

X-ray diffraction investigation of phase stability in the Co–Cr–O and the Fe–Co–Cr–O systems in air at 1323 K

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Received 7 April 2005; received in revised form 24 April 2005; accepted 27 April 2005

Available online 7 July 2005

Abstract

Mixtures of Co_3O_4 , Cr_2O_3 , and Fe_2O_3 were annealed in air for times up to 147 h at 1323 K. Phase analysis was performed using X-ray diffraction.

The mixtures of Cr_2O_3 and Co_3O_4 powders reacted forming mixed oxides with the spinel structure. In addition to an oxide with the spinel structure an oxide with the rock salt structure was identified in the cobalt-rich mixtures, suggesting that these compositions belong to a two-phase field in the Cr–Co–O phase diagram. In the Cr-rich mixtures, both non-reacted Cr_2O_3 and CoCr_2O_4 were identified.

The decomposition temperatures of Co_3O_4 , Co_2CrO_4 , and $\text{Co}_{1.5}\text{Cr}_{1.5}\text{O}_4$ were estimated with thermogravimetry. On the basis of the results obtained a part of the Cr–Co–O phase diagram was constructed.

Incorporation of Fe cations in the Co–Cr spinel was observed to expand the spinel lattice. Qualitative phase analyses of the Fe–Cr–Co oxide mixtures indicate that connecting the phase fields in the Fe–Co–O and Cr–Co–O system gives a fair prediction of the phase fields in the Fe–Cr–Co–O system at 1323 K (in air).

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Keywords: Phase diagram; Mixed Co–Cr oxides/spinel; Mixed Fe–Co–Cr oxides/spinel

1. Introduction

One of the candidate materials for the interconnector in solid oxide fuel cell (SOFC) stacks is high chromium containing metallic substrate coated with a Co_3O_4 [1] or a Co-containing perovskite (e.g. LaCoO_3 [1], $(\text{La},\text{Sr})\text{CoO}_3$ [1–3]) layer. Oxidation of the interconnector material occurs during operation of SOFCs at high temperature. In this respect the coating/substrate interaction and the coating/oxidizing atmosphere interaction become of importance. Crystallographic and thermodynamic data relating to the Co–Cr–O and Fe–Co–Cr–O systems are scarce. Previously, the solid solution of Cr_2O_3 and Co_3O_4 with the spinel structure (hereafter denoted spinel) has been studied at temperatures between

773 and 1173 K [4–7]. Various Cr,Co-spinel compositions were synthesised, mainly from the nitrates of Co and Cr by prolonged annealing at a given temperature [4–6] and characterised. Makkonen [4] obtained spinels after 240 h at 1173 K, Bracconi et al. [5] after 500 h at 1123 K and O'Neill [6] after 40 h at 1073 K. Hanck and Laitinen [7] obtained Co_2CrO_4 by constant current electrolysis of K_2CrO_4 with CoCl_2 at 773 K. The lattice parameters, a , of the mixed Cr–Co-spinels as reported in the literature and those identified in the present work are collected in Fig. 1. The solid line in Fig. 1 was calculated using the equation O'Neill [6] obtained from a least squares regression of his data (cf. Eq. (1)).

$$a(\pm 0.0002)/\text{Å} = 8.0832 + 0.2641 x_{\text{Cr}} - 0.0147(x_{\text{Cr}})^2, \\ x_{\text{Cr}} = \text{Cr}^{3+}/(\text{Cr}^{3+} + \text{Co}^{3+}) \quad (1)$$

The lattice parameter follows Vegard's law [8], i.e. increases linearly proportional to the fraction of the Cr-cations in the spinel. Magnetic susceptibility and neutron diffraction

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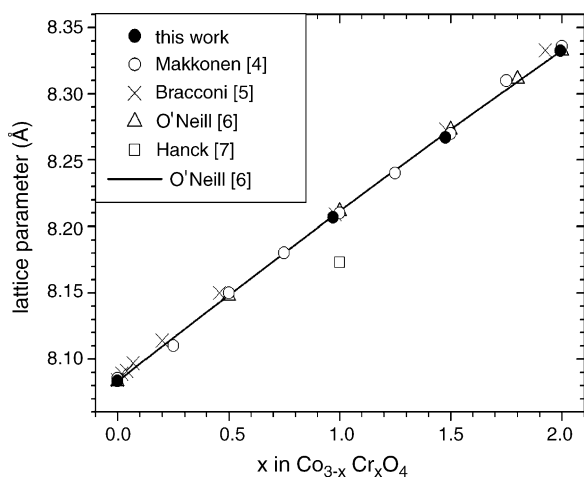


