Thermal Expansivity and High-Temperature Oxidation Resistance of Fe–Cr–W Alloys

Masami Ueda and Hitoshi Taimatsu[†]

Sumitomo Special Metals Co. Ltd., Suita 564-0043, Japan

[†]Department of Materials Science and Engineering, Faculty of Engineering and Resource Science, Akita 010-8502, Japan

The heat-resistant alloys were investigated for the use of the separator in solid oxide fuel cells. To find out those alloys which have low thermal expansivity close to zirconia, the Fe–Cr–W system was surveyed with respect to the thermal expansion up to 1273 K and the oxidation resistance at 1273 and 1373 K. In the compositional range above 15 mass%Cr, the average coefficient of thermal expansion was low in the alloys containing 7 to 10 mass%W, and especially low, $12 \times 10^{-6} \text{ K}^{-1}$ or less, in the alloy containing about 9 mass%W. This is because, below the Curie temperature the expansivity is depressed due to ferromagnetism, while above the Curie temperature it is intrinsically low. Fe–18 mass%Cr–7 mass%W was found to have very good oxidation resistance comparable to the commercial superalloys of forming Cr_2O_3 scales, but Fe–18 mass%Cr–9 mass%W had poorly adherent scales.

(Received July 2, 1999; In Final Form October 5, 1999)

Keywords: iron-chromium-tungsten alloys, thermal expansivity, lattice constant, Curie temperature, magnetization, heat-resistant alloys, oxidation resistance, solid oxide fuel cell separator

I. Introduction

Solid oxide fuel cells (SOFCs) using zirconia electrolytes have attracted considerable attention as highly efficient energy generators that produce the minimized pollutant gases. Planar SOFCs, which present many more technical problems than tubular SOFCs do, have been investigated intensively because of their high power densities. Each single cell in a planar SOFC is composed of a cathode, an electrolyte, and an anode. Since they are exposed in oxidizing and/or reducing atmospheres at an operating temperature near 1273 K, only a few materials are applicable to them. At present, for example, the following materials are considered⁽¹⁾⁽²⁾: SrO-doped LaMnO_3 as a cathode, Y_2O_3 -doped ZrO_2 (YDZ) as an electrolyte and Ni-YDZ cermet as an anode. One single cell is connected to another with a separator (interconnector) which has important functions of conducting electricity and separating an oxidizing gas, *e.g.* air, and a fuel gas. As a separator, one of electrically conductive ceramics LaCrO_3 is a candidate, and is widely used in trial SOFCs because it is very close in thermal expansivity to YDZ and stable in both oxidizing and reducing atmospheres at high temperatures. For LaCrO_3 , however, it is not easy to obtain dense sintered bodies by usual sintering techniques. In comparison with LaCrO_3 , metallic materials are very workable, machinable, impermeable and thermally-conductive, but in general they have high thermal expansivity and low oxidation resistance at high temperatures. Because of these reasons, especially in thermal

expansivity, metallic separators have not been developed in SOFCs except for Cr-base alloys⁽³⁾⁽⁴⁾ with very poor ductility which are prepared by powder-metallurgical processes in similar manner as for ceramics. To apply metallic materials to the separator of SOFC, therefore, the function of low thermal expansivity must be additively given to heat-resistant alloys.

As summarized in Fig. 1 as the results for the preliminary thermal expansion experiments, the oxidation-resistant alloys with fcc lattices SUS 304 and Inconel X-750 have much higher thermal expansion coefficients than YDZ, while the thermal expansion coefficient of the alloy with a bcc lattice SUS 430 is closer to that of YDZ because of its coarse packing in atoms and short distance between atoms. The average coefficient of thermal expansion of SUS 430 in the temperature range between

Fig. 1 Thermal expansion $\Delta L/L_0$ of ZrO_2 -8 mol% Y_2O_3 , SUS 430, Inconel X-750 and SUS 304.

