

## Copper – Iron – Platinum

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### Introduction

A diagram of primary crystallization in the ternary system Cu-Fe-Pt was proposed for the first time by [1909Jae], but the earliest experimental studies were by [1941Nem] and [1943Nem2]. They used thermal analysis, optical microscopy hardness measurement, electrical resistivity and temperature coefficient determination. The thermoelectric power with respect to Pt, the extension and the tensile strength of the alloys were also determined.

Four isopleths were produced which suggested that all Cu-Fe-Pt alloys form solid solutions at high temperatures except for Pt poor alloys with less than 20 at.% Pt. The compound FePt was found to separate out of the solid solution and penetrates deep into the ternary system with a suggestion of the formation of a ternary compound  $\text{FePt}_2\text{Cu}$  at about 1200°C. This ternary compound was seen on investigation of the section Pt-(50 at.% Cu + 50 at.% Fe), forming an unbroken series of solid solutions with FePt and limited solutions with PtCu [1941Nem, 1943Nem2]. These data were included in the reviews [1951Sol], [1969Gue] and [1979Cha], but as stated in [1979Cha], by that time, the existence of the ternary compound hadn't been confirmed.

Interest in this system and the proposed compound continued [1973Cab]. Tulameenite is a naturally occurring deposit of the composition  $\text{FePt}_2\text{Cu}$  adding weight to the hypothesis that this ternary compound exists [1973Cab, 1991Cab, 2002Tol, 2002Coo, 2002Gar, 2004Dis]. [1973Cab] conducted an extensive XRD, EPMA and optical microscopical study of tulameenite, but it was not until the work of [1986Sha] that the true nature of the material came to light. Through XRD, EPMA, TEM and DTA studies, they determined the relationship between  $\text{FePt}_2\text{Cu}$  and the rest of the ternary system. Arc-melted samples were homogenized at 1200°C for 3 months before quenching into water, followed by a further heat treatment at 1200°C for 1 week, followed by slow cooling ( $10^\circ\text{C}\cdot\text{d}^{-1}$ ) to 1000°C where they were held for a further 3 months. Some samples were cooled to 600°C and held for 6 months before quenching. They postulated that the single phase region of  $\text{FePt}_2\text{Cu}$  extends all the way to FePt at 1000°C and the  $\text{FePt}_2\text{Cu}$  composition lies in a two phase field at 600°C. This would suggest that the ternary compound is in fact an extension of the binary compound. Later work [1986Sha] confirmed that this is the case with the binary and “ternary” compounds being isomorphous.

Little thermodynamic study has taken place on this system. [1989Par] measured the activity of Cu along composition lines of constant Fe/Pt ratios by Knudsen cell effusion. [2004Wil] used electronic structure calculations to calculate the Gibbs energy of mixing along the  $\text{Fe}_{1-x}\text{Cu}_x\text{Pt}$  section, suggesting phase separation with a critical temperature of 450°C.

Experimental investigations of phase equilibria and thermodynamics are listed in Table 1.

### Binary Systems

Binary systems Cu-Fe, Cu-Pt and Fe-Pt are accepted from [2006Tur], [2006Kuz] and [Mas2], respectively.

### Solid Phases

The  $L1_0$ -FePt ordered phase extends into the ternary system by just over 30 at.% Cu at 1000°C and includes the composition  $\text{FePt}_2\text{Cu}$ . Thus, there is no ternary compound in this system. The ordering temperature of the  $L1_0$  phase falls with increasing Cu content [2002Mae]. At the  $\text{FePt}_2\text{Cu}$  composition, the ordering temperature falls to 1150°C [1986Sha]. It proved to be impossible to retain the high-temperature disordered fcc structure by quenching [1986Sha].

In rapidly cooled polycrystalline material the grains are subdivided into twin-related domains with {101} habit to compensate for the stress set up by the tetragonal distortion. Colonies of small twins are found within larger twins on three levels of scale, and it is suggested that these smaller twins are formed by

successive re-ordering of a previously ordered matrix during cooling [1986Sha]. Cu substitutes for Fe in the FePt lattice [1986Sha, 2004Wil]. Early crystallographic work indicates 4 atoms per unit cell in the structure of the  $L1_0$  compound, but later work by [1990Bay] did not reveal any additional reflections to indicate Fe and Cu ordering. No information is available on the solubility of Cu in either  $\text{Fe}_3\text{Pt}$  or  $\text{FePt}_3$ .

