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Structural and phase equilibria studies in the system Pt-Fe-Cu and the occurrence of tulameenite (Pt_2FeCu)

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ABSTRACT. The crystal structure and compositional limits of the ternary compound Pt_2FeCu (tulameenite), formed either by quenching from above the critical temperature of 1178 °C or by slow cooling, have been investigated using X-ray diffraction, transmission electron microscopy, differential thermal analysis and electron probe microanalysis.

The crystal structure of Pt_2FeCu, established using electron density maps constructed from the measured and calculated intensities of X-ray diffraction patterns of powdered specimens, has the (000) and $(\frac{1}{2}\frac{1}{2}0)$ lattice sites occupied by Pt atoms and the $(\frac{1}{2}0\frac{1}{2})$ and $(0\frac{1}{2}\frac{1}{2})$ sites occupied by either Cu or Fe atoms in a random manner. The resulting face-centred tetragonal structure undergoes a disordering transformation at the critical temperature to a postulated non-quenchable face-centred cubic structure. Stresses on quenching, arising from the ordering reaction, are relieved by twinning along {101} planes or by recrystallization along with deformation twinning; always involving grain boundary fracturing.

Phase relations in the system Pt-Fe-Cu have been investigated through the construction of isothermal sections at 1000 and 600 °C. At 1000 °C there is an extensive single phase region of solid solution around Pt_2FeCu and extending to the binary composition PtFe. At 600 °C the composition Pt_2FeCu lies just outside this now reduced area of solid solution in a two-phase field. Comparison of the experimental results with data for tulameenite suggests that some observed compositions may be metastably preserved. The occurrence of fine veinlets of silicate or other gangue minerals in tulameenite is suggested to result from grain boundary fracturing on cooling below the critical temperature of 1178 °C and to be evidence of a magmatic origin.

KEYWORDS: tulameenite, system Pt-Fe-Cu, crystal structure.

THE presence of a distinct compound in the Pt-Fe-Cu ternary system, with a composition of Pt_2FeCu, was originally proposed by Nemilov and Rudnitskii (1944), but the compound was not identified as a mineral (tulameenite) until the work of Cabri *et al.* (1973) on natural alloys from the platinum-gold placer deposits of the Tulameen River in British Columbia which were further described by Raicevic and Cabri (1976). Tulameenite occurs associated with cubic Fe-Pt natural alloys as rounded to irregular areas up to 400 μm in diameter, as free grains, or as grains with complex inclusions. Cabri *et al.* (1973) measured the lattice parameters of both natural and synthetic samples of Pt_2FeCu. Their analysis shows that tulameenite has a tetragonal cell with dimensions of a 3.891 and c 3.577 Å. Cabri *et al.* (1973) also concluded that tulameenite has a range of composition with minor Ir replacing Pt and with Ni replacing Fe.

Mineral concentrates from the Tulameen district were further studied by Shahmiri *et al.* (1980) who found that the platinum group minerals (PGMs) occur as discrete grains and nuggets up to 2-3 mm in diameter. Cubic platinum-iron (Pt_3Fe) forms the bulk of the PGMs, with tulameenite as a minor intergrown phase. Electron microprobe analysis of the Pt_2FeCu gave compositions clustered around the ideal composition as shown in fig. 1.

The work described in this paper was initiated to determine the Pt-Fe-Cu phase diagram especially in the region around Pt_2FeCu and thus to determine the compositional range of tulameenite, and also to determine the structure of Pt_2FeCu and some of the structural changes which may occur following different thermal treatments of this material.

