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Immiscibility in the NiFe₂O₄–NiCr₂O₄ spinel binary

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Abstract

The solid solution behavior of the Ni(Fe_{1-n}Cr_n)₂O₄ spinel binary is investigated in the temperature range 400–1200 °C. Non-ideal solution behavior, as exhibited by non-linear changes in lattice parameter with changes in *n*, is observed in a series of single-phase solids air-cooled from 1200 °C. Air-annealing for 1 year at 600 °C resulted in partial phase separation in a spinel binary having n=0.5. Spinel crystals grown from NiO, Fe₂O₃ and Cr₂O₃ reactants, mixed to give NiCrFeO₄, by Ostwald ripening in a molten salt solvent, exhibited single-phase stability down to about 750 °C (the estimated consolute solution temperature, T_{cs}). A solvus exists below T_{cs} . The solvus becomes increasingly asymmetric at lower temperatures and extrapolates to *n* values of 0.2 and 0.7 at 300 °C. The extrapolated solvus is shown to be consistent with that predicted using a primitive regular solution model in which free energies of mixing are determined entirely from changes in configurational entropy at room temperature.

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1. Introduction

Hydrothermal transport of metal ions in the water–steam circuit of power plants is influenced by the solubility behavior of metal oxides that are part of the corrosion layer formed on the materials of construction. Since most of the metals used in these plants are multicomponent alloys, their oxides are multicomponent as well. In the case of Fe–Ni–Cr alloys, the corrosion oxides are spinels: AB_2O_4 , where A= Fe, Ni and B=Fe, Cr.

Mixing in spinel binaries is complicated by the existence of two sublattice sites: octahedral and tetrahedral. Solid solutions having three different cation distribution patterns between the sites are known: normal, random and inverse. Although a regular solution model has been successfully applied to predict divalent cation mixing in inverse $(Ni_nFe_{1-n})Fe_2O_4$ and normal $(Ni_nFe_{1-n})Cr_2O_4$ spinel binaries, the regular solution parameter is relatively insignificant (1.6 kJ/mol, as per Ref. [1]) and the ideal mixing formula provides adequate estimates of the free energies of mixing over virtually all temperatures of interest to the power plant chemist.

On the other hand, the mixing of trivalent cations in these spinel binaries occurs non-ideally because each end member spinel has a different cation arrangement: ferrites are inverse, while chromites are normal. Mixing will not only cause changes in cation distribution, but the regular solution parameter becomes much larger (11.0 kJ/mol, as per Ref. [1]) and a region of immiscibility occurs at power plant water temperatures. Thus, a more complete mixing model is required to provide accurate estimates for the free energies of mixing.

As a first step in developing a mixing model for spinel binaries that share a common divalent cation, accurate experimental measurements are required to characterize their immiscibility behavior: consolute solution temperature (T_{cs}) and solvus. Available data [2] indicate that $T_{cs} = 880 \,^{\circ}\text{C}$ for the Fe(Fe_{1-n}Cr_n)₂O₄ binary; the solvus at 300 $\,^{\circ}\text{C}$ being represented by *n* values of 0.1 and 0.7. These compositions agree closely with those found in the duplex spinel oxide layers on corroding stainless steel surfaces [3]: (Fe_{0.8}Ni_{0.2})(Fe_{1-n}Cr_n)₂O₄ where *n*=0.05 and 0.7. Data have yet to be reported for the NiFe₂O₄–NiCr₂O₄ binary, although complete mixing is known to occur at temperatures as low as 950 $\,^{\circ}\text{C}$ [4] and analysis of the duplex spinel oxide on a corroding nickel base NiCrFe alloy indicates the compositions *n*=0.1 and 0.8 [5].

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2. Experimental

Spinel immiscibility was investigated using two approaches: (1) air-annealing a series of single-phase solid solutions of Ni(Fe_{1-n}Cr_n)₂O₄ having $0.1 \le n \le 0.9$ at 600 °C that had been synthesized at 1200 °C and (2) reacting 2:1:1 molar ratio mixtures of NiO, Fe₂O₃ and Cr₂O₃ in a molten salt solvent at temperatures in the range 400–900 °C. The existence of multiple spinel phases was detected using a combination of X-ray diffraction, energy dispersive X-ray spectrometry (EDX) and electron microprobe analyses (EMPA).

