Oxidation Resistance、Electrical Property and Dilatometry of STS321 Stainless Steel for SOFC Interconnect Candidate

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Abstract: The paper offered a promising high temperature-resistant stainless steel, STS321 (FeCr18Ni9Ti), as interconnect of solid oxide fuel cell (SOFC) working at intermediate or low temperature and investigated its cycle oxidation property in air. The research shows the steel is almost hardly oxidized on condition of less 700℃. The mass of steel is constant since oxidative protective scale produced at 800℃with time length 1000 h. However, oxidative protective scale decomposed due to volatilization and detached from the steel substrate, losing shielding function once the temperature attains to 900℃. The mass of the steel also dropped. The electrical resistance increases tardily when temperature is below 600℃, However, quickly when temperature exceeds 600℃, reaching 1.3 $\Omega\cdot cm^2$, indicating that the STS321 stainless steel can be as below 600℃. The dilatometry is 22.5×10^{-6} per centigrade. The research demonstrates STS321 stainless steel is a promising interconnect candidate for intermediate and low temperature SOFC (400-600℃) in aspect of oxidation resistance at least.

Keywords: STS321 stainless steel; SOFC interconnect; property

1. Introduction

It is self-evident that developing fuel cell technologies is useful to tackle energy and environmental problems, thereinto，SOFC is just a kind of promising fuel cell, which can be used as power station as well as mounted on automobiles, replacing the using internal-combustion engines[Zhang Xiongwen, Li Guojun, Li Jun, Feng Zhenping. Numerical study on electric characteristics of solid oxide fuel cells. Energy Conversion and Management, 2007, 48: 977-989][Y. Inui, T. Matsumae, H. Koga, K. Nishiura. High performance SOFC/GT combined power generation system with CO_2 recovery by oxygen combustion method. Energy Conversion and Management, 2005,46: 1837-1847][Yohei Tanaka, Akihiko Momma, Ken Kato, Akira Negishi, Kiyonami Takano, Ken Nozaki, Tohru Kato. Development of electrical efficiency measurement techniques for 10kW-class SOFC system: Part I. Measurement of electrical efficiency Energy Conversion and Management, 2009,50:458–466][Yohei Tanaka, Akihiko Momma, Ken Kato, Akira Negishi, Kiyonami Takano, Ken Nozaki, Tohru Kato. Development of electrical efficiency measurement techniques for 10 kW-class SOFC system: Part II. Uncertainty estimation . Energy Conversion and Management, 2009, 50: 467-478.] [Comas Haynes, William J. Wepfer. `Design for power' of a commercial grade tubular solid oxide fuel cell. Energy Conversion & Management, 2000, 41: 1123-1139]. Power density of the current SOFC attains to 1.8 w/cm^2 at most. It is capital cost to restrict it from commercial utilization, and interconnects, known as most expensive $LaCrO_3$ ceramic, which is also the most stable material so far, account for 70-80% of the whole expenditure of the whole SOFC system [1].

There are two causes to prompt the researches of using metallic alloys as interconnect candidates: One is that doped-CeO_2 exacted perfect performance to replace ZrO_2 as SOFC electrolyte[2]; another is that the configuration of SOFC are transforming from electrolyte-supported to anode-supported one , the thickness of electrolyte dropped to 20-30 μm from 150 μm [D.P. Lim, D.S.Lim, J.S.Oh, I.W.Lyo. Influence of posttreatments on the contact resistance of plasma-sprayed $La_{0.8}Sr_{0.2}MnO_3$ coating on SOFC metallic interconnector. Surface & Coatings Technology, 2005, 200: 1248-1251] The two causes results in the reduction of working temperature from 1000℃ to 400-600℃.[Yoon Jong-Seol, Lee Jun, Hwang Hae-Jin, Whang Chin-Myung, Moon Ji-Woong, Kim Do-Hyeong. Lanthanum oxide-coated stainless steel for bipolar plates in solid oxide fuel cells (SOFCs). Journal of Power Sources, 2008, 181: 281–286] At the meantime, metallic alloys present their own characters as good workability, low cost, high intensity, high heat conductivity and electrical conductivity.