Experimental methods

The various alloys and the ternary compound were prepared from spectrographically pure elements. The alloy compositions were chosen to cover the entire ternary system. Pure powdered elements were weighed out in quantities sufficient to prepare a total of one gram of alloys of the desired composition. The samples were melted and cast in a vacuum-arc furnace, were

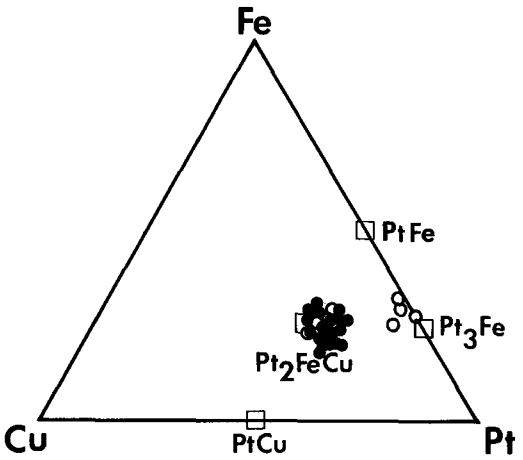


FIG. 1. Plot to show the compositions of natural Pt–Fe and Pt–Fe–Cu alloys including tulameenite. Circles are analyses of natural phases, squares are the stoichiometric compositions PtFe and Pt_2FeCu. Data are from Cabri *et al.*, 1973 (open circles); Shahmiri *et al.*, 1980 (closed circles).

equilibrated at 1200 ± 5 °C in a muffle furnace for three months, and were subsequently quenched in iced water.

The homogenized alloys were cut in half and each half was sealed inside a silica tube. They were given additional heat treatment at 1200 ± 5 °C for one week and then slowly cooled at 10 °C/day. One set reached 1000 °C after 20 days, and then was held for a further period of three months before being finally quenched. The second set of alloys was continuously cooled at 10 °C/day to 600 °C and held at that temperature for a further period of six months before subsequently being quenched.

To study the ternary compound Pt_2FeCu in greater detail, 10 g of the compound was synthesized in a manner identical to the alloys. The compound was equilibrated either at 1200 ± 5 °C (for three months) or 1400 °C ± 5 °C (for ten days) before being finally quenched.

An X-ray diffractometer using Co-$K\alpha$ radiation and an iron β-filter was employed throughout the present investigation to measure lattice parameters and to determine the crystal structure of stoichiometric Pt_2FeCu. The true lattice parameters were obtained using the $\cos^2\theta$ correction function (King and Massalski, 1962). Whenever the integrated intensity measurements were required, either a planimeter was used to measure peaks on graphically recorded data, or integrated intensities were measured directly by numerical data output from a computer-controlled diffractometer step scan. A scan rate of 0.1°/min was used in the latter case.

Samples were hot mounted in conductive bakelite, mechanically ground and polished to $\frac{1}{4}$ μm finish. During this process samples briefly attained temperatures of *c.*120 °C; since in these alloys diffusion is very slow at such low temperatures, the samples would not have been affected by this treatment. Etching in aqua-regia of various strengths was used as part of the examination in polished section.

Electron microprobe analysis was carried out using a Cambridge Instruments Microscan V microanalyser operated at 20 keV with a beam current of 50 nA. Analyses were carried out using pure Pt ($L\alpha$, λ = 1.313 Å), Fe ($K\alpha$, λ = 1.936 Å) and Cu ($K\alpha$, λ = 1.540 Å), as standards. The intensity ratios were corrected to true concentrations using the computer programme of Duncumb and Jones (1969).

To study some of the microstructures of the compound Pt_2FeCu, thin foils were examined with a JEOL 100 B transmission electron microscope (TEM) operating at 100 keV. Different electropolishing solutions were used in specimen preparation, but due to the high atomic number of the specimen and its resistance to chemical attack, only two out of ten attempts produced electron-transparent samples. An alternative technique of ion-beam thinning was employed. Discs of 3 mm diameter were spark-machined and then ground on 1200 grade silicon carbide paper to a thickness of 100–200 μm. The energy of the ion beam employed was 3–5 keV and the time required to thin-down samples suitable for TEM examination was 3–72 hours. The ion-beam thinning procedure was carried out with Ion-Tech equipment.