Fig. 1. The lattice parameter of the $\text{Co}_{3-x}\text{Cr}_x\text{O}_4$ spinel measured at room temperature vs. the Cr content (x). The lattice parameters represented by the solid line were calculated using Eq. (1) [6].

data strongly suggest that Co_3O_4 [9], $\text{Co}_{3-x}\text{Cr}_x\text{O}_4$ [5] and CoCr_2O_4 [10] are normal spinels at room temperature. Hence, the Cr^{3+} -cations are expected to be located at the same positions as the Co^{3+} -cations [4].

The phase stability (in air) of the various types of oxides in the Fe–Co–O system is shown in Fig. 2 as a function of the fraction of Fe-cations [11]. It shows that spinel Co_3O_4 transforms to CoO with the rock salt structure (hereafter named rock salt) at about 1173 K [11]. At 1323 K, the $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ spinel is monophasic for $0.67 < x < 1.46$; monophasic rock salt develops for $x > 2.45$ [11].

Mössbauer spectroscopy of $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ showed that for $x \leq 1$ the Co^{2+} -cations replace the Fe^{2+} -cations, whereas for $x > 1$ it is the Fe^{3+} -cations, which are replaced by the Co^{3+} -cations. The Co^{3+} -ions were only found on octahedral interstices with respect to the anion sublattice [11]. Rietveld refinement of X-ray diffraction patterns obtained from CoFe_2O_4 and FeCo_2O_4 powders indicated that Fe^{3+} -cations and Co^{2+} -cations are distributed over the tetrahedral and octahedral positions (with respect to the anion sublattice) [12].

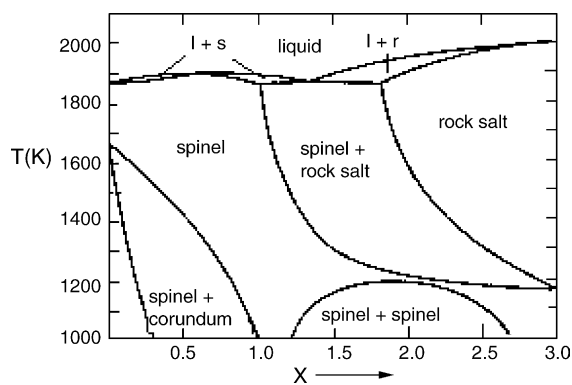


Fig. 2. [11] The Fe–Co oxide phase diagram in air at 1000–2100 K. x is x in $\text{Co}_x\text{Fe}_{3-x}\text{O}_{4\pm\delta}$.

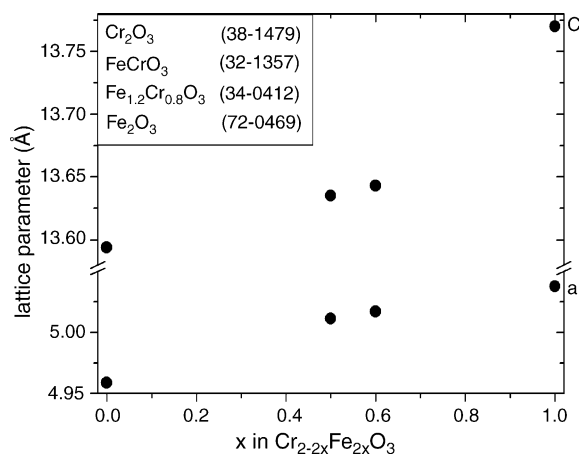


Fig. 3. The lattice parameter of $\text{Cr}_{2-x}\text{Fe}_x\text{O}_3$. Data from the JC-PDS database.

Thermodynamically, Fe_2O_3 and Cr_2O_3 are the most stable oxides of Fe and Cr, respectively, in air at 1323 K (and at temperatures below). The oxides form a continuous series of solid solutions according to the Fe–Cr–O phase diagram [13]. Lattice parameters of $\text{Cr}_{2-2x}\text{Fe}_{2x}\text{O}_3$ from the JC-PDS database show that substituting Cr-ions with Fe-ions in an oxide with the corundum structure (henceforth entitled corundum) results in larger a - and c -lattice parameters as shown in Fig. 3.

