The corrosion resistance of Fe_3Al-based iron aluminides in molten glasses

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Abstract

Corrosion resistance of iron aluminides was investigated in molten soda-lime glass and molten lead glass. Iron aluminides with different additives and comparative steel (EN X8CrNi 25-21) were tested in laboratory conditions and compared. The corrosion resistance was determined using measurement of weight change and change of surface. The tinting of molten glasses is important to describe the interaction between the molten glass and the investigated materials. The alloys Fe25Al5Cr and Fe28Al3Cr0.02Ce have very good corrosion resistance against both glasses. The preferential oxidation of aluminium is typical for all tested iron aluminides and generated alumina slows down corrosion of these alloys. The plunger for molten glass output control was produced from Fe25Al2Cr and the application plant test of plunger has been running in lead molten glass. Damage of the surface is typical for doped Zr iron aluminide.

Key words: iron aluminide (Fe_3Al type), corrosion resistance, molten soda-lime glass, molten lead glass

1. Introduction

Fe_3Al-based iron aluminides have been studied as candidates for high-temperature structural applications in glass making. The main advantages of Fe_3Al-type iron aluminides compared to chromium-nickel steels are low material costs, low density and corrosion resistance at high temperature [1]. On the other hand, these alloys have low ductility at room temperature and low high-temperature strength. However, these disadvantages can be partly suppressed by off-stochiometric composition (e.g. 28 at.% Al) and ternary additives (especially chromium) in combination with grain refinement agents such as Ce.

Alloys based on Fe_3Al and FeAl have excellent oxidation resistance at high temperatures. High-temperature corrosion resistance of alloys based on Fe-Al in oxidation media is caused by creation, maintenance of intact and adherent layer of Al_2O_3 [2]. Minimum aluminium content for pure binary Fe-Al alloy is approx. 16–19 at.%. Aluminium content of investigated iron aluminides is satisfactory to originate continuous aluminium oxide layer. The temperatures for the formation of high-quality protective of α-Al_2O_3 layer are 800–900 °C. Alloying can influence corrosion resistance of iron aluminides, too. Chromium addition in amount greater as 4 at.% deteriorates corrosion resistance [3]. Vice-versa, cerium has positive effect on corrosion resistance of iron aluminides based on Fe_3Al at temperatures above 1000 °C [4].

The corrosion resistance of materials based on Fe40–45at.%Al in molten glass was tested in the Czech Republic in the early fifties of the last century, see e.g. [5]. Results of corrosion resistance were very good but high content of carbon was a disadvantage for using in molten glass. Therefore this material was used for parts of furnaces, which were not in contact with molten glass (for example burners, holders etc.).

Special requirements necessary for the use of metals and alloys in molten glass are namely high

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Table 1. Chemical composition of the alloys

Materials		Chemical composition							
		Al	C	Ce	Zr	Cr	Mn	Ni	Fe
Fe25Al5Cr	wt.%	14.20	0.02	–	–	5.63	max. 0.45	–	Bal.
	at.%	25.41	0.08	–	–	5.23	max. 0.40	–	Bal.
Fe28Al3Cr0.02Ce	wt.%	16.13	0.04	0.06	–	2.85	0.46	–	Bal.
	at.%	28.39	0.16	0.02	–	2.60	0.40	–	Bal.
Fe28Al3Cr0.5Zr	wt.%	17.39	0.05	–	0.47	3.72	0.20	–	Bal.
	at.%	28.06	0.2	–	0.53	2.85	0.26	–	Bal.
EN X8CrNi25-21 (ČSN 417 255)	wt.%	–	max. 0.20	–	–	24.00–26.00	1.50	19.00–22.00	Bal.
	at.%	–	max. 0.92	–	–	25.37–27.48	1.50	17.79–20.60	Bal.

corrosion resistance at high temperatures (to 1200 ℃), low tint of glass, low generation of bubbles and proper values of mechanical strength [6] and creep properties at high temperatures [7].

