Iron – Oxygen – Lead

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Introduction

Ferrites, non-metallic solid magnetic materials, are the complex compounds of the iron oxide Fe_2O_3 with oxides of other metals by their chemical compositions. By their magnetic properties the ferrites are the analogues of ferromagnetics but they possess lower densities and lesser losses on the eddy currents. That's why ferrites are widely used in radio engineering, electronics and super high frequent technology productions. With a view to optimization of alloys compositions selection for preparation of ferrites information about phase relations in the corresponding ternary and multicomponent systems is of a great importance. Among these systems the Fe-O-Pb system plays a considerable role, but information concerning phase relations is quite scanty. It is presented in literature by a partial isobaric section in air [1984Sha], the solubility of lead in liquid iron in the presence of oxygen [1995Li] and the constitution of the PbO-Fe_2O_3 temperature-composition section [1955Coc, 1957Ber, 1960Mar, 1962Mou, 1978Mex, 1984Sha, 1986Nev]. Phase contents of the alloys and crystal structures of the identified intermediate phases were studied by [1928Joh, 1938Ade, 1955Coc, 1957Ber, 1960Mar, 1962Mou, 1978Mex, 1984Sha, 1986Nev, 1988Ara, 1997Dor, 1998Cla, 1998Hua, 2000Dia, 2001Dia, 2002Car, 2002Mar, 2003Cas, 2004Dia, 2005Pal]. Data on thermodynamic properties were experimentally obtained by [1986Nev] and [1995Li]. The applied experimental methods as well as the studied temperature and composition ranges are presented in Table 1. Literature information concerning the Fe-O-Pb system was reviewed in [1989Rag]. Further determination of the phase equilibria character is necessary, in particular, on the constitution of the temperature-composition sections formed by Fe_2O_3 with lead oxides Pb_3O_4, $Pb_{12}O_{17}$, $Pb_{12}O_{19}$ and PbO_2.

Binary Systems

Phase diagrams of the Fe-O and Fe-Pb systems are accepted from [Mas2]. Constitution of the O-Pb system is accepted on the basis of [1998Ris] assessment data (Fig. 1).

Solid Phases

Crystallographic data about known unary, binary and ternary phases are compiled in Table 2. Compositions of the all reported ternary phases lie along the PbO-Fe_2O_3 section. Existence of the τ_1, τ_2 and τ_3 phases was established certainly during both crystal structures and phase relations studies. In particular, data about the τ_1 phase were reported by [1955Coc, 1957Ber, 1962Mou, 1978Mex, 1984Sha, 1986Nev], about the τ_2 phase - by [1928Joh, 1957Ber, 1960Mar, 1962Mou, 1984Sha, 1986Nev], as well as concerned the τ_3 phase - by [1938Ade, 1957Ber, 1960Mar, 1962Mou, 1978Mex, 1984Sha, 1986Nev, 1997Dor, 1998Cla, 2000Dia, 2001Dia, 2002Mar, 2003Cas, 2004Dia, 2005Pal]. Also information about the τ_4 and τ_5 existence was presented by [1955Coc], but later it was shown by [1962Mou] that the τ_2 and τ_3 phases possess homogeneity ranges covering the compositions of the τ_4 and τ_5 phases. Data about the existence of the τ_6 and τ_7 phases ([1960Mar] and [1978Mex, 1999Hsu], respectively) were not confirmed by investigations of phase relations along the PbO-Fe_2O_3 temperature-composition section [1984Sha, 1986Nev].

Invariant Equilibria

On the basis of a dissociation process studies it was established by [1984Sha] that equilibria with the participation of the following phases take place: L + τ_2 + τ_3 + β at 1315°C, L + βPb_3O_4 + αPbO + τ_1 at 455°C, L + βPb_3O_4 + τ_1 + τ_2 at 430°C and L + βPb_3O_4 + τ_3 + β at 410°C. Also equilibria with the participation of the PbO_x-based phase with inexact stoichiometry were reported. The character of all the respective invariant reactions is not established.

Liquidus, Solidus and Solvus Surfaces

Phase relations at subsolidus temperatures in the range of compositions adjacent to the PbO-Fe_2O_3 section were schematically shown by [1984Sha]. It was established that the βPb_3O_4 phase takes part in equilibria with the τ_1, τ_2 and τ_3 phases and with the β phase.