Only few investigations were dedicated to the Fe–Co–Cr oxide system. The investigations mainly focus on the cation distribution in the spinel phase [12,13]. Rietveld refinement of room temperature neutron diffraction data obtained from CoFeCrO_4 suggested that Cr^{3+} -ions were located in the octahedral sites, whereas Co^{2+} -ions and Fe^{3+} -ions were distributed over the remaining octahedral and tetrahedral sites [14]. In situ Mössbauer spectroscopy of slowly cooled (10 K/h) $\text{CoFe}_{1.9}\text{Cr}_{0.1}\text{O}_4$ showed that cation site exchange occurred during heating for temperatures above 295 K [15].

In the present work the oxide phases developing in the Co–Cr–O and Fe–Co–Cr–O systems were investigated under conditions of relevance for SOFC cathode conditions.

2. Experimental

2.1. Synthesis of the mixed oxides

Mixtures of 1 g were prepared from Co_3O_4 (manufacturer: Alfa Aesar, purity > 99.7%, grain size: $d_{p,\text{average}} = 7.5 \mu\text{m}$), Cr_2O_3 (manufacturer: Merck, purity > 99%, grain size: $d_{p,\text{average}} = 2.3 \mu\text{m}$) and Fe_2O_3 (manufacturer: Alfa Aesar, purity > 99.945%, grain size: $d_{p,\text{average}} = 6.8 \mu\text{m}$) in the cation ratios given in Tables 1 and 2. The powders were crushed and mixed in a mortar for approximately 5 min. The Co–Cr oxide mixtures were placed in Al_2O_3 containers and annealed three times at 1323 K in air. In the 1st and the 3rd run, the powders were heated at 100 K/h and cooled at 300 K/h. In the 2nd run,

Table 1
The investigated cobalt and chromium cation ratios

	Co:Cr 1:5	Co:Cr 1:2	Co:Cr 1:1	Co:Cr 2:1	Co:Cr 5:1
Co	1.00	1.00	1.00	1.97	4.83
Cr	5.08	1.98	0.97	1.00	1.00

the heating rate was 200 K/h and the powders were quenched in air after the annealing. The annealing time after reaching 1323 K was 56 h in the 1st run, 85 h in the 2nd and 6 h in the 3rd.

The Fe–Cr–Co oxide mixtures were annealed twice. The mixtures were held at temperature for 56 h in the 1st run and 72 h in the 2nd run. The heating and cooling rates were 100 and 300 K/h in the 1st run and 200 K/h and air quenching in the 2nd run.

The 2nd anneal was carried out to ensure that the mixtures had reached equilibrium, whereas the purpose of the 3rd anneal was to investigate whether the cooling rate had an influence on the phase constitution of the powders. In-between two successive anneals, the mixtures were re-mixed in a mortar for approximately 5 min.

2.2. Synthesis from the nitrates of Co and Cr

The powder was produced according to the glycine–nitrate combustion method [16]. An aqueous solution of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (manufacturer: Alfa Aesar, purity: 99.999%) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (manufacturer: Merck, purity: 99%), respectively, were prepared. The metal concentration was determined by transforming a known amount of each solution into the pure oxide by annealing the solution for 5 h at 1073 K in air. A Cr–Co solution with the metal ratio Cr:Co equal to 1:2.09 was mixed with glycine. Water was evaporated until combustion occurred, during which the powder was formed. The powder was annealed for 65 h at 1123 or 1323 K and quenched in air.

2.3. X-ray diffraction analysis

The annealed mixtures were characterised with X-ray diffraction (XRD) at room temperature. Silicon powder was used as a reference in the XRD measurements following the 1st and 2nd run. The XRD measurements were performed on an STOE (θ – θ) diffractometer with Cu $\text{K}\alpha$ radiation. The diffractometer was equipped with an energy disperse detector. The diffractograms were obtained in the 2θ range 15–90°

Table 2
The investigated iron, chromium and cobalt cation ratios

	Fe:Cr:Co 1:6:3	Fe:Cr:Co 1:4:2	Fe:Cr:Co 1:1:2	Fe:Cr:Co 1:2:4	Fe:Cr:Co 1:3:6
Co	3.00	2.00	1.97	3.95	6.10
Cr	6.00	4.00	1.00	1.95	3.04
Fe	1.00	1.00	1.00	1.00	1.00

or 10–100°. The 2θ -step size was either 0.05° (1st run, slits: 8 and 0.3 mm) or 0.03° (2nd and 3rd run, slits: 8 and 0.15 mm).