[†] Department of Materials Science and Engineering, Faculty of Engineering and Resource Science, Akita 010-8502, Japan.

303 and 1273 K is $13.45 \times 10^{-6} \text{ K}^{-1}$. This value is rather low in different heat-resistant alloys. However, the average coefficient of thermal expansion of YDZ $10.62 \times 10^{-6} \text{ K}^{-1}$ is still lower by 27% than that of SUS 430. To find out the ductile heat-resistant metallic materials having both low thermal expansivity and good oxidation resistance at high temperatures as the separator of SOFC, consequently, candidates should be searched on the basis of the following guides: (1) Fe should be selected as a base metal because Ni and Co are essentially high in thermal expansivity, (2) oxidation resistance must be maintained by the Cr addition because Al brings about the formation of Al_2O_3 scales with very low electrical conductivity, and (3) elements which have low thermal expansivity and maintain bcc structure in Fe should be added. Thus, we searched for several alloy systems which are expected to have low thermal expansivity up to 1273 K, and then found out the promising compositions in the Fe–Cr–W system. In this paper, we describe the results of thermal expansion measurements and oxidation tests in the Fe–Cr–W system, and discuss which compositions are suitable for the separator.

II. Experimental

A phase diagram after Gustafson⁽⁵⁾ for the Fe–Cr–W system at 1273 K is shown in Fig. 2. When alloys consist of a single γ phase or mixtures of α and γ phases, transformations from bcc to fcc during heating and the reverse during cooling give rise to abrupt volume changes. In this study, therefore, compositions except for γ and $\alpha + \gamma$ regions were surveyed.

Starting materials for preparing Fe–Cr–W alloys were electrolytic iron (99.98 mass%), electrolytic chromium (99.85 mass%), and tungsten (99 mass%). Weighed metals were placed in alumina crucibles and were melted in a vacuum induction furnace. Ingots were hot-rolled into plates 8 mm in thickness at 1473 K. The composi-

Fig. 2 Phase diagram in the Fe–Cr–W system after Gustafson⁽⁵⁾.

Table 1 Chemical composition of the Fe–Cr–W alloys.

Alloy designation	Composition (mass%)					
	C	Si	S	Mn	Cr	W
Fe-5Cr-7W	0.001	0.054	<0.001	0.009	5.04	6.97
Fe-10Cr-7W	0.001	0.059	0.001	0.008	10.58	7.15
Fe-10Cr-9W	0.001	0.006	0.001	<0.001	9.53	8.99
Fe-15Cr-9W	0.001	0.009	0.001	<0.001	14.91	9.39
Fe-18Cr	0.001	0.055	0.001	0.005	18.32	—
Fe-18Cr-1W	0.001	0.013	0.001	0.006	17.93	0.96
Fe-18Cr-4W	0.001	0.010	0.001	0.004	17.77	3.94
Fe-18Cr-7W	0.001	0.009	0.001	0.003	17.74	7.11
Fe-18Cr-8W	0.001	0.011	0.001	0.002	18.12	8.04
Fe-18Cr-9W	0.001	0.011	0.001	0.002	17.62	8.99
Fe-18Cr-10W	0.001	0.014	0.001	0.002	17.91	9.97
Fe-18Cr-15W	0.001	0.015	0.001	0.002	18.08	15.06
Fe-18Cr-20W	0.002	0.019	0.001	<0.001	18.57	19.08
Fe-25Cr-7W	0.001	0.049	0.001	0.007	24.35	7.08
Fe-25Cr-9W	0.001	0.013	0.001	<0.001	24.72	8.65
Fe-28Cr	0.001	0.058	0.001	0.004	28.60	—
Fe-30Cr-9W	0.001	0.013	0.001	<0.001	29.60	8.49
Fe-35Cr-7W	0.001	0.051	0.001	0.007	34.57	6.99

tions and designations of the alloys prepared are given in Table 1. Commercial SUS 430 (Fe–18 mass%Cr), SUS 304 (Fe–18 mass%Cr–8 mass%Ni), Inconel X-750 (Ni–15 mass% Cr–7 mass% Fe–2.5 mass% Ti–1 mass% Nb + Ta–0.7 mass%Al), and ZrO_2 –8 mol% Y_2O_3 were also used to obtain fundamental thermal expansion data for the development of metallic separators.

