DEFECT FORMATION AND THERMAL EXPANSION OF
PEROVSKITES ON THE BASIS OF LaCrO₃
FOR SOLID OXIDE FUEL CELLS

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ABSTRACT

Perovskites on the basis of LaCrO₃ are of interest as ceramic interconnect materials for the development of Solid Oxide Fuel Cells (SOFCs). The interconnects are exposed to oxidising and reducing atmospheres under operating conditions. Oxygen vacancy formation was determined as a function of oxygen partial pressure between 1 bar and 10⁻²² bar at temperatures between 900 and 1100°C. Different perovskite compositions made of (La,Ca/Sr)CrO₃, La(Cr,Mg)O₃, La(Cr,Mg/Cu/Co,Al)O₃, and (La,Ca)(Cr,Al)O₃ were investigated. Defect models were evaluated to describe the oxygen vacancy formation and the respective thermodynamic data were determined. The results are used to explain existing literature data on the isothermal expansion of LaCrO₃ based perovskites under reducing conditions.

INTRODUCTION

LaCrO₃ base perovskites are of interest as ceramic interconnect materials for the development of solid oxide fuel cells (SOFCs) (1). The interconnects are exposed to oxidising and reducing atmospheres under operating conditions. On annealing in reducing atmospheres, the LaCrO₃ base perovskites lose oxygen and form oxygen vacancies. The charge neutrality is maintained by changes in the valence state. The change in the valence and the oxygen vacancy concentration in reducing environments leads to volume expansion (2-6), which can result in residual stresses in the interconnects of SOFCs under operating conditions. However, it should be noted that compositional changes allow to suppress at least to a certain extent the volume expansion (6).

The main goal of this work is to determine the oxygen vacancy formation and to provide a better understanding of the structural changes in LaCrO₃ base perovskites related with a reduction of oxygen partial pressure. In this respect, the correlation between defect formation and isothermal volume expansion is also elaborated. The compositions shown in Table 1 were investigated.

EXPERIMENTAL

Powders of different substituted lanthanum chromite compositions LCC, LSC20, LCCA, LCCuA, and LCCoA (definition of acronyms cf. Table 1) were synthesised by solid-state reaction from the corresponding nitrates. The chemical composition of the samples after...
preparation was confirmed by chemical analysis (ICP-OES). The phase composition was checked by X-ray diffraction, XRD.

**Table 1. Sample compositions and labels.**

| Label | Doped on A and B site | Label |
|-------|-----------------------|-------|
| Lao.90Ca0.10CrO3-δ | Lao.80Sr0.20Cr0.97V0.03O3-δ | LSCV |
| Lao.80Ca0.20CrO3-δ | Lao.95Ca0.05Cr0.84Al0.16O3-δ | LCCA |
| Lao.80Sr0.20CrO3-δ | Lao.79Mg0.05Al0.16O3-δ | LCMA |
| Lao.79Cu0.05Al0.16O3-δ | LCCuA |
| Lao.79Co0.05Al0.16O3-δ | LCCoA |

The LSCV and LCMA perovskites (cf. Table 1) were obtained as slabs and discs with high density. Riso National Laboratory, Denmark, provided LSCV and H. Bausinger, Dornier, Friedrichshafen, Germany, the LCMA variant. For details with respect to the LCMA source see Ref. 6.

The formation of oxygen vacancies at elevated temperatures was studied by isothermal thermogravimetry as a function of oxygen partial pressure at different temperatures between 900 and 1100°C. The weight change of a given composition was measured with a thermo-balance system. Cylindrical samples of the compositions listed in Table 1 with a weight between 1500 mg to 2500 mg were used for the thermogravimetric measurements. The weight change was measured to an accuracy of ±0.1 μg with a Mettler UMT5 balance. Different oxygen partial pressures were adjusted and maintained by using the H2/H2O/Ar system with flow rates of about 30 ml/min and fixed by means of an electrochemical pump which was also used as an oxygen sensor. The pump/sensor was arranged downstream before the balance. The pO2 was additionally monitored by passing the exit gases through a calibrated oxygen sensor. Each sample was heated to the measurement temperature in an oxidizing atmosphere and allowed to equilibrate before stepwise change of pO2.