Peak positions were assessed by careful visual inspection of each individual line profile. Relative intensities (I_R) are defined with respect to the strongest peak. STOE's software package was used for peak calibration and calculation of the lattice parameters. The positions of the Si peaks (4–7 peaks) were compared with the theoretical positions of Si; deviations from theoretical positions were described as a function of 2θ with a straight line. The lattice parameters of the phases developed were determined by minimisation of the absolute difference of the 2θ values.

2.4. Thermal analysis

The decomposition temperatures of Co_3O_4 , “Cr:Co 1:2” (Section 2.2) and “Co:Cr 1:1” were determined with thermogravimetry (TGA), using a Netzsch STA 409C/D. The heating rate was 300 K/h up to 773 K; thereafter the heating rate was 60 K/h. The temperature, where the sample weight started to fall, was taken as an indication of the decomposition temperature.

3. Results

3.1. The Cr–Co oxide mixtures

The lattice parameters and the relative intensities of the oxide phases identified after each annealing treatment of the Cr–Co oxide mixtures are given in Table 3. The “Cr:Co 2:1” and “Cr:Co 1:1” mixtures are homogeneous spinel phases after the 2nd anneal. In the “Cr:Co 5:1” mixture coexistence of the same spinel phase as for the “Cr:Co 2:1” mixture and non-reacted Cr_2O_3 were observed. The lattice parameter of the spinel phase identified in the “Cr:Co 5:1” and the “Cr:Co 2:1” mixtures is comparable to the value reported for CoCr_2O_4 (JC-PDS 22-1084): $a = 8.3299 \text{ \AA}$. The lattice parameter found for the homogeneous spinel phase identified in the “Cr:Co 1:1” mixture could not be compared to any of the Cr–Co-spinel phases reported in the JC-PDS database.

In the “Cr:Co 1:2” and “Cr:Co 1:5” mixtures two spinel phases and a rock salt phase were identified. The relative intensities of the identified phases did not change from the 1st to the 3rd anneal of “Cr:Co 1:2” mixture, which strongly suggests that the reaction has completed during the 1st anneal.

The identified spinel phases have lattice parameters smaller than those observed for the spinel phase in the “Cr:Co 1:1” mixture and for CoCr_2O_4 . The smallest lattice parameters observed for a spinel phase, are slightly larger than reported for Co_3O_4 ($a = 8.084 \text{ \AA}$; JC-PDS 43-1003). It is noted that the lattice parameter of the starting powder Co_3O_4 is in accordance with the reported JC-PDS value. The largest of the lattice parameters found for the spinel phases in the “Cr:Co 1:2” and “Cr:Co 1:5” mixtures is larger than the value reported for Co_2CrO_4 ($a = 8.17 \text{ \AA}$; JC-PDS 24-0326). The lat-

Table 3

The lattice parameter (a , c) (± 0.001 Å) and the relative intensity (I_R) of the starting materials and of the oxides formed during annealing of the chromium and cobalt oxide mixtures in air

Cr:Co	Anneal	Corundum (R- $\bar{3}c$)			Spinel (Fd $\bar{3}m$)		Rock Salt (Fm $\bar{3}m$)	
		a (Å)	c (Å)	I_R	a (Å)	I_R	a (Å)	I_R
Cr ₂ O ₃		4.959	13.594	1				
5:1	1	4.959	13.591	0.73	8.333	1		
	2	4.959	13.594	0.69	8.333	1		
	3							
2:1	1	4.961	13.591	0.01	8.333	1		
	2				8.333	1		
	3				8.331	1		
1:1	1				8.312 & 8.263	0.2 & 1		
	2				8.267	1		
	3				8.267	1		
1:2	1				8.249 & 8.090	1 & 0.24	4.268	0.05
	2							
	3				8.249 & 8.089	1 & 0.25	4.265	0.05
1:5	1				8.227 & 8.087	0.47 & 1	4.261	0.12
	2				8.241 & 8.094	0.58 & 0.12	4.262	1
	3				8.234 & 8.088	0.62 & 1	4.267	0.13
Co ₃ O ₄				8.084	1			

Anneal 1: 100 K/h—56 h at 1323 K—300 K/h. Anneal 2: 200 K/h—85 h at 1323 K—air quenching. Anneal 3: 100 K/h—6 h at 1323 K—300 K/h.

tice parameter of the rock salt phase is slightly larger than that of CoO ($a = 4.26$ Å; JC-PDS 43-1004). In the diffractograms obtained after the second run, i.e. after quenching from the annealing temperature, the fraction of rock salt phase is considerably higher than in the diffractograms of the slowly cooled samples. The reverse applied for the fraction of spinel phase with lattice parameter of approximately 8.09 Å: a larger abundance of spinel phase in the diffractograms of the slowly cooled samples. This observation indicates that the spinel with $a = 8.09$ Å developed during cooling, as a result of a conversion of rock salt CoO to spinel Co₃O₄.

