

Heat treatment influence on corrosion resistance of Fe₃Al intermetallic phase based alloy

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Received 15.03.2006; accepted in revised form 30.04.2006

Materials

ABSTRACT

Purpose: In this paper attention was paid to determine the corrosion resistance of Fe₃Al intermetallic phase based alloy in corrosive medium of liquid hydrochloric acid with 0.2% concentration and sulphuric acid with 3% concentration. Research of material susceptibility to surface activation in the pipeline of corrosion processes are conducted. Work is continuation of earlier research of corrosion resistance evaluation tests for FeAl intermetallic phase based alloy in liquid HCl and H₂SO₄ corrosive medium.

Design/methodology/approach: In the corrosion research electrolyser, potentiostat „Solartron 1285” and computer with „CorrWare 2” software were used. Results of the research were worked out with „CorrView” software. The potentials values were determined in relation to normal hydrogen electrode (NEW). The temperature of the solutions was kept on 21°C level. The recording of potential/density of current - time curve was conducted for 300 s.

Findings: The results of research conducted in 0.2% HCl solution, the best electrochemical corrosion resistance were showed by samples after annealing during 72 hours. It was confirmed by the lowest value of corrosion current density, low value of passive current density, pitting corrosion resistance much higher than in other samples.

Practical implications: The last feature is the reason to conduct the research for this group of materials as corrosion resistance materials. Especially FeAl and Fe₃Al intermetallic phase based alloys are objects of research in Poland and all world during last years.

Originality/value: The goal of this work was to determine the influence of homogenizing treatment time on corrosion resistance of Fe₂₈Al intermetallic phase based alloy in 0.2% HCl and 3% H₂SO₄ solutions. Homogenizing treatment was conducted in temperature of 1050°C during: 24, 48, 72 and 96 h.

Keywords: Metallic alloys; Corrosion; Electron microscopy; Microstructure

1. Introduction

Search of new engineering materials is connected with determining of physical-chemical properties, which one of most important is corrosion resistance [1-5]. Research conducted during last years in group of intermetallic phase based materials showed corrosion resistance in oxygen and sulphur medium in increased temperatures [4]. Research of resistance in medium of liquid acid solutions were published in few articles. Initial research of

corrosion resistance showed different mechanism of corrosion processes]. Physical-chemical aspects recognition of reactions during corrosion processes can allow to characterize [6-15].

The methods for decreasing the velocity of corrosion among other things by using surface passivation phenomenon. In this work corrosion resistance of Fe₃Al intermetallic phase based alloy were characterized in medium of 0.2% HCl and 3% H₂SO₄ solutions. Research of susceptibility to surface activation during corrosion processes were conducted. Homogenizing treatment time influence on corrosion resistance of Fe₂₈Al was tested.

This work is continuation of previous research of corrosion resistance evaluation for FeAl intermetallic phase based alloy in liquid acid solutions of HCl and H₂SO₄ [3, 4].

2. Material and methodology

The goal of this work was to determine the influence of homogenizing treatment time on corrosion resistance of Fe28Al intermetallic phase based alloy in 0.2% HCl and 3% H₂SO₄ solutions. Homogenizing treatment was conducted in temperature of 1050°C during: 24 h 48 h 72 h 96 h

The research programme included:

1. Potentiostatic examinations.
2. Galvanostatic examinations.
3. Potentiodynamic examinations.
4. Cyclic voltammetry.
5. Evaluation of surface condition after corrosion tests.

In the corrosion research electrolyser, potentiostat "Solartron 1285" and computer with "CorrWare 2" software were used. Results of the research were worked out with "CorrView" software. The potentials values were determined in relation to normal hydrogen electrode (NEW). The temperature of the solutions was kept on 21°C level. The recording of potential/density of current - time curve was conducted for 300 s. Samples polarization was conducted in range from potential smaller by 300 mV from normal potential to 500 mV in case of the test in 0.2% HCl solution as well as to 2000 mV in case of 3% H₂SO₄ solution. Rate of changing the potential amounted 10 mV/min in each case. Observations of the surface state were conducted using scanning electron microscope HITACHI S4200 with magnifications from 30 to 1000.

3. Results and analysis of research results

The results of cyclic voltammetry are presented in table 1. The results of potentiodynamic research for alloy examined in 0.2% HCl solution are presented in table 2 and these for 3% H₂SO₄ are presented in table 3. Table 4 presents results of the surface state after corrosion tests.

Analysis of the potentiodynamic and galvanostatic research of Fe28Al in 3% H₂SO₄ solution shows on susceptibility of tested alloy to surface activation. Exception were samples after annealing during 72 h, which have susceptibility to surface passivation. In case of samples annealed during of 96 hours activation was slow, in the rest of cases much faster. Susceptibility to surface activation could be considered as disadvantageous property, because damage of surface and passive layer can develop the acceleration of corrosion processes. Taking susceptibility to passivation or activation of surface into consideration, the best properties have samples after homogenizing treatment during 72 hours, next during 96 hours.

