Iron – Sodium – Oxygen

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Introduction

Knowledge of the phase equilibria in the iron-sodium-oxygen system and free energies of formation of sodium ferrites at elevated temperatures is necessary, in the first instance, with a view to analyze the corrosion behavior of sodium in nuclear reactors and to address the problem of scabbing and scaffolding in blast furnaces that is due to high alkali content. Information about phase relations in the Fe-Na-O system is presented in literature by the Fe_3O_4-$NaFeO_2$ quasibinary section [1984Dai2], liquidus surface of the partial FeO-Fe_2O_3-$NaFeO_2$ system [1984Dai2], isothermal sections and phase relations at different temperatures and composition ranges [1975Cla, 1976Bal2, 1977Kni, 1981Lin, 1984Dai2, 1986Igu, 1993Sri, 1999Kal, 2003Hua2, 2003Lyk] and temperature-composition sections [1940Kni, 1960The, 1962The, 1984Dai1, 1984Dai2]. Crystal structure data obtained by powder- or single crystal X-ray diffraction are published by [1959Col, 1960The, 1962Roo, 1962The, 1963Sch, 1967Rom, 1970Gro, 1971Tsc, 1974Bar, 1974Rie, 1975Cla, 1975Kol, 1976Bal1, 1976Bal2, 1977Bra, 1977Kni, 1978Bra1, 1978Bra2, 1978Bra3, 1980Kes, 1981Kes, 1981Oka, 1985Fru, 1986Igu, 1997Ded, 2002Ama, 2003Sob1, 2003Sob2]. Thermodynamic aspects of the Fe-Na-O system are reflected in [1970Gro, 1977Kni, 1977Sha, 1981Lin, 1984Ban, 1984Dai1, 1984Dai2, 1985Ban1, 1985Ban2, 1987Yam, 1988Bha, 1996Zha, 1999Kal, 2003Hua1, 2003Hua2, 2003Lyk]. The applied experimental techniques as well as the studied temperature and composition ranges are listed in Table 1. Reviews of literature data present information concerning phase equilibria and crystal structures [1989Rag], thermodynamics [1981Lin, 1999Kal] as well as systematics of crystal structures of the Fe-Na-O phases [1978Zve, 1982Bau, 1998Wu, 2000Mat, 2003Mue].

In future further studies are desirable on the liquidus and solidus surfaces in the area FeO-Na_2O-NaO_3-Fe_2O_3 as well as on invariant equilibria. More details of isothermal sections at different temperatures would be useful. New informations may help to find new practical applications of sodium ferrites.

Binary Systems

The Fe-Na, Fe-O and Na-O binary systems are accepted as compiled in [Mas2]. The assessment of the Na-O system is published with more details by [1987Wri]

Solid Phases

Crystallographic data of all known unary, binary and ternary solid phases are compiled in Table 2. Compositions of the all reported ternary phases, except the τ_9 and τ_{12} phases, lie along the Na_2O-FeO or Na_2O-Fe_2O_3 sections. The composition of the τ_6 phase, established by [1959Col, 1962The, 1999Kal] as "$Na_{10}Fe_{16}O_{29}$", was later refined by [1962Roo, 1967Rom, 1987Yam, 1996Zha, 1999Kal] to be "$Na_3Fe_5O_9$". For the τ_2 phase the standard Gibbs energy of formation was determined by [1984Dai1] using emf, but no crystal structure data are known. For many of the ternary phases the temperature range of stability is not known, except the temperature of preparation. The crystal structures of the phases τ_{11}, τ_{12} and τ_{13} also are unknown and need further experimental clarification.

Quasibinary Systems

The section Fe_2O_3-Na_2O is quasibinary, at least in solid state at lower temperatures. In the range Fe_2O_3-$NaFeO_2$ [1940Kni, 1984Dai1] assume a simple eutectic near 1150°C and Na/(Na+Fe) = 0.36, whereas [1960The, 1962The] found in solid state the τ_6 phase, stable between 1100 and 755°C. Additionally they found a metastable solid solution of Na_2O in γFe_2O_3, decomposing on heating above 650°C. The pure Fe_2O_3 before melting decomposes into Fe_3O_4 and O_2 gas. Thus the two-phase field L + Fe_2O_3 must end before it reaches the Fe_2O_3 side of the section. The liquidus temperature of $NaFeO_2$ is

assumed as 1330°C [1940Kni, 1984Dai1]. Between $NaFeO_2$ (τ_1'''-τ_1') and Na_2O there are at least five more phases in this quasibinary section, well established by the determination of their crystal structures: $Na_4Fe_2O_5$ (τ_4), $Na_{14}Fe_6O_{16}$ (τ_8), Na_3FeO_3 (τ_{10}), $Na_8Fe_2O_7$ (τ_5) and Na_5FeO_4 (τ_7). On the temperature ranges of stability and on equilibria with melt no experimental data are published for these phases. A further phase, τ_{13}, between τ_6 and τ_1', postulated by [1981Lin], was denied by [1962The, 1999Kal]. In Fig. 1 the Fe rich part of this section is constructed. The equilibria between gas, liquid, Fe_2O_3 and Fe_3O_4 must be taken as tentative only. The Fe rich liquid, due to Fe^{+2} ions does not reach the section and Na rich liquid may dissolve more O than corresponding to the section, due to peroxide or ozonide ions known in the binary Na-O liquid. On the transition between both cases data are lacking.

The section FeO-Na_2O is quasibinary in the range Na_2FeO_2-Na_2O [1984Dai1, 1984Dai2]. Between Na_2FeO_2 and FeO it is clearly a not quasibinary isopleth, Fig. 2. At lower temperatures also the range Na_2O to Na_4FeO_3 looses the quasibinary character. [2003Hua2] calculated an invariant reaction: Na(liq) + Na_4FeO_3 ⇌ Na_2O + (αFe) at 421°C. This temperature may be a reasonable estimate. [1993Sri] found this reaction experimentally and located it somewhere between 353 and 487°C.

The Fe_3O_4-$NaFeO_2$ section is approximately quasibinary. The Fe_3O_4 phase has some homogeneity range towards a composition $NaFe_5O_8$, corresponding to the spinel structure of γFe_3O_4, in which the divalent Fe^{+2} ions may be replaced by $0.5(Fe^{+3} + Na^{+1})$. Due to the difference between this direction and the section plane the tie lines of the two-phase fields containing γFe_3O_4 are slightly outside the section plane. Contrary to a strictly quasibinary section all these fields contain a trace of FeO and thus are three-phase fields. Figure 3 shows this approximately quasibinary section as published by [1984Dai2] with correction of a typing error. The horizontal lines at ca. 1150 and 980°C correspond to the invariant four-phase equilibria L ⇌ γFe_3O_4 + αFeO + τ_1''' and τ_1''' ⇌ τ_1'', γFe_3O_4, αFeO, respectively.