3.2. “Cr:Co 1:2” oxide powder obtained from the nitrates of Co and Cr

The obtained powder was very inhomogeneous and consisted of green and black particles. After annealing at 1323 K the powder consisted of two spinel phases ($a = 8.248$, 8.092 Å) and a rock salt phase ($a = 4.265$ Å), which is equivalent to the result obtained by mixing of the Cr₂O₃ and Co₃O₄ oxide powder. Only one spinel phase was identified after annealing at 1123 K. The lattice parameter was 8.207 Å, which is larger than that reported for Co₂CrO₄ ($a = 8.17$ Å, JC-PDS 24-0326).

3.3. Thermal analysis of selected powders

Co₃O₄ transformed to CoO at 1163 K. A weight loss is observed due to oxygen release.

The weight started to decrease at 1270 K for the “Cr:Co 1:2” oxide mixture and at 1426 K for the “Co:Cr 1:1” oxide mixture. The weight continued to decrease until the heating was stopped, indicating that the phase transformation was not completed when thermal analysis was terminated. In

the selected samples a transformation from Co-rich spinel to Co-rich rock salt phase is held responsible for the observed weight loss. This interpretation is consistent with the low temperature XRD results for low and high cooling rates (cf. Table 3).

3.4. The Fe–Cr–Co oxide mixtures

The lattice parameters and the relative intensities of the oxide phases identified after annealing of the Fe–Cr–Co oxide mixtures are given in Table 4.

A single oxide phase was obtained after annealing of the “Fe:Cr:Co 1:1:2” mixture at 1323 K. CoFeCrO₄ is the only ternary Fe–Cr–Co oxide included in the JC-PDS database ($a = 8.34$ Å, 28-1234). Both the composition and the lattice parameter of this spinel differ from those identified in the “Fe:Cr:Co 1:1:2” mixture. The X-ray diffractogram of the “Fe:Cr:Co 1:1:2” spinel phase is shown in Fig. 4.

Annealing of the “Fe:Cr:Co 1:6:3” and “Fe:Cr:Co 1:4:2” mixtures resulted in the development of both corundum and spinel phases. The spinel peaks in the diffractograms showed a low intensity shoulder at higher 2θ values, especially after quenching. This is attributed to in-homogeneities in the spinel phase (perhaps caused by cation exchange during cooling). The lattice parameters of the identified phases in the two mixtures are similar and the phases may very likely be the same. As compared to the spinel phase in the “Fe:Cr:Co 1:1:2” mixture, the lattice parameter of the spinel phases in the “Fe:Cr:Co 1:6:3” and “Fe:Cr:Co 1:4:2” mixtures is much larger; the lattice parameter of the corundum phase is slightly larger than that of the Cr₂O₃ starting powder.

Two spinel phases and a rock salt phase formed during annealing of the “Fe:Cr:Co 1:2:4” and “Fe:Cr:Co 1:3:6” mixtures. Both spinel phases have lattice parameters smaller than

Table 4

The lattice parameter (a , c) ($\pm 0.001 \text{ \AA}$) and the relative intensity (I_R) of the oxides formed during annealing of the “Fe:Cr:Co” oxide mixtures in air

Fe:Cr:Co	Anneal	Corundum ($R - \bar{3}c$)			Spinel ($Fd\bar{3}m$)		Rock Salt ($Fm\bar{3}m$)	
		a (\AA)	c (\AA)	I_R	a (\AA)	I_R	a (\AA)	I_R
1:6:3	1	4.971	13.673	0.02	8.350	1		
	2	5.000	13.614	0.02	8.347	1		
1:4:2	1	4.894	13.934	0.03	8.353	1		
	2	4.988	13.673	0.06	8.357	1		
1:3:6	1				8.269 & 8.098	1 & 0.08	4.259	0.03
	2				8.265	1	4.259	0.13
1:2:4	1				8.274 & 8.096	1 & 0.05	4.270	0.01
	2				8.273	1	4.261	0.07
1:1:2	1				8.299	1		
	2				8.297	1		

Anneal 1: 100 K/h—56 h at 1323 K—300 K/h. Anneal 2: 200 K/h—72 h at 1323 K—air quenching.

the “Fe:Cr:Co 1:1:2” and larger than Co_3O_4 . The rock salt phase has a lattice parameter somewhat larger than that of CoO . The spinel phase with a lattice parameter of approximately 8.10 \AA is present in larger amounts after slow cooling than after quenching. The reverse is observed for the rock salt phase. This suggests that the spinel phase forms as a result of a rock salt to spinel transition during cooling.