The solution of metal in molten glass has mostly the character of oxidation [8]. The oxidation in molten glass differs from oxidation in gaseous environment because generally protective scales are not formed on the surface during corrosion in molten glass. The process of corrosion can be measured as a weight loss (weight change), while the formed oxides immediately dissolve in the neighbouring molten glass where their concentration may increase up to saturation level. This is the process, which takes place near metallic parts inserted into the molten glass.

The aim of the present paper is to describe corrosion resistance of alloys based on Fe_3Al (with different composition) in molten soda-lime glass and molten lead crystal. The results are compared with steel EN X8CrNi25-21, which is now frequently used in molten glasses.

2. Experimental procedure

The iron aluminides of different composition (Table 1) were tested for corrosion resistance and that was compared to steel EN X8CrNi25-21. The samples were cylinders (ø 12 mm × 18 mm long) machined from sheets 13 mm thick, which were prepared by rolling at 1200 ℃. The grains are elongated in the rolling direction (Fig. 1). The structure after corrosion tests (holding at 1200 ℃) is recrystallized.

The test samples were placed in alumina crucibles, which were prior filled with scrap glass, in the furnace. All tests were carried out at 1200 ℃. The corrosion tests were performed in different mol-

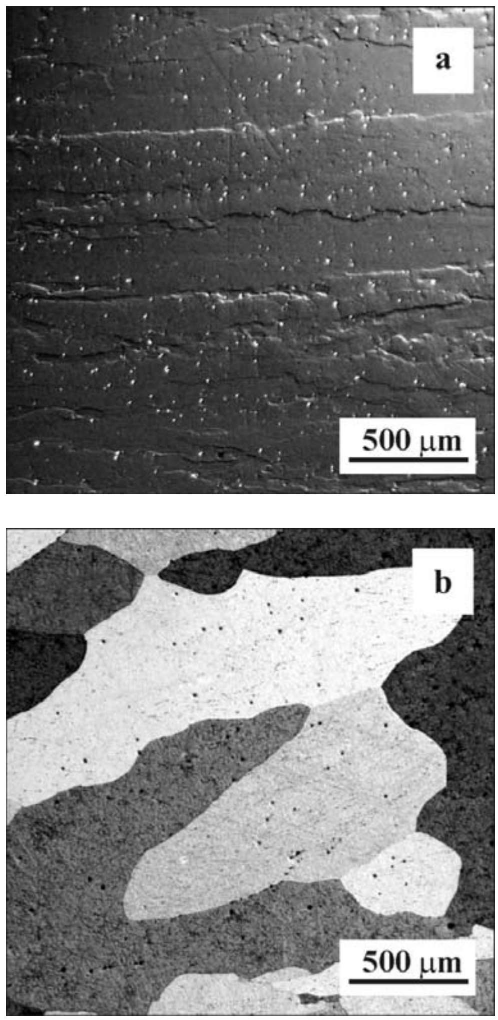

Fig. 1. (a) Structure of Fe28Al3Cr0.02Ce – Mastermet reagent, (b) structure of Fe28Al3Cr0.02Ce (to the right) after corrosion test in molten lead glass at 1200 ℃/72 h – Rollason's reagent.

T a b l e 2. Chemical composition of the glasses before tests; viscosities of molten glasses at 1200 °C

Composition (wt.%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	Viscosity log η (dPa)
Soda-lime glass (transparent container glass)	74.03	1.67	0.05	10.08	0.54	0.62	12.68	0.13	2.67
Composition (wt.%)	SiO_2	Na_2O	K_2O	BaO	PbO	ZnO	As_2O_3	Er_2O_3	Viscosity log η (dPa)
Lead crystal	53.0	2.5	10.8	0.7	32.0	0.7	0.2	0.018	3.28