Results of cyclic voltammetry in 3% H₂SO₄ solution show that corrosion processes in tested samples can accelerate with time – this should be considered as disadvantageous property of tested alloy. In samples after homogenizing treatment during 24 hours, initially significant than slower increase of corrosion processes velocity was observed. It is confirmed by increase of recorded current density values in individual ranges for potentiodynamic curves. In case of samples annealed during 48 and 96 hours after initial, significant increase of corrosion processes velocity, stabilization of corrosion velocity was observed.

Corrosion velocity in samples after annealing during 72 hours was stable, next insignificantly accelerated to stabilized at last. The best properties were proved by samples after homogenizing treatment during 72 hours, next 96 and 48. The worst were samples after homogenizing treatment during 24 hours.

Samples after annealing during 72 hours were characterized by the lowest density of corrosion current in 3% H₂SO₄ solution. Density of corrosion current for samples after annealing during 96 and 48 hours was higher by order of magnitude, for samples after annealing during 24 hours was higher by two orders of magnitude. Magnitudes of current density for both observed peaks on potentiodynamic curves were similar for all samples. This magnitudes were significantly higher than values of current density in prepassive and passive range. Thus very important magnitude is width of individual ranges: prepassive and passive. On the basis of Pourbaix chart analysis first peak can be combined with Fe⁺² → Fe⁺³ reaction, second peak with Fe⁺³ → Fe⁺⁶ [4] reaction. All of tested samples show similar magnitude of current density in prepassive range. Width of the range was not equal – for samples after annealing during 48 and 72 hours the width was significantly bigger than for samples after annealing during 24 and 96 hours.

Table 1.
Results combination of cyclic voltammetry

Time of homogenizing	0.2% HCl solution	3% H ₂ SO ₄ solution
24h	increase, decrease than stabilization of recorded current density quantity	initially slow than significant increase of recorded current density quantity
48h	gradual decrease of recorded current density quantity	initially very large increase than stabilization of recorded current density quantity
72h	gradual increase of recorded current density quantity	initially stabilization than significant increase and stabilization of recorded current density quantity
96h	initial increase than decrease of recorded current density quantity	initially very large increase than stabilization of recorded current density quantity

where: E_{cor} - corrosion potential; i_{cor} - density of corrosion current; E_{cp} - critical potential of passivation, i_{cp} - critical current density of passivation, E_p - potential of passivation, i_p - current density in passivation range, E_{np} - puncture potential

Table 2. Results of potentiodynamic research in 0.2% HCl solution for Fe28Al

Time of homogenizing	E_{cor} [mV]	i_{cor} [$\mu\text{A}/\text{cm}^2$]	peak	
			E_{cp} [mV]	I_{cp} [$\mu\text{A}/\text{cm}^2$]
24h	-554.4	64.3	-501.1	195.0
48h	-566.2	77.8	-480.0	673.2
72h	-405.9	9.6	-324.0	28.2
96h	-554.6	19.9	-481.2	178.9
	E_p [mV]	I_p [$\mu\text{A}/\text{cm}^2$]	E_{np} [mV]	
24h	-173.4	8.4	-132.3	
48h	-340.0	168.1	-202.2	
72h	-265.8	26.4	47.0	
96h	-373.4	48.8	-347.0	

Table 3. Results of potentiodynamic research in 3% H₂SO₄ solution for Fe28Al

Time of homogenizing	E_{cor} [mV]	i_{cor} [mA/cm^2]	prepassive			peak 1	
			E_1 [mV]	E_2 [mV]	i_{p1} [$\mu\text{A}/\text{cm}^2$]	E_{cp1} [mV]	i_{cp1} [mA/cm^2]
24h	-132.2	1.3	365.7	509.7	13.1	-459.7	7.0
48h	-566.4	0.26	17.3	766.9	17.0	-397.7	2.9
72h	-565.9	0.01	60.0	705.0	16.5	-104.5	2.5
96h	-583.0	0.32	303.4	775.0	14.1	-470.0	3.0
	E_{cor} [mV]	i_{cor} [mA/cm^2]	passive			peak 2	
			E_1 [mV]	E_2 [mV]	i_{p2} [$\mu\text{A}/\text{cm}^2$]	E_{cp2} [mV]	i_{cp2} [mA/cm^2]
24h	-132.2	1.3	1378	1522	37.8	1327	0.38
48h	-566.4	0.26	1400	1550	68.9	1140	0.16
72h	-565.9	0.01	1350	1573	96.9	1256	0.20
96h	-583.0	0.32	1314	1542	78.4	1193	0.23

where: E_1 , E_2 - beginning and the end of prepassive and passive range, i_{p1} - density of current in prepassive range, i_{p2} - density of current in passive range, E_{cp1} - critical potential of passivation for first peak, i_{cp1} - critical current density of passivation for first peak, E_{cp2} - critical potential of passivation for second peak, i_{cp2} - critical current density of passivation for second peak

Passive layer on samples surface is much tighter and stable in case of samples after annealing during 48 and 72 hours. Polarization of this samples e.g. as a result of local concentration cells appearing, is not causing significant increase of corrosion velocity, like in other samples. Samples after annealing during 24 hours were characterized by the lowest magnitude of current density in passive range. For samples after annealing during 48 and 96 hours this magnitude was similar. The worst properties were shown by the samples after annealing during 72 hours but the differences were not significant. Width of passive range for all samples was similar and much smaller than in prepassive range. Thus the rising layer wasn't tight and didn't protect the alloy from corrosion. All of the samples were characterized by similar, high puncture potential. Analysis of surface state after corrosion

research shows, than in each case corrosion first of all is proceeding on grains boundaries. The development of corrosion processes can lead to falling out individual grains, thereby expose next grains boundaries, what probably have influence on acceleration of corrosion processes.