Factually, researches on employing alloy as SOFC interconnect are multiple, involving Mg、Ca、Sr、Ti、V、Cr、Mn、Fe、Co、Ni、Cu、Al、Si、Ge as much as 14 elements so far, including mainly Cr-based alloy [Norbert H. Menzler, Doris Sebold, Mohsine Zahid,

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Sonja M. Gross, Thomas Koppitz. Interaction of metallic SOFC interconnect materials with glass-ceramics sealant in various atmospheres. Journal of Power Sources, 2005, 152: 156-167], Fe-based alloy Ni-based alloy. Wherein, G. Cabouro et al. [2] researched oxidation and electrical properties on Fe-30Cr alloy, holding that the electrical resistance of the alloy is 0.03Ωcm^2 and considering its resistance can drop 10 times while using Y_2O_3 as coating. Lee et al. [3] studied the properties of Hayness230 and SS310 steel , drawing that Cr_2O_3 and $MnCr_2O_4$ are the main contents in the oxide scale after being oxidized for 1000 h at 750 ℃ , measured specific electrical resistance as 0.1Ωcm^2. S. J. Greng el al. [4] investigated the feasibility that Haynes 242 alloy as SOFC interconnect , arguing the oxidation behavior observe parabola law, weight gain increased along promotion of oxidation temperature and the most outward layer is non-entirely coating NiO scale even though the coating have little effect to refrain from oxidation.

Nowadays, Cr-based alloys are widely recognized as producing Cr_2O_3 protective scale at high 900℃. Cr_2O_3 scale has good conductivity, while the volatilizable oxide can react with cathode contents into $MnCr_2O_4$ spinel so as to drop the SOFC property. At the same time, the increasing oxide scale raised electrical resistance.

The oxidation of alloy is ineluctable. If the ceramic coating was applied on the metallic alloys surface, not only are the oxidations of the metallic alloys avoided, but also the cost will drop. Therefore, the ceramic coating will be the future trend to assemble interconnects. Despite requirements of ceramic coating, the chosen alloy should be high oxidation resistant, low electrical resistant and low dilatant. Hence, we selected thermal STS321 stainless steel, the alloy has not been not tested before with high potential, as research object to explore its oxidation resistance, electrical resistance and thermal dilatancy, providing a basis for the further coating.

2. Experiment

The STS321 stainless steel plate with thickness 4.0mm , whose composition is seen in Table.1, were lathed into a few dozen 10 mm diameter, 4 mm thickness cylinder samples, ultrasonically cleaned in acetone, and then dried for evaluation.

Table1. Nominal composition of the STS321 (wt%)

C	Si	Mn	P	S	Cr	Ni	Ti
0.08	1.00	2.00	0.045	0.03	17.0	13.0	0.4

The specimens were weighed in a XT220A Precisa electronic balance made in Swiss with minimum 0.01 g before the oxidation experiments proceeding at CM-1 crucible melting stove. The weighed specimen were put into the stove when the desired temperature attained and taken out until the scheduled time reached, cooled in air, weighed to get mass gain. The surface of specimen was characterized by SEM equipment accompanying X-ray EDX analysis facility. The electrical resistance was measured through KEITHELEY 2000 digital multimeter, whereas, thermal dilatometry measurement was carried out by CT60 dilatometer (25-800℃, one centigrade per second) made in France.