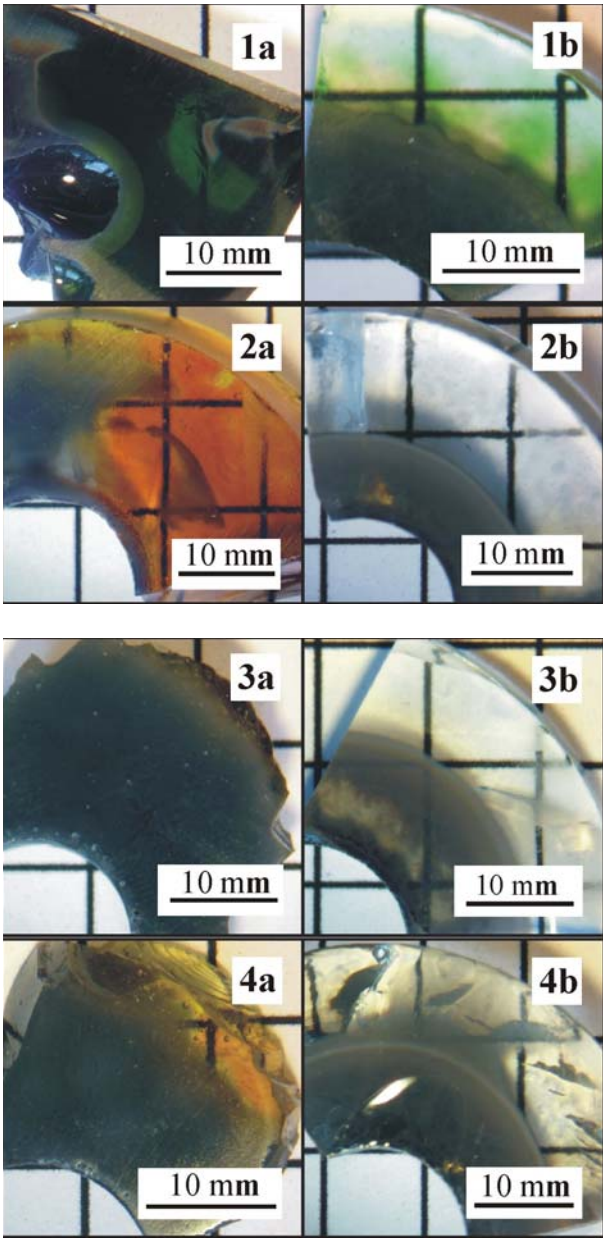

Fig. 2. The tinting of soda-lime glass (a) and lead crystal (b) after interaction with alloys, time interval 168 h; 1 – EN X8CrNi25-21, 2 – Fe25Al5Cr, 3 – Fe28Al3Cr0.02Ce, 4 – Fe28Al3Cr0.5Zr.

ten glasses (Table 2) for time intervals: 24, 48, 72, 96, 168 hours. After each test the crucibles were cooled down in furnace, subsequently carefully broken and the glass separated from surface of alloys except for Fe28Al3Cr0.5Zr. The corrosion resistance was determined using measurement of the weight change and change of surface roughness. Change of chemical composition of glasses was measured by EDX.

3. Results and discussion

3.1. Corrosion resistance of tested alloys

Describing of tinting by the interaction between alloys and glasses is very important. The tinting of both glasses after 168 hours is obvious in Fig. 2. (colour version on the website). The cylindrical samples were situated (tinting the glass) in lower left corner. Soda-lime glass is tinted more intensively than lead crystal after interaction with alloys.

Iron aluminides tint glasses mainly to grey. Yellow-brown tint of soda-lime glass was also observed after corrosion test with iron aluminides. This colour is little intensive (glass is still transparent) and it is typical for soda-lime glass after interaction with Fe25Al5Cr. On the contrary, comparative steel tinted both glasses to dark green. The dark green tint of steel was caused especially by Cr_2O_3, which dissolves very quickly from steels to molten glass. Only a small quantity of Cr_2O_3 tints very intensively [8]. In the picture you can see bubbles in the scrap of soda-lime glass. In preference carbon reacted with SO_3 during interaction steel with soda-lime glass and gases (CO_2 and SO_2) generated.