Isothermal Sections

The solubility of lead in the liquid iron in the presence of oxygen was studied by [1995Li] at the temperatures of 1550, 1600 and 1650°C and various oxygen contents. The obtained dependences are shown in Fig. 2. A rise in lead solubility with increasing oxygen content and temperature was observed. Using the method of linear regression, the following functions lg(at.%){Pb} were evaluated as $-0.51 + 0.50 \cdot \{at.\% O\} \pm 0.025$ at 1550°C, $-0.43 + 0.67 \cdot \{at.\% O\} \pm 0.089$ at 1600°C and $-0.36 + 0.76 \cdot \{at.\% O\} \pm 0.038$ at 1650°C.

Temperature – Composition Sections

The PbO-Fe_2O_3 temperature - composition section being named as quasibinary in many publications, does not possess quasibinary character on the Fe_2O_3 side because this phase melts incongruently in the boundary binary Fe-O system. The section shown in Fig. 3 after [1989Rag] is based on the data of [1986Nev] in the PbO rich part and [1962Mou] in the Fe_2O_3 rich side. Another version of the PbO-Fe_2O_3 phase diagram was constructed by [1984Sha] on the basis of dissociation curves projections. The character of the phase relations at low temperatures needs further verification using different physico-chemical experimental techniques.

Thermodynamics

Enthalpies of melting ΔH^S_{melt} of the τ_1, τ_2 and τ_3 phases were calculated by [1986Nev] using the solution of equations following from the equilibrium conditions of coexisting phases. These values were obtained as 22.24 kJ·mol^{-1}, 49.92 kJ·mol^{-1} and 61.67 kJ·mol^{-1}, respectively. The enthalpies of formation of the τ_3 phase from oxides ($\Delta_f H$) or from simple substances ($\Delta_f H_{298}$) were calculated by [1992Rez] by approximate methods using the enthalpies of the change of cation coordination in the formation of the compounds from simple oxides. The reported values are 37 kJ·mol^{-1} and –5115 kJ·mol^{-1}, respectively. In the study of lead solubility in liquid iron, [1995Li] have calculated the activity coefficient f^o_{Pb} and the interaction parameter e^o_{Pb} at the temperatures of 1550, 1600 and 1650°C (Table 3).

Notes on Materials Properties and Applications

In case Pb is used as heat exchanger liquid in steel tubes of a nuclear reactor, the system is interesting in case of oxygen contamination of the cooling system producing oxide compounds which are radioactive and may be deposited in cool parts of the tubing system causing unwanted levels of radiation in the outer parts of the reactor system.

Because of their particular magnetic properties, ferrites, in particular, lead-containing, find many industrial applications, in the first instance as magneto-electric materials. Information concerning investigations of the Fe-O-Pb materials properties is collected in Table 4. [1957Ber] studied dependence of magnetic energy on the temperature of sintering for alloys with different PbO:Fe_2O_3 ratios [1957Ber] and observed a maximum energy values at the composition PbO-$4Fe_2O_3$. The corresponding dependences of the residual magnetic induction and the coercive force were also constructed by [1957Ber]. Magnetic measurements on the epitaxial films with the composition $Fe_{12.9}PbO_{22.9}$ were carried out by [1997Dor]. These objects exhibit magnetically isotropic behavior in the film plane with magnetic remanence to saturation magnetization divided by 4π ratio M(r)/M(s) = 88 ± 2.9% and coercive field H_c = 198.94 ± 7.72 kA·m^{-1}. However, the films were anisotropic with respect to the film normal such that the *c* crystallographic axis is a magnetically hard direction and all directions normal to the *c* axis are magnetically easy. The saturation magnetization (4πM (s)) value for the films is 0.063 T at room temperature. Magnetic properties of thin films with the