Invariant Equilibria

[1984Dai2] constructed the liquidus surface of the FeO-Fe_2O_3-$NaFeO_2$ partial system. These authors mention four invariant four-phase reactions. In Fig. 4 the corresponding reaction scheme is tentatively constructed. It covers the area Fe-Na_2FeO_2-$NaFeO_2$-Fe_2O_3. The τ_6 phase is tentatively included, assuming no participation in an invariant equilibrium. The three-phase equilibria of the quasibinary part Na_2O-Na_2FeO_2 can be approximated as degenerate four-phase equilibria with Fe in equilibrium. By this consideration the congruent melting point of Na_2FeO_2 in the quasibinary part of the Na_2O-FeO section is also a degenerate maximum of the three-phase equilibrium L + Fe + Na_2FeO_2. Thus only the formation of the three-phase equilibrium L + τ_1 + τ_2 remains unsolved in the reaction scheme. The compositions of liquid in the invariant equilibria are too unprecise to justify a tabulation. In Fig. 4 the polymorphic transformations of (Fe) and $NaFeO_2$ (τ_1) are neglected. As at both compositions all phases are nearly stoichiometric, all these transformations are degenerate with the equations (δFe) ⇌ (γFe), (γFe) ⇌ (αFe), τ_1''' ⇌ τ_1'' or τ_1'' ⇌ τ_1'. All other phases participating remain in equilibrium at higher and lower temperatures without taking part at the reactions. Phase τ_{12} was not mentioned by [1984Dai2] and is not implemented in Fig. 4.

Outside the range of Fig. 4 the existence of the invariant four-phase equilibrium L(Na) + Na_4FeO_3 ⇌ (Fe) +Na_2O is well established, its temperature is inside the interval 487-353°C [1993Sri], but could not be located more precisely.

Liquidus, Solidus and Solvus Surfaces

The liquidus surface projection of the partial FeO-Fe_2O_3-$NaFeO_2$ system is shown in Fig. 5, based on [1984Dai2]. Isotherms at the temperatures of 1300, 1400 and 1500°C are plotted. No data concerning solidus or solvus surfaces were found in literature.

Isothermal Sections

The isothermal section of the partial Fe-Fe_2O_3-$NaFeO_2$ system at 1000°C is shown in Fig. 6, as constructed by [1986Igu], based on experimental studies of the FeO-Na_2O solid solution in equilibrium with Ar-H_2-H_2O mixtures. The shapes of the single phase fields of the FeO-Na_2O and Fe_3O_4-Na_2O solid

solutions agree well with the findings of [1975Cla, 1976Bal2, 2003Lyk], except, that [1976Bal2, 2003Lyk] postulate the existence of τ_{12}, which is not mentioned by [1975Cla, 1984Dai2, 1986Igu]. [1986Igu] also ignored the τ_6 phase, which is reported to be stable at 1000°C [1962The, 1999Kal].
Participation of the τ_6 phase in equilibria at 1000°C was also reported in the works of [1960The] and [1962The, 1999Kal] devoted to constitution of the $NaFeO_2$-Fe_2O_3 temperature-composition section. The partial isothermal section at 1000°C in the FeO-Fe_3O_4-$NaFe_5O_8$-$NaFeO_2$ range was also experimentally constructed by [2003Lyk]. These authors report the τ_{13} phase, but do not show the τ_6 phase. In general, their data conform to the data of [1986Igu] satisfactorily. In their studies of corrosion of steel by liquid Na [1977Kni] found at 650°C the τ_3 phase in equilibrium with (αFe) and liquid sodium, while at 400°C the tie line Na-τ_3 is replaced by an equilibrium between Na_2O and (αFe). In the calculations of [2003Hua2] the corresponding four-phase reaction was located at 421°C. [1993Sri] experimentally confirmed this four-phase reaction to happen between 353 and 487°C. [1981Lin] used the SOLGAMIX-PV computer program to calculate phase equilibria in the temperature range from 447 to 607°C in the partial Na-Na_2O-Fe_2O_3-Fe system. They reported the ternary phases τ_1, τ_2, τ_3, τ_5, τ_6, τ_7, τ_{10} and τ_{13} to take part in equilibria in this temperature interval. However, they do not mention the eutectoid decomposition of FeO at 570°C, due to which FeO should not take part in equilibria far below 570°C. The 595°C isothermal section, constructed by [1984Dai2] from their experimental data (Fig. 7), differs as far as the three iron oxides FeO, Fe_3O_4 and Fe_2O_3 all are in equilibrium with $NaFeO_2$ (τ_1), whereas [1981Lin] show them in equilibrium with $Na_3Fe_5O_9$ (τ_6) or $Na_4Fe_6O_{11}$ (τ_{13}). [1984Dai2] left the phases τ_4, τ_8, τ_{10}, τ_5 and τ_7 outside their investigated range. [2003Hua2] published six calculated isothermal sections between 25 and 727°C. In this calculation they did not include the phases τ_2, τ_4, τ_6, τ_8, τ_9, τ_{11}, τ_{12} and τ_{13}. The thermodynamic dataset used for the calculation is published. Apart from the excluded phases these sections agree well with Fig. 7. The phase τ_5 appears to be stable only above 364°C and the invariant reaction L(Na) + Na_4FeO_3 ⇌ Fe +Na_2O is located at 421°C. Some of the dashed lines in the O rich part of Fig. 7 may be replaced by equilibria with Na- and O rich liquid.

Temperature – Composition Sections

Besides the partially or approximately quasibinary sections shown in Figs. 1 to 3 the temperature-composition section $NaFeO_2$-FeO is shown in Fig. 8 based on data of [1984Dai1, 1984Dai2]. The authors qualify this section as qualitative representation of the phases in this section.

Thermodynamics

Information about thermodynamic properties of the Fe-Na-O alloys is widely represented in the literature. Data concerned the reactions are listed in Table 3. The chemical equilibria of gas-slag reactions have been studied by [1984Ban, 1985Ban1, 1985Ban2] to clarify the effect of soda on the thermodynamic properties of slags in the hot metal treatment. The FeO-Na_2O slags were studied at 1610°C being equilibrated with p_{CO2} = 1.013 bar by using a platinum crucible. The influence of slag composition on the activity of iron oxide and the Fe^{3+}/Fe^{2+} ratios has been determined. It has been clarified, that the results can be expressed in terms of the Lumsden's regular solution model over a wide range of compositions. [1984Dai1], besides the results presented in Table 3, also have estimated the standard Gibbs energies of formation of the compounds Na_2FeO_4, Na_2FeO_2 and Na_4FeO_3 referred to the pure elements iron, sodium and oxygen.
Table 4 presents results of vapor pressure measurements. The oxygen and sodium partial pressures were calculated by [1984Dai1] from the Gibbs energy functions. [1984Dai2] obtained an expression for the oxygen partial pressure of the three-phase equilibrium α + (Fe) + $Na_2Fe_2O_4$ in the temperature range 760 to 910°C. Oxygen and sodium potential ranges at 650°C for the stability of selected equilibria in the Fe-Na-O system were determined by [1977Kni].
[2003Lyk] proposed a thermodynamic model for solid solutions of sodium in the α phase, that provides a possibility to establish a relation between the equiliubrium oxygen pressure, composition of the α phase and temperature.
Thermodynamic calculations of isothermal sections of the Fe-Na-O system at the temperatures up to 727°C were carried out by [2003Hua2] using the Thermo-Calc code. Thermodynamic data of the ternary phases

Na_4FeO_3(s), Na_3FeO_3(s), Na_5FeO_4(s) and $Na_8Fe_2O_7$(s) have been assessed and compiled to a database by reviewing literature data together with DSC and vapor pressure measurements conducted by the authors themselves.

