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High Temperature Corrosion of Type 316 L Stainless Steel with Molten Carbonate. The Effect of Alkaline Earth Carbonate Addition

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Received January 16, 1996 ; Accepted March 13, 1996

1 INTRODUCTION

The molten carbonate fuel cell (MCFC) is expected to be a high efficiency power generation device with low pollutant emission. Molten carbonate used as its electrolyte, which composition is conventionally $\text{Li}_2\text{CO}_3\text{:K}_2\text{CO}_3=62\text{:}38$ ((mol%)), separates anode and cathode gas environment and provides ionic conductivity under the MCFC operation. Some properties (e.g. melting point, conductivity, surface tension, corrosivity, etc.) of the carbonate as the electrolyte affect the performance and/or lifetime of the MCFC. That is, it causes some problems such as NiO cathode dissolution and corrosion of component materials. In MCFC technology, corrosion of materials is one of the life-limiting problems, since corrosion in the MCFC proceeds continuously with consumption of electrolyte as well as cell materials at the same time. Especially, the separator plates in an MCFC stack are exposed to the most severe conditions, since they are contact with molten carbonate as well as both oxidizing and reducing conditions and must retain adequate electronic conductivity.

Recently, the addition of the alkaline earth carbonates into $(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3$ has been reported to be effective to reduce the NiO solubility into the melt under cathode environment¹⁾. The addition will be expected, necessarily, to affect the other properties of $(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3$. Few reports were, however, known about the effect of

the additions on corrosion of the MCFC components²⁾.

This paper reports the effect of addition of alkaline earth carbonate in $(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3$ on corrosion rate and corrosion products of type 316L stainless steel under the cathode environment in out-of-cell test.

2 EXPERIMENTAL

A sheet of commercially available type 316L stainless steel (SS 316L), of thickness 0.5 mm, served as corrosion specimen. Its chemical composition is listed in Table 1. The sheet was cut into 10×20 mm specimens, polished with wet abrasive paper up to #1000, washed and decreased with acetone, and dried. Chemical reagent grade Li_2CO_3 , K_2CO_3 , CaCO_3 , SrCO_3 and BaCO_3 , which purity were >99.0%, >99.5%, >99.99%, >99.9% and >99.9%, respectively, served for preparation of mixed carbonates. After these carbonates were dried for 12 hours at 523 K in the air, they were mixed as $\text{Li}_2\text{CO}_3\text{:K}_2\text{CO}_3=62\text{:}38$ (mol%) and $(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3\text{:}(\text{CaCO}_3, \text{SrCO}_3 \text{ or } \text{BaCO}_3)=90\text{:}10$ (mol%). From now on they are referred to as Li/K, Li/K/Ca, Li/K/Sr and Li/K/Ba, respectively. Each mixed carbonate was previously melted at 923 K under CO_2 atmosphere in high purity alumina crucible ($\text{Al}_2\text{O}_3 > 99.5\%$), quenched and ground. The compositions of the carbonates were confirmed after melt by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Specimens were coated with 5 mg/cm² carbonate with ethanol and hung in alumina crucible. Specimens in the crucible were set in the furnace for corrosion test. The out-of-cell corrosion test was carried out under the cathode environment

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Key Words : High Temperature Corrosion, Molten Carbonate Fuel Cell, Stainless Steel, Alkaline Earth Carbonate

Table 1 Chemical composition in wt% of SS 316L used.

C	P	S	O	N	Si	Mn	Mo	Ni	Cr	Fe
0.022	0.0029	0.010	0.0060	0.0262	0.65	1.01	2.14	12.01	17.02	Bal.

(CO₂:O₂=67:33 (vol%), 300 cm³/min flow) at 923 K for 100, 200 and 500 hours.

After the test, the deposit of carbonate melt was observed to remain on the specimen. Each specimen was washed in distilled water to remove the carbonate. The solution was analyzed quantitatively by ICP-AES to examine the elements which dissolved from the specimen into the carbonate. Weight change due to corrosion is calculated by weighing the specimen before and after the test without carbonate. The surface and cross section of each specimen were observed by SEM and analyzed by energy dispersive electron probe microanalysis (EPMA). Corrosion products on the each specimen before and after removal of carbonate were identified by X-ray diffraction (XRD) with a fixed incident angle.

3 RESULTS AND DISCUSSION

Results of weight gains of the specimens with time are shown in Fig. 1. Though Cr was only detected in all the melts after the test as the element dissolved from the specimen using ICP-AES analysis, the analysis showed the weight changes due to the dissolution of Cr into melts were less than 0.3 mg, which were negligibly small. The weight of all the specimens increases with time. The weight gains with the addition of each alkaline earth carbonate are always less than those without the addition. It shows that the addition of CaCO₃, SrCO₃ or BaCO₃ decreases the corrosion of SS 316L. No remarkable difference is, however, found among the weight gains due to the corrosion in all the additions. On the contrary, only minor differences in corrosion of SS 310S between with the addition of 5 mol% BaCO₃ and without the addition have been shown²⁾. Among various rate equations, all the weight gains with time always best fit the parabolic rate one:

$$x^2 = k_p \cdot t$$

where x is the weight gain (mg), k_p the parabolic rate constant (mg²/h), and t the time exposed (h). Each k_p for corrosion of SS 316L under ambient 67% CO₂+33% O₂ at 923 K with the melts is calculated in Table 2.

The surface observation using SEM after the test showed that all the specimens were covered with the facet corrosion products and there was no significant difference of morphology among the corrosion products at the same duration with each composition of all the melts. The corrosion products for Li/K were identified as LiFeO₂, LiFe₅O₈ and LiCrO₂ by XRD and were similar to those for Li/K/Ca, Li/K/Sr and Li/K/Ba. NoCa, Sr or

Fig. 1 Weight gain as a function of time for SS 316L specimens coated with different carbonate deposits (5 mg/cm²) reacted at 923 K in 67% CO₂+33% O₂. Li/K (●), Li/K/Ca (○), Li/K/Sr (□), Li/K/Ba (△), calculated according to the parabolic rate equation (—).

Table 2 Parabolic rate constants for corrosion of SS 316L under ambient 67% CO₂+33% O₂ at 923 K with various carbonate deposits (5 mg/cm²).

Composition of carbonates (mol%)	Parabolic rate constant, k_p , (mg ² /h)
Li ₂ CO ₃ : K ₂ CO ₃ = 62 : 38	1.3×10^{-1}
(Li _{0.62} K _{0.38}) ₂ CO ₃ : CaCO ₃ = 90 : 10	6.5×10^{-2}
(Li _{0.62} K _{0.38}) ₂ CO ₃ : SrCO ₃ = 90 : 10	6.8×10^{-2}
(Li _{0.62} K _{0.38}) ₂ CO ₃ : BaCO ₃ = 90 : 10	6.4×10^{-2}

Ba compound was found in the corrosion products for Li/K/Ca, Li/K/Sr or Li/K/Ba.

The EPMA results showed that the structure of corrosion products consisted of two layers. The inner and outer layers were identified as LiFeO₂ and LiFe₅O₈, and LiCrO₂, respectively, in all the melt systems.

No dependence of corrosion products on the carbonate compositions suggested that the change of the melt properties such as activity of oxidizing species and solubility of gases depending on the addition would rather play important roles in the corrosion mechanism. The addition effect on the melt properties of the Li-K carbonate system should be elucidated to understand the corrosion behavior furthermore.

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