**RESULTS**

Figures 1-4 show the results of the thermogravimetric measurements on the defect formation for a temperature of 1000°C. The weight change caused by the vacancy formation and the total weight of the sample investigated were used to compute the oxygen nonstoichiometry of the different perovskites. Stoichiometric composition was assumed for an atmosphere of air at a pressure of 1 bar. The loss of oxygen observed for the different materials is described by the defect equilibria listed in Table 2 using the Kröger-Vink notation. The equilibrium constants of these reactions are used to obtain model relations describing the measurement results shown in Figures 1-4. The measurement points in these figures are fitted well by these equations yielding the equilibrium constant of the reactions shown in Table 2. The full lines shown in these
figures result from the fitting, the respective equilibrium constants are listed in Table 2. Details of the defect models and the fitting procedure are reported in Refs 7, 8, and 9.

Measurements at 900°C and 1100°C as well as at 900°C and 950°C (for LCCoA) were carried out in addition to those at 1000°C for some of the perovskite materials listed in Table 1. Equilibrium constants are evaluated in the same way as described for 1000°C. The temperature dependence of the equilibrium constant is given as:

$$K = \exp\left(\frac{-\Delta G^\circ}{RT}\right) = \exp\left(\frac{\Delta S^\circ}{R}\right) \cdot \exp\left(\frac{-\Delta H^\circ}{RT}\right)$$

where $\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$ are the changes of the Gibbs energy, the enthalpy, and the entropy, respectively, of the reactions considered. The values of $\Delta H^\circ$ and $\Delta S^\circ$, therefore, result from the slope and the intercept, respectively, of the plot $\ln(K)$ vs. $1/T$ and are given in Table 2.

Table 2. Temperature range of measurements of oxygen vacancy formation as well as reactions of defect formation together with their thermodynamic properties (equilibrium constant $K^\circ$, enthalpy change, $\Delta H^\circ$, and entropy change, $\Delta S^\circ$) for different perovskite compositions.

| Composition (cf. Table 1) | Temp. range, K | Reaction | $K^\circ$ at 1273 K, and reference | $\Delta H^\circ$, kJ/mol | $\Delta S^\circ$, J/K/mol |
|---------------------------|----------------|----------|-----------------------------------|--------------------------|--------------------------|
| LCC10 1173- 1373          |                | $O'_6 + 2Cr'_6 \rightleftharpoons V'_6 + 1/2O_2(g) + 2Cr'_6$ | 1.63$\times$10$^4$ (7)   | 301.2 (7)                | 86.4 (7)                |
| LCC20 1273                |                | $O'_6 + 2Cr'_6 \rightleftharpoons V'_6 + 1/2O_2(g) + 2Cr'_6$ | 2.58$\times$10$^4$ (7)   | -                        | -                        |
| LCCA 1173- 1373           |                | $O'_6 + 2Cr'_6 \rightleftharpoons V'_6 + 1/2O_2(g) + 2Cr'_6$ | 1.13$\times$10$^7$ (9)   | 232.2                    | 49.4                    |
| LCMA 1173- 1373           |                | $O'_6 + 2Cr'_6 \rightleftharpoons V'_6 + 1/2O_2(g) + 2Cr'_6$ | 1.55$\times$10$^7$ (8)   | 241.3                    | 58.9                    |
| LSC20 1173- 1373          |                | $O'_6 + 2Cr'_6 \rightleftharpoons V'_6 + 1/2O_2(g) + 2Cr'_6$ | 4.99$\times$10$^8$ (9)   | -                        | -                        |
| LSCV 1173- 1373           |                | $O'_6 + 2Cr'_6 \rightleftharpoons V'_6 + 1/2O_2(g) + 2Cr'_6$ | 1.45$\times$10$^4$ (9)   | 388                      | 155                      |
|                           |                | $O'_6 + 2V'_6 \rightleftharpoons V'_6 + 1/2O_2(g) + 2V'_6$ | 3.48$\times$10$^{12}$ (9) | -                       | -                        |
|                           |                | $Cr'_6 + V'_6 \rightleftharpoons Cr'_6 + V'_6$ | 1.55$\times$10$^4$ (9)   | -                        | -                        |
| LCCoA 1173- 1273          |                | $O'_6 + 2Cr'_6 \rightleftharpoons V'_6 + 1/2O_2(g) + 2Cr'_6$ | 3$\times$10$^4$ (9)      | 225.6                    | 90                       |
|                           |                | $O'_6 + 2Co'_6 \rightleftharpoons V'_6 + 1/2O_2(g) + 2Co'_6$ | 1.2$\times$10$^9$ (9)     | 220.3                    | 13                       |
|                           |                | $Cr'_6 + Co'_6 \rightleftharpoons Cr'_6 + Co'_6$ | 6.01$\times$10$^3$ (9)    | 3.5                      | -38                      |
| LCCuA 1273                |                | $O'_6 + 2Cu'_6 \rightleftharpoons V'_6 + 1/2O_2(g) + 2Cu'_6$ | 2.47$\times$10$^4$       | -                        | -                        |
|                           |                | $O'_6 + 2Cu'_6 \rightleftharpoons V'_6 + 1/2O_2(g) + 2Cu'_6$ | 4.69$\times$10$^{14}$    | -                        | -                        |
DISCUSSION