composition of $Fe_{12}PbO_{19}$ prepared by deposition on Si\SiO_2 and sapphire substrates were studied by [2000Dia] and [2001Dia], respectively. The influence of the substrate temperature (550-775°C) and the oxygen pressure (1-3 mbar) on the magnetic properties during the deposition was reported by [2000Dia]. The χ type lead hexaferrite films with high saturation magnetization and high coercive field (302.39 $kA \cdot m^{-1}$) were grown using a substrate temperature of 700°C and a pressure of 3.0 mbar of oxygen, while moderate value of coercive field of the thin films deposited on sapphire substrate at 700°C under 3.0 mbar partial pressure of high purity oxygen was 198,94 $kA \cdot m^{-1}$ [2001Dia]. The optimum value of coercive field of the $Fe_{12}PbO_{19}$ powder obtained by [2004Dia] using modifications to the traditional ceramic route was 318.31 $kA \cdot m^{-1}$ at 900°C. It was concluded that at temperatures higher than 900°C the magnetic properties are drastically affected as a consequence of the volatility of PbO. Phase formation during self-propagating high-temperature synthesis of ferrites was studied by [2002Mar]. The combustion temperature was 1267°C, the average front velocity was $9 \cdot 10^{-4}$ $m \cdot s^{-1}$, the obtained intermediate phases were FeO, Fe_3O_4 and Fe_4PbO_7. The value of coercivity was 48 $kA \cdot m^{-1}$. Results of tunneling magnetoresistance effect studies in the Fe-O-Pb granular films were presented by [1998Cla, 1999Hsu, 2000Hsu]. The dynamics of the 2*b* site in the $Fe_{12}PbO_{19}$ compound was investigated by [1998Cla] on polycrystalline and oriented single-crystal samples above the Curie temperature.

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

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1928Joh] as quoted by [1962Mou]	X-ray diffraction	Fe_4PbO_7
[1938Ade]	X-ray Laue and rotation techniques	$Fe_{12}PbO_{19}$
[1955Coc] as quoted by [1960Mar] and [1989Rag]	optical microscopy	The PbO-Fe_2O_3 section
[1957Ber]	X-ray Debye-Scherrer studies, thermal analysis, magnetic steel tester measurements	875-1275°C, the PbO-Fe_2O_3 section
[1960Mar]	Thermal analysis, metallography, powder X-ray diffraction	The PbO-Fe_2O_3 section
[1962Mou]	X-ray diffraction (Norelco diffractometer), DTA	600-1400°C, the PbO-Fe_2O_3 section
[1978Mex]	Solid state reactions studying, thermogravimetry, X-ray diffraction	The PbO-Fe_2O_3 section
[1984Sha]	Thermobalance, X-ray diffraction	The PbO-Fe_2O_3 section
[1986Nev]	DTA, X-ray diffraction, crystal growth studying	The PbO-Fe_2O_3 section
[1995Li]	Gas-light Tammann furnace measurements of solubility	1550, 1600, 1650°C, the Fe rich corner
[1997Dor]	X-ray diffraction (standard and grazing incidence), Rutherford back-scattering spectrometry	600°C, room temperature, the $Fe_{12.9}PbO_{22.9}$ thin films
[1998Cla]	Comparative Fe-57 Mössbauer spectroscopy (polycrystalline and oriented single-crystal samples)	477-707°C, $Fe_{12}PbO_{19}$
[1998Hua]	Method of manufacturing granular films	whole range of compositions

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[2000Dia]	Pulsed laser ablation deposition	550-775°C, $Fe_{12}PbO_{19}$
[2001Dia]	Pulsed laser ablation deposition, X-ray diffraction	700°C, $Fe_{12}PbO_{19}$
[2002Car]	Optical microscopy, scanning electron microscopy, electron probe microanalysis, X-ray diffraction, Mössbauer spectroscopy	476°C, Fe-O-Pb thin layers
[2002Mar]	Self-propagating high-temperature synthesis, X-ray diffraction, thermal analysis, chemical analysis, magnetic properties determination, density measurements, arrested front method	$Fe_{12}PbO_{19}$
[2003Cas]	Laser ablation deposition	700°C, $Fe_{12}PbO_{19}$ thin films
[2004Dia]	Mössbauer spectroscopy, X-ray diffraction	> 800°C, $Fe_{12}PbO_{19}$
[2005Pal]	Ceramic method, Rietveld refinement X-ray diffraction	$Fe_{12}PbO_{19}$