Results and discussion

The ternary compound Pt_2FeCu. X-ray diffractometer data for Pt_2FeCu quenched from 1200 °C after 3 months' heat-treatment showed the same reflections reported by Cabri *et al.* (1973) for Pt_2FeCu. These include certain mixed-index reflections [e.g. (001), (110) ...] in addition to the peaks due to the face-centred cubic (f.c.c.) structure and reveal that an ordering transition has occurred in the system. A differential thermal analysis (DTA) study of the homogenized sample was undertaken. This study involved heating the sample to 1300 °C at a rate of 7 °C per minute, cooling to 1100 °C at 1 °C per minute, to 900 °C at 2 °C per minute, and then to room temperature at 5 °C per minute. It showed that a significant endothermic reaction occurs on heating (and exothermic reaction on cooling) and the critical temperature of this transition, attributed to the ordering process, is 1178 ± 5 °C. All attempts to retain the disordered structure by means of fast-quenching were unsuccessful as the subsequent X-ray analysis showed the presence of superlattice lines. It appeared, therefore, that Pt_2FeCu has similar behaviour to the binary compound PtFe which orders on quenching from above *c.*1300 °C (Lipson *et al.*, 1941). The X-ray trace of the Pt_2FeCu was indexed using a Bunn Chart and shown to be due to a face-centred tetragonal (f.c.t.) lattice. The lattice parameters and axial ratio were determined as:

$$a = 3.805\ (\pm 0.001),\ c = 3.595\ (\pm 0.001)\ \text{Å},$$
$$c/a = 0.923.$$

The structure of tulameenite ought strictly to be referred to a smaller unit cell with $a' = a/\sqrt{2}, c' = c$