Oxygen Vacancy Formation and Defect Structure

Figures 1-4 show that the experimental results obtained are excellently represented by the selected defect models (see Table 2). The chromite compositions investigated can be divided into two different groups according to the nature of the dopants. The first group consists of the compositions, which contain the alkaline earth metal Ca, Sr or Mg as a dopant. The particularity of the defect structure of such chromites is that tetravalent chromium is formed under oxidizing conditions as a result of charge compensation due to acceptor doping in accordance with the Verwey principle (10). The process of oxygen release from the chromite lattice under reducing conditions is, therefore, accompanied by the transition of Cr$^{4+}$ to Cr$^{3+}$ according to the “small polaron” reaction (Table 2). There is a general trend for this group that the vacancy concentration at low oxygen potential increases if the content of the alkaline earth metals is raised as shown in Figure 2. It is interesting to note that the results obtained for LCMA containing 5 per cent Mg on B site and those of LCCA containing the same amount of Ca agree with each other in practical terms (Figure 3). In contrast to this, the result obtained for LSC20 and LSCV deviate from each other significantly although these chromites have the same Sr content on A sites. This can be explained by the influence of the vanadium on B site in LSCV. Vanadium seems to accept the 4+ state of oxidation easier as compared to Cr thereby compensating in part the negative charge induced by the Sr$^{2+}$ presence on A site (3 per cent of the Sr content). This means LSCV shows the same behavior as La$_{0.83}$Sr$_{0.17}$CrO$_3$ at high and intermediate oxygen partial pressures as it is demonstrated in Figure 1 by the comparatively good agreement between the measurement results and the “small polaron” model using a reduced Sr content. However, the results shown in Figure 1 are in favor of the selected defect model, which allows also the reduction V$^{4+}$ $\rightarrow$ V$^{3+}$. This reduction seems to start at very low oxygen partial pressures.

The Co- and Cu-doped chromites, LCCoA and LCCuA, form the second group of chromites. Unlike the compounds from the first group, the second group chromites does not contain alkaline earth metals which could provide Cr$^{4+}$ cations as a result of charge compensation in accordance with the Verwey principle. However, the existence of tetravalent charge carriers follows from the results of electrical conductivity and thermopower measurements for LaCr$_{1-x}$Co$_x$O$_3$ (11). This means that some amount of the Cr$^{4+}$ cations can be produced by the reaction Cr$^{3+}$ + Co$^{3+}$ = Cr$^{4+}$ + Co$^{2+}$ similar to Jonker’s proposal for La(Mn,Co)O$_3$ (12). The fit results shown in Figure 3 confirm this assumption. Moreover, the site occupancy for LCCoA at 1273 K calculated in air by the use of the equilibrium constants listed in Table 2 shows good agreement with that from thermopower measurements (11). The results mentioned above for Co-doped chromites allow the conclusion that the loss of oxygen in reducing environment is accompanied by both Cr$^{4+}$ $\rightarrow$ Cr$^{3+}$ and Co$^{3+}$ $\rightarrow$ Co$^{2+}$ transitions.