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 $Fe_{1-x-y}Pb_xO_y$	*cI*2 $Im\bar{3}m$ W	a = 293.15	[Mas2] $x = 0$, $0 < y \leq 2.9\cdot10^{-4}$, T = 1528°C [Mas2]
(γFe) (h_1) 1394 - 912 $Fe_{1-x-y}Pb_xO_y$	*cF*4 $Fm\bar{3}m$ Cu	a = 364.67	[Mas2] $x = 0$, $0 < y \leq 9.4\cdot10^{-5}$, T = 1371°C [Mas2]
(αFe) (r) < 912 $Fe_{1-x-y}Pb_xO_y$	*cI*2 $Im\bar{3}m$ W	a = 286.65	at 25°C [Mas2] $x = 0$, $0 < y \leq 8\cdot10^{-6}$, $T \approx$ 912°C [Mas2]
(εFe) > $1.3\cdot10^5$ bar	*hP*2 $P6_3/mmc$ Mg	a = 246.8 c = 396	at 25°C [Mas2]
(βPb) < 327.502 $Fe_xPb_{1-x-y}O_y$	*cF*4 $Im\bar{3}m$ Cu	a = 495.02	at 25°C [Mas2] $x = 0$, $0 < y \lesssim 10^{-6}$, $T \approx$ 327°C [Mas2] $y = 0$, $0 < x \lesssim 2.5\cdot10^{-4}$, $T \approx$ 910°C [E]
(αPb) > $1.03\cdot10^5$ bar	*hP*2 $P6_3/mmc$ Mg	a = 326.5 c = 538.7	at 25°C [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
α, $Fe_{1-x}O_x$ (wüstite) 1424 - 570	*cF*8 $Fm\bar{3}m$ NaCl	 *a* = 430.88	*x* = 0.5126 to 0.5457 [Mas2] in the alloy $Fe_{48.5}O_{51.5}$, *T* = 20°C [E]
		a = 428.00	in the alloy $Fe_{47.2}O_{52.8}$, *T* = 20°C [E]
γFe_3O_4 (h) 1596 - 580	*cF*56 $Fd\bar{3}m$ $MgAl_2O_4$	 *a* = 840	57.1 to 58.02 at.% O [Mas2] [E]
βFe_3O_4 (r) < 580	*mC*224 *Cc* βFe_3O_4	-	~57.1 at.% O [Mas2]
αFe_3O_4 (hp) > $2.5 \cdot 10^{-5}$ bar	*m**14	-	~57.1 at.% O [Mas2]
β, Fe_2O_3 < 1457	*hR*30 $R\bar{3}c$ Al_2O_3	 *a* = 503.42 *c* = 1374.83	59.82 to ~60 at.% O [Mas2] at 600°C [Mas2, V-C2]
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]
μ (Fe-O)	*tP*60 $P4_32_12$	-	metastable; ~60 at.% O; labelled as "γFe_2O_3" [Mas2]
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]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
βPbO (h)	*oP*8		50 at.% O, labelled as "PbO-M" [Mas2, 1998Ris]
~887 - ~489	*Pbma*		
	or	*a* = 547.6	[1961Lec1]
	Pbcm	*b* = 474.3	
	βPbO	*c* = 587.6	
		a = 548.9	at *T* = 27°C [H]
		b = 475.5	
		c = 589.1	
αPbO (r)	*tP*4		50 at.% O, labelled as "PbO-L" [Mas2, 1998Ris]
≲ 489	*P*4/*nmm*		
	αPbO	*a* = 396	[1961Lec2]
		c = 501	
		a = 397.59	at *T* = 27°C [H]
		c = 502.3	
		a = 397.2	[1989Rag]
		c = 501.8	
βPb_3O_4 (r)	*tP*28		57.1 at.% O, labelled as "Pb_3O_4-*T*" [Mas2, 1998Ris]
595 - (–103)	$P4_2/mbc$		
	βPb_3O_4 (r)	*a* = 881.5	at *T* = 25°C [S]
		c = 656.5	
		a = 880.6	[1989Rag]
		c = 656.4	
αPb_3O_4 (l)	*oP*28		57.1 at.% O, labelled as "Pb_3O_4-R" [Mas2]
< –103	*Pbam*		
		a = 912.4	at *T* = – 268°C [1988Wri, 2001Guz]
		b = 846.7	
		c = 656.7	
		a = 881.89	[1989Rag]
		b = 880.68	
		c = 656.36	
γ, $Pb_{12}O_{17}$	*oP28*		58.6 at.% O [Mas2, 1998Ris]
361 - < 0	$Pmc2_1$*?*	*a* = 778	[1988Wri, 2001Guz]
		b = 1098	
		c = 1148	