4. Discussion

4.1. Phase stability in Cr–Co oxide mixtures

The lattice parameters of the spinel phase with $a = 8.09 \text{ \AA}$ and the rock salt phase, identified in the “Cr:Co 1:2” and “Cr:Co 1:5” mixtures, are slightly larger than those of the Co_3O_4 starting powder and CoO , respectively. Since the lattice parameter of the Co–Cr spinel phases increases with increasing Cr-content (Fig. 1), it is expected that this spinel phase contains some Cr-cations. The Cr-content is estimated

to 1 at.% using Eq. (1). Since the spinel phase results from a rock salt to spinel transition during cooling, it is expected that the rock salt phase contained a similar amount of Cr-cations at high temperature. At 1273 K CoO in air can maximally dissolve 1 at.% Cr [17].

The lattice parameter of the “Cr:Co 1:1” spinel and CoCr_2O_4 agrees excellently with those reported in the literature on spinels with similar composition (cf. Fig. 1). The data in Fig. 1 suggest that annealing of the “Cr:Co 1:2” and “Cr:Co 1:5” mixtures results in a single spinel phase. In the corresponding literatures [2–5], the spinels were mainly synthesised from metal ion nitrates, which resulted in mixing of the metal ions on an atomic scale. It could be argued that the coexistence of three oxide phases instead of a single spinel phase after 147 h of annealing of the “Cr:Co 1:2” and “Cr:Co 1:5” mixtures at 1323 K is due to insufficient homogenisation time for the present oxide mixtures. In this respect it should be mentioned that annealing of the “Cr:Co 1:2” oxide powder, obtained from the nitrates of Co^{2+} and Cr^{3+} , for 65 h at 1323 K also showed the occurrence of two spinel phases and a rock salt phase. It is noted that the temperature was higher and that the reaction time was longer than in the investigation of O’Neill [6] for the synthesis of Co_2CrO_4 . Furthermore, using the same annealing time (65 h) for a powder at 1123 K, a single spinel phase formed. Clearly, insufficient reaction time at 1323 K cannot explain the occurrence of more than one oxide phase. Instead the results suggest that a two-phase field, containing a spinel phase and a rock salt phase occurs in Cr–Co oxide system at 1323 K in air, rather than a continuous series of solid solutions ranging from Co_3O_4 to CoCr_2O_4 . The observation of a continuous weight decrease for temperatures above 1270 K during the TGA measurements of “Cr:Co 1:2” oxide powder, obtained from the nitrates of Co^{2+} and Cr^{3+} (65 h at 1123 K), corroborate this interpretation and indicate that the fraction of rock salt phase increases with temperature.

Using Eq. (1), the minimum Cr-content of the mixed spinel phase is estimated at approximately 19 at.% (at 1323 K), at lower Cr-contents a two-phase region of this spinel phase and

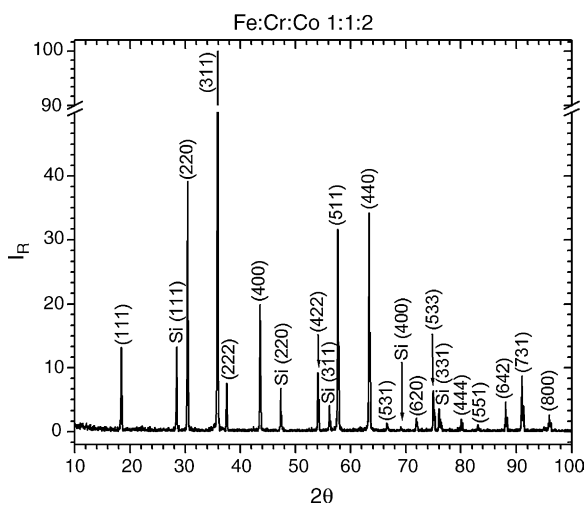


Fig. 4. The X-ray diffractogram of the “Fe:Cr:Co 1:1:2” spinel. The Si-peaks are obtained from Si-reference powder.