The defect structure of the Cu-doped chromite LCCuA differs significantly from that of the other compositions investigated (Table 2). Two particularities have to be highlighted in this respect. Firstly, LCCuA remains slightly understoichiometric with respect to oxygen at 1273 K in air. The second particularity consists in the lack of the change of the Cr$^{3+}$ oxidation state over the complete oxygen partial pressure range investigated (see Table 2). In contrast to this, copper changes its oxidation state continuously from 3+ via...
2+ to 1+ if the oxygen partial pressure decreases. The reactions for the formation of oxygen vacancies in LCCuA shown in Table 2 proceed simultaneously. The first point of inflection of the curve shown in Figure 4 at an oxygen partial pressure \( p(O_2) = 10^{-11} \) atm corresponds to equal concentrations of \( \text{Cu}^{3+} \) and \( \text{Cu}^{2+} \). The second point of inflection is observed at \( p(O_2)=10^{-17} \) atm when the concentration of the \( \text{Cu}^{3+} \) becomes equal to that of \( \text{Cu}^{1+} \) and, therefore, the concentration of the \( \text{Cu}^{2+} \) starts to decrease if the oxygen partial pressure is further diminished.

**Correlation Between Defect Structure and Isothermal Expansion**

The isothermal expansion determined as a function of the oxygen partial pressure at 1000°C for different chromite compositions and reported in Refs. (6) and (7) is used in the present study to determine the correlation between the isothermal expansion and the defect structure described in the preceding Section. The formation of oxygen vacancies at low oxygen partial pressures is accompanied by the reduction of \( \text{Cr}^{4+} \) to \( \text{Cr}^{3+} \) for all chromites of the first group defined in the preceding Section. For this reason, there are two possible mechanisms according to which the observed isothermal expansion can be explained. The first mechanism is a dimensional one, which consists in the increase of the mean size of the chromium cations due to the substitution of large \( \text{Cr}^{3+} \) for small \( \text{Cr}^{4+} \) by the reduction. The second mechanism is the coulomb repulsion between \( \text{Cr} \) cations because of the oxygen vacancy formation (5). In order to reveal which of the mechanisms mentioned above contributes most to the lattice expansion the average size of the B site cations is plotted versus the oxygen partial pressure. The respective changes in radii (Figure 5) were computed by taking into account the ionic radii of the B site cations (13) and their concentration which was determined on the basis of the defect structure evaluated for the different chromite compositions (see Section Results). The crystal ionic radii (13) accepted for the B site cations in octahedral coordination (\( CN=6 \)) are \( r(C_{\text{Cr}^{3+}})=0.755 \) Å, \( r(C_{\text{Cr}^{4+}})=0.69 \) Å, \( r(C_{\text{O}})=0.78 \) Å, and \( r(C_{\text{O}})=0.72 \) Å. Crystal radii are employed in this paper, instead of effective ionic radii used in our previous paper (9), because of their close correspondence to the physical size of ions in solids (9). Figure 6 summarizes results on isothermal expansion obtained from the literature (6,7). The comparison of Figs 6 and 5 reveals that the trend in the expansion behavior (Figure 6) and the trend in the change of average radius of the B site cations (Figure 5) are similar. The isothermal expansion and the change of average radius of the B site cations increase at constant oxygen partial pressure if the alkaline earth metal content is raised. On other hand, if the chromites contain the same amount of a dopant, such as in LCMA and LCCA, they have about the same expansion and average change in radius under similar conditions, indifferently whether the dopant is on A or B site.

According to the simple defect model accepted for compounds with an alkaline earth metal as dopant the decrease of the \( \text{Cr}^{4+} \) content at the same oxygen vacancy concentration is independent of the nature, lattice site, and concentration of the dopant. The change of the average radius of the B site cations for such chromites, therefore, agrees well at the same value of oxygen nonstoichiometry (Figure 7). Moreover, this figure shows a strong linear dependence of the change of the average radius from the oxygen nonstoichiometry. A similar relation has to be expected between the isothermal expansion and the oxygen vacancy concentration if the change of the average B site cation radius contributes most to the isothermal expansion. Figure 8 shows the isothermal expansion plotted for all alkaline earth metal doped chromites versus the oxygen partial pressure.
nonstoichiometry. The Figure reveals that in spite of the scatter which may be caused by experimental errors there is a linear trend in the expansion as function of the oxygen nonstoichiometry. The relation $\Delta L/L_0=0.15(\Delta R/R_0)$ can be used to predict the isothermal expansion as it is shown by Figure 9.