PtCu dissolves about 4.3 mass% Fe [1979Cha],  $\text{PtCu}_3$  also dissolves a small quantity of iron [1943Nem1]. Crystallographic data for solid phases in the system are given in Table 2.

### Isothermal Sections

Isothermal sections of the Cu-Fe-Pt ternary system at 1000 and 600°C, based on the work of [1985Sha] are shown in Figs. 1 and 2. At 1000°C there is a single phase region based on FePt extending far into the ternary system. Modification to the section presented in [1986Sha] is necessary, however, in order to take into account equilibria involving  $\text{FePt}_3$ . At 600°C, equilibria involving the PtCu and  $\text{PtCu}_3$  binary phases are also included, although dissolution of the third element in these compounds is fairly small [1979Cha, 1941Nem].

### Temperature – Composition Sections

Two vertical sections CuPt - FePt and Pt - 50Cu50Fe (at.%) were constructed by [1941Nem, 1943Nem2] and included in the review [1969Gue]. However, there are inconsistencies between these sections and the binary systems, particularly Cu-Pt. In fact, their measurements of the CuPt-FePt section disagree with their own determination of the liquidus and solidus of the Cu-Pt binary. For these reasons, the sections have not been included here. Electronic structure calculations were used by [2004Wil] to calculate the Gibbs free energy of mixing of disordered  $\text{Fe}_{1-x}\text{PtCu}_x$  alloys. This enabled the calculation of a temperature-composition section revealing phase separation with a critical temperature of approximately 177°C. The section is given in Fig. 3. It should be noted that this behavior has yet to be seen experimentally.

### Thermodynamics

The partial pressures of Cu in the system Cu-Fe-Pt in the temperature range 1240 to 1360°C have been measured by the Knudsen effusion technique and the thermodynamic properties of this system at 1300°C have been derived [1989Par]. The activities of Fe in solid solutions at 1300°C were calculated by Gibbs-Duhem integration of the Cu activities. The experimental alloys were prepared from Cu (99.999 mass%), Fe (99.999 mass%) and Pt (99.99 mass%) by induction melting in an alumina crucible under an Ar atmosphere. The alloy buttons were then homogenized in a  $\text{H}_2$  atmosphere for 5 to 30 days at 900 to 1300°C.

The iso- $a_{\text{Cu}}$  lines and the iso- $a_{\text{Fe}}$  lines in the Cu-Fe-Pt system are shown in Figs. 4 and 5, respectively (the dashed lines in these figures are the estimated solidus and liquidus lines at 1300°C).

### Notes on Materials Properties and Applications

The alloys of the Cu-Fe-Pt enriched by Pt have practical interest as materials for electrical contacts [1943Nem1]. Ordered alloys of this system are good candidate materials for ultrahigh recording density in terms of both high magnetic anisotropy energy and preparation without high-temperature treatment [2004Kai]. According to the data of [2004Wil], the magnetocrystalline anisotropy falls smoothly with increasing Cu content, both for small and large additions of Cu. The calculations point to Cu as a promising material with which it is possible to reduce the prohibitively high ordering temperature of  $L1_0$  FePt while not adversely affecting the magnetic properties. Furthermore, experimental data on the lower bound for the ordering temperature of the  $L1_0$  phase in FePt alloyed with Cu may aid in the future commercial viability of this material.

The catalytic activity of Cu-Fe-Pt ternary alloy was investigated using an electrochemical method in a polymer electrolyte fuel cell by [2000Shi]. It was established that the electrode prepared using a Cu-Fe-Pt alloy catalyst showed higher cell performance than unalloyed Pt.

Brief details of some studies of materials properties in Cu-Fe-Pt alloys are given in Table 3.