Notes on Materials Properties and Applications

Sodium ferrites have been used, in particular, as reference electrodes in conjunction with sodium-iron-conducting solid electrolytes and, more recently, in sodium and antimony sensors, because of their good electronic conductivity [1996Kal, 1996Zha, 1999Kal], which produces a rapid response of the sensor. Literature data about properties of the Fe-Na-O alloys concern mainly the magnetic properties (Table 5). The magnetic interaction in the structural units $\{Fe_2O_7\}^{8-}$, built of two corner-sharing FeO_4 tetrahedra, in the τ_5 phase was studied by [1981Kes] in the temperature range from 4.2 to 500 K (–269 to 27°C). The hypothesis of magnetically isolated $\{Fe_2O_7\}^{8-}$ groups was corroborated by Mössbauer spectroscopy between 1.5 and 77 K (–271.7 and –196°C). Authors of [1967Rom] have determined that the τ_6 phase crystals possess antiferromagnetic properties and a possible arrangement of magnetic spins was discussed. Magnetic properties of the τ_7 phase are reported in [1980Kes] and [1985Fru]. The susceptibility obeys a Curie-Weiss law down to 4.2 K, within experimental error, with effective magnetic moment $\mu_{eff} = 5.83 \cdot \mu_B$, very close to the spin-only value $5.92 \cdot \mu_B$, and the Curie temperature is $\theta = -13$ K. At low temperature the magnetic ordering takes place (the Néel temperature $T_N = 5.40$ K). Authors of [1975Cla] and [1976Bal2] have investigated magnetic properties of alloys from the Fe-Fe_2O_3-$NaFeO_2$ partial system annealed at 1000°C. It was established, in particular, that with increasing sodium content of the alloys the Néel temperature values decrease. In opinion of [1997Ded], the Fe-Na-O system is prospective for the study of derivatives of iron in higher oxidation states. The use of oxidizer in abundance in solid-state oxidation synthesis can get novel information about valent possibilities of transition metals. For the first time the data about quadrupole and magnetic interactions of iron in higher oxidation state in the Fe-Na-O system (the Na_2O_2-Fe_2O_3 section) were obtained by [1997Ded].

Miscellaneous

The mechanism of iron transport by liquid sodium in non-isothermal loop system was studied by [1975Kol]. The loop system was constructed from an AISI Type 316 steel. The sodium was heated from 400°C to 700°C in the heated zone of the system and cooled down reversibly in the cooled zone. In the cooled zone four specimen holders were invariably mounted, the exposition temperatures being 650, 600, 500 and 400°C. Based on the obtained results a model for the transport of iron from the heated zone to the cooled zone was proposed.

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Table 1: Investigations of the Fe-Na-O Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1940Kni] as quoted by [1984Dai1]	Thermal analysis	The $NaFeO_2$-Fe_2O_3 section
[1960The]	X-ray diffraction	300-700°C, $NaFeO_2$-Fe_2O_3 section
[1962Roo] as quoted by [1999Kal]	Crystal structure studies	$Na_3Fe_5O_9$
[1962The]	Dilatometry, X-ray diffraction	≤ 1300°C, $NaFeO_2$-Fe_2O_3 section
[1963Sch]	X-ray diffraction, solubility tests	room temperature, $NaFeO_2$-Fe_2O_3 section
[1967Rom]	X-ray diffraction (single crystals, Weissenberg goniometer), Patterson methods, heavy-atom technique	1100°C, room temperature, complete crystal structure of $Na_3Fe_5O_9$
[1970Gro]	X-ray diffraction, solution calorimetry	500-600°C, ΔH of Na_4FeO_3
[1971Tsc]	X-ray diffraction	450°C, 650°C, three phases in the Na_2O-$NaFeO_2$ section
[1974Bar]	X-ray diffraction	> 600°C, Na_4FeO_3 as corrosion product of Na steel
[1974Rie]	Guinier X-ray diffraction	crystal structure of Na_4FeO_3
[1975Cla]	X-ray diffraction, chemical analysis	1000°C, Fe-Fe_2O_3-$NaFeO_2$ partial system
[1976Bal1] as quoted by [2003Lyk]	Crystal structure studies	$NaFe_2O_3$
[1976Bal2]	X-ray diffraction, chemical analysis	1000°C, the Fe-Fe_2O_3-$NaFeO_2$ partial system
[1977Bra]	X-ray diffraction	crystal structure of $Na_4Fe_2O_5$
[1977Kni]	Bendix “time of flight” mass spectrometer vapor pressure measurements (Knudsen cell unit attachment)	Partial pressures of Na and O, 350-600°C, 0 to 60 at.% O
[1977Sha] as quoted by [1981Lin, 1999Kal]	Emf	522-775°C, $NaFeO_2$
[1978Bra1]	X-ray Guinier-Simon diffraction technique (single crystals)	crystal structure of Na_5FeO_4
[1978Bra2]	X-ray diffraction (rotation of single crystal, Weissenberg, precision filming techniques)	crystal structure of $Na_{14}Fe_6O_{16}$
[1978Bra3]	X-ray Guinier-Simon diffraction technique (single crystals)	crystal structure of $Na_8Fe_2O_7$

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1981Oka]	X-ray diffraction, kinetics of transformation	$NaFeO_2$
[1984Ban]	Slag-iron equilibria studies	FeO-Fe_2O_3-Na_2O partial system
[1984Dai1]	Emf, acid-solution calorimetry	500-1400°C, whole range of compositions
[1984Dai2]	X-ray diffraction, DTA, high-temperature microscopy, emf	500-1400°C, whole range of compositions, phase diagram and thermodynamics
[1985Ban1]	Gas-slag reactions studying	1610°C, FeO-Fe_2O_3-Na_2O partial system
[1985Ban2]	Gas-slag reactions studying	1610°C, FeO-Fe_2O_3-Na_2O partial system
[1985Fru]	Magnetic structure by neutron diffraction	≤ –173°C, Na_5FeO_4
[1986Igu]	Reduction and fire flame techniques	1000°C, FeO-Fe_2O_3-Na_2O partial system
[1987Yam]	Emf	577-1227°C, Fe_2O_3-Na_2O section
[1988Bha]	Emf	350-600°C, Na_4FeO_3
[1993Sri]	Pseudo-isopiestic equilibrations, in-sodium equilibrations, DTA, solid state reactions, X-ray diffraction	< 700°C, 0 to 60 at.% O
[1996Zha] as quoted by [1999Kal]	Emf	≤ 1050°C, Fe_2O_3-$Na_3Fe_5O_9$ section
[1997Ded]	Mössbauer spectroscopy, EPR, X-ray diffraction	≤ 480°C, Na_2O_2-Fe_2O_3 section
[1999Kal]	Emf, isothermal equilibration, X-ray diffraction	$NaFeO_2$-Fe_2O_3 section
[2002Ama]	X-ray diffraction (rotation of single crystal)	$Na_9Fe_2O_7$
[2003Hua1]	High temperature mass spectrometry (Knudsen effusion), X-ray diffraction	25-447°C, Na_4FeO_3
[2003Lyk]	Emf	827-1027°C, FeO-Fe_3O_4-$NaFeO_2$ partial system
[2003Sob1]	X-ray diffraction (single crystal)	Na_3FeO_3
[2003Sob2]	X-ray diffraction (single crystal)	Complete crystal structure of Na_3FeO_3