The substitution of Co or Cu for Cr in lanthanum chromite instead of an alkaline-earth metal as a dopant leads to a significant change of the defect structure (cf. Section Results). These chromites should, therefore, show an isothermal expansion behavior different from that of chromites doped with an alkaline earth metal.

Isothermal expansion of LCCoA was determined for an oxygen partial pressure, which covers also the conditions of a fully occupied oxygen sublattice (6). This is not the case for LCCuA which shows significant oxygen vacancy formation at $p(O_2)=10^4$ bar (Figure 4) the highest oxygen partial pressure adjusted in the isothermal expansion measurements. The correlation between the oxygen vacancy formation and the isothermal expansion is, therefore, only considered for LCCoA. The isothermal expansion is compared with that of LCCA due to the similar composition (5 per cent dopant) of LCCA and LCCoA. Figures 10 and 11 show the oxygen partial pressure dependences of the isothermal expansion and the computed relative change of the average radius of the B-site ions, respectively, for LCCoA and LCCA. The calculated change of the B-site ionic radii is based on the concentrations of different species and their effective ionic radii (13). The radii for Co$^{2+}$ and Co$^{3+}$ were adopted in octahedral coordination ($CN=6$) as: $r_{Co^{2+}}=0.75$ Å (HS), $r_{Co^{3+}}=0.79$ Å (LS) and $r_{Co^{2+}}=0.885$ Å (HS), where LS and HS correspond to low and high spin state, respectively. Figure 11 shows the results for the two spin states, since it was not known whether Co$^{2+}$ exists in low or in high spin state. Figure 11 may indicate that the presence of the Co$^{2+}$ high spin state is doubtful for LCCoA because the relative change of the average radius of the B-site ions for this state is twice as large than the one calculated for the Co$^{2+}$ low spin state. A Co$^{2+}$ high spin state would lead to an expansion significantly higher than the dependence shown in Figure 11. The trends in the expansion curves are in good agreement with those of the average radius of the B-site ions for both compounds, if the computation of the change of the average radius is based on the presence of the Co$^{2+}$ low spin state. Not only the expansion onsets and the onsets of the change of the B-site ionic average radius are consistent with each other for the Co$^{2+}$ low spin state, but also the intersections of the expansion and radius change curves are observed at about the same oxygen partial pressure ($log(p_{O_2}/atm)=-16$). The change of average radius of the B-site ions and the isothermal expansion plotted versus the oxygen nonstoichiometry for both LCCA and LCCoA are shown in Figs 12 and 13, respectively. The comparison of these figures reveals that the trends in the diagrams are obviously consistent with each other. The consistencies mentioned above indicate that the expansion observed in the (La, Ca)(Cr, Co, Al)O$_3$ system is mainly determined by the relative change of the average B-site ionic radius as it was observed for the other chromite systems mentioned above.

CONCLUSIONS

Oxygen vacancy formation in nine LaCrO$_3$ base perovskites of different composition (Table 1) was determined and correlated with data on the isothermal expansion.
Thermomechanical measurements on selected compositions revealed the influence of oxygen vacancies on the mechanical stability.

Defect models were developed which describe the oxygen vacancy formation in the different perovskites. Enthalpy and entropy changes were evaluated for the reactions of the defect formation. The perovskites investigated can be divided into two groups. The chromites containing Ca, Sr or Mg (first group) essentially release oxygen by the transition $\text{Cr}^{4+}$ to $\text{Cr}^{3+}$ according to the “small polaron” reaction. The composition LSCV may additionally show the transition $\text{V}^{4+}$ to $\text{V}^{3+}$ at very low oxygen partial pressures. The chromites with no addition of alkaline earth metals but Co or Cu (second group) lead to significant changes in the defect structures since Co and especially Cu tend to reduce their oxidation state. The results obtained on oxygen non-stoichiometry of doped chromite compositions showed the large impact of the nature of the dopants on the defect structure of these chromites.

The correlation between the oxygen non-stoichiometry and the isothermal expansion reveals that the latter can be understood by the change of the average B site cation radius of the perovskites, which is obtained from the defect structure.