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
δ, $Pb_{12}O_{19}$ 335 - 54	*mP*62 *Pc*? or $P2_1/c$	 *a* = 773 *b* = 1083 *c* = 1147 β = 88.77°	61.3 at.% O [Mas2, 1998Ris] in the alloy $PbO_{1.57}$ [E]
		a = 775.3 *b* = 1084.8 *c* = 1150.2 β = 88.93°	[S]
		a = 1150 *b* = 1084.3 *c* = 777.3 β = 91.08°	[1988Wri, 2001Guz]
βPbO_2 251 - < 0	*tP*6 $P4_2/mnm$ TiO_2 (rutile)	 *a* = 491 *c* = 336	66.1 to 66.7 at.% O, with a small amount of hydrogen; labelled as "PbO_2-I" [Mas2, 1998Ris] [E]
		a = 495.5 *c* = 338.3	[S]
		a = 495.56 *c* = 338.67	1988Wri, 2001Guz]
		a = 495.78 *c* = 338.78	[1989Rag]
αPbO_2 (hp)	*cF*12 $Fm\bar{3}m$ CaF_2	-	metastable; about 66.7 at.% O; contains a small amount of hydrogen; labelled as "PbO_2-III" [Mas2]
θ (Pb-O)	*m*** $P2_1$ *or* $2_1/m$	-	metastable; 50 at.% O [Mas2]
ρ (Pb-O)	*o***	-	metastable; 50 at.% O; labelled as "PbOα" [Mas2]
σ (Pb-O)	*o***	-	metastable; 57.1 at.% O [Mas2]
ξ (Pb-O)	*o***	-	metastable; 57.1 to 61.1 at.% O; labelled as "PbO_n" [Mas2]
ζ (Pb-O)	Pseudocubic	-	metastable; 58.6 at.% O [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Δ, Pb_2O_3, 1 bar hydrostatic pressure	*mP*20 $P2_1/a$	 *a* = 781.4 *b* = 562.5 *c* = 846.6	metastable; 60 at.% O [1961Whi] [1988Wri, 2001Guz]
ϱ (Pb-O)	Pseudocubic	-	metastable; 61.3 at.% O [Mas2]
ϱ' (Pb-O)	*m***	-	metastable; 61.3 at.% O [Mas2]
ϕ (Pb-O)	*oP*12 *Pbcn* Nb_2FeO_6	-	metastable; about 66.7 at.% O; contains a small amount of hydrogen; labelled as "PbO_2-II" [Mas2]
* τ_1, $Fe_2Pb_2O_5$ 870 - ~650	*t***	*a* = 779 *c* = 1585 *a* = 780 *c* = 1582	[1957Ber, 1962Mou] [1978Mex] labelled as "δ" [1962Mou]
* τ_2, Fe_4PbO_7 880 - 750	*h***	*a* = 1186 *c* = 4714	[1928Joh, 1962Mou] labelled as "γ" [1962Mou]
* τ_3, $Fe_{12}PbO_{19}$ ~1315 - ~760	*hP64* $P6_3/mmc$	 *a* = 588 *c* = 2302 *a* = 512 *c* = 2367 *a* = 588.5 *c* = 2306.6 *a* = 592 *c* = 2322 *a* = 587 *c* = 2312	[1938Ade] in the $Fe_{12.9}PbO_{22.9}$ epitaxial films deposited at *T* = 600°C [1997Dor] in the $Fe_{12}PbO_{19}$ thin films deposited at *T* = 700°C [2001Dia] [2002Mar] [2002Mar] labelled as "β" [1962Mou]
* τ_4, $Fe_{10}Pb_2O_{17}$	-	-	[1955Coc]
* τ_5, $Fe_{10}PbO_{16}$	-	-	[1955Coc]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
* τ_6, Fe_8PbO_{13}	*h***	*a* = 662 *c* = 1019	[1960Mar]
* τ_7, Fe_6PbO_{10}	*h***	*a* = 591 *c* = 2352	[1978Mex]