Samples for thermal expansion measurements were prepared in the shape of cylinders 3 mm in diameter and 50 mm in length, which were rectangular to the rolling direction. These samples were normalized at 1173 K in H_2 for 3.6 ks. Thermal expansion was measured from 303 to 1273 K. Average thermal expansion coefficients were calculated from expansion data in this temperature range.

Samples for X-ray diffraction analysis were prepared in the shape of disks 30 mm in diameter and 8 mm in thickness. They were normalized at 1273 K in Ar for 3.6 ks, quenched in water, and finished with #1000 emery paper. The samples were surveyed with an X-ray diffractometer (Rigaku RINT2200) using Mo $K\alpha$ radiation.

Samples for magnetization measurements were prepared in the shape of cylinders 2 mm in diameter and 2 mm in thickness. They were annealed at 1273 K in Ar for 3.6 ks and then quenched in water. Magnetization of the samples was measured with a vibrating sample magnetometer (Toeiogyo, VSM-3) at a magnetic field strength of 1.2 MA m^{-1} where it is saturated.

Thermal analysis was made for samples in the shape of disks 2.5 mm in diameter and 1 mm in thickness. Their magnetic transformation temperatures were determined with a thermogravimetric analyzer (Mettler TG50) by heating them in a magnetic field.

Oxidation tests were done at 1273 and 1373 K in air for samples with the shape of plates 10 mm in width, 20 mm in length and 2 mm in thickness, finished with a diamond paste of 2 μm .

III. Results and Discussion

1. Thermal expansivity

Thermal expansion is measured in the temperature range from 303 to 1273 K. A polynomial up to T^3 is usually used for representation of the experimental data as a function of temperature⁽⁶⁾. The alloys examined in this study are slightly changed in expansion behavior above their Curie temperatures, as described later. Therefore, data of the expansion $\Delta L/L_0$ were fitted for the polynomial up to $T^4a + bT + cT^2 + dT^3 + eT^4$. Results are summarized in Table 2. Change in the average coefficient of thermal expansion of the alloys with about 18 mass%Cr as a function of W concentration is shown in Fig. 3. The average expansion coefficient is decreased with increasing the W concentration, and becomes a minimum of $11.92 \times 10^{-6} \text{ K}^{-1}$ near 9 mass%W. Above this concentration, the thermal expansion coefficient is increased, and is then decreased. Changes in the average coefficients of thermal expansion of the alloys with constant W concentrations of about 7 and 9 mass% as a function of Cr concentration are shown in Fig. 4. The average coefficients of thermal expansion for both the alloy systems are decreased with increasing the Cr concentration, and above 18 mass%Cr become constant. The average coefficients of thermal expansion of all the alloys examined are summarized in Fig. 5, in terms of the iso-coefficient contours. A low thermal expansion region where the average coefficient of thermal expansion is $12 \times 10^{-6} \text{ K}^{-1}$ or a little less expands from 15 mass%Cr toward the high Cr side along about 9 mass%W like a valley. This region corresponds to that of α phase near and along the solubility curve of W shown in Fig. 2.