Powder X-ray diffraction (XRD) analyses were performed using a Rigaku Dmax B system equipped with a diffracted-beam graphite monochromator. Copper K_{α} radiation ($\lambda_1 = 1.54056$ Å, $\lambda_2 = 1.54439$ Å) was used; step size was 0.024°. A silicon internal standard was included in each analysis to ensure highly accurate 20 measurements. Microchemical analyses of individual crystal grains were performed using: (1) EDX (Oxford Link, thin window spectrometer Model 6227) with integration times around 100 s; suitably corrected for absorption/fluorescence (ZAF) and (2) EMPA (JEOL 8200) at an accelerating voltage of 20 kV.

2.1. Single-phase annealing

This effort started with ceramic syntheses of stoichiometrically pure powders of NiFe₂O₄ (950 °C, 3 h) and NiCr₂O₄ (1200 °C, 4 h). XRD confirmed the absence of the reactant oxides NiO, Fe₂O₃ and Cr₂O₃. Nickel ferrite was single-phase cubic, while nickel chromite exhibited a tetragonal structure. The cubic structure of NiCr₂O₄ is known to distort into a tetragonal structure below 47 °C due to the Jahn–Teller effect [6]. The two powders were then mixed in desired proportions to give a series of single-phase solutions of Ni(Fe_{1-n}Cr_n)₂O₄ with *n* values of 0.1, 0.3, 0.4, 0.5, 0.6, 0.8 and 0.9. Five grams of each dry powder mix were cold pressed into a 1-in. diameter pellet at 20,000 psi and sintered at 1200 °C for 12 h in an

Table 1 Lattice parameters of solid solutions in the NiFe₂O₄–NiCr₂O₄ binary

air furnace to form the desired series of single-phase solid solutions. After air cooling, a piece of each pellet was ground into a fine powder and analyzed by XRD to establish lattice parameter and confirm the absence of $NiFe_2O_4$ and $NiCr_2O_4$ reactants.

The n=0.5 material was then subjected to various heat treatments at lower temperatures and longer periods of time: 800 °C/1 week, 700 °C/2 weeks and 650°C/1 month. After each treatment, a small portion of the pellet was ground into a fine powder and examined by XRD to determine if any changes had occurred in the shapes of the higher angle peaks. Since no changes were detected, the entire series of single-phase solid solutions was subjected to extended annealing periods at 600 °C (6 and 12 months).

2.2. Molten salt synthesis

This effort started by dry-mixing 2:1:1 molar ratio mixtures of reagent grade powders of NiO, Fe₂O₃ and Cr₂O₃ in excess quantities of various LiCl/KCl salt mixtures. Mixing was accomplished by tumbling with zirconia balls in a plastic bottle. After the pre-mixing operation was completed, the powder mixture was poured into a platinum crucible, covered with a platinum lid and placed in an air furnace. Four spinel formation periods were tested: 700 °C (1 month in 30/70 LiCl/KCl), 600 °C (1 month in 50/50 LiCl/KCl), 500 °C (2 months in 60/40 LiCl/KCl) and 400 °C (6 months in 60/40 LiCl/KCl). The molar ratios selected for the solvent salts were a compromise between melting point (620, 460 and 350 °C, respectively, as per Ref. [7]) and the need for low vapor pressure at test temperature. Despite these precautions, approximately 20% of the solvent salt evaporated during the spinel formation period.

Upon removal from the furnace, the reacted oxide–salt mixture was dissolved in deionized water and the spinel oxide product was recovered by filtration. The oxide product was thoroughly washed to remove all traces of chloride, rinsed with isopropanol and dried. This synthesis produced an extremely fine-grained oxide powder.