The corrosion resistance was determined by measurement of weight change. Weight loss is typical for all alloys with the exception of iron aluminide alloyed by Zr. Weight gain of iron aluminide alloyed by Zr is due to glued-on thin layer of glass on the surface of specimen, therefore the corrosion cannot be quantified. Other specimens for iron aluminides have lower weight loss than comparative steel (Figs. 3 and 4). The rate of solution in molten glass is very important parameter. The slopes of curve show that alloys Fe25Al5Cr and Fe28Al3Cr0.02Ce have smaller rate of solution in

T a b l e 3. The rate of solution in molten glasses

Glass	Temperature (℃)	Fe25Al5Cr (mm/year)	Fe28Al3Cr0.02Ce (mm/year)	EN X8CrNi25-21 (mm/year)
Lead crystal	1200	0.5	0.8	1.0
Soda-lime glass	1200	0.9	1.2	1.9
	1350	No measurement	2.6	11.2

T a b l e 4. The roughness parameters of boundaries between alloys and glasses, D_{C1000} average compass dimension (multiplied by 1000), STD average standard deviation and R_t average maximum roughness

Glass, time period	Fe25Al5Cr			Fe28Al3Cr0.02Ce			Fe28Al3Cr0.5Zr			EN X8CrNi25-21		
	D_{C1000} (–)	STD (μm)	R_t (μm)	D_{C1000} (–)	STD (μm)	R_t (μm)	D_{C1000} (–)	STD (μm)	R_t (μm)	D_{C1000} (–)	STD (μm)	R_t (μm)
Before the test	1016	0.8	3.7	1018	0.8	4.7	1017	0.7	3.2	1012	0.6	3.3
Lead crystal, 168 h	1010	1.7	7.6	1017	2.6	11.0	1057	8.4	36.2	1042	2.5	12.1
Soda-lime glass, 168 h	1020	2.0	8.3	1023	2.7	13.1	1037	10.8	46.1	1036	8.8	34.0

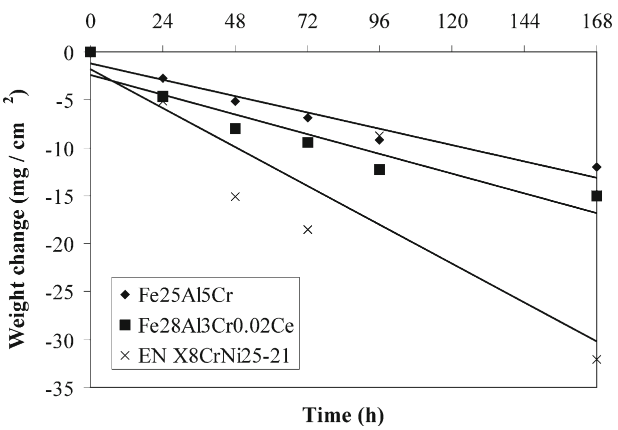

Fig. 3. The dependence of weight loss on time in soda-lime glass at 1200 ℃.

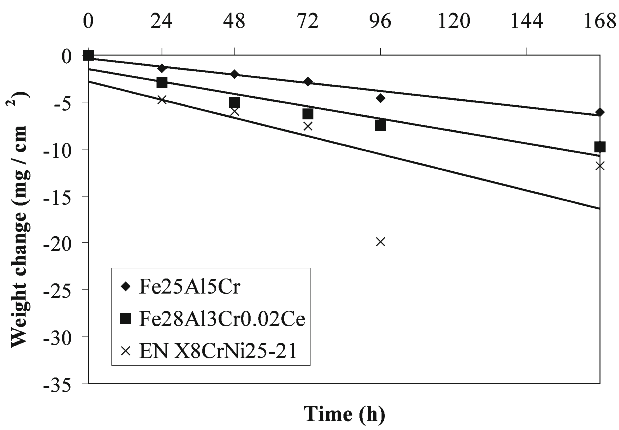

Fig. 4. The dependence of weight loss on time in lead crystal at 1200 ℃.

both glasses than comparative steel. The difference of solution rate is greater at 1350 ℃ in soda-lime glass, see Table 3.