Thermal expansivity is related to interaction between

atoms; that is, strong atomic bonding yields low thermal expansivity. Therefore, crystal structure of the Fe-Cr-W alloys at about 18 mass%Cr, which were obtained by normalizing at 1273 and then quenching in water, was examined by X-ray diffractometry. Only α phase was detected except for Fe-18Cr-8W in which very weak peaks relating to the Fe_2W phase were found. As shown in Fig. 2, the Fe_2W phase should thermodynamically precipitate at W concentrations above about 10 mass% at 1273 K. The reason for this is that the W concentration in the alloys (max. 6.85 at%, solubility in $\alpha \sim 3$ at%) is lower than that in Fe_2W . Lattice constants for α phases of the Fe-Cr-W alloys at about 18 mass%Cr are shown in Fig. 6. The lattice constant is anomalously low at 8 to 10 mass%W, and as a whole it tends to be decreased with increasing the W concentration. In these alloys, W makes the lattice small although it has a larger atomic size than Fe and Cr. This suggests that atomic bonding becomes strong with increasing the W concentration, especially at

Fig. 3 Average coefficient of thermal expansion α of the Fe-Cr-W alloys containing about 18 mass%Cr.

Table 2 Thermal expansion $\Delta L/L_0$ of the Fe-Cr-W alloys. $\Delta L/L_0 = a + bT + cT^2 + dT^3 + eT^4$ (T : 303–1273 K).

Alloy designation	$a/10^{-3}$	$b/10^{-6}$	$c/10^{-8}$	$d/10^{-11}$	$e/10^{-15}$
Fe-5Cr-7W	-1.380	-1.541	2.544	-1.932	5.752
Fe-10Cr-7W	-1.942	2.196	1.783	-1.443	4.891
Fe-10Cr-9W	-2.044	3.043	1.572	-1.288	4.345
Fe-15Cr-9W	-2.064	3.501	1.404	-1.144	3.896
Fe-18Cr	-1.761	1.062	2.014	-1.644	5.613
Fe-18Cr-1W	-2.246	4.606	1.183	-0.958	3.584
Fe-18Cr-4W	-1.840	1.755	1.883	-1.703	6.267
Fe-18Cr-7W	-2.057	3.675	1.319	-1.083	3.987
Fe-18Cr-8W	-1.807	1.551	1.922	-1.723	6.153
Fe-18Cr-9W	-1.709	1.272	1.875	-1.593	5.364
Fe-18Cr-10W	-1.953	2.742	1.602	-1.406	5.072
Fe-18Cr-15W	-0.037	-10.414	4.661	-4.372	15.391
Fe-18Cr-20W	-1.450	-1.343	2.750	-2.711	10.199
Fe-25Cr-7W	-1.741	0.923	2.145	-2.062	7.834
Fe-25Cr-9W	-2.540	6.819	0.672	-0.596	2.648
Fe-28Cr†	-1.830	1.584	1.985	-1.945	8.075
Fe-30Cr-9W	-2.413	6.560	0.577	-0.435	2.016
Fe-35Cr-7W	-1.810	2.602	1.467	-1.335	5.543

† 303–1073 K.

Fig. 4 Average coefficient of thermal expansion α of the Fe-Cr-W alloys containing about 7 and 9 mass%W.

8 to 10 mass%. When comparing Figs. 5 and 6, the average expansion coefficient and the lattice constant obviously resembles each other in their changes with the W concentration. Consequently, it is likely that atomic bonding becomes strong in the low expansion region.

All the alloys examined in this study are ferromagnetic. In ferromagnetic alloys, as widely known as the Invar effect, thermal expansivity is low below the Curie temperatures. Above the Curie temperatures, since the alloys have already lost ferromagnetism, they expand at high rates. This low expansivity below the Curie temperatures is caused by spontaneous volume magnetostriction where lattice distortion counteracts the normal lattice thermal expansion. Curie temperatures of the Fe-Cr-W alloys at about 18 mass%Cr are shown in Fig. 7. The Curie temperature is in the range between about 900 and 950 K, and is a little decreased with increasing the W