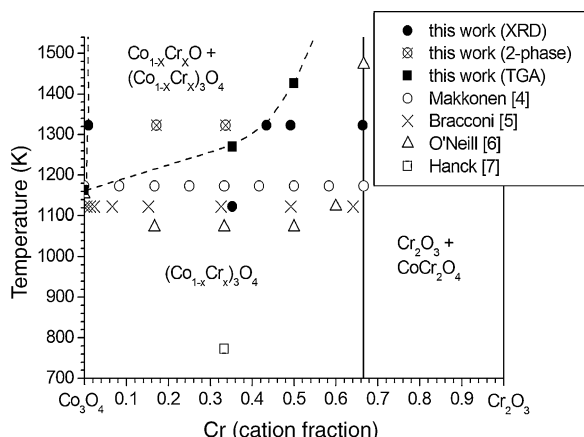


Fig. 5. An illustration of the Cr–Co–O phase diagram in air (the dashed line represents an approximate boundary for the two-phase field between the rock salt and the spinel).

a rock salt phase, containing appr. 1 at.% Cr, forms. Since the lattice parameter of the corundum phase obtained in the “Cr:Co 5:1” mixture is similar to that of the Cr_2O_3 starting powder, it is suggested that Co-cations is not dissolved in Cr_2O_3 to any appreciable extent.

Data relating to the phase stability of oxides in the Co–Cr–O system in air are summarized in Fig. 5. The squares represent the temperatures at which Co_3O_4 , Co_2CrO_4 and $\text{Co}_{1.5}\text{Cr}_{1.5}\text{O}_4$ start to decompose into spinel and rock salt phases. A tentative shape of the spinel + rock salt two-phase region is indicated as well.

4.2. Phase stability in Fe–Cr–Co oxide mixtures

The lattice parameters of the spinel and corundum phases developed in the “Fe:Cr:Co 1:6:3” and “Fe:Cr:Co 1:4:2” mixtures are larger than those in the CoCr_2O_4 and the Cr_2O_3 starting powders. Since the CoCr_2O_4 is the mixed Cr–Co-spinel with the largest lattice parameter (cf. Fig. 1) this shows that the spinel lattice has expanded upon incorporating iron cations. Analogously, lattice parameters for the corundum phase larger than for the Cr_2O_3 starting powder, strongly indicate that iron is incorporated in the corundum phase (cf. Fig. 3: iron expands the lattice).

The lattice parameters of the main spinel phase identified in the “Fe:Cr:Co 1:3:6”, “Fe:Cr:Co 1:2:4” and “Fe:Cr:Co 1:1:2” mixtures (Table 4) are larger than those obtained for the “Cr:Co 1:2” mixture, which has the same Cr:Co ratio (Table 3). Fig. 6 shows that the lattice parameter of these spinel phases increases linearly with the Fe-content.

A Gibbs triangle in the Fe–Cr–Co–O system at 1323 K is given in Fig. 7. The diagram has been constructed by connecting the phase field boundaries of the Cr–Co–O system suggested in Fig. 5 (the black circles in Fig. 7) with the Fe–Co–O [11] (the black squares in Fig. 7) and the Fe–Cr–O [13] systems at 1323 K in air. The phase constitution in relation to the composition of the “Fe:Cr:Co” mixtures studied

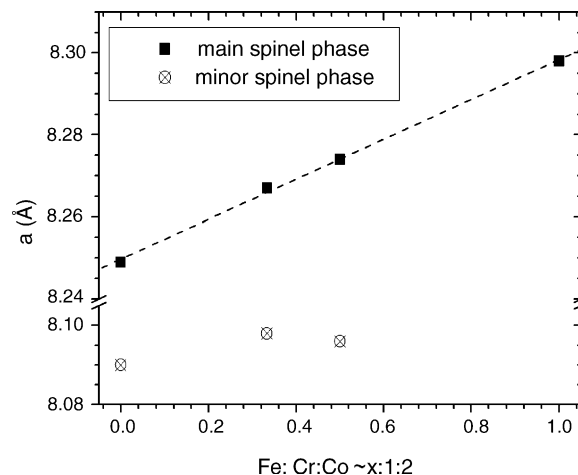


Fig. 6. The lattice parameters of the spinel phases obtained after annealing the “Cr:Co 1:2”, “Fe:Cr:Co 1:3:6”, “Fe:Cr:Co 1:2:4” and “Fe:Cr:Co 1:1:2” mixtures at 1323 K in air vs. the Fe-content.

in this work is plotted into the diagram; they are labelled with their cation ratio numbers only.