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Figure 1. Nonstoichiometry of $\text{La}_{0.80}\text{Sr}_{0.20}\text{CrO}_{3.5}$ (LSC 20) and $\text{La}_{0.80}\text{Sr}_{0.20}\text{Cr}_{0.97}\text{V}_{0.03}\text{O}_{3.5}$ (LSCV) at 1000°C. Fitted curves result on the basis of defect models (see text).

Figure 2. Nonstoichiometry of $\text{La}_{0.95}\text{Ca}_{0.05}\text{Cr}_{0.84}\text{Al}_{0.16}\text{O}_{3.5}$ (LCCA), $\text{La}_{0.90}\text{Ca}_{0.10}\text{CrO}_{3.5}$ (LCC10), and $\text{La}_{0.80}\text{Ca}_{0.20}\text{CrO}_{3.5}$ (LCC20) at 1000°C. Fitted curves result on the basis of defect models (see text).
Figure 3. Nonstoichiometry of \( \text{LaCr}_0.79\text{Co}_{0.05}\text{Al}_{0.16}\text{O}_{3-\delta} \) (LCCoA), \( \text{La}_{0.95}\text{Ca}_{0.05}\text{Cr}_{0.04}\text{Al}_{0.16}\text{O}_{3-\delta} \) (LCCA), and \( \text{LaCr}_0.79\text{Mg}_{0.05}\text{Al}_{0.16}\text{O}_{3-\delta} \) (LCMA) at 1000°C. Fitted curves result on the basis of defect models (see text).

Figure 4. Nonstoichiometry of \( \text{LaCr}_0.79\text{Co}_{0.05}\text{Al}_{0.16}\text{O}_{3-\delta} \) (LCCoA) and \( \text{LaCr}_0.79\text{Cu}_{0.05}\text{Al}_{0.16}\text{O}_{3-\delta} \) (LCCuA) at 1000°C. Fitted curves result on the basis of defect models (see text).
Figure 5. Relative change of the average radius of the B site cations as function of the oxygen partial pressure $p(\text{O}_2)$ for different perovskite compositions (cf. Table 1).

Figure 6. Linear isothermal expansion as function of the oxygen partial pressure $p(\text{O}_2)$ for different perovskite compositions (cf. Table 1) at 1000°C.
Figure 7. Relative change of the average radius of the B site cations as function of the oxygen nonstoichiometry $\delta$ for different perovskite compositions (cf. Table 1).

Figure 8. Linear isothermal expansion as function of the oxygen oxygen nonstoichiometry $\delta$ for different perovskite compositions (cf. Table 1) at 1000°C.
Figure 9. Linear isothermal expansion as function of the relative change of the average radius of the B site cations for different perovskite compositions (cf. Table 1) at 1000°C.

Figure 10. Linear isothermal expansion as function of the oxygen partial pressure \(p(O_2)\) for \(\text{La}_{0.95}\text{Ca}_{0.05}\text{Cr}_{0.84}\text{Al}_{0.16}\text{O}_{3.3}\) (LCCA) and \(\text{LaCr}_{0.79}\text{Co}_{0.05}\text{Al}_{0.16}\text{O}_{3.3}\) (LCCoA) at 1000°C.
Figure 11. Relative change of the average radius of the B site cations as function of the oxygen partial pressure $p(O_2)$ for $La_{0.95}Ca_{0.05}Cr_{0.84}Al_{0.16}O_{3-δ}$ (LCCA) and $LaCr_{0.79}Co_{0.05}Al_{0.16}O_{3-δ}$ (LCCoA) for different spin states at 1000°C.

Figure 12. Relative change of the average radius of the B site cations as function of the oxygen partial pressure for $LaCr_{0.79}Co_{0.05}Al_{0.16}O_{3-δ}$ (LCCoA) and $LaCr_{0.95}Ca_{0.05}Al_{0.16}O_{3-δ}$ (LCCA) at 1000°C.
Figure 13. Linear isothermal expansion as function of the oxygen nonstoichiometry $\delta$ for $\text{La}_{0.95}\text{Ca}_{0.05}\text{Cr}_{0.84}\text{Al}_{0.16}\text{O}_{3.5}$ (LCCA) and $\text{LaCr}_{0.79}\text{Co}_{0.05}\text{Al}_{0.16}\text{O}_{3.5}$ (LCCoA) at 1000 °C.