concentration. There is not such a particular change as that found in the thermal expansion coefficient. Slopes of thermal expansion curves, *i.e.* thermal expansion coefficients, of all the alloys measured tend to be increased above the Curie temperatures. Thermal expansion curves of the Fe-Cr-W alloys at about 18 mass%Cr are shown in Fig. 8. Below the Curie temperatures, the thermal expansion curves is almost the same. Above the Curie temperatures, the alloys in the low expansivity region such as Fe-18Cr-8W, Fe-18Cr-9W and Fe-18Cr-10W expand at not so high rates as Fe-18Cr-4W, Fe-18Cr-15W and Fe-18Cr-20W. Since these alloys are ferromagnetic, instantaneous thermal expansion coefficients above the Curie temperatures reflect on their normal lattice thermal expansivity. This suggests that the expansivity of the alloys in the low expansion region is not only depressed due to ferromagnetism but is intrinsically low. Since the differences between 1273 K, a typical operation temperature in SOFCs, and the Curie temperatures are 220 to 270 K, expansion behavior above the Curie temperatures strongly affects the average

Fig. 5 Iso-coefficient contours for the average coefficients of thermal expansion (303–1273 K) of the Fe-Cr-W alloys. The average coefficient of Fe-28Cr (28.60 mass%Cr) was estimated from the data obtained up to 1073 K.

Fig. 6 Lattice constant a of the Fe-Cr-W alloys containing about 18 mass%Cr.

Fig. 7 Curie temperature T_c of the Fe-Cr-W alloys containing about 18 mass%Cr.

Fig. 8 Thermal expansion $\Delta L/L_0$ of the Fe-Cr-W alloys containing about 18 mass%Cr.

Fig. 9 Magnetization $4\pi I$ of the Fe-Cr-W alloys containing about 18 mass%Cr or about 9 mass%W.

coefficients of thermal expansion.

Saturation magnetization reflects on intrinsic structure of substances. As shown in Fig. 9, the saturation magnetization of the alloys containing about 18 mass%Cr is steeply decreased with increasing the W concentration above 10 mass%. This corresponds to the compositional change from α to $\alpha + \text{Fe}_2\text{W}$. However, there are not such particular changes as in the thermal expansivity and the lattice constant.

As shown in Fig. 5, the low expansion region is relatively wide near 9 mass%W above 15 mass%Cr. In addition, workability is a little bad above 25 mass%Cr. Therefore, the alloys containing about 18 mass%Cr and 7 to 10 mass%W are promising materials. Fe-18Cr-9W had the lowest average coefficient of thermal expansion $11.92 \times 10^{-6} \text{ K}^{-1}$ of these alloys. This value is only 12% higher than that of the YDZ $10.62 \times 10^{-6} \text{ K}^{-1}$. For Fe-18Cr-7W, Fe-18Cr-8W, and Fe-18Cr-10W also, the differences are 17%, 15% and 15% respectively, and are not so serious in the compatibility of thermal expansion with YDZ.

2. Oxidation resistance

Oxidation tests were done mainly for Fe-18Cr-7W and Fe-18Cr-9W. This is because Fe-18 mass%Cr-7 to 10 mass%W alloys had low thermal expansivities and volatile W oxides may possibly generate at high W concentrations above 10 mass%. Fe-18Cr-7W had well adherent scales after oxidation at 1273 and 1373 K. For Fe-18Cr-9W, however, scale spalling occurred during cooling after oxidation. X-ray diffraction studies revealed that the scales of Fe-18Cr-9W consisted of only Cr_2O_3 and those of Fe-18Cr-7W were a mixture of Cr_2O_3 and a small amount of FeCr_2O_4 .

Mass gain data for Fe-18Cr-7W at 1273 and 1373 K are shown in Fig. 10. After long periods of oxidation time at 1373 K, the mass gain data deviated from the parabolic rate law $\Delta m^2 = k_p t$. This is due to the scale thinning by CrO_3 evaporation, which is a typical feature in high-temperature oxidation for Cr_2O_3 -forming al-

Fig. 10 Change in mass gain Δm^2 with time at 1273 and 1373 K.