### Miscellaneous

The 'compound'  $\text{FePt}_2\text{Cu}$  with minor substitution of Pd, Rh, Ir and Ni is a naturally occurring minor constituent of platinum ores and placers (mineral tulameenite) [1973Cab, 1976Ura, 1985Sha, 1990Bay, 1991Cab, 2000Joh, 2002Coo, 2002Tol, 2004Dis]. An alloy with the composition  $\text{FePt}_2\text{Cu}$  commonly occurs as prismatic and needle-shaped crystals at the outer margin of altaite ( $\text{PbTe}$ ) [2002Coo]. This mineral is ferromagnetic [1973Cab]. According to [1973Cab], tulameenite has a range of composition with minor amounts of Ir replacing Pt and with Ni replacing Cu and Fe. Minor amounts of Sb was also detected in some grains. Studies along the  $\text{FePt}_2\text{Cu}$ - $\text{FePt}$  join by [1985Sha] indicate that the maximum substitution of Fe for Cu in tulameenite is up to between  $\text{Fe}_{1.68}\text{Pt}_2\text{Cu}_{0.32}$  and  $\text{Fe}_{1.28}\text{Pt}_2\text{Cu}_{0.72}$ . Comparison of the experimental results with data for the tulameenite mineral suggests that some observed compositions may be metastably preserved [1985Sha].

Tulameenite is white in reflected light in oil and air [1973Cab]. No birefractance could be observed and the mineral is very weakly anisotropic.

The Cu-Fe-Pt films show a high coercivity ( $H_C$ ) of around 5 kOe at 300°C, whereas the  $H_C$  of Fe-Pt films is still several hundred oersted at this temperature and starts increase to around 4.5 kOe at 400°C [2002Mae, 2005Che]. Cu-Fe-Pt films show a large  $H_C$  value at around 15 at.% Cu.

The Mössbauer spectra of alloys of 0.1 and 1 at.%  $^{57}\text{Fe}$  in Cu with 5 at.% Pt have been obtained by [1971Win]. Analysis shows electric field gradients and changes in the isomer shift with Pt neighbors that can be explained by the increased density of states due to the virtual bound state on the Pt impurity.

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**Table 1:** Investigations of the Cu-Fe-Pt Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1941Nem, 1943Nem2]	Thermal analysis, hardness measurements, electrical resistance	Isopleths $\text{Fe}_{0.5}\text{Pt}_{0.5}\text{-Pt}_{0.5}\text{Cu}_{0.5}$ , $\text{Pt-Fe}_{0.5}\text{Cu}_{0.5}$
[1973Cab]	XRD, EPMA	$\text{Pt}_2\text{FeCu}$ composition and alloys of the $\text{PtFe-Pt}_2\text{FeCu}$ section
[1985Sha]	XRD, TEM, EPMA, DTA	Equilibria involving $\text{Pt}_2\text{FeCu}$
[1986Sha]	XRD, TEM, EPMA, DTA	Crystal structure and morphology of $\text{Pt}_2\text{FeCu}$
[1989Par]	Weight loss Knudsen cell	Activity of Cu in ternary alloys from 1239 - 1360°C
[2002Mae]	XRD	Structure of $\text{PtFe}$ with added Cu
[2004Wil]	Total energy calculations - Korringa-Kohn-Rostoker method	Phase separation in the $\text{Fe}_{1-x}\text{Cu}_x\text{Pt}$ section