%NiCr ₂ O ₄	As sintered		1 Mo at 650 °C		6 Mo at 600 °C		12 Mo at 600 °C	
	a_0 (Å)	FWHM (deg)	a_0 (Å)	FWHM (deg)	a_0 (Å)	FWHM (deg)	a_0 (Å)	FWHM (deg)
0	8.3391	0.22						
10	8.3328	0.20	8.3310	0.21	8.3313	0.23	8.3304	0.23
30	8.3164	0.22	8.3140	0.23	8.3139	0.23	8.3135	0.25
40	8.3102	0.21	8.3063	0.24	8.3064	0.24	_	_
50	8.3090	0.18	8.3023	0.18	8.3006	0.19	(8.3033	$(0.43)^{a}$
60	8.3088	0.24	8.3043	0.28	8.3037	0.29	8.3042	0.30
80	8.3175	0.28	8.3156	0.31	8.3157	0.30	8.3138	0.26
90	8.3190	0.26	8.3184	0.28	8.3181	0.28	8.3182	0.29
100	8.3186 ^b	_						

^a Presence of multiple phases indicated by increased FWHM of the [8, 4, 4] $K_{\alpha 1}$ peak.

^b Equivalent cubic cell dimension to give same volume as observed for tetragonal cell (a_0 =8.2616 Å, c_0 =8.4337 Å).



Fig. 1. Deconvolution of [8, 4, 4] spinel peak in partially transformed Ni(Fe_{0.5}Cr_{0.5})₂O₄ solid solution, air-annealed for 1 year at 600 °C. Note the appearance of a new phase(s) at $2\theta = 130.7^{\circ}$.

3. Results

3.1. Single-phase annealing

Lattice parameters of the (cubic) spinel phases, determined from a whole pattern fit of XRD peak positions for five high angle reflection planes: [9,3,1], [8,4,4], [10,2,0], [9,5,1] and [10,2,2], are compared in Table 1. Also included in Table 1 are the peak widths (full width at half maximum, FWHM) of the [8,4,4] peak. Except for the n=0.5 solid annealed for 1 year at 600 °C, no evidence of phase separation is observed.

Fig. 1 plots the results of a spectral deconvolution of the [8,4,4] spinel peak from the n=0.5 sample. Doublet peaks are observed for each phase because copper K_a radiation has two wavelengths, i.e. K_{a1} and K_{a2}, which are readily distinguishable at large 20 values. The fitted peak positions correspond to lattice parameters of 8.3066 and 8.3015 Å for two spinel phases. Their relative intensities indicate that the two phases are present in the approximate proportion 25 and 75 mol%, respectively. The first represents the new phase(s), while the second corresponds to the original spinel. In other words, only about one-fourth of the original, single-phase spinel has separated into immiscible solids.

A 'calibration curve' is constructed in Fig. 2 to permit spinel composition to be estimated from lattice parameter based on averages of Table 1 results. Included in Fig. 2 are data points at n=0.25, 0.50 and 0.75 reported previously for single-phase solid solutions synthesized at 950 °C [4]. Fig. 2 indicates that the new lattice parameter (8.3066 Å) is consistent with two spinel phases having compositions n=0.45 and n=0.55. Electron microprobe results confirmed the chromium-rich solvus composition as Ni(Fe_{1-n}Cr_n)₂O₄, where $n=0.53\pm0.01$.

3.2. Molten salt syntheses

XRD analyses of reaction products from the molten salt syntheses revealed the presence of spinel oxides having very broad diffraction peaks, along with minor amounts of unreacted NiO. Spectral deconvolutions of the [8,4,4] spinel and [4,2,2] NiO peaks, present in the vicinity of $2\theta \approx 130^\circ$, are shown in Fig. 3 on the basis that two spinel peaks were present. Fitting two peaks instead of one reduced



Fig. 2. Lattice parameters of Ni(Fe_{1-n}Cr_n)₂O₄ spinel solid solutions. Uncertainty bands were derived by averaging Table 1 measurements; data from Ref. [4] are plotted as squares. Non-linearity is characteristic of non-ideal solid solutions.

the average FWHM value from 1.08 to 0.88° , see Table 2. Although the amount of improvement is marginal, support for the correctness of this interpretation is provided by means of an additional molten salt synthesis at 900 °C, where complete mixing was expected. The resulting FWHM value for a spinel known to be single-phase (0.7°), and the knowledge that all crystals grown by the molten salt process had approximately the same sizes $(0.5-5 \mu m, \text{ see Fig. 4})$, rules out an explanation that peak broadening was caused by a much smaller crystal size [8].