3 Results and discussion

3.1 Oxidation of STS321 specimen

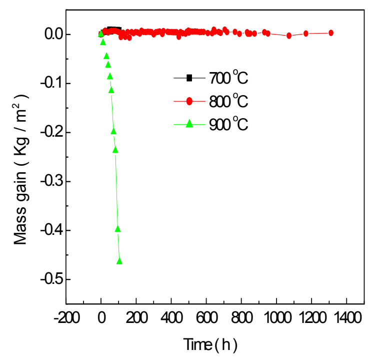

Fig.1 Relation between mass gain and oxidation time on STS321 specimens

It can be seen from Fig.1 that mass gain of STS321 specimen was constant when temperature was 700℃. The specimen was hardly oxided at 700℃ with the heating time.However, the mass gain of the specimen at 800℃ was fluctuating within 200 hours, indicating oxidation scale was forming. After that, the oxidation curve was almost a straight line even for 1000 h, mass gain rose as small as 0.15%, indicating the formed scale was excellent for protecting the substrate from oxidation. STS321 alloy are suitable for intermediate temperature SOFC (400-800℃). However, oxidative protective scale decomposed due to volatilization and detached from the steel substrate , losing shielding function once the temperature attains to 900℃. The mass of the steel also dropped.

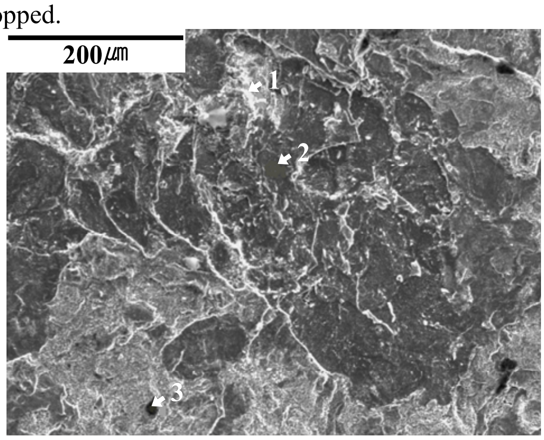

Fig.2 SEM micrograph of the surface oxide morphology

of STS321 oxided in air at 900 ℃ for 100 h

EDX analysis results for the three sections in Fig.2 are seen in Table.2.

Table.2 EDX results for the three layers of Fig.2 (mol%)

	Fe	Cr	Ni	Ti	O
1	47.08	41.94	2.92	0	4.82
2	0	0	0	0	116.53
3	15.31	16.23	5.23	0	62.34

Surface 2 was found through SEM micrograph incorporating EDX analysis to be mainly constituted by ferric oxide, chromium oxide and nickel oxide. Whereas, amount of Ni element in the intermediate layer 3 is 2 times that in the substrate 1, proving that Ni enriched in the specimen surface, which increased oxidation-resistant ability of STS321 specimen. Therefore, the specimen is stable below 800℃. There is no Ti element in EDX analysis, maybe because amount of Ti is small and no enrichment in the surface.

3.2 Change of electrical resistance of STS321 specimen before and after oxidation

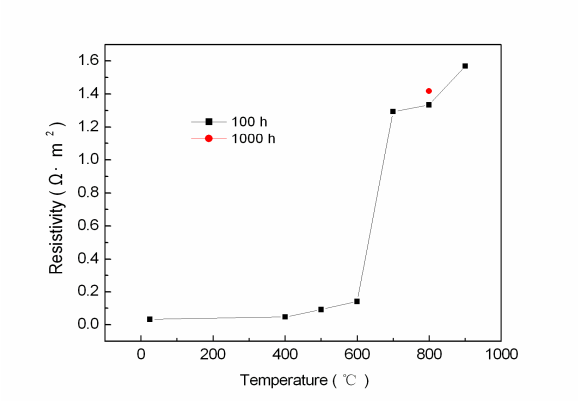

Fig.3. Change of electrical resistance of STS321 specimen with the temperature

Electrical resistance of STS321 specimen increased with temperature (seen in Fig.3), which are caused by thicker scale yielded at higher temperature. Under the experimental conditions, the electrical resistance rose slowly when the temperature was below 700℃.After that, when temperature was beyond 700℃, electrical resistance enhanced drastically due to the shaped oxide scale. When the heating temperature is 700℃, 800 ℃ and 800 ℃ with prolonged time up to 1000 h, the oxide scales have been formed without being demolished, therefore, electrical resistance increased tardily with the rising temperature as well as the thicking scale. The electrical resistance added only 0.0837Ω·m^2 at 800℃ for 1000 h comparing the STS321 specimen without oxidation. However, when temperature added up to 900℃, the electrical resistance rose rapidly for a second time because severe oxidation occurred on the STS321 substrate, losing protective oxidation scale. The oxygen can reacted with the substrate permeating the oxidation scale.

