PHASES IN THE Pt-Fe SYSTEM

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It is known that in the system Pt-Fe the complete solid solution series, $(Pt,Fe)_{ss}$, exists above T > 835˚C, and three ordered compounds, Pt_3Fe, PtFe, $PtFe_3$, are formed in the subsolidus field. $(Pt,Fe)_{ss}$ is characterized by disordered cubic structure of Cu type (Sp.gr.Fm3m). Pt_3Fe has the ordered cubic structure of Cu_3Au type (Sp.gr.Pm3m). PtFe is tetragonal phase (Sp.gr.P4/mmm). According to L.Cabri and M.Fether [1] minerals corresponding to all these phases are: ferroan platinum, (Pt,Fe), isoferroplatine, Pt_3Fe, and tetraferroplatine, PtFe. Pt–Fe minerals are very important platinum group minerals for various geological occurrences – Alaskan (Uralian) ultramafites complexes, ofiolites massifs, differentiated mafic intrusions etc. Information about composition and characteristics of Pt-Fe minerals could be found in numerous publications (A.Genkin, L.Cabri, Z.Johan, T.Augé, H.Prichard, O.Thalhammer, M.Tarkian, A.Mochalov, K.Malitch, G.Garuti, E.Anikina, G.Shcheka and many others), but however some questions remain not clear. Beside stoichiometric isoferroplatinum, Pt_3Fe, and tetraferroplaatinum, PtFe, there are natural phases with other formulae. Even A.G.Betekhtin noted that ferroplatinum from Nizhny Tagil placers is characterized by ratio Pt:Fe= 1:1 – 2:1 [2]. Such ratio for “polyxene” (according to modern classification ferroan platinum) varies from 3:2 till 3:1.

Some explanations of this fact could be done: 1) Pt_2Fe is another ordered phase in the system Pt-Fe; 2) the composition «Pt_2Fe» corresponds not to the homogeneous compound, but to the fine “Pt_3Fe + PtFe” intergrowth; 3) Pt_2Fe is the ferroan platinum stable under particular conditions. If Pt_2Fe is really a new phase in Pt-Fe system, it should be the compound with particular ordered structure. If it is an intergrowth Pt_3Fe+PtFe, the x-ray diagram should contain reflexes characteristic for these phases. In the case of third version there are only reflexes typical for Fm3m cell. It is necessary to note that the system Pt – Fe is well studied: the high temperature field is occupied by the solid solution, and if Pt_2Fe is a new phase, it should have the structure derived from the cubic structure of Cu.

For check if “Pt_2Fe”is homogeneous, and if so, has it the ordered structure, the x-ray diffraction data were obtained using Gandolfi chamber for Pt_2Fe nuggets from some Russian ultrabasic massifs (Inagli, Konder, Guli, and Nizny Tagil - all from the collection of K.Malich), and from Youbdo complex, Ethiopia. The same nuggets were also investigated with SEM +EDD (JSM-5300 + Link ISIS).

The composition of Pt-Fe natural alloys: $Pt_{2\pm x}Fe$, 0<x<0.2 (9 nuggets), Pt_3Fe_2 (1 nugget), and Pt_3Fe (5 nuggets). It is shown that composition “Pt_2Fe” characterizes either ferroan platinum, or the mixture of Pt_3Fe and PtFe. Except principal reflexes that belong to non-ordered ferroan platinum, (Pt,Fe), the majority of nugget x-ray diagrams contain additional reflexes characteristic for native osmium, natural Os-Ir-Ru and Ru-Os-Ir alloys, laurite, and some other PGM inclusions in Pt_2Fe matrix. It should be noted that principal reflexes on some x-ray diagrams are broad (i.e. $d_\alpha \sim 2.20$ Å). Only x-ray powder data of one very small nugget from Nizhny Tagil with composition ~ Pt_3Fe_2 correspond to two phases - Pt-Fe, cubic and tetragonal. This confirms the first version, and the opinion of I.Zhernovski et al. [3].

Other x-ray diagrams contain only reflexes of face-centered cubic cell [(111), (200), (220), (222) и (331)]. Any reflexes characterized neither ordered cubic Pt_3Fe (Pm3m), nor tetragonal PtFe (P4/mmm) structures are observed. Therefore according to the nomenclature of L.Cabri & M.Feather [1] all studied “Pt_2Fe” nuggets except one from Nizhny Tagil, are ferroan platinum with disordered face centered cubic structure (Fm3m). Cell parameter, a_o, calculated on the base of cubic close packed structure, Fm3m, is in a good agreement with published data for cubic Pt-Fe compounds [1,3]. Variations of a_0 of natural (Pt,Fe) alloys in comparison with synthetic compounds are caused by small impurities of Os, Ir, Rh, Pd, Cu, and Ni, and are determined by atomic radius of isomorphous element. The mutual correlation “a_0, Å – [Fe+Ni+Cu], at. %” is weakly negative.