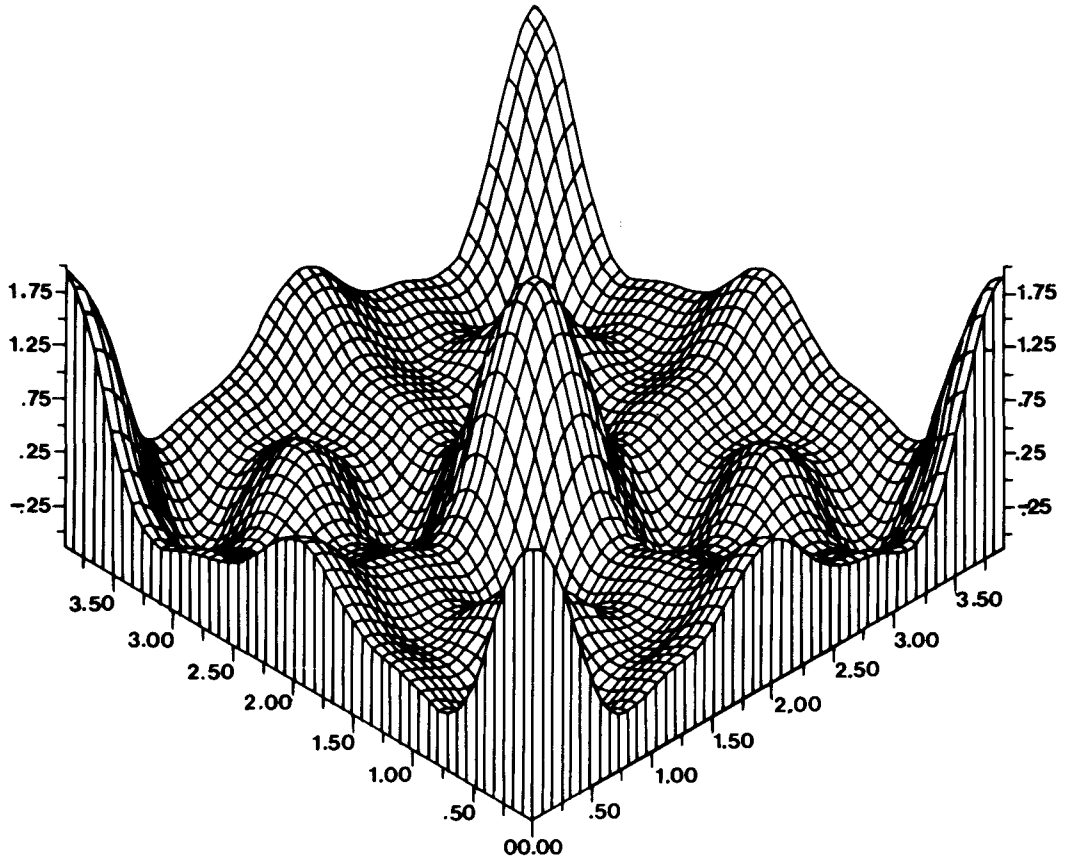


FIG. 2. Electron density map for Pt_2FeCu.

and, indeed, Cabri *et al.* (1977) have noted that tulameenite can be satisfactorily indexed in this way. This is a body-centred tetragonal structure cell, crystallographically equivalent to the one employed in the present work which is universally used to allow easy comparison with otherwise identical f.c.c. disordered alloys.

To determine the crystal structure of Pt_2FeCu, electron density maps from the calculated and measured intensities of two different samples (one sample annealed at 1200 °C for 3 months and the other at 1000 °C for three months) were plotted (fig. 2). The calculated and measured electron densities proved to be identical. The (000) and $(\frac{1}{2}\frac{1}{2}0)$ sites of the projection can easily be identified as being occupied by platinum atoms, but it was not possible to discriminate between Fe and Cu atoms as occupants of $(\frac{1}{2}0\frac{1}{2})$ or $(0\frac{1}{2}\frac{1}{2})$ lattice sites, although the anomalous scattering factor (Cullity, 1978) was taken into consideration.

A first interpretation of the data is that Cu and Fe are randomly distributed with the Pt atoms at fixed atomic sites, and that the ordering transition is due to the Pt adopting an ordered arrangement relative to Cu and Fe. In other words, the ordering reaction produces a layered structure cell similar to that observed in AuCu (Hansson and Barnes, 1964), or PtFe (Lipson *et al.*, 1941), i.e. the Fe/Cu and Pt atoms occupy alternate (001) planes (fig. 3).

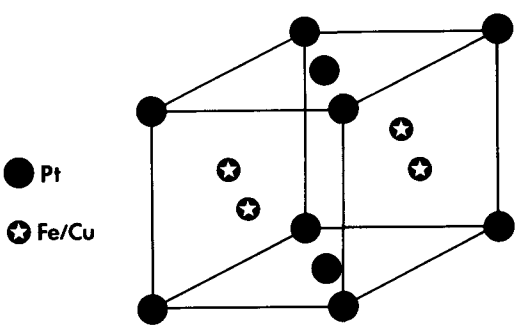


FIG. 3. Proposed crystal structure of the ordered tetragonal phase Pt_2FeCu (the mineral tulameenite).

No high-temperature X-ray techniques have been used to study the disordered phase, but it is presumed that the high-temperature structure is disordered face-centred cubic (f.c.c.), although it could not be proved by quenching. However, assuming that the mean volume per atom remains constant, a hypothetical lattice parameter of $a_0 = 3.792$ Å was calculated for the disordered face-centred cubic phase at room temperature.

Examination of the Pt_2FeCu in polished section shows that different grain structures are obtained depending upon the previous heat-treatments. After homogenization, etched samples show coarse grains and, within them, twin-bands. These twin-bands are thought to be stress-relief twins resulting from the ordering reaction that has produced a crystal lattice with lower symmetry than the disordered phase, i.e. it is the mechanism by which the material releases the stress resulting from the shape change due to the formation of anisotropic ordered domains in an isotropic matrix.