Table 3: Values of Activity Coefficient and Interaction Parameters Referring to O [1995Li]

T [°C]	% $\{Pb\}^{Fe\text{-}Pb}$	f°_{Pb}	e°_{Pb}
1550	0.31	3.23	– 0.50
1600	0.38	2.66	– 0.67
1650	0.43	2.31	– 0.76

Table 4: Investigations of the Fe-O-Pb Materials Properties

Reference	Method/Experimental Technique	Type of Property
[1957Ber]	Magnet steel tester measurements	Residual magnetic induction, coercive force, magnetic energy
[1997Dor]	Vibrating sample magnetometer, SQUID magnetometer static magnetic techniques	Magnetic anisotropy, magnetic remanence, coercive field, saturation magnetization
[1998Cla]	Comparative Fe-57 Mössbauer spectroscopy	Dynamics of the 2*b* site
[1998Hua]	Magnetic resistivity measurements	Magnetic resistivity
[1999Hsu]	Magnetic resistivity measurements	Magnetic resistivity
[2000Dia]	Saturation magnetization and coercive field measurements	Saturation magnetization, coercive field
[2000Hsu]	Tunneling magnetoresistance measurements	Tunneling magnetoresistance
[2001Dia]	Saturation magnetization and coercive field measurements	Saturation magnetization, coercive field
[2002Mar]	Coercive field measurements	Coercive field
[2004Dia]	Saturation magnetization and coercive field measurements	Saturation magnetization, coercive field