Microchemical analyses performed concurrently with the above SEM examinations (i.e. EDX) confirmed that the reaction product crystals contained the expected elements (O, Fe, Cr and Ni). More importantly, some crystals had



Fig. 3. Deconvolution of the [8,4,4] spinel XRD peak for 50/50 nickel ferrite–nickel chromite mixtures precipitated in molten salt: (a) 700 °C/1 month, (b) 600 °C/1 month, (c) 500 °C/2 month and (d) 400 °C/6 months. The two lowest 2θ peaks represent [6,2,0] reflections from the internal silicon standard; unreacted NiO [4,2,2] appears at $2\theta \approx 129^{\circ}$. Note the appearance of a third spinel at 400 °C in the vicinity of $2\theta \approx 126^{\circ}$.



Cr/Fe > 1, while others had Cr/Fe < 1. A summary of the solvus determined for the NiFe₂O₄–NiCr₂O₄ binary by both EDX and EMPA is given in Table 3.

4. Discussion

4.1. Single-phase region

Solid solutions in the nickel ferrite–nickel chromite binary exhibit a V-shaped variation in lattice parameter with changes in composition. This non-ideal behavior may be explained by considering each pure component as a solvent phase and following changes in cation distribution between octahedral and tetrahedral sites as mixing takes place. These distributional changes are expected to occur as a result of competition for octahedral sites. Transition metal cations exhibit a preference for octahedral sites (OSPE) based on number of d-elections and the splitting of their energy levels between an upper e_g doublet (destabilized) and a lower t_{2g} triplet (stabilized). Ranking OSPEs on a scale of 0–100, based on Dunitz and Orgel [9], gives $Cr^{3+} = 100$, $Ni^{2+} =$ 55, $Fe^{2+} = 10$ and $Fe^{3+} = 0$.

Starting with the inverse distribution in stoichiometric nickel ferrite, initial substitution of Cr^{3+} ions for Fe³⁺ ions is expected to occur only on Fe³⁺ ions located in octahedral sites. The Ni²⁺ cations should remain on octahedral sites, because they have a greater OSPE than Fe³⁺. This behavior is manifested by linear decreases in lattice parameter until *n* reaches 0.5 and all of the Fe³⁺ ions that were originally on octahedral sites have been replaced. Lattice parameter contractions occur because the substituting Cr^{3+} cation is smaller than the Fe³⁺ cation being replaced, see Table 4.

Table 2 XRD parameters of spinels formed by molten salt synthesis

LiCl/KCl ratio	Temp/time conditions	Spinel characteristics		
		a_0 (Å)	FWHM (deg)	
0/100	900 °C/1 day	8.310	0.70	
30/70	700 °C/1 month	8.308	1.20	
50/50	600 °C/1 month	8.310	0.92	
60/40	500 °C/2 months	8.317	1.13	
60/40	400 °C/6 months	8.309	1.08	
Refit, assuming tw	vo phases			
30/70	700 °C/1 month	8.304	0.78	
		8.327	1.03	
50/50	600 °C/1 month	8.309	0.61	
		8.314	1.14	
60/40	500 °C/2 months	8.306	0.89	
		8.319	0.71	
60/40	400 °C/6 months	8.308	0.72	
		8.322	1.16	

NiO, Fe₂O₃ and Cr₂O₃ reactants mixed in molar ratios of 2:1:1.

In the ideal, cubic close-packed arrangement of oxygen anions in the spinel lattice the octahedral bond length is greater than the tetrahedral bond length by a factor of 1.155, i.e. $2/\sqrt{3}$. However, minor structural adjustments occur in real spinels to accommodate cation size differences between the two sites. Based on spinel geometrical relationships, bond lengths may be determined from the unit cell dimension (a_0) and oxygen positional parameter (u), see Hill et al. [10]:

tet. bond length = $a_0\sqrt{3}(u - 1/8)$

oct. bond length = $a_0(3u^2 - 2u + 3/8)^{1/2}$

The ideal spinel has

u = 1/4

. Given the unit cell dimension of NiFe₂O₄ in Table 1, which is known to represent an inverse spinel, and accepting the ionic radius of Fe³⁺(tet)=0.49 Å as accurate, gives