Additionally, the values of electrical resistance will drop if the pressure on the probe is larger.

The assembled single cell or stack will endure high pressure up to a dozen of mega pa, hence, the real electrical resistance would decrease further. For the intermediate temperature (400-800℃) SOFC , the values of electrical resistance are acceptable.

3.3 Dilatometry of the STS321 specimen at 800℃

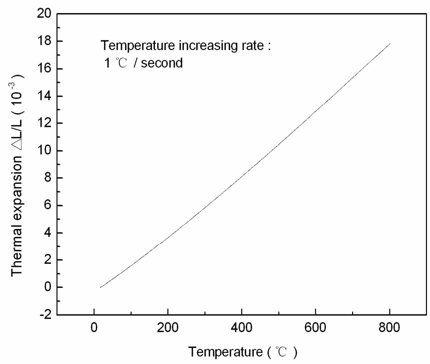

Fig.4 Variation of thermal dilatometry of STS321 specimen with temperature

The thermal dialtometry of the STS321 specimen is 22.5×10^{-6} per centigrade, which is in the same magnitude as that of electrolyte, ZrO_2 , 10.5×10^{-6} per centigrade. The value of the STS321 is lower than that of FeAl alloy[1], but higher than most of alloys. The thermal dialtometry of Cr-containing stainless steel is about 12×10^{-6}, and the thermal dialtometry of SOFC components is about 10.13×10^{-6}. The mismatch can be solved by the particular stack design [6].

4. Conclusions

The research shows the steel is almost hardly oxidized on condition of less 700℃. The mass of steel is constant since oxidative protective scale produced at 800℃ with time length 1000 h. However, oxidative protective scale decomposed due to volatilization and detached from the steel substrate , losing shielding function once the temperature attains to 900℃. The mass of the steel also dropped. The electrical resistance increases tardily when temperature is below 600℃, However, quickly when temperature exceeds 600℃, reaching 1.3 Ω· cm^2 , indi-

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cating that the STS321 stainless steel can be as below 600℃. The dilatometry is 22.5×10^{-6} per centigrade. The research demonstrates STS321 stainless steel is a promising interconnect candidate for intermediate and low temperature SOFC(400-600℃) in aspect of oxidation resistance at least. It is also a good material to be coated by ceramic in a bid to be interconnect for SOFC.

5. Acknowledgements

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References

[1] Zhu W. Z., Deevi S. C.. Development of interconnect materials for solid oxide fuel cells. Materials Science and Engineering, 2003, A348: 227-243
[2] Na Ai, Zhe Lu, Kongfa Chen et al. Low temperature solid oxide fuel cells based on $Sm_{0.2}Ce_{0.8}O_{1.9}$ film fabricated by slurry spin coating. Journal of Power Sources, 2006, 159(1): 637-640
[3] G. Cabouro, G. Caboche, S. Chevalier, P. Piccardo. Opportunity of metallic interconnects for ITSOFC: Reactivity and electrical property. Journal of Power Sources, 2006, 156(1): 39-44
[4] Li Jian, Pu Jian, Xie Guangyuan, Wang Shunxu, Xiao Jianzhong. Heat resistant alloys as interconnect materials of reduced temperature SOFCs. Journal of Power Sources, 2006, 157(1): 368-376
[5] S. J. Greng, Zhu J.H., Lu Z.G.. Evaluation of Haynes 242 alloy as SOFC interconnect materials. Solid State Ionics, 2006, 177: 559-568