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(δFe) (h_2) 1538 - 1394	*cI*2 $Im\bar{3}m$ W	a = 293.15	[Mas2], dissolves 0.029 at.% O at 1528°C
(γFe) (h_1) 1394 - 912	*cF*4 $Fm\bar{3}m$ Cu	a = 364.67	[Mas2], dissolves 0.0098 at.% O at 1392°C
(αFe) (r) < 912	*cI*2 $Im\bar{3}m$ W	a = 286.65	T = 25°C [Mas2], dissolves 0.00008 at.% O at 912°C
(εFe) (hp) > $1.3\cdot10^5$ bar	*hP*2 $P6_3/mmc$ Mg	a = 246.8 c = 396	T = 25°C [Mas2] High pressure phase
(βNa) (r) 97.8 - (–233)	*cI*2 $Im\bar{3}m$ W	a = 428.865	T = 25°C [1987Wri]
(αNa) (l) < –233	*hP*2 $P6_3/mmc$ Mg	a = 376.7 c = 615.4	T = –268°C [1987Wri]
α, $Fe_{1-x}O_x$ (wüstite) 1424 - 570	*cF*8 $Fm\bar{3}m$ NaCl		x = 0.5126 to 0.5457 [Mas2], dissolves 8 at.% Na (as Na_2O) at 1000°C [1976Bal]
		a = 430.88	$Fe_{48.5}O_{51.5}$, 20°C [E]
		a = 428.00	$Fe_{47.2}O_{52.8}$, 20°C [E]
		a = 431	$Fe_{47.35}O_{52.65}$, 1000°C, $p_{O2} = 1.2\cdot10^{-15}$ bar [1975Cla]
$Na_y(Fe_{1-x}O_x)_{1-y}$		a = 433	x = 0.5265, y = 0.0537, T = 1000°C, $p_{O2} = 1.2\cdot10^{-15}$ bar [1975Cla]
		a = 434.5	x = 0.5265, y = 0.1020, T = 1000°C, $p_{O2} = 1.2\cdot10^{-15}$ bar [1975Cla]
γFe_3O_4 (h) 1596 - 580	*cF*56 $Fd\bar{3}m$ $MgAl_2O_4$	a = 843.96	57.1 to 58.02 at.% O [Mas2] at 25°C [V-C2] Fe replaced by 0 to 3.5 at.% Na, at 1000°C in equilibrium with Ar-H_2-H_2O mixture [1986Igu]
βFe_3O_4 (r) < 580	*mC*224 *Cc* βFe_3O_4	-	~57.1 at.% O [Mas2]
αFe_3O_4 (hp) > $2.5\cdot10^5$ bar	*m**14	-	~57.1 at.% O [Mas2] High pressure phase

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
β, Fe_2O_3 < 1457	*hR*30 $R\bar{3}c$ Al_2O_3	*a* = 503.42 *c* = 1374.73 *a* = 503.5 *c* = 1372	59.82 to ~60 at.% O [Mas2] *p* = 1 bar [V-C2] [1981Oka]
ε (Fe-O)	*c***	-	metastable; ~51.3 to ~53.5 at.% O [Mas2]; labelled as "P′ (wüstite)" [Mas2]
η (Fe-O)	*mP*500? $P2_1/m$	-	metastable; ~52 to ~54 at.% O [Mas2]; labelled as "P′′ (wüstite)" [Mas2]
κ (Fe-O)	*hR*6 $R\bar{3}$ NiO (l)	-	metastable; 51.3 to 53.2 at.% O [Mas2]; labelled as "wüstite (low-temperature)" [Mas2]
λ (Fe-O)	*cI*80 $Ia\bar{3}$ Mn_2O_3	-	metastable; ~60 at.% O; labelled as "βFe_2O_3" [Mas2]
γFe_2O_3	*tP*60 $P4_32_12$	*a* = *c* = 833 *a* = *c* = 833.9 *a* = *c* = 840.7	metastable; ~60 at.% O; labelled also as μ (Fe-O) [1981Oka] *T* = 300°C [1960The] *T* = 380°C [1960The]
ν (Fe-O)	*m*100*	*a* = 1299 *b* = 1021 *c* = 844 β = 95.33°	metastable; ~60 at.% O; labelled as "εFe_2O_3" [Mas2] [S]
γ, Na_2O < 1134 ± 4	*cF*12 $Fm\bar{3}m$ CaF_2	*a* = 556	33.3 at.% O [Mas2] [E]
βNa_2O_2 (h) 675 - (~512)	*cF*12 $Fm\bar{3}m$ CaF_2	*a* = 666 *c* = 993	~50 at.% O; labelled as "Na_2O_2-II" [Mas2] [1989Rag]
αNa_2O_2 (r) ≲ 512	*hP*9 $P\bar{6}2m$ Fe_2P	*a* = 620.7 *c* = 447.1 *a* = 620.8 *c* = 446.9	~50 at.% O; labelled as "Na_2O_2-I" [Mas2] [E] [1989Rag]
γNaO_2 (r) 552 - (–50)	*cF*8 $Fm\bar{3}m$ NaCl	*a* = 549	~66.7 at.% O; labelled as "NaO_2 (I)" [Mas2] *T* = 25°C [E]
βNaO_2 (l_1) (–50) - (–77)	*cP*12 $Pa\bar{3}$ FeS_2 (pyrite)	*a* = 546	~66.7 at.% O; labelled as "NaO_2 (II)" [Mas2] *T* = –70°C [E]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
αNaO_2 (l_2) < –77	*oP*6 *Pnnm* FeS_2 (marcasite)	 *a* = 426 *b* = 554 *c* = 344	~66.7 at.% O; labelled as "NaO_2 (III)" [Mas2] *T* = –100°C [E]
θ (Na-O) < –77	*oP*6 *Pnnm* FeS_2 (marcasite)	-	metastable; ~50 at.% O; labelled as "Na_2O_2-Q" [Mas2]
ρ, NaO_3	*tI** *I*4/*mmm*	 *a* = 1043 *c* = 688 *a* = 1165 *c* = 766	~75 at.% O [Mas2] [1962Kuz] [1964Kuz]
τ_1'''', $NaFeO_2$ (h_2) 1330 - 1010	-	-	by dilatometry distinguished from τ_1'' [1962The]
τ_1'', β$NaFeO_2$ (h_1) 1010 - 760	*oP*16 *Pna*2_1	*a* = 567.2 *b* = 731.6 *c* = 537.7	[1981Oka]
τ_1', α$NaFeO_2$ (r) < 760	*hR*12 *R*$\bar{3}$*m* $CsICl_2$	*a* = 301.9 *c* = 1593.4 *a* = 302.5 *c* = 1609.4	[1981Oka] [2000Mat]
τ_2, Na_2FeO_2 < 801	-	-	[1984Dai1]
τ_3, Na_4FeO_3	*mC*32 *Cc* Na_4FeO_3	*a* = 1096 *b* = 582 *c* = 822 β = 114°	single crystals prepared at 630°C, 10 d [1974Rie]
τ_4, $Na_4Fe_2O_5$	*mP*44 *P*2_1/*n* $Na_4Fe_2O_5$	*a* = 1187 *b* = 567 *c* = 917 β = 104.5°	single crystals prepared at 600°C, 6 d [1977Bra]
τ_5, $Na_8Fe_2O_7$	*mP*68 *P*2_1/*c* $Na_8Ga_2O_7$	*a* = 872 *b* = 1102 *c* = 1010 β = 107.7° *a* = 870 *b* = 1101 *c* = 1009 β = 107.6°	[1977Bra] single crystals prepared at 600°C, 7 d [1978Bra1]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
τ_6, $Na_3Fe_5O_9$ 1100 - 755	*mC*68 *C*2/*c* $Na_3Fe_5O_9$	*a* = 1339 *b* = 1207 *c* = 529 β = 89.17°	single crystals prepared at 1100°C [1967Rom] labelled as "$Na_{10}Fe_{16}O_{29}$" [1959Col, 1962The, 1999Kal]
τ_7, Na_5FeO_4	*oP*80 *Pbca* Na_5FeO_4	*a* = 1033 *b* = 597 *c* = 1808	single crystals prepared at 650°C, 7 d [1978Bra2]
		a = 1026.7 *b* = 591.3 *c* = 1780	*T* = –173°C [1985Fru]
		a = 1027.9 *b* = 592.3 *c* = 1791.4	*T* = –270.5°C [1985Fru]
τ_8, $Na_{14}Fe_6O_{16}$	*aP*36 $P\bar{1}$ $Na_{14}Fe_6O_{16}$	*a* = 1142 *b* = 827 *c* = 595 α = 109.3° β = 87.7° γ = 111.4°	single crystals prepared at 650°C, 7 d [1978Bra3]
τ_9, $Na_9Fe_2O_7$	*oP*72 $Pca2_1$ $Na_9Fe_2O_7$	*a* = 956.2 *b* = 999.1 *c* = 1032.3	single crystals prepared at 450°C [2002Ama]
τ_{10}, Na_3FeO_3	*mP*28 $P2_1/n$ Na_3FeO_3	*a* = 579.9 *b* = 1265.9 *c* = 582.8 β = 116.02°	single crystals prepared at 650°C, 14 d, no single phase product available [2003Sob1, 2003Sob2]
τ_{11}, $NaFe_5O_8$	*cF*56 ? $Fd\bar{3}m$? $MgAl_2O_4$?	-	[1975Cla, 1976Bal2, 1986Igu]. Inside metastable solid solution of γFe_2O_3 after [1960The]
τ_{12}, $NaFe_2O_3$ < 1047	-	-	[1976Bal1, 2003Lyk]
τ_{13}, $Na_4Fe_6O_{11}$	-	-	[1981Lin]. Phase does not exist after [1999Kal]