$$Ni^{2+}(oct) + Fe^{3+}(oct) = 1.294 \text{ Å}$$

Since the sum differs by 0.04 Å from that predicted using the cation radii tabulated by Shannon [11], our lattice parameter measurements of the NiFe₂O₄–NiCr₂O₄ binary were used to provide internally consistent estimates of ionic radii. Starting with the expectation that the substituting Cr^{3+} (0.615 Å) is replacing Fe³⁺ in only octahedral sites, octahedral bond lengths were calculated from the measured lattice parameters and plotted versus mole fraction chromite (0 < *n* < 0.5). The linear behavior shown in Fig. 5 allows radii of Ni²⁺ (oct) and Fe³⁺ (oct) to be determined as 0.655 and 0.639 Å, respectively. These results show that the Shannon-recommended radius of $Ni^{2+}(oct)$, i.e. 0.69 Å, is too high by about 0.03 Å.

In the case of nickel chromite as solvent, Cr^{3+} ions are replaced with Fe^{3+} ions, and initial substitution occurs by placing Fe^{3+} on tetrahedral sites. Equivalent amounts of Ni²⁺ are displaced from tetrahedral to octahedral sites because OSPE for Ni²⁺ is greater than for Fe^{3+} . In other words, the octahedral sites vacated by Cr^{3+} are filled by Ni²⁺, with the end result that the substituting Fe^{3+} appear on tetrahedral sites.

Given the (equivalent) cubic unit cell dimension for NiCr₂O₄ which corresponds to a normal spinel, and accepting the ionic radius of $Cr^{3+}(oct)=0.615$ Å as accurate, gives $Ni^{2+}(tet) = 0.537$ Å. This estimate differs from the Shannon-recommended value (0.55 Å) by about 0.01 Å. Additional interatomic distance calculations were performed for chromite-rich solid solutions $(0.5 < n \le 1)$ using the refined radius for Ni²⁺(oct) and the expectation that the substituting Fe^{3+} ions go only to tetrahedral sites. Calculated tetrahedral bond lengths based on the measured lattice parameters exhibit a linear behavior when plotted versus mole fraction chromite, see Fig. 5. The resulting radius of $Fe^{3+}(tet) = 0.494 \text{ Å}$ is virtually identical to that recommended by Shannon (0.49 Å). Thus, only the radius of Ni^{2+} (tet) was revised, see Table 4. It is noteworthy that decreases in the lattice parameter of the chromite-rich spinels observed with increasing concentrations of ferrite (see Fig. 2) occur because shrinkage of the tetrahedral bond more than offsets increases in octahedral bond length (see Fig. 5). Such behavior was not observed in the $Fe(Fe_1)$ $_{n}$ Cr $_{n}$) $_{2}$ O₄ binary [12].

4.2. Two phase region

A consolute solution temperature appears in the nickel ferrite-nickel chromite spinel binary around 750 °C. This value is slightly lower than that observed in the analogous iron system (880 °C, [2]). The solvus, which began at n = 0.5, became increasingly asymmetric with respect to decreases in temperature and extrapolates to n=0.2 and 0.7 at 300 °C. Kinetics of the phase separation process, being controlled by ionic diffusion, are extremely slow at temperatures below about 950 °C. It is impractical to measure the process at ambient temperature since times on a geological scale would be required. Even at 600 °C, only one-quarter of a supersaturated, single-phase, solid solution was observed to separate after 1 year of testing.

A more practical method, which relies on a molten salt solvent and the Ostwald ripening mechanism, was found to grow spinel crystals of adequate size in a much shorter time period. Spinel formation occurred under nearly equilibrium conditions due to the low degree of supersaturation required for crystal growth. The synthesis, however, is not 'clean', since minor amounts of unreacted NiO were found in all reaction products. This result indicates that the spinel

Table 3



Fig. 4. SEM photographs of the Ni(Fe_{1-n}Cr_n)₂O₄ crystals formed in molten LiCl/KCl: (a) 900 °C/1 day, (b) 700 °C/1 month, (c) 600 °C/1 month and (d) 500 °C/2 months.