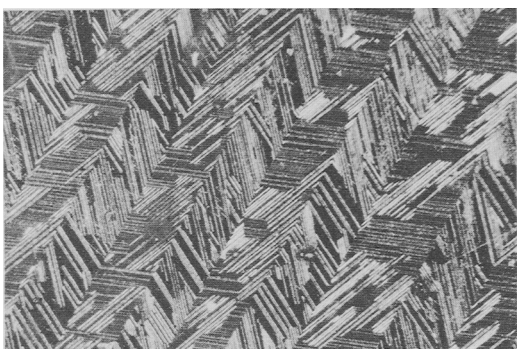


FIG. 4. Photomicrograph of Pt_2FeCu quenched from 1400 °C after annealing for 10 days. Etched section in plane polarized light at 350 × magnification.

Fig. 4 shows a polarized light photomicrograph of a typical area of a homogenized Pt_2FeCu sample. Each grain seems to be completely divided into narrow parallel bands which, in turn, are also subdivided by much finer bands.

Fig. 5 is a typical bright-field photomicrograph of Pt_2FeCu viewed under the TEM, and shows differently oriented ordered domains. Trace analysis in conjunction with selected area diffraction patterns from these revealed that the bands were twin related with $\{101\}$, $\langle 110 \rangle$ twinning shear. This is a similar relationship to that found in the AuCu, PtCo, and PtFe systems (Hansson and Barnes, 1964; Newkirk *et al.*, 1950; Lipson *et al.*, 1941). Any thermal treatment below the critical temperature resulted in stress-induced recrystallization and no further twinning was observed. Such a mechanism, where it is incorporated with the deformation twins, is another mode of stress-relief.

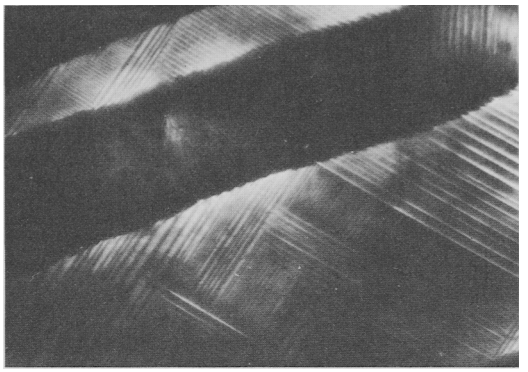


FIG. 5. Bright-field electron micrograph of Pt_2FeCu showing ordered domains in different orientations (17 000 × magnification).

Another important feature observed is that of grain-boundary fracture. This occurs regardless of the heat-treatment involved. When either quenched or slowly cooled specimens are viewed optically, very fine cracks are observed along the grain boundaries. Further annealing and quenching propagates the existing cracks or initiates new cracks. Fig. 6 shows the intercrystalline fracturing of a Pt_2FeCu sample quenched five times from the homogenization temperature.

The grain boundary fracturing is a mechanism for the release of further ordering stresses or the stresses of the ordered domains when they impinge. Such mechanisms occur when the combinations of recrystallization and deformation twins are not compatible with the stress build-up following heat treatment and set up when domain coalescence occurs.

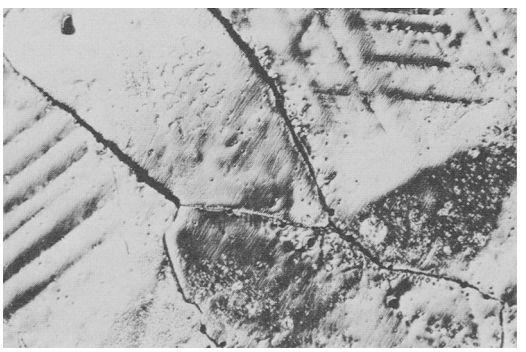


FIG. 6. Photomicrograph of thermally etched Pt_2FeCu showing grain boