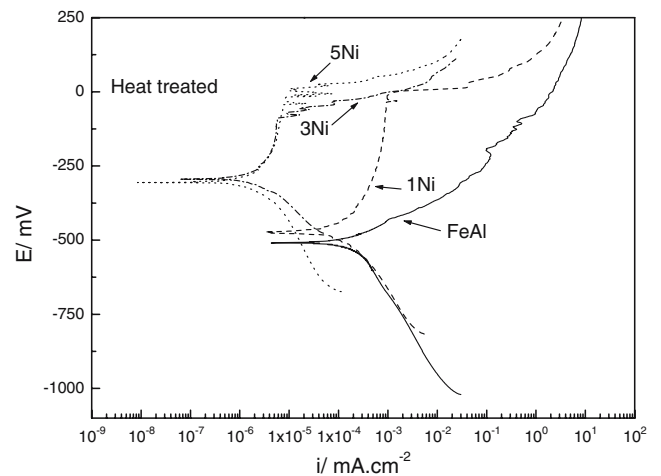


Fig. 3 Effect of Ni content on the polarization curves of annealed FeAl intermetallic alloys

metallics; Fig. 2 shows that, for FeAl-base alloy, the anodic current density starts to increase from the free corrosion potential value, E_{corr} , up to a value around 5×10^{-5} mA/cm², at a potential value of -625 mV. After this potential, the anodic current density reaches a more or less constant value, around 10^{-4} mA/cm² of passive region up to a potential value of -426. After this potential, the breakdown of the passive layer occurs, as manifested by a sudden increase in the anodic current density. This breakdown potential corresponds to the onset of pitting corrosion, and this potential is called pitting potential, E_{pit} . For iron aluminides without heat treatment, both the E_{corr} and E_{pit} values increase with the nickel contents. The passive current density for iron aluminides decreased with the nickel contents too. For the heat-treated aluminides, both the E_{corr} and E_{pit} values followed a similar tendency than those for aluminides without heat treatment, although the difference between these values for samples with 3 and 5Ni was marginal. The passive region for the heat-treated FeAl alloy has disappeared this time, so there is not a breakdown or pitting potential.

Table 2 summarizes the average values of the free corrosion and the pitting potential values, together with the

Table 2 Fundamental parameters obtained from the polarization curves for the different FeAl-based intermetallics

Sample	E_{corr} (mV)	E_{pit} (mV)	$E_{pit} - E_{corr}$ (mV)
FeAl	-670	-426	244
FeAl+1Ni	-414	-76	338
FeAl+3Ni	-350	-45	305
FeAl+5Ni	-300	-39	261
FeAl HT	-503	-	-
FeAl+1Ni HT	-467	-2	465
FeAl+3Ni HT	-307	-7	300
FeAl+5Ni HT	-295	2	297

size of the passive region as given by the difference between these two values. We can see that the probability for pitting to occur as given by the E_{pit} value is decreased by both the increase in the Ni contents and by heat treating the specimens. The width of the passive region for unalloyed FeAl intermetallic is also increased in the same way.

Measurements of E_{corr} value during 14 days confirmed these tendencies, as shown in Figs. 4 and 5. Regardless the heat treatment, the E_{corr} values for FeAl and FeAl+1Ni followed a behavior very similar during the 14 days, being always the value for the alloy without Ni more active. The E_{corr} value for the FeAl+3Ni tended towards more active values, whereas for the FeAl+5Ni, the opposite was true, i. e., the E_{corr} value tended towards more positive values. On the other hand, for heat-treated aluminides followed a very similar pattern as the one observed for the samples without heat treatment, as can be seen in Fig. 5, with the exception that, in the last 4 days, the E_{corr} value for the FeAl+5Ni alloy was made more active after reaching the most positive values.

The change on the I_{corr} value with time for the specimens without and with heat treatment is given in Figs. 6 and 7, respectively. Figure 6 shows that, for iron aluminides without heat treatment, the I_{corr} value decreases as the Ni contents increase, reaching a maximum value with the alloy containing 5Ni almost ten times higher than the unalloyed aluminide. A very similar behavior was observed for heat-treated samples: The I_{corr} value decreased as the Ni contents in the alloy increased, although at the last days of testing, the corrosion resistance for the alloys containing Ni was very similar to each other (Fig. 7). This time, the difference in corrosion rate for unalloyed intermetallic and the one with 5Ni was ten times too. It can be seen that the difference in the corrosion rates among the aluminides with and without heat treatment was marginal.

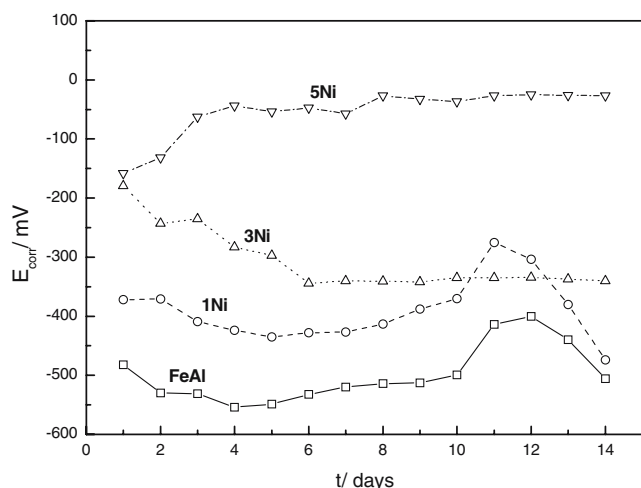


Fig. 4 Effect of Ni additions on the variation of E_{corr} with time for FeAl intermetallic alloys

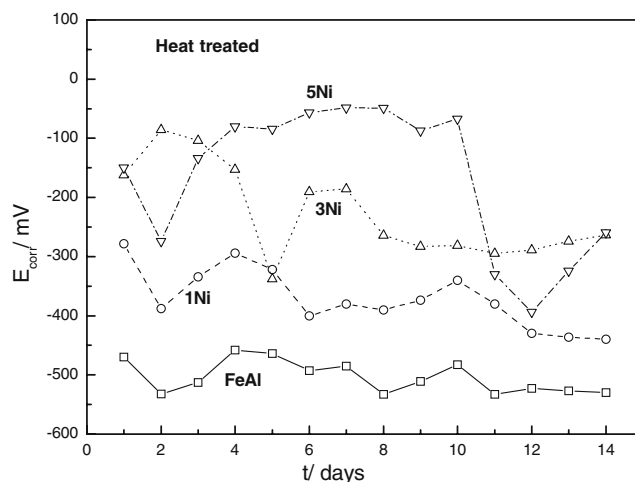


Fig. 5 Effect of Ni additions on the variation of E_{corr} with time for heat-treated FeAl intermetallic alloys

A more detailed study of the tendency towards pitting type of localized corrosion was performed by using ECN in current. The series time for the current is given in Figs. 8 and 9. The FeAl-base alloy showed transients of intensity lower than 10^{-5} mA/cm² with very high frequency, and very few transients of higher intensity and low frequency, typical of localized corrosion such as pitting [23]. With the addition of 1 or 5Ni, the intensity and frequency of the transients typical of pitting type of corrosion increased, meaning that the sites for film breakdown and possibility for pitting to occur have increased. With the addition of 3Ni, the number of transients is similar to the shown by specimens with either 1 or 5Ni, but the intensity is one order of magnitude lower.

For the annealed FeAl-base alloy, the time series shows only transients with low intensity, two orders of magnitude lower than the FeAl-base alloy without heat treatment, and very high frequency, showing no transients characteristic of pitting corrosion. Therefore, the tendency

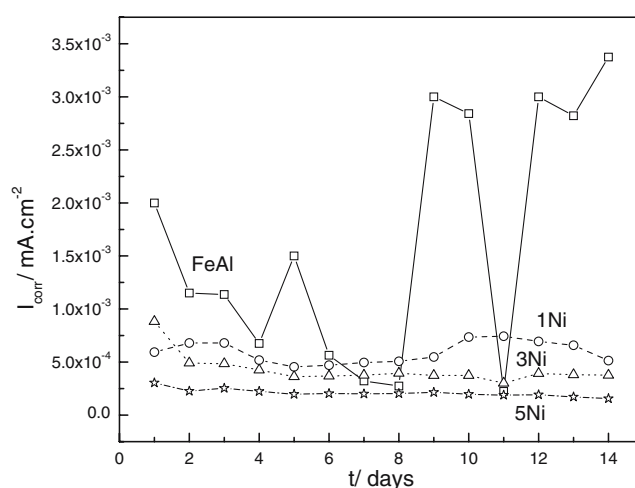


Fig. 6 Effect of Ni additions on the variation of I_{corr} with time for FeAl intermetallic alloys

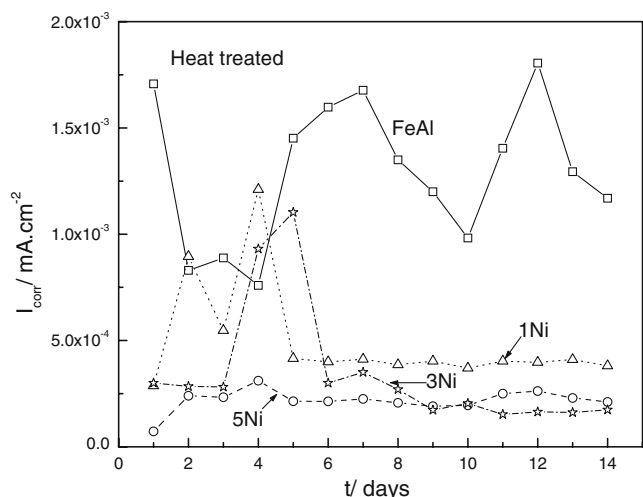


Fig. 7 Effect of Ni additions on the variation of I_{corr} with time for heat-treated FeAl intermetallic alloys

towards pitting corrosion has disappeared now, just like it had been shown by the corresponding polarization curve by this specimen (Fig. 3). With the addition of 1 or 3Ni, the time series shows now some transients with higher intensity, two orders of magnitude, and low frequency, meaning that the susceptibility for pitting corrosion to occur has increased. When 5Ni is added, however, the tendency towards pitting type of corrosion decreases, as the time series is very similar to the one shown by the FeAl-base alloy, with a few transients of high intensity and low frequency, typical of pitting corrosion [23].

The above results were confirmed by SEM analysis of the corroded surface of different specimens as shown in Fig. 10. This figure shows the surfaces of specimens with 1 and 5Ni, with and without heat treatment. We can see that, as evidenced by polarization curve in Fig. 2 and the time series shown in Fig. 8, the FeAl alloy containing 5Ni

showed any evidence of pitting corrosion, unlike the corresponding specimen with heat treatment, which did not show any evidence of pits. In the case of specimen with 1Ni, it is evident that, by heat treating the specimen, the number of pits is decreased considerably. The pits were randomly distributed on the specimens surface, and the size of them was more or less the same on the different specimens regardless its chemical composition or heat treatment.

In general terms, it has been shown that the resistance to uniform corrosion in iron aluminides type FeAl increases by alloying them with Ni, and this resistance increases with the increase in the Ni contents. By annealing at 400 °C, the corrosion resistance of this FeAl intermetallic was not greatly affected. Normally, additions of Ni have been reported to increase the corrosion resistance of iron-base alloys in acidic solution, sea water, and alkaline solutions [16]. This corrosion resistance has been reported to be due to the establishment a more stable passive layer. Frangini and Masci [24] have shown that additions of some ternary elements to FeAl intermetallics such as Cr or Ti improve the Al_2O_3 protectiveness by suppressing spalling of these scales. Additionally, they showed that, if Ni is added, there will be some diffusion of Ni outwards rather than diffusion inwards of Al, thus, preventing the formation of voids on the surface that could lead to a scale spalling. Normally, additions of Ni have been reported to increase the corrosion resistance of iron-base alloys in molten salts [7, 8]. This corrosion resistance has been reported to be due to the establishment a more stable passive layer in addition to the formation of voids as explained above.

As it can be seen in Figs. 2 and 3, by increasing the nickel contents, the passive current density is decreased with respect to the passive current exhibited by the unalloyed FeAl base alloy regardless of the heat treatment.

Fig. 8 Noise in current for the different alloys without thermal annealing

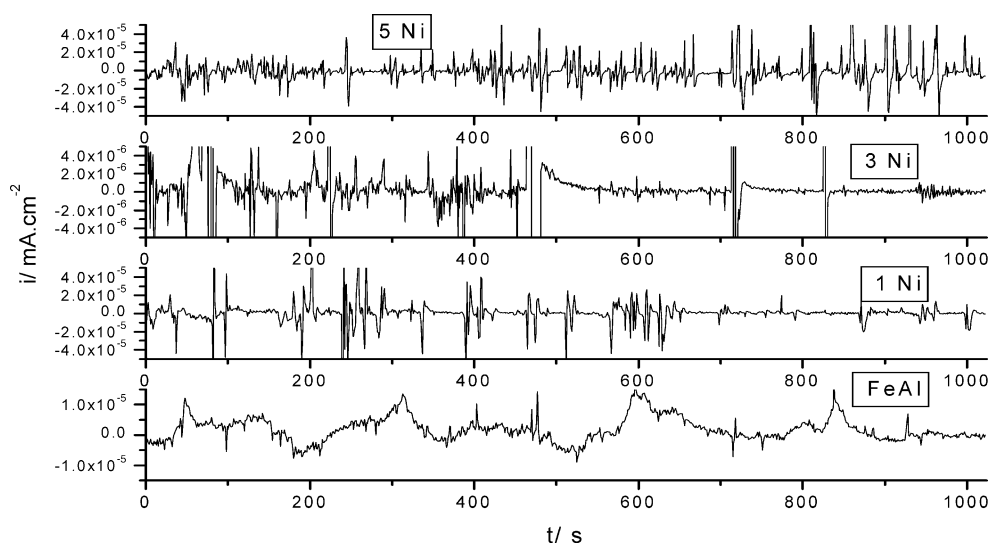
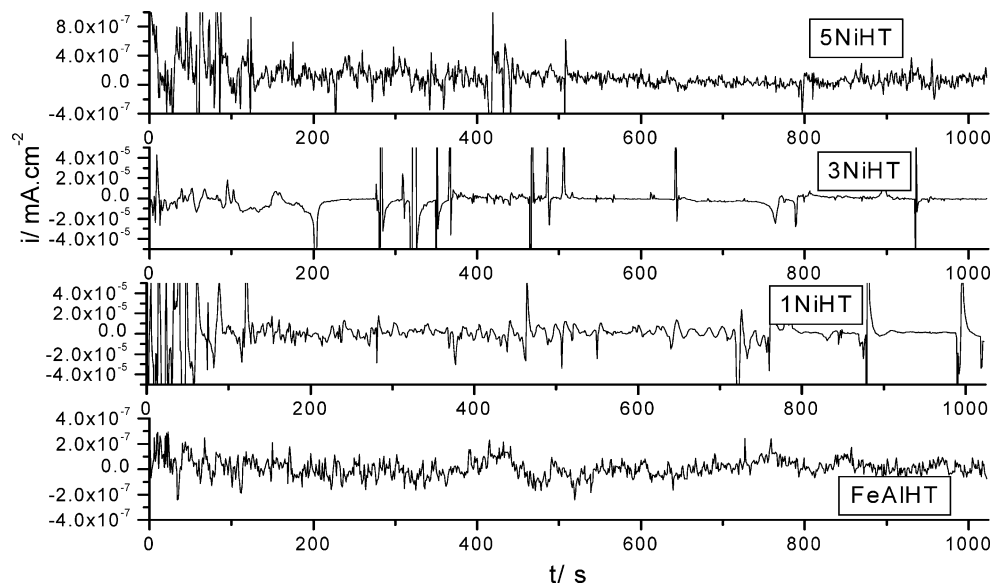


Fig. 9 Noise in current for the different thermal-annealed alloys

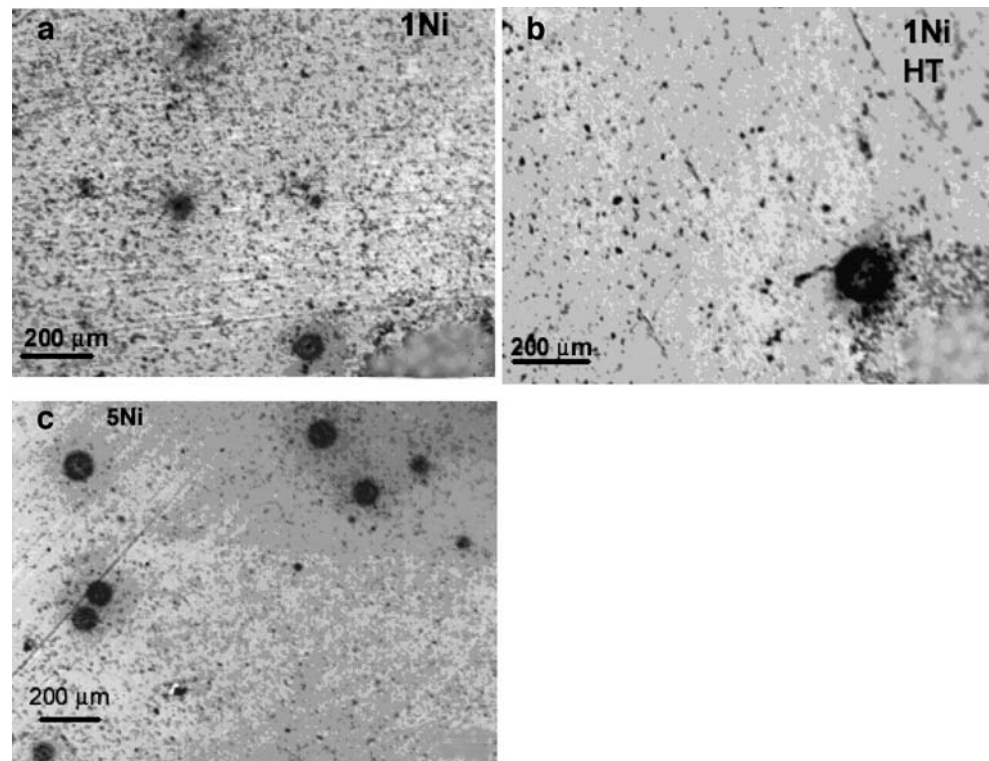


This beneficial effect of Ni addition is more evident for the case of annealed specimen, where the passive current density was decreased by more than four orders of magnitude. This may be because, by annealing the specimens, the number of thermal vacancies is minimized, and thus, the number of voids on the surface is lower, and the anchoring of the passive film to the metal surface is improved [24].

On the other side, however, as mentioned earlier, with the presence of precipitates, the establishment of micro-

electrochemical galvanic cells between the coupling of FeAl matrix and Fe_3AlC or Al_2O_3 particles, the susceptibility towards pitting type of corrosion is enhanced because the precipitates can act either active anodes or cathodes. When they act as cathodes, the surrounding matrix will corrode, and when they act as active anodes, the precipitates themselves will corrode away. If the number of precipitates is decreased somehow, like in the case of annealed FeAl+5Ni, the number of active sites which will act as anodes will be lowered, decreasing the tendency

Fig. 10 SEM micrographs of the corroded specimens showing in **a** FeAl+1Ni, **b** heat-treated FeAl+1Ni, and **c** FeAl+5Ni



towards pitting type of corrosion. By heat treating the specimens, the precipitates present in the FeAl-base alloy were drastically lowered. In FeAl intermetallic without heat treatment, there were elongated Fe₃AlC particles inside the grain boundaries together with Al₂O₃ particles along the grain boundaries. When they were heat-treated, the amount of the precipitates was decreased, and they were spherical and homogeneously distributed. This more homogeneous distribution of particles could serve for a better anchoring of the protective external Al₂O₃ layer. Similarly, Salazar et al. [9] showed that, by annealing the specimens, the formation of thermal vacancies was minimized; thus, with the presence of less vacancies on the surface, the adhesion or anchoring of the protective alumina layer is now improved.

Conclusions

The effect of additions of 1, 3, and 5 at.% Ni to the FeAl intermetallic alloy with and without a thermal-annealing heat treatment on both uniform and localized corrosion in a simulated human fluid solution has been investigated. Results have shown that, irrespective of the heat treatment, the free corrosion potential and the pitting potential values increased with additions of Ni. The passive current and corrosion current density were reduced too with additions of Ni. The susceptibility towards pitting type of corrosion was lowered significantly for the heat-treated FeAl-base and FeAl+5Ni alloys. This was because by adding Ni, the adhesion of external protective layer was improved by avoiding the formation of voids on the surface. By annealing the specimens, on the other hand, decreased the corrosion rate because it reduced the amount of particles precipitated and they were more homogeneously distributed; thus, a better anchoring of the external protective layer was promoted. Thermal annealing helped to reduce the corrosion rate by minimizing thermal vacancies and reducing the number of voids.

References

1. Noebe RD, Bowman RR, Nathal MV (1993) *Int Mater Rev* 38:193
2. Miracle DB (1993) *Acta Metall Mater* 41:649
3. Nachmann JF, Buehler WJ (1955) in *Naval Ordnance Laboratory, NAVORD Report*, 4130
4. Kayser FX (1957) *Ford Motor Company, WADC-TR-57-298*
5. Duffy ER, Nachman JF (1976) *National Technical Information Service, PB-259-253*
6. Bondeau RG (1987), *AFWAL-TR-87-40009*, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio
7. Tortorelli PF, Bishop PS (1991) In: Jones RH, Ricker RE (eds) *Environmental effects on advanced Materials, the minerals, metals and materials society*, Warrendale, P.A.: 91
8. Tortorelli PF, Natesan K (1998) *Mater Sci Eng* 258A:115
9. Salazar M, Albitzer A, Rosas G, Perez R (2003) *Mat Sci Eng* 351A:154
10. Buchanan RA, Kim KG, Ricker RE, Heldt LA (1994) *Aqueous corrosion of intermetallic alloys*. In: Stoloff NS, Sikka VK (eds) *Physical metallurgy and processing of intermetallic alloys*. Chapman and Hall, pp 517–521
11. Garcia-Alonso MC, Lopez MF, Escudero ML, Gonzalez-Carrasco JL, Morris DG (1999) *Intermetallics* 7:185
12. Lopez MF, Escudero ML, Vida E, Pierna AR, Marzo FF (1997) *Electrochim Acta* 42:659
13. Lopez MF, Gutierrez A, Alonso-Garcia MC, Escudero ML (1998) *J Mater Res* 13:3144
14. Sharma G, Gaonkar KB, Sing PR (2007) *Mater Lett* 61:971
15. Yang H, Yang K, Zhang B (2007) *Mater Lett* 61:1154
16. Zhou YL, Ninomi M, Akahori T, Fukui H, Toda H (2005) *Mater Sci Eng* 398A:28
17. Choubrey A, Basu B, Balasubramaniam R (2004) *Mat Sci Eng* 379A:234
18. Choubrey A, Basu B, Balasubramaniam R (2005) *Trend Biomater Artif Organs* 18:64
19. Li YH, Rao GB, Rong LJ, Li YY, Ke W (2003) *Mat Sci Eng* 363A:336
20. Ray WY, Ho JPY, Liu X, Chung CY, Kelvin KC, Yeung WK (2005) *Mat Sci Eng* 390A:444
21. Liu C, Xin Y, Tang G, Chu K (2007) *Mat Sci Eng* (in press)
22. Stearn M, Geary AL (1958) *J Electrochem Soc* 105:638
23. Anonymous (1996) "Electrochemical Noise Measurement for Corrosion Applications," *ASTM Symposium on Electrochemical Noise*, Montreal, May 1994, ASTM STP 1277
24. Frangini S, Masci A (2004) *Surf Coat Technol* 184:31