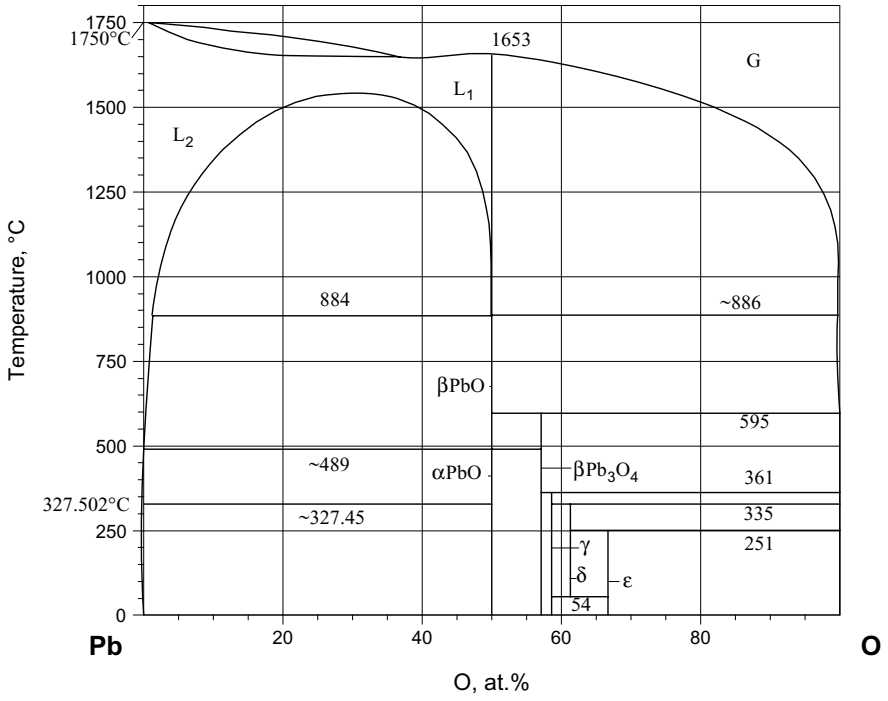

Fig. 1: Fe-O-Pb. The O-Pb phase diagram

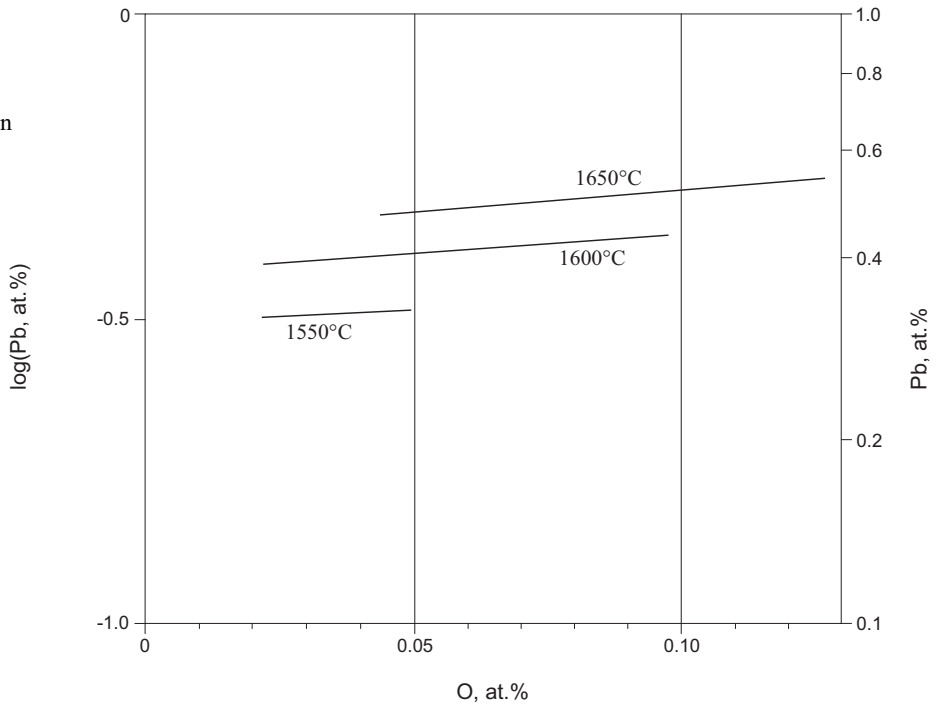

Fig. 2: Fe-O-Pb. Lead solubility as a function of oxygen content in liquid iron at 1550, 1600 and 1650°C

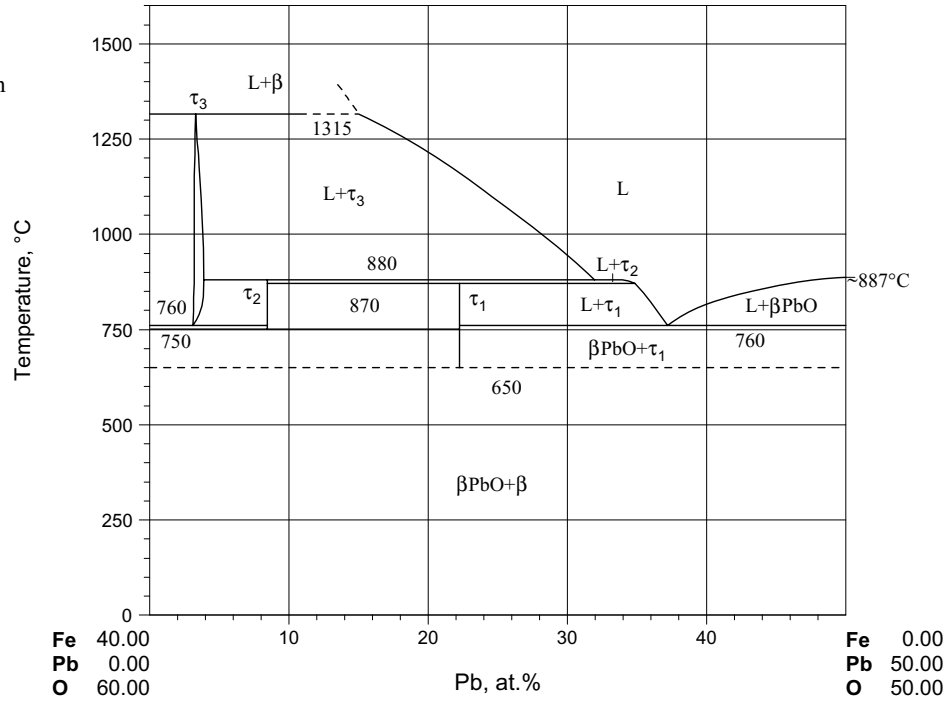

Fig. 3: Fe-O-Pb. Temperature - composition section $PbO\text{-}Fe_2O_3$