Table 3: Thermodynamic Data of Reactions or Transformations

Reaction or Transformation	Temperature [°C]	Quantity, per mole of atoms [kJ, mol, K]	Comments
$FeO(s) + 2Na_2O(s) \rightarrow Na_4FeO_3$ (s)	25°C	$\Delta H = -13.12 \pm 0.3$ kJ·mol^{-1}	[1970Gro] acid solution calorimetry
$3Na_2O(s) + Fe(s) \rightarrow Na_4FeO_3(s) + 2Na(l)$	500-600	$\Delta G = 49.89 - 0.07 \cdot T$	[1970Gro] derived from acid solution calorimetry

Reaction or Transformation	Temperature [°C]	Quantity, per mole of atoms [kJ, mol, K]	Comments
$Na_4FeO_3(s) \rightarrow NaFeO_2(s) + Na_2O(s) + Na(l)$	500-600	$\Delta G = 93.02 - 0.01 \cdot T$	[1970Gro] derived from acid solution calorimetry
$Ca(s) + 2NaF(s) + 2FeO(s) \rightarrow Na_2FeO_2(s) + CaF_2(s) + Fe(s)$	522-775	$\Delta G = -776.6 + 0.208 \cdot T$	[1977Sha, 1981Lin, 1999Kal] emf
$Na_2O(s) + Fe_2O_3(s) \rightarrow Na_2Fe_2O_4(s)$	522-775	$\Delta G = -171.970 - 0.009456 \cdot T$	[1977Sha, 1999Kal] emf
	500-1400	$\Delta G = -86 - 61.89 \cdot 10^{-3} \cdot T$	[1984Dai1] emf
	657-774	$\Delta G = -160.2 - 0.003909 \cdot 10^{-3} \cdot T$	[1987Yam] emf
	774-1005	$\Delta G = -157.2 - 1.332 \cdot 10^{-3} \cdot T$	[1987Yam] emf
	1005-1132	$\Delta G = -147.3 - 13.37 \cdot 10^{-3} \cdot T$	[1987Yam] emf
	362-512	$\Delta G = -237.425 + 83.1 \cdot 10^{-3} \cdot T$	[1996Zha, 1999Kal] emf
	561-731	$\Delta G = -247.086 + 89.435 \cdot 10^{-3} \cdot T$	[1996Zha, 1999Kal] emf
	657-725	$\Delta G = -232.582 + 69.61 \cdot 10^{-3} \cdot T$	[1999Kal] emf
$FeO(s) + Na_2O(s) \rightarrow Na_2FeO_2(s)$	500-1400	$\Delta G = -119.106 + 0.114 \cdot T$	[1984Dai1] acid-solution calorimetry
$FeO(s) + 2Na_2O(s) \rightarrow Na_4FeO_3(s)$	500-1400	$\Delta G = -147.998 + 0.165 \cdot T$	[1984Dai1] acid-solution calorimetry
$1/2\ \{5Fe_2O_3(s) + 3Na_2O(s)\} \rightarrow Na_3Fe_5O_9(s)$	< 1132	$\Delta G = -(248.6 \pm 1.1) - (2.447 \pm 1.188) \cdot 10^{-3} \cdot T$	[1987Yam] emf
	752-864	$\Delta G = -153.978 + 32.32 \cdot 10^{-3} \cdot T$	[1999Kal] emf
$4Na(l) + Fe(s) + 3/2O_2(g) \rightarrow Na_4FeO_3(s)$	450-600	$\Delta G = -1212.202 + 0.3511 \cdot T$	[1988Bha] emf
$Na_4FeO_3(s) \rightarrow Na_3FeO_3(s) + Na(g)$	317-444	$\Delta G\ (Na_4FeO_3) = -11168.629 + 0.33834 \cdot T$	[2003Hua1] Knudsen cell effusion

Table 4: Vapor Pressure Measurements

Phase(s)	Temperature [°C]	Pressure [bar]	Comments
Fe(s), FeO(s), $Na_2Fe_2O_4(s)$	600	$\log_{10}(p_{O2}) = -25.27$	[1984Dai1] tabulated data
	600	$\log_{10}(p_{Na}) = -7.14$	
	900	$\log_{10}(p_{O2}) = -19.6$	
	900	$\log_{10}(p_{Na}) = -1.24$	
Fe(s), $Na_2Fe_2O_4(s)$, $Na_2FeO_2(s)$	600	$\log_{10}(p_{O2}) = -29.85$	
	600	$\log_{10}(p_{Na}) = -2.56$	
Fe(s), $Na_2FeO_2(s)$, $Na_4FeO_3(s)$	600	$\log_{10}(p_{O2}) = -29.95$	
		$\log_{10}(p_{Na}) = -2.50$	
$Na_2Fe_2O_4(s)$, $Na_4FeO_3(s)$, $Na_2FeO_2(s)$	600	$\log_{10}(p_{O2}) = -29.69$	
		$\log_{10}(p_{Na}) = -2.56$	
Fe(s), Na(l), $Na_4FeO_3(s)$	600	$\log_{10}(p_{O2}) = -32.55$	
		$\log_{10}(p_{Na}) = -1.53$	