The surface roughness of samples was measured after the exposure to molten glass. The corroded surface was observed using light optical microscopy. The boundary curve (see Fig. 5) was described by a software tool. For a quantification of the metal roughness fractal geometry and statistic tools were used. The dividing curve generated is described by a fractal dimension (a compass dimension multiplied by 1000, D_{C1000}, for details see [9]) that expresses the degree of complexity of the interface between alloy and glass by means of a single number. Also average standard deviation (STD) of all the curves and average maximum roughness of all the curves (R_t) are used for the statistical description [10]. These parameters are given in Table 4.

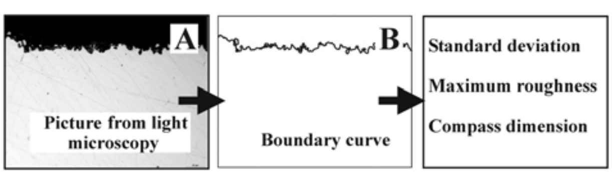

Fig. 5. Description of boundary curve.

The values of roughness parameters show that all testing materials are less damaged after interaction in lead molten glass than in molten soda-lime glass. Low roughness parameters of iron aluminides (Fe25Al5Cr, Fe28Al3Cr0.02Ce) are obvious from all results. Austenitic steel (EN X8CrNi25-21) has similar values as Fe28Al3Cr0.02Ce after interaction in lead molten glass but surface of this steel is more damaged after interaction in soda-lime molten glass. In the case of Fe28Al3Cr0.5Zr, the damaged surface layer is very thick. Probably this is caused by selective surface corrosion. The detrimental effect of Zr on oxidation resistance of iron aluminides is realized also in [11].

3.2. Corrosion mechanism of iron aluminides

Diffusion of aluminium from samples and preferential oxidation of aluminium are typical for all tested iron aluminides. The reaction of Al with SiO_2 causes a formation of Al_2O_3 and Si in both glasses. Al_2O_3 layer is formed at the glass/alloy interface, which is partially protected against further solution of iron aluminides. In addition alumina, which is concentrated near the surface of samples, increases viscosity and also slows down corrosion of these alloys.

The generated Si small particles cause grey tint of soda-lime glass. If a reducing effect of aluminium is lower, aluminium reacts with SO_3 and Fe_2O_3 and the yellow-brown tint of soda-lime glass generates. Small bubbles in soda-lime glass are caused by the reaction Al with SO_3, too.

In the case of a lead crystal, Al reacts especially with PbO and the reaction causes a formation of Al_2O_3 and Pb. The reaction of aluminium with SiO_2 also takes place at the same time. Small particles of Pb and Si formed grey area around the sample.

Higher corrosion rates of all tested alloys in soda-lime glass are caused by different chemical composition, especially by the content of SO_3 (Table 2) because corrosion resistance of majority of metals decreases with increasing content of SO_3 [8]. Viscosity of glasses also has influence on rates of alloy solution because diffusion and glass flow are slowed down with increasing viscosity. But lower viscosity of lead crystal than that of soda-lime glass does not increase solution rate of alloys in lead crystal too much (see Table 2).

All tested iron aluminides have sufficient content of aluminium for good corrosion resistance in molten glass. Differences of aluminium content in iron aluminides are small and lower content of Al can cause only shorter oxidation lifetime of iron aluminides in molten glasses. Therefore alloying elements (Cr, Zr, Ce) probably have an effect on corrosion rate. For understanding of the effect of alloying elements on corrosion mechanism of iron aluminides in tested molten glasses, further studies and analysis are necessary.