Fig. 11 Temperature dependence of parabolic rate constant k_p for Fe-18Cr-7W, SUS 430, Fe-Cr alloys⁽⁸⁾, and Cr_2O_3 -forming superalloys⁽⁹⁾.

loys⁽⁷⁾. Parabolic rate constants obtained from the data for a short oxidation time for Fe-18Cr-7W and SUS 430 are shown in Fig. 11, together with data reported for Fe-Cr alloys⁽⁸⁾ and several commercial Cr_2O_3 -forming superalloys⁽⁹⁾, N 155 (Fe-21Cr-20Co-19Ni-2.7Mo-2.4W-1.4Mn, mass%), DH 242 (Ni-19Cr-1.3(Nb+Ta)-1Si, mass%) and Hastelloy X (Ni-22Cr-18Fe-9Mo-1.5Co, mass%). The parabolic rate constants for Fe-18Cr-7W are smaller than those of the binary Fe-Cr alloys and are close to those for the superalloys. Therefore, Fe-18Cr-7W has oxidation resistance comparable with the Cr_2O_3 -forming superalloys which contain no element nor compound greatly effective to improve the oxidation resistance, e.g. rare earth elements or their oxide particles.

Although the defect structure and diffusion mechanism of Cr_2O_3 at high temperatures are not clarified, the

results of high-temperature oxidation of Cr_2O_3 suggest that major defect species are Cr^{3+} vacancies⁽¹⁰⁾; the doping effect well explains the influences of the alloying addition of Li, Fe, Al and Ti on the oxidation of Cr. For W, stable cations at high temperatures are W^{4+} and/or W^{6+} , which have higher valences than Cr^{3+} . This indicates that W would increase the oxidation rate. In this study, however, W had evidently the better effect on the oxidation resistance of Fe–Cr alloys. A similar effect is reported in Co–15Cr–W alloys⁽¹¹⁾: increase in the W content from 15 to 30 mass% markedly reduced the oxidation rate constant. The high refractory metal Mo in the same group as W induced catastrophic oxidation in Fe–Cr–Mo alloys⁽¹²⁾. This is due to the formation of liquid MoO_3 (1074 K) and Cr_2O_3 dissolution by this liquid. On the other hand, W additions did not induce catastrophic oxidation of Ni–Cr⁽¹³⁾ and Co–Cr alloys⁽¹¹⁾, because the melting temperature of WO_3 (1745 K) is much higher than that of MoO_3 .

As shown above, Fe–18Cr–7W has good oxidation resistance competitive with the commercial superalloys. SOFCs are operated near 1273 K. Since they are postulated to be used for commercial electric generators, materials in them should bear operating for 144 Ms (40000 h). If the volatilization loss of Cr_2O_3 and the resulting acceleration of oxidation are not taken in consideration, mass gain after 144 Ms will be 120 g m^{-2} according to the parabolic rate law. Taking into account that the mass gain is due to oxygen in the Cr_2O_3 scale, this value corresponds to 73 μm in thickness for the scale (density of $\text{Cr}_2\text{O}_3 = 5.21 \text{ Mg m}^{-3}$, density of oxygen in $\text{Cr}_2\text{O}_3 = 1.65 \text{ Mg m}^{-3}$). Consequently, since the resistivity of Cr_2O_3 at 1273 K is in the range between 0.19 and $1.7 \Omega \text{ m}^{(14)}$, the resistance of the scale per 1 m^2 arrive at 1.4×10^{-5} to $1.2 \times 10^{-4} \Omega \text{ m}^2$ (0.14 – $1.2 \Omega \text{ cm}^2$). If a current density of 1000 A m^{-2} (0.1 A cm^{-2}) passes through a single cell, the resistance causes an voltage drop of 0.014 to 0.12 V. Since output voltage is probably in the range between 0.5 and 1 V in a single cell, the estimated resistance after 144 Ms is somewhat high. Though Fe–18Cr–7W is superior in thermal expansivity and oxidation resistance, further modifications, e.g. raising oxidation resistance and/or lowering electrical resistivity of scales themselves, will be necessary for actual use. In addition, Fe–18Cr–9W may be the best of a series of the Fe–Cr–W alloys, if its oxidation resistance is considerably improved. Coating of a conductive oxide $\text{La}_{0.85}\text{Sr}_{0.15}\text{CoO}_3$, which is also one of cathode materials, is effective for lowering the electrical resistivity⁽¹⁵⁾.