Table 5: Investigations of the Fe-Na-O Materials Properties

Reference	Method/Experimental Technique	Type of Property
[1967Rom]	Magnetic property studies, Mössbauer spectroscopy	Magnetic susceptibility, magnetic ordering of the τ_6 phase
[1975Cla]	Faraday magnetic technique	Magnetic susceptibility of the Fe-Fe_2O_3-$NaFeO_2$ partial system phases
[1976Bal2]	Faraday magnetic technique	Magnetic susceptibility of the Fe-Fe_2O_3-$NaFeO_2$ partial system phases
[1980Kes]	Magnetic property studies, Mössbauer spectroscopy	Magnetic susceptibility, magnetic ordering of the τ_7 phase
[1981Kes]	Magnetic property studies, Mössbauer spectroscopy	Magnetic susceptibility, magnetic ordering of the τ_5 phase
[1985Fru]	Neutron diffraction	Magnetic structure of the τ_7 phase
[1997Ded]	Mössbauer spectroscopy	Magnetic structure of Na_2O_2-Fe_2O_3 section phases, quadrupol interactions

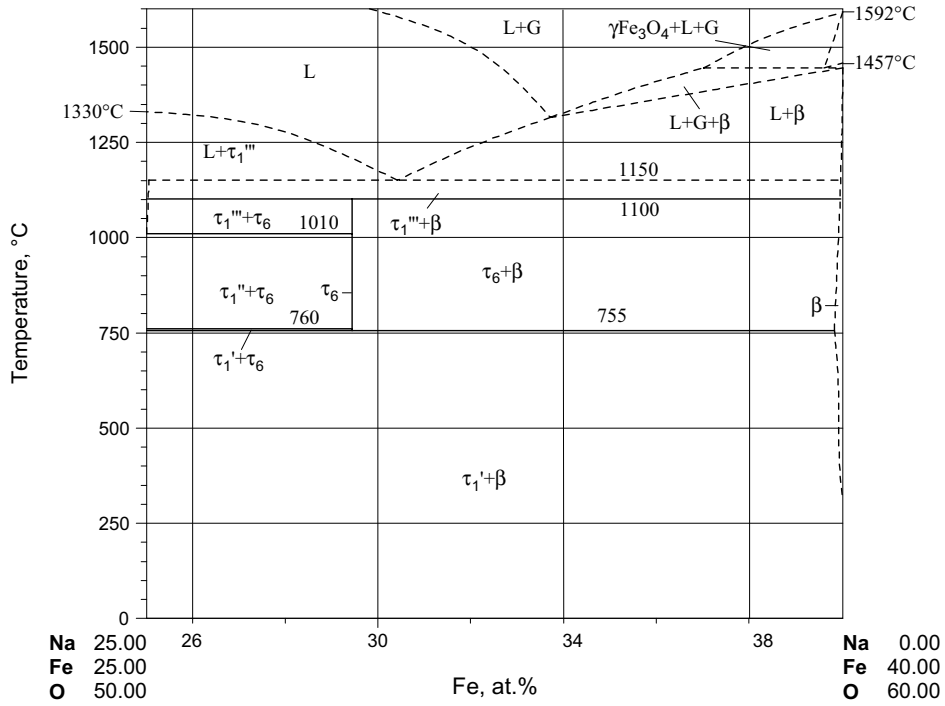

Fig. 1: Fe-Na-O. The partially quasibinary section $NaFeO_2$ - Fe_2O_3

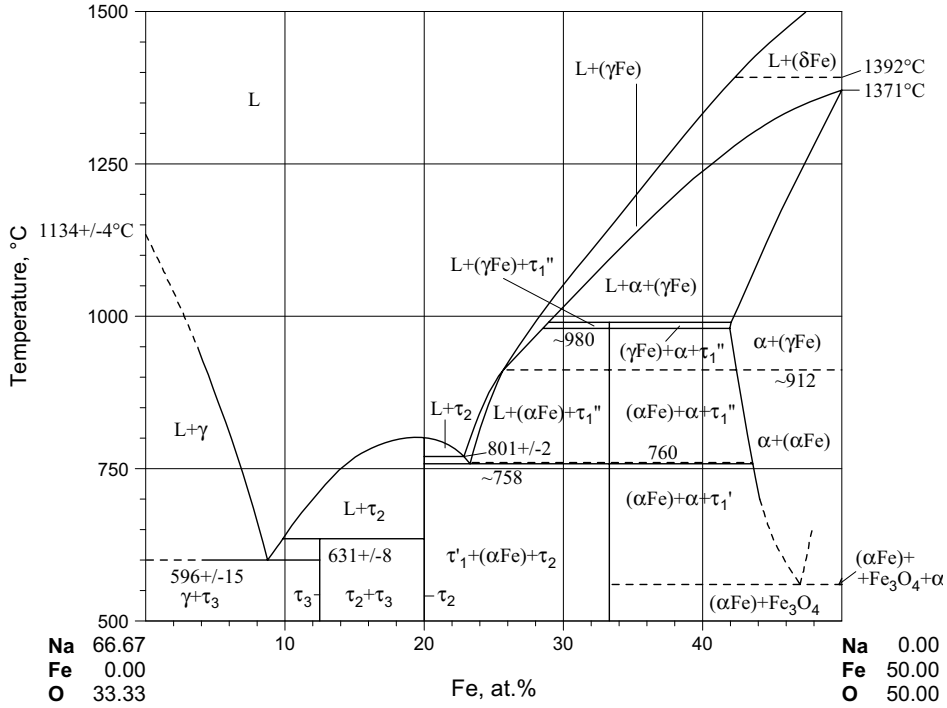

Fig. 2: Fe-Na-O. The partially quasibinary section Na_2O - FeO

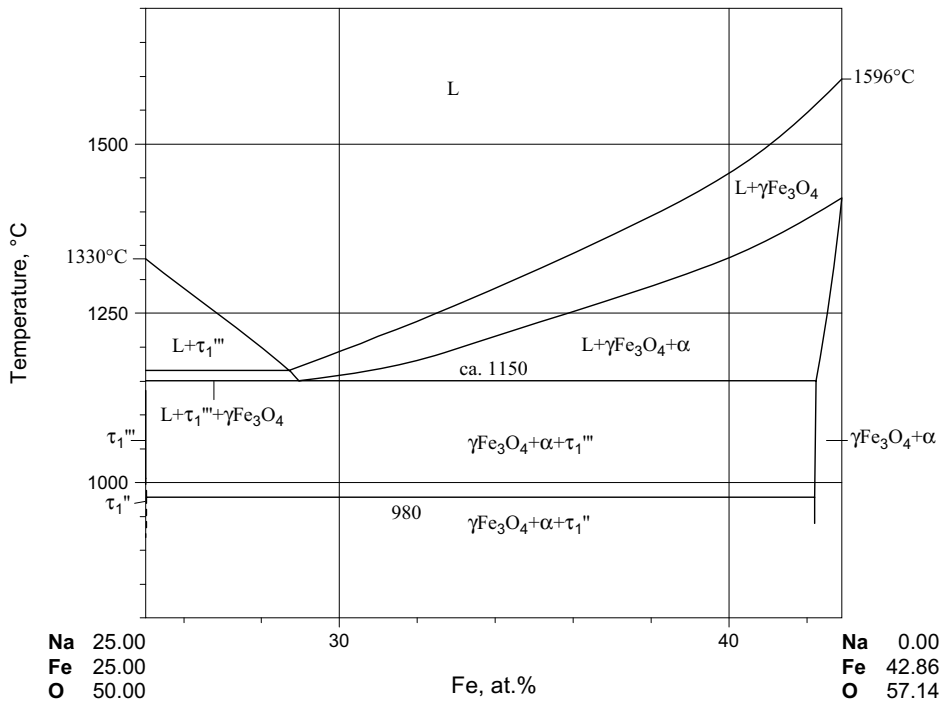

Fig. 3: Fe-Na-O. The approximately quasibinary section Fe_3O_4-$NaFeO_2$

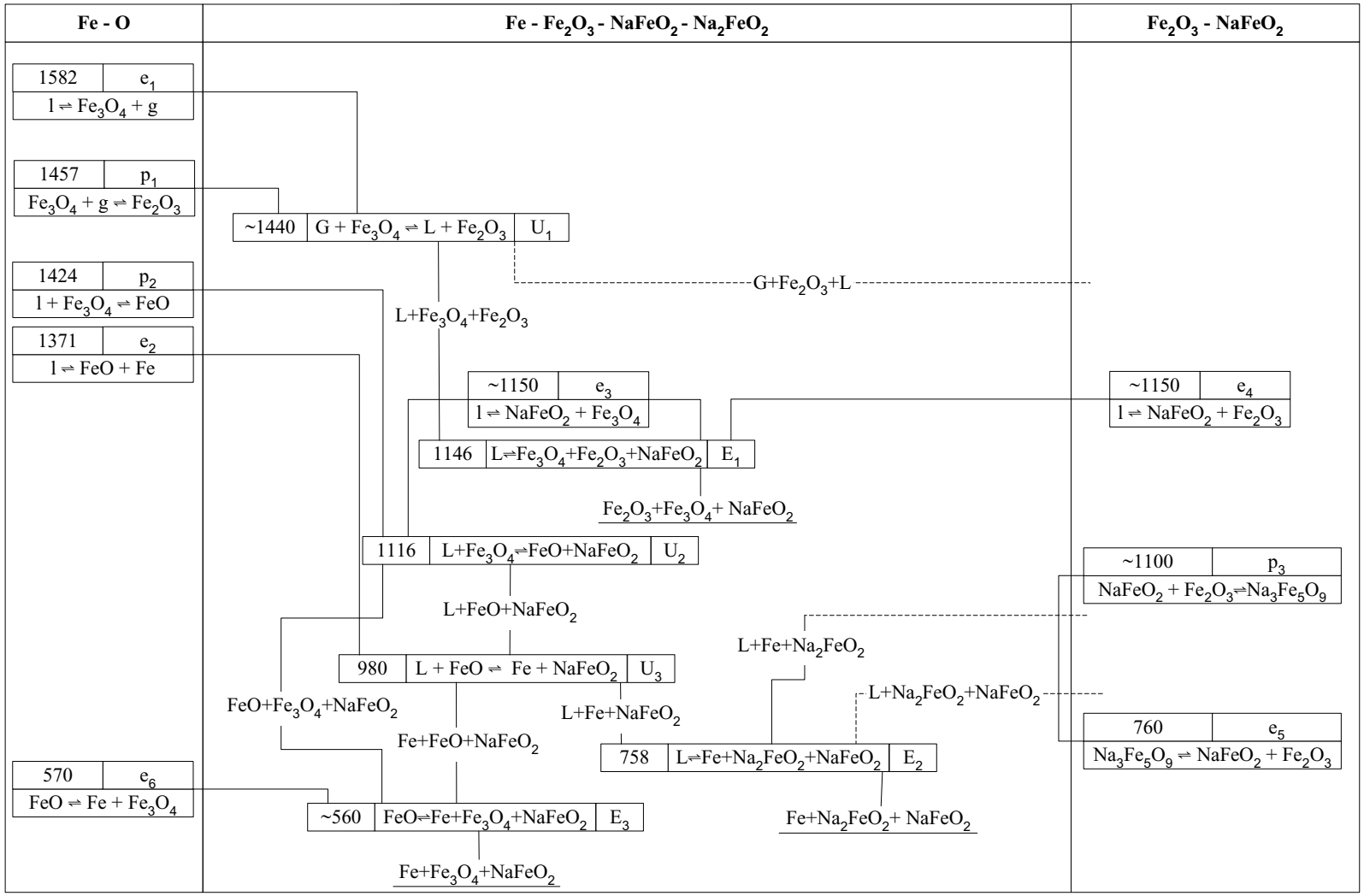

Fig. 4: Fe-Na-O. Reaction scheme of the partial system Fe-Fe_2O_3-$NaFeO_2$-Na_2FeO_2. The phases (αFe), (γFe) and (δFe) are not distinguished and called Fe. Also τ_1', τ_1'' and τ_1''' are not distinguished and called $NaFeO_2$.

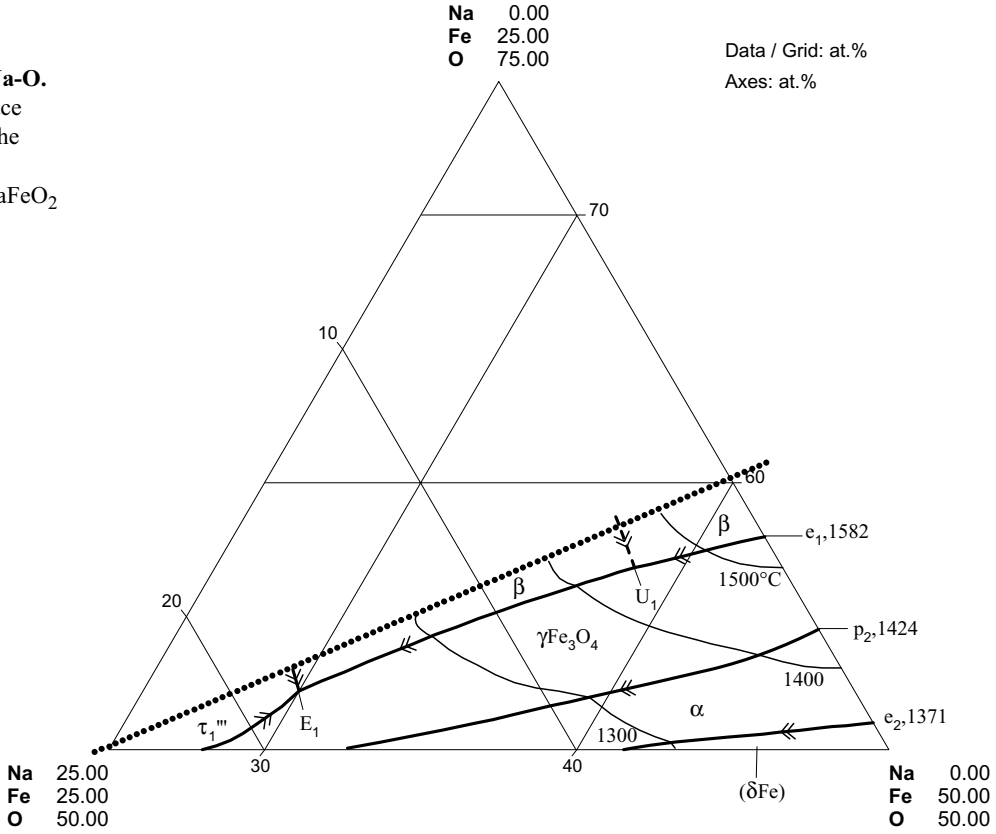

Fig. 5: Fe-Na-O. Liquidus surface projection of the partial FeO-Fe_2O_3-$NaFeO_2$ system