**Table 2:** Crystallographic Data of Solid Phases

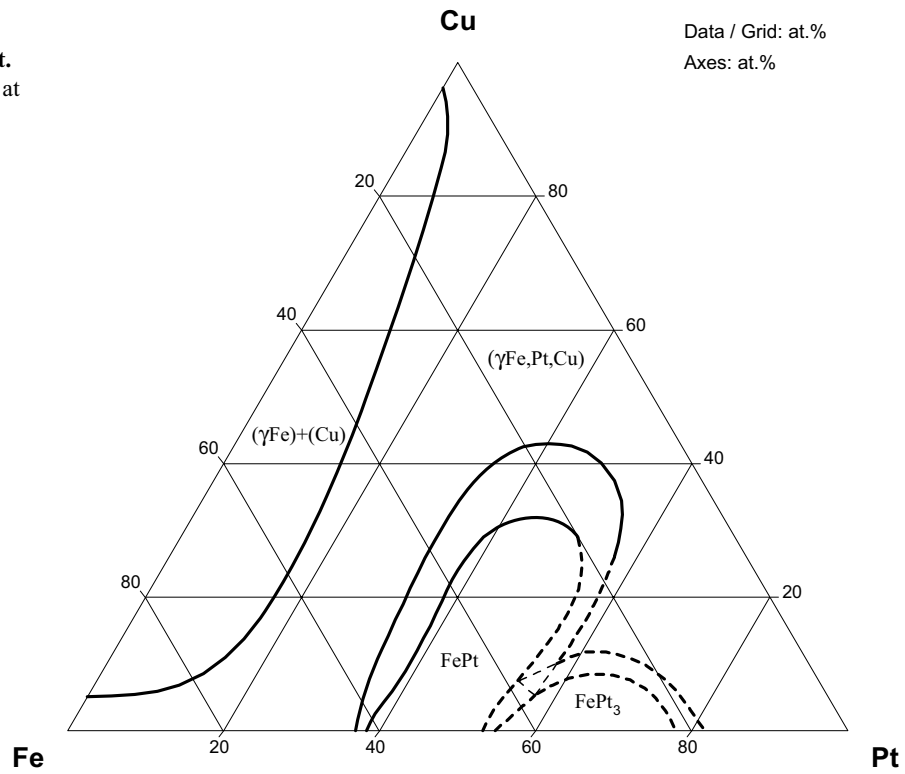
Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
( $\epsilon\text{Fe}$ )	$hP2$ $P6_3/mmc$ Mg	$a = 246.8$ $c = 396.0$	at 25°C, 13 GPa [Mas2]
( $\delta\text{Fe}$ ) 1538 - 1394	$cI2$ $Im\bar{3}m$ W	$a = 293.15$	[Mas2]
( $\gamma\text{Fe}_x\text{Pt}_{(1-x-y)}\text{Cu}_y$ )	$cF4$ $Fm\bar{3}m$ Cu	$a = 361.46$ to $392.36$ $x = 0$ , [2006Kuz] $a = 364.67$ to $392.36$ $y = 0$ ,	
( $\gamma\text{Fe}$ ) 1394 - 912		$a = 364.67$	at 915°C [V-C2, Mas2]
(Pt) < 1769.0		$a = 392.36$	at 25°C [Mas2]
(Cu) < 1084.62		$a = 361.46$	at 25°C [Mas2]; melting point [1994Sub]
( $\alpha\text{Fe}$ ) < 912	$cI2$ $Im\bar{3}m$ W	$a = 286.65$	at 25°C [Mas2]
PtCu < 816	$hR32$ $R\bar{3}m$ CuPt	$a = 1071.3$ $c = 1319.2$	[Mas2, V-C2]
$\text{PtCu}_3$ $\leq 735$	$cP4$ $Pm\bar{3}m$ $\text{AuCu}_3$	$a = 368.8$	at 25 at.% Pt, 250°C [2006Kuz]
1-D LPS $\leq 650$	$tP28$ $P4mm$ $\text{Cu}_3\text{Pd}$	?	[2006Kuz]; most probably - not unique phase but a set of closely related phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Fe <sub>3</sub> Pt ≤ 820	<i>cP4</i> <i>Fm<math>\bar{3}m</math></i> AuCu <sub>3</sub>	$a = 373.0$	[Mas2], [V-C2]
FePt ≤ 1300	<i>tP2</i> <i>P<sub>4</sub>/mmm</i> AuCu	$a = 384.1$	[Mas2] [V-C2]
FePt <sub>2</sub> Cu < 1200	<i>tP4</i> <i>P<sub>4</sub>/mmm</i> AuCu	$a = 389.1 \pm 0.2$ $c = 357.7 \pm 0.2$ $a = 388.5 \pm 0.1$ $c = 358.8 \pm 0.1$ $a = 389.5$ $c = 359.5$	[1973Cab, V-C2]; mineral tulameenite [1973Cab]; synthetic compound [1986Sha, V-C2]; annealed at 1200°C for 3 months [1985Sha]
		$a = 380.5 \pm 0.1$ $c = 359.5 \pm 0.1$	[1991Cab]
		$a = 390.18 \pm 0.07$ $c = 358.45 \pm 0.13$	[1990Bay]
	<i>tP2</i> <i>P<sub>4</sub>/mmm</i> ?	$a = 274.77 \pm 0.04$ $c = 358.70 \pm 0.03$	[1985Sha]
	<i>c**</i> ? ?	$a = 379.2$ $a = 385.0$	[2000Shi]
FePt <sub>3</sub> ≤ 1350	<i>cP4</i> <i>Pm<math>\bar{3}m</math></i> AuCu <sub>3</sub>	$a = 387.2$	[V-C2]

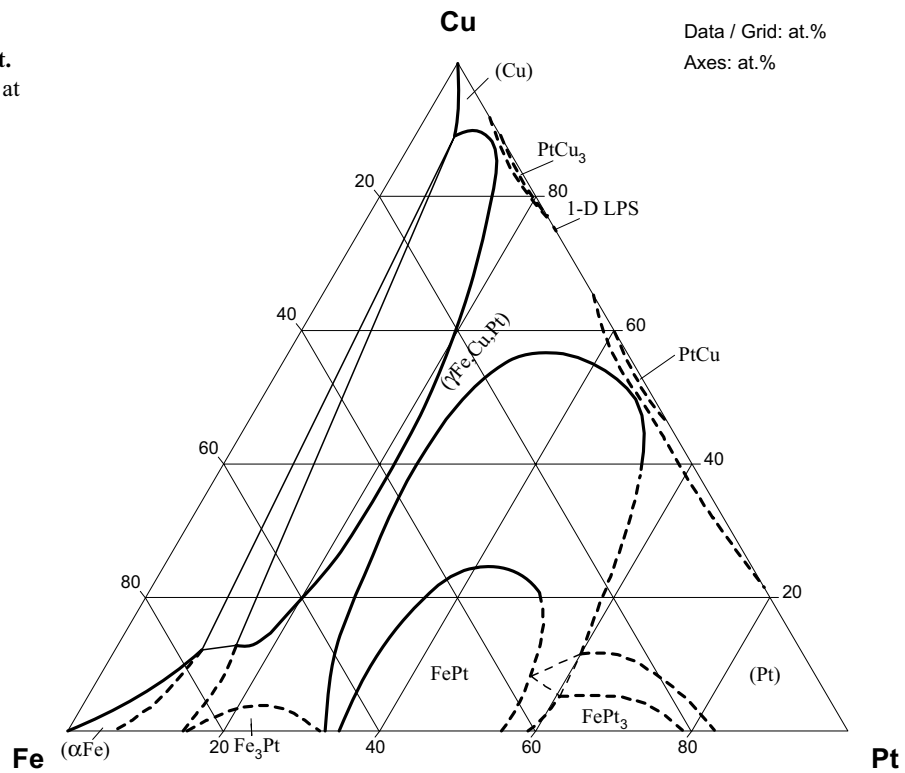
**Table 3:** Investigations of the Cu-Fe-Pt Materials Properties

Reference	Method/Experimental Technique	Type of Property
[1941Nem, 1943Nem2]	Hardness measurements, tensile and ductility measurement, electrical resistance, thermopower.	Mechanical and electrical properties with respect to composition and temperature.
[1971Win]	Mössbauer studies	Spectra and hyperfine field distributions of 1.4, 1 and 0.2 at.% Fe in Cu-5Pt
[1973Cab]	Ore microscopy, hardness measurement.	Reflectance, microhardness
[2002Mae]	Vibrating sample magnetometry	Magnetic properties of PtFe with respect to Cu addition
[2004Wil]	Total energy calculations	Magneto-crystalline anisotropy as a function of Cu in Fe <sub>1-x</sub> Cu <sub>x</sub> Pt
[2005Che]	Vibrating sample magnetometer	Coercivity change diffusion of Cu into PtFe thin film.

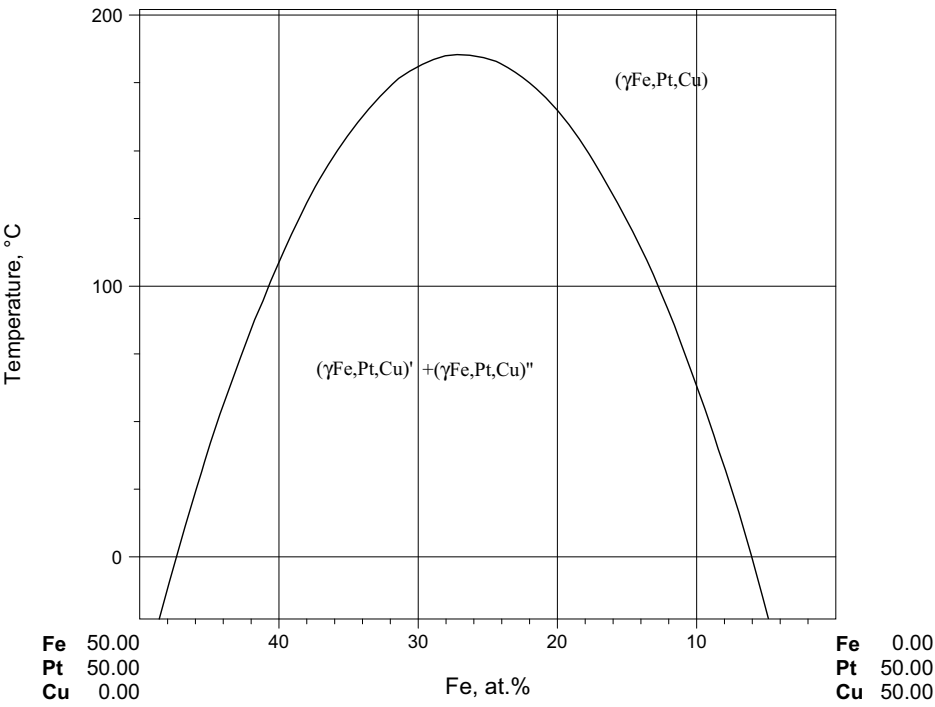
**Fig. 1: Cu-Fe-Pt.**  
Isothermal section at  
1000°C



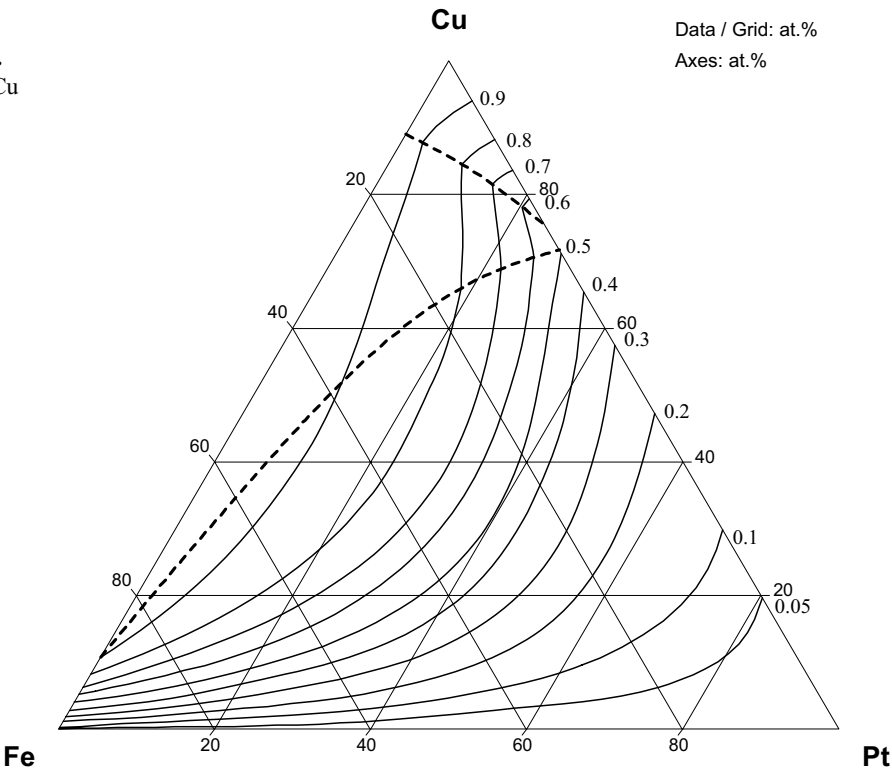
**Fig. 2: Cu-Fe-Pt.**  
Isothermal section at  
600°C



**Fig. 3: Cu-Fe-Pt.**  
Calculated vertical  
section for  
FePt - PtCu



**Fig. 4: Cu-Fe-Pt.**  
Isoactivity lines of Cu  
at 1300°C





**Fig. 5: Cu-Fe-Pt.**  
Isoactivity lines of Fe  
at 1300°C