IV. Conclusion

Thermal expansion of Fe–Cr–W alloys were measured up to 1273 K to find out the alloys having low thermal expansivities close to zirconia, and alloys having such thermal expansivities were tested for oxidation resistance at 1273 and 1373 K to use them as separators of SOFCs. A low thermal expansion region where alloys have average coefficients of thermal expansion of $12 \times 10^{-6} \text{ K}^{-1}$ or a little less expanded from 15 mass%Cr toward the high Cr side along about 9 mass%W like a valley. This region corresponded to that of α phase near and along the solubility curve of W in the phase diagram of the Fe–Cr–W system. In the alloys having low thermal expansivities, the expansivity is depressed due to ferromagnetism below the Curie temperatures and is intrinsically low above the Curie temperatures. For Fe–18 mass%Cr–9 mass%W, which had the lowest expansion coefficient of the alloys containing about 18 mass%Cr, scale spalling occurred during cooling after oxidation. The oxidation resistance of Fe–18 mass%Cr–7 mass%W was as good as that of commercial superalloys forming Cr_2O_3 scales.

REFERENCES

- (1) H. Taimatsu and H. Kaneko: Bulletin of the Japan Institute of Metals, **11** (1992), 984–990.
- (2) N. Q. Minh: J. Amer. Ceram. Soc., **76** (1993), 563–588.
- (3) W. Köck, H.-P. Martinz, H. Greiner and M. Janousek: Proceedings of the 4th International Symposium on Solid Oxide Fuel Cells, Ed. by M. Dokiya, O. Yamamoto, H. Tagawa and S. C. Singhal, Proceedings Vol. 95-1, The Electrochem Soc., Pennington, (1995), pp. 841–849.
- (4) J. Urbanek, M. Miller, H. Schmidt and K. Hilpert: Proceedings of the 2nd European Fuel Cell Forum, Ed. B. Thorstensen, Oslo, European SOFC Forum, Oberrohrdorf, (1996), 503–512.
- (5) P. Gustafson: Met. Trans. A, **19A** (1988), 2531–2546.
- (6) Y. S. Touloukian, R. K. Kirby, R. E. Taylor and P. D. Desai: *Thermophysical Properties of Matter Vol. 12*, IFI/Plenum, New York, (1975).
- (7) N. Birks and G. H. Meier: *Introduction to High Temperature Oxidation of Metals*, Edward Arnold, London, (1983), 80–83.
- (8) E. J. Felten: J. Electrochem. Soc., **108** (1961), 490–495.
- (9) S. K. Rhee and A. R. Spencer: Met. Trans., **1** (1970), 2021–2023.
- (10) P. Kofstad: Nonstoichiometry, *Diffusion and Electrical Conductivity in Binary Metal Oxide*, Robert E. Krieger Publishing, Malabar, (1983), 203–208.
- (11) M. E. El-Dahshan, D. P. Whittle and J. Stringer: Corros. Sci., **16** (1976), 77–82.
- (12) S. S. Brenner: J. Electrochem. Soc., **102** (1955), 16–21.
- (13) M. E. El-Dahshan, D. P. Whittle and J. Stringer: Corros. Sci., **16** (1976), 83–90.
- (14) A. Holt and P. Kofstad: Solid State Ionics, **69** (1994), 127–136.
- (15) T. Kadowaki, T. Shiomitsu, E. Matsuda, H. Nakagawa and H. Tsuneizumi: Solid State Ionics, **67** (1993), 65–69.