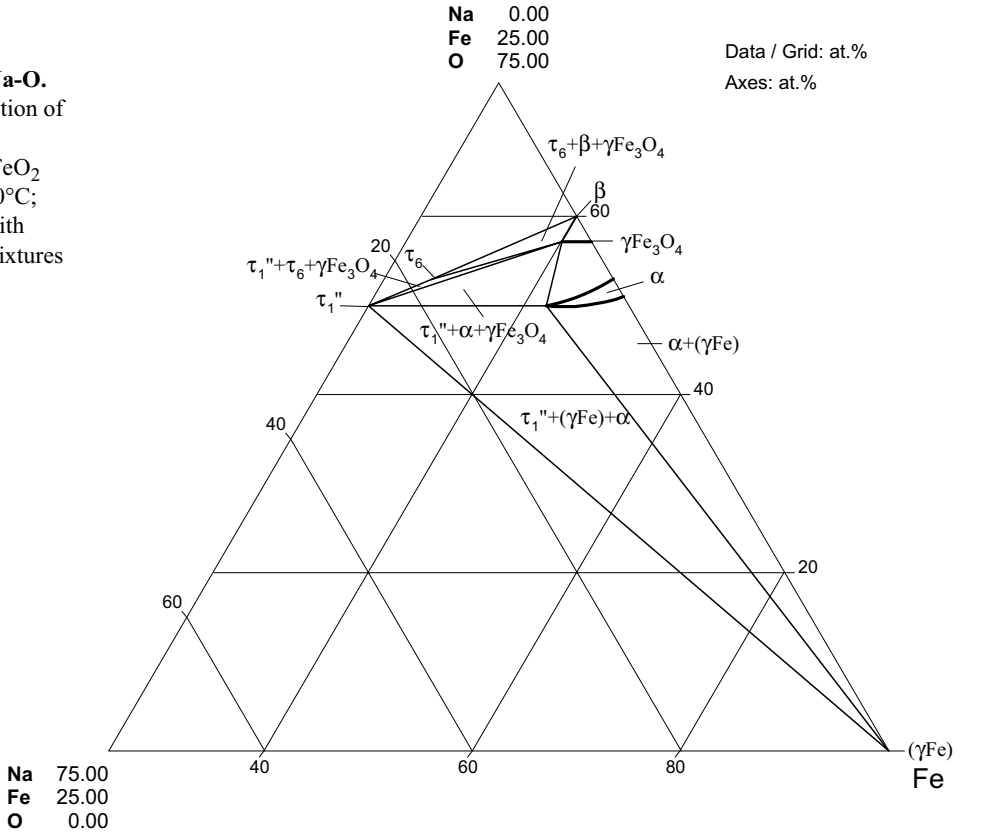

Fig. 6: Fe-Na-O. Isothermal section of the partial Fe-Fe_2O_3-$NaFeO_2$ system at 1000°C; equilibrated with Ar-H_2-H_2O mixtures

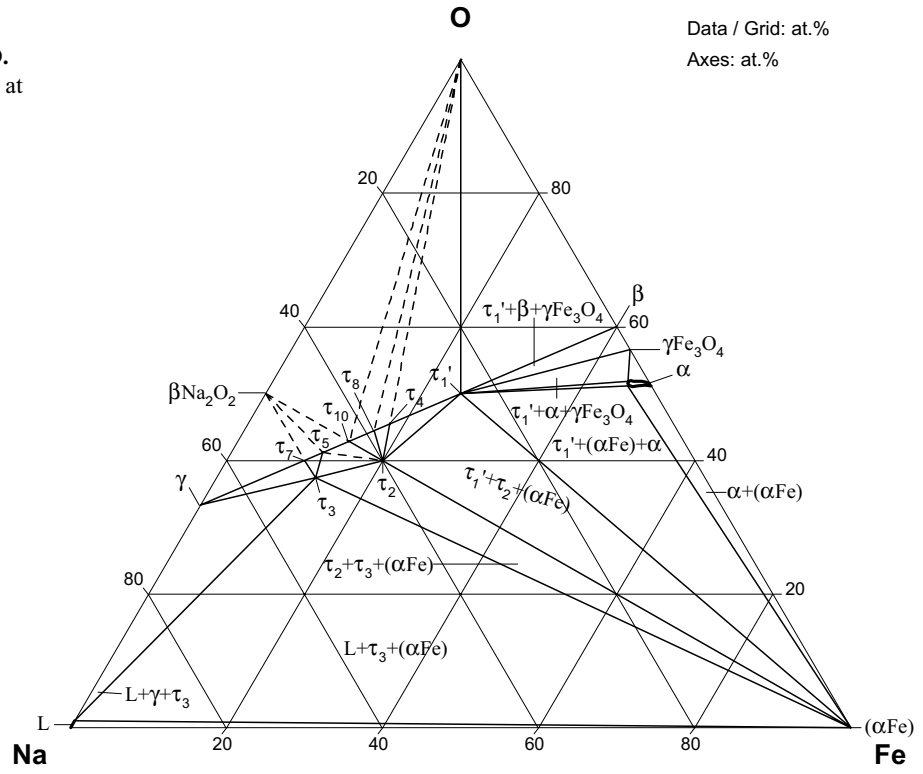

Fig. 7: Fe-Na-O. Isothermal section at 595°C

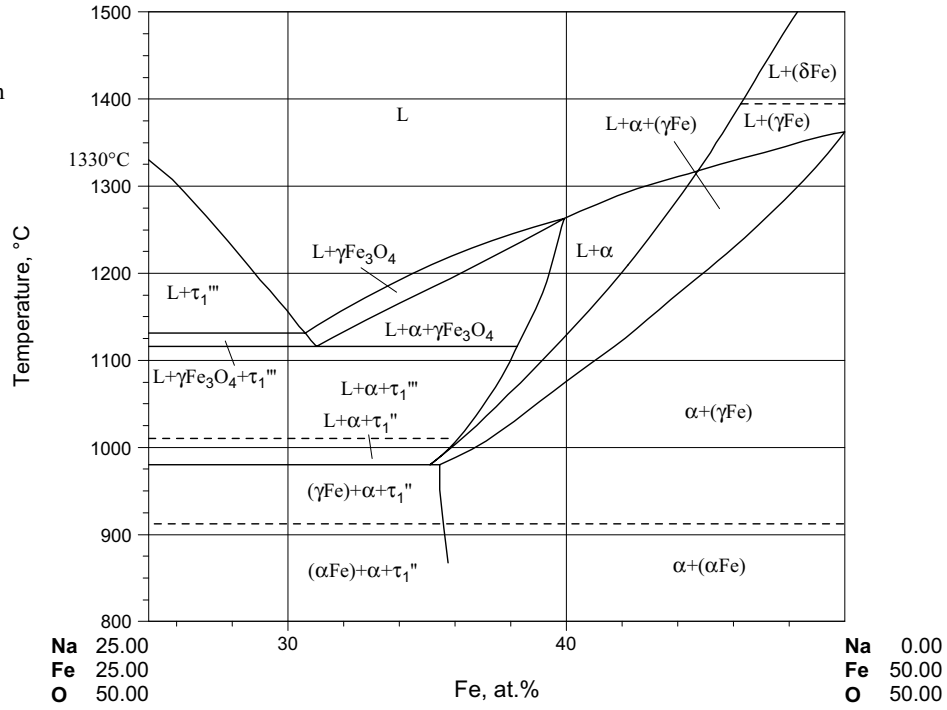

Fig. 8: Fe-Na-O. Temperature - composition section $NaFeO_2$-FeO