It is evident that the “Fe:Cr:Co 1:1:2” (“112”) mixture lies within the homogeneous spinel phase field. It is therefore not surprising that only one phase is identified. Likewise, the isothermal section of the quasi-ternary system predicts that the “Fe:Cr:Co 1:2:4” (“124”) and the “Fe:Cr:Co 1:3:6” (“136”) mixtures are within a two-phase field where a rock salt phase and a spinel phase coexist in equilibrium, which was indeed found.

Corundum and spinel phases developed during the annealing of the “Fe:Cr:Co 1:4:2” (“142”) and the “Fe:Cr:Co 1:6:3” (“163”) mixtures, which also is in accordance with their location in the quasi-ternary diagram. The results indicate that connecting the phase field of the Cr–Co–O, the Fe–Co–O, and the Fe–Cr–O systems provides a useful prediction of the

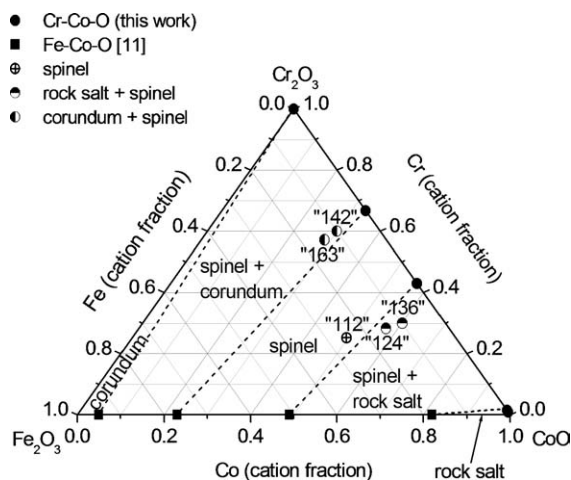


Fig. 7. Comparison of the Cr–Co–O, Fe–Co–O [11], and Fe–Cr–O [13] systems at 1323 K in air and the phases identified in the “Fe:Cr:Co” mixtures annealed at 1323 K in air. The numbers refer to the cation ratios of the mixtures.

phase boundaries in the Fe–Cr–Co–O system at 1323 K in air.

4.3. The use of Co, Cr, (Fe)-containing components in SOFCs cathode environment

On start-up and operation of SOFCs, an interaction is expected to occur between the interconnect material and its neighbouring component (i.e. coating, contact layer, or cathode). Co–Cr spinel layers have been observed to develop as a result of reaction diffusion between the Cr₂O₃ oxide layer formed on the steel interconnector and Co-containing coatings [1–3]. Such layers are also likely to develop in the contact areas between a Co-containing cathode, i.e. La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O₃, and a non-coated steel interconnector. It is common to heat up to a temperature higher than the operation temperature at the start-up of a SOFC stack with glass sealings, which have to be softened in order to deform. The layers should stay compact and well adhering to the metal as well as to the cell. Thus, it is important to avoid phase changes (or at least any big changes in molar volume of the involved phases) during start-up as well as during operation (i.e. thermal cycling) as this may introduce additional stress, which in worst case can result in loss of electric contact in the SOFC.

The work presented here is believed to be a useful contribution to the necessary background knowledge for SOFC stack developers.

5. Conclusion

Literature data strongly suggest that the mixed Co–Cr oxides form a continuous series of solid solutions with the spinel structure ranging from Co₃O₄ to CoCr₂O₄ in air at 1023 and 1173 K. The present work shows that the Cr–Co–O phase diagram at 1323 K contains a two-phase field where a rock salt phase, containing approximately 1 at.% Cr, and a spinel phase with a Cr content of approximately 19 at.% coexist. The lattice parameter of the Cr–Co-spinel increases

with increasing Cr-content in accordance with existing literature.

Substitution of Fe-cations into a Cr–Co-spinel results in an expansion of the spinel lattice. Phase analyses of Fe–Cr–Co oxide mixture showed a new Fe:Cr:Co (1:1:2) spinel with a lattice parameter: $a = 8.298 \text{ \AA}$. A pragmatic prediction of the isothermal section at 1323 K of the Fe–Cr–Co oxide phase diagram in air is obtained by connecting the phase boundaries in the Cr–Co oxide, the Fe–Co oxide and the Fe–Cr oxide phase diagrams. This is in a favourable correspondence with the experimental phase constitution.

These data contributes to a basis for designing the composition and the processes of protective contact coatings on FeCr stainless steels for interconnectors in SOFC stacks.

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