Table 4. Results of surface observations after corrosion tests and tests results of corrosion products

Time of homogenizing	0.2% HCl solution	3% H ₂ SO ₄ solution
24h	evenly spread corrosion products, etched grains boundaries, empty places after grains are present	big corrosion products are present near grains boundaries, etched grains boundaries
48h	corrosion products are grouped along grains boundary, small corrosion pits are present	corrosion products are grouped along grains boundary, etched grains boundaries
72h	a few small corrosion products are evenly spreaded, deep corrosion pits are present	small and evenly spreaded corrosion products, empty places after grains are present
96h		big and grouped corrosion products, no corrosion pits, partially etched grains boundaries

Summarizing the results of research conducted in 3% H₂SO₄ solution, the best corrosion resistance was shown by the samples after annealing during 72 hours. It was confirmed by the lowest value of corrosion current density, low value of current density in prepassive range with large width of this range, susceptibility to surface passivation and relatively stable direction of corrosion processes course. Samples after annealing during 96 and 48 hours also showed good corrosion resistance. The lowest corrosion resistance in 3% H₂SO₄ solution was shown by the samples after annealing during 24 hours.

Analysis of the potentiodynamic and galvanostatic research of Fe28Al in 0,2% HCl solution shows on susceptibility of tested alloy to surface activation. In case of samples after homogenizing treatment during 72 and 96 hours activation of surface was very slow, in case of samples after annealing during 24 and 48 hours activation was much faster. Susceptibility to surface activation for tested samples could be considered as disadvantageous property, but samples after annealing during 72 and 96 hours showed better properties than others.

Results of cyclic voltammetry in 0,2% HCl solution showed that for samples after homogenizing treatment during 24 hours, corrosion processes are accelerated with time, than corrosion velocity was stable. Similarly in case of samples after annealing during 72 hours gradually increase of corrosion velocity was observed. In case of samples annealed during 96 hours after initial acceleration, significant decrease of corrosion processes velocity was recorded. The best properties were shown by the samples

after homogenizing treatment during 48 hours – gradually decrease of corrosion processes velocity was observed.

Samples after annealing during 72 hours were characterized by the lowest density of corrosion current in 0,2% HCl solution. Value of corrosion current density for samples after annealing during 96 hours was two-times higher, for other samples it was six- or seven-times higher. On potentiodynamic curves the peak was observed. On the basis of Pourbaix chart analysis this peak can be combined with $\text{Fe}^{+2} \rightarrow \text{Fe}^{+3}$ reaction [4]. The difference between value of passive corrosion current density and value of passive current density was not big only for samples after annealing during 72 hours. For the rest of samples these differences were bigger. Samples after annealing during 24 hours were characterized by the lowest passive current density, but the width of passive range was very small in this case. However samples after annealing during 72 hours were characterized by the widest passive range and low passive current density from all tested samples. It can be supposed that alloy polarization didn't have influence on significant acceleration of corrosion processes. Samples after annealing during 72 hours were characterized by the highest pitting corrosion resistance. It was confirmed by the highest value of puncture potential. For rest of samples this value was significantly lower – only insignificantly higher than value of passivation potential. It can be supposed that samples after homogenizing treatment during 24, 48, and 96 hours will be characterized by low pitting corrosion resistance in 0,2% HCl solution. In case of samples after annealing during 72 hours pitting corrosion resistance will be much higher. Analysis of surface state after corrosion tests showed the presence of corrosion pits. Not large size and big depth was characteristic for this pits. Course of corrosion processes along grains boundaries was observed in samples after annealing during 24 hours and it was the cause of grains falling out.

Conducted research showed, that time of homogenizing treatment had crucial influence on corrosion resistance of Fe28Al in medium of H_2SO_4 and HCl solution. This influence can be combine with structural changes. The highest corrosion resistance for both solutions was observed for samples after homogenizing treatment during 72 hours.

4. Conclusions

1. Time of homogenizing treatment has a crucial influence on corrosion resistance of Fe28Al alloy in medium of H_2SO_4 and HCl solution.
2. The highest corrosion resistance in both solutions is observed for samples after homogenizing treatment during 72 hours.
3. Fe28Al alloy has higher corrosion resistance for reacting with SO_4^{2-} ions, than for reacting with Cl^- ions.
4. Fe28Al alloy has low pitting corrosion resistance in HCl solutions, with exception of samples after homogenizing treatment during 72 hours.

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