Inferred spinel oxide compositions $(Ni_yFe_{1-y})(Fe_{1-n}Cr_n)_2O_4$ based on lattice parameter and microprobe analyses								
Temp/time conditions	Solvus/phase	EDX results		EMPA results		XRD results		
		n	у	n	У	n	у	
900 °C/1 day	_	0.50 ± 0.02	1.03 ± 0.04	-	_			
700 °C/1 month	Fe-rich	0.47 ± 0.02	0.95 ± 0.05	-	-	0.17	n.a	
	Cr-rich	0.56 ± 0.04	0.88 ± 0.03	-	-	0.57	n.a	
600 °C/1 month	Fe-rich	0.38 ± 0.03	0.90 ± 0.03	0.40 ± 0.03	0.87 ± 0.04	0.33	n.a	
	Cr-rich	0.64 ± 0.06	0.78 ± 0.06	0.62 ± 0.03	0.76 ± 0.12	0.67	n.a.	
500 °C/2 month	Fe-rich	0.40 ± 0.04	1.00 ± 0.10	0.33 ± 0.04	0.81 ± 0.12	0.26	n.a.	
	Cr-rich	0.63 ± 0.07	0.87 ± 0.07	-	-	0.61	n.a.	
400 °C/6 months	Fe-rich			0.28 ± 0.09	0.84 ± 0.19	0.23	n.a.	
	Cr-rich			0.67 ± 0.07	*	0.64	n.a.	

*Cr-rich spinel phase combined with (unreacted) NiO; Ni(II) spinel stoichiometry assumed to be unity.

Table 4 Ionic radii in spinels (Å)

Ion	Radius (Å)			
	Tet.	Oct.		
Ni ²⁺	0.54	0.655		
Fe ³⁺	(0.49)	0.64		
Cr ³⁺	_	(0.615)		
O ²⁻	(1.38)	(1.40)		

Values in parentheses are taken from [11].

formation reaction did not proceed to completion and that partial reduction of Fe(III) to Fe(II) may have occurred. Results of the 400 °C synthesis were more complex, as evidence for the presence of a third spinel reaction product was observed, see Fig. 3d. The composition of this phase remains in doubt, however, since its lattice parameter, i.e. 8.473 Å, is beyond the range of the Ni(Cr_nFe_{1-n})₂O₄ and Fe(Cr_nFe_{1-n})₂O₄ binaries.

4.3. Entropy of mixing at room temperature

An expression for the entropy of mixing (ΔS_{mix}) may be determined by considering purely configurational aspects of the cation distributions summarized above. Following previous work, see [13,14], the configurational entropy of a spinel is given by applying the Temkin formula [15], which assumes random mixing of cations on each site

 $-S/R = \Sigma b_s (m_i \ln m_i)_s$



Fig. 5. Octahedral and tetrahedral bond lengths (M–O) in the Ni(Fe₁– $_n$ Cr_n)₂O₄ spinel binary determined from lattice parameter measurements and octahedral site preference energies.

where m_i is the fraction of species *i* on site s, $b_s = 1$ for the tetrahedral site and two for the octahedral sites. Note that three sites exist in each spinel (AB₂O₄). The cation distribution parameters and configurational entropy for the two crystallographically distinct regions discussed above are given by:

	Ion	Tet	Oct	Sum
Ferrite-rich	Ni ²⁺	0	1	1
Region I	Fe ³⁺	1	1 - 2n	2 - 2n
0 < n < 0.5	Cr ³⁺	0	2n	2n
	Sum	1	2	3

$-S/R = (1 - 1)^{-1}$	$-2n)\ln(1-2)$	$n)+2n\ln n-(2-$	-2n)ln 2	
	Ion	Tet	Oct	5

	Ion	Tet	Oct	Sum
Chromite- rich	Ni ²⁺	2n - 1	2 - 2n	1
Region II	Fe ³⁺	2 - 2n	0	2 - 2n
0.5 < n < 1	Cr ³⁺	0	2 <i>n</i>	2 <i>n</i>
	Sum	1	2	3