Since Pt-Fe alloys from placers associated with ultrabasic massifs often have the composition Pt_2Fe, it should be interesting to know if this composition could be an indicator of primary formation or characterizes late processes. For analyse the composition and structure peculiarities of (Pt,Fe) minerals from Youbdo, Ethiopia, some nuggets were investigated using JEM 5300 + INCA. Samples were presented by complex polymineral grains, often with Fe-Mn oxides/hydroxide “shirt” [4, 5].

The “primary” (Pt,Fe) alloy is Pt_3Fe (isoferroplatinum?), sometimes with first wt.% of iridium and osmium. Practically all nuggets have new-formed inclusions of Pt-Fe minerals along the peripheral and broken zones of nuggets. The new formed (Pt,Fe) minerals differ from primary by highest Cu content and by the ratio "Pt:(Fe+Cu)". More dense centre has the composition ($Pt_{3-x}Fe$), and does not contain any Cu. The copper concentration in peripheral zone of the same nugget is increased till 3.94 Wt. %. The main phase and broken parts of other grain contain 1.3 and 6.54 Wt. % of Cu correspondingly. Cu enriched areas are characterized by "Pt:(Fe+Cu)" ratio close to 2:1.

Beside "isoferroplatinum", Pt_3Fe, and "Pt_2Fe", nuggets from Youbdo contain cuproan ferronickelplatinum, [$Pt_2(Fe,Ni,Cu)$], with various copper content up to tulameenite, Pt_2FeCu), and tetraferroplatinum, PtFe. Other PGM associated with Pt-Fe-(Ni,Cu) compounds are (Os,Ir,Pt); (Au,Ag); PdBi, $PdBi_2$, Bi, CuAu, Ag_2Au, Ag_2Au_3; $PtAs_2$, (Rh,Pt); Pd, (Pt,Pd); Cu_3Zn_2; (Rh,Ir)AsS; Ir(As,Sb)S; Pt_3Sb; PdSb; OsS_2, as well as apatite, chromite, hematite, and Fe-Mn oxides. Based on such association "secondary" Pt-Fe alloys could be formed at the temperatures not higher than ~ 400-500°C.

According to data of Pt-Fe-S-O system experimental study under hydrothermal conditions at 300-600°C [6] the stability fields of (Pt,Fe) alloys and Mss are very close in sulphur fugacity. At the diagram "$lgfS_2$-T" the equilibrium line "(Pt,Fe)/Pt_3Fe" is higher than "PtFe/$PtFe_3$" one only for 4 log units. The "Pt_3Fe +PtFe mixture" and ferroan platinum, "Pt_2Fe", are stable in the field of intermediate $lgfS_2$ values (between these two lines).

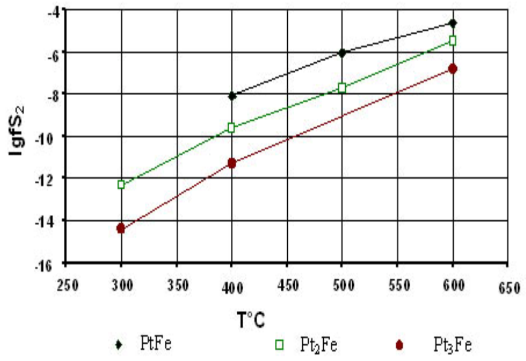

Fig.1. Stability of (Pt,Fe) phases in the "$lgfS_2$ – T" field (after [6])

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References

1. *Cabri L.G., Feather M.* Platinum-iron alloys: a nomenclature based on a study of natural and synthetic alloys // Canadian Mineralogist. V. 13. 1975. P. 117-126.

2. *Betekhtin A.G.* // Platina. AN SSSR. 1935 (in Russian).

3. *Zhernovsky I.V., Mochalov A.G., Rudashevsky N.S.* Phase heterogeity of isoferroplatinum rich in iron // Doklady Academii Nauk SSSR. V. 283. 1985. P. 1096-2000.

4. *Cabri L.G., Criddle A.J., Laflamme J.H.G., Bearne G.S., Harris D.C.* Mineralogical study of complex Pt-Fe nuggets from Ethiopia // Bulletin de Mineralogie. V. 104. 1981. P. 508-525.

5. *Evstigneeva T.L., Kudrjavtsev A.S., Rudashevsky N.S.* PGM from Youbdo (Ethiopia): new data // Mineralogitcheskij Zhurnal. 14. 1992. P. 29-41 (in Russian).

6. *Evstigneeva T.L., Nekrasov I.Ya., Laputina I.P.* Phase relationships in the system Pt-Fe-S-O // Doklady Academii Nauk SSSR. V. 308. 1989. P. 440-444 (in Russian).

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