3.3. Application plant tests

The application plant tests also run in lead molten glass at present because alloys Fe25Al5Cr and Fe28Al3Cr0.02Ce have very good corrosion resistance. The plungers for molten glass output control from glass furnace were casted from iron aluminide base on Fe_3Al. Final shapes of plungers were produced by investment casting to save cost production. The as-cast plunger from Fe25Al2Cr is cyclically heated up from room temperature to working temperature. The working temperature of molten glass is 900–1050 ℃ and temperature of furnace atmosphere is 1130–1150 ℃. The plunger is now used without damage for 79 cycles (i.e. 312 hours at service temperature) under these conditions.

4. Conclusions

1. Alloy Fe25Al5Cr has better corrosion resistance against both molten glasses (soda-lime molten glass and lead molten glass) than the steel EN X8CrNi25-21. The alloy Fe25Al5Cr tinted less intensively both glasses and the rate of solution and damage of surface were the lowest.

2. Alloy Fe28Al3Cr0.02Ce offers better resistance also to soda-lime glass than EN X8CrNi25-21. It dissolves slower and the surface is smoother. On the other hand, the corrosion resistance of iron aluminide with Ce to lead molten glass is comparable to steel EN X8CrNi25-21.

3. The alloy Fe28Al3Cr0.5Zr has different results of corrosion resistance. Thin layer of glass is glued on the samples of iron aluminides with Zr therefore the corrosion cannot be quantified. Large damage of samples surface is typical for this type of iron aluminide.

4. The preferential oxidation of aluminium is typical for all tested iron aluminides. Generated alumina formed a layer at the glass/alloy interface, which partially protected iron aluminides against further solution. In addition, alumina around samples increases viscosity and it also slows down corrosion of these alloys.

5. Tested iron aluminides have sufficient content of aluminium for good corrosion resistance in molten glass. Small differences among corrosion rates of tested iron aluminides are probably caused by alloying elements (Cr, Zr, Ce).

6. The good laboratory results stimulated the application plant tests of iron aluminide based on Fe_3Al run in lead molten glass. Iron aluminides (especially Fe25Al5Cr) could replace heat resistant steels for applications in soda-lime molten glass to 1200 ℃. Feeder plungers, parts of gatherer and elements for mechanical homogenizing of molten glass are the prospective applications.

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References

[1] McKAMEY, C. G.—DeVAN, J. H.—TORTORELLI, P. F.—SIKKA, V. K. J.: Mater Res, *6*, 1991, p. 1779.
[2] TORTORELLI, P. F.—NATESAN, K.: Mat. Sci. Eng., *A258*, 1998, p. 115.
[3] LEE, D. B.—KIM, G. Y.—KIM, G. J.: Mat. Sci. Eng., *A339*, 2003, p. 109.
[4] XINQUAN, Y.—YANGSHAN, S.: Mat. Sci. Eng., *A363*, 2003, p. 30.
[5] UXA, V.: Sklář a keramik, *6*, 1956, p. 225 (in Czech).
[6] HOTAŘ, A.—KRATOCHVÍL, P.: Kovove Mater., *40*, 2002, p. 45 (in Czech).
[7] KRATOCHVÍL, P.—HANUS, P.—HAKL, J.—VLASÁK, T.: Kovove Mater., *42*, 2004, p. 73.
[8] KIRSCH, R.: Metals in Glassmaking. Amsterdam, Elsevier Science Ltd. 1993.
[9] MANDELBROT, B. B.: The Fractal Geometry of Nature. 2nd ed. New York, Freeman WH and Co. 1982.
[10] HOTAŘ, V.—NOVOTNÝ, F.: In.: Proceedings of 11th International Conference on Fracture. Ed.: Carpinteri, A. Turin, CCI Centro Congressi Internazionale s.r.l. 2005, p. 588.
[11] STEIN, F.—PALM, M.—SAUTHOFF, G.: Intermetallics, *13*, 2005, p. 1275.