 $-S/R = (2n-1)\ln(2n-1) + 2n\ln n + 4(1-n)\ln(1-n) + (2-2n)\ln 2$

Configurational entropy for each stoichiometric endmember spinel follows directly from the above: NiFe₂O₄ $(n=0; -S/R=2 \ln 2)$ and NiCr₂O₄ (n=1; -S/R=0). Finally, the entropy of mixing is determined from configurational entropy of the mixture by subtracting the mole fraction weighted sum of configurational entropies of the two end-member spinels being mixed. Thus, for Region I (0 < n < 0.5)

$$-\Delta S_{\text{mix}}/R = (1-2n)\ln(1-2n) + 2n\ln n$$

and for Region II (0.5 < n < 1)

$$-\Delta S_{\text{mix}}/R = (2n-1)\ln(2n-1) + 2n\ln n + 4(1-n)\ln(1-n) + 4(1-n)\ln 2$$

Fig. 6 plots the resulting entropies of mixing and compares them to entropies of mixing calculated using the ideal mixing formula:

$$(-\Delta S_{\text{mix}}/R)_{\text{ideal}} = 2[n \ln n + (1-n)\ln(1-n)]$$

4.4. Primitive mixing model

A primitive mixing model may be constructed at room temperature by assuming the enthalpy of mixing to be zero (i.e. close to ideal) and accounting for changes in cation configurational entropy during mixing as determined from the above analysis:

$$\Delta G_{\rm mix} = \Delta H_{\rm mix} - T \Delta S_{\rm mix}$$

 $\Delta G_{\rm mix}(298) = 0 - 298.15R(\Delta S_{\rm mix}/R)$

Since ΔG_{mix} (298) is a multiple of ΔS_{mix} (298), construction of a common tangent line in Fig. 6 also enables the solvus in the spinel binary to be determined at 298.15 K. This condition occurs at nickel chromite mole



Fig. 6. Estimated entropies of mixing (ΔS_{mix}) in the nickel ferrite–nickel chromite spinel binary based on changes in configurational entropy. Ideal entropies of mixing are shown as a dashed line.

fractions n=0.28 and 0.67. As shown in Fig. 7, the general agreement between experimentally determined solvi and a rough estimate of the solvus at room temperature means that a credible database has been obtained to facilitate development of an accurate thermodynamic model for spinel mixing.



Fig. 7. Measured solvus in the Ni(Fe_{1-n}Cr_n)₂O₄ spinel binary: EDX (open circles) and EMPA (filled circles). Arrows show solvus predicted from configurational entropy changes based on observed cation distributions between octahedral and tetrahedral sites at room temperature.

5. Conclusions/significance

An experimental methodology, based on Ostwald ripening in a molten salt solvent, has been successfully applied to investigate immiscibility in the Ni(Fe_{1-n}Cr_n)₂O₄ spinel binary. A comparison of solvi in the NiFe₂O₄-NiCr₂O₄ and Fe₃O₄-FeCr₂O₄ [2] spinel binaries reveals that the chromite-rich solvi are nearly identical ($n \approx 0.7$) in both systems, while the ferrite-rich solvus in the nickel system may contain slightly more chromite than in the iron system (n= 0.2 vs. 0.1). This result is consistent with previous analyses [3,5] which indicate that the outer layer corrosion films on nickel base NiCrFe alloys contain a higher percentage of Cr(III) than those on stainless steels, i.e. n=0.1 vs. 0.05, in tests at 260 °C.

Consolute solution temperatures in the Ni(Fe₁₋ $_n$ Cr_n)₂O₄ and Fe(Fe_{1-n}Cr_n)₂O₄ binaries appear to be associated with the onset of magnetic ordering which occurs below 600 °C in stoichiometric NiFe₂O₄ and Fe₃O₄. Magnetic ordering causes the moments of the tetrahedral Fe³⁺ ions to align antiparallel to the moments of the octahedral Fe³⁺ (and Fe²⁺) ions [16]. As shown previously [17], inclusion of this effect in the O'Neill-Navrotsky spinel mixing model [1] results in more accurate predictions of consolute solution temperature (600 °C) and solvus (i.e. n=0.05 and 0.70 at 500 °C) in the Fe(Fe_{1-n}Cr_n)₂O₄ spinel binary. Future work is needed to demonstrate similar agreement for the solvus in the Ni(Fe_{1-n}Cr_n)₂O₄ binary. Completion of this work will allow accurate free energies (and solubility calculations) to be obtained for metal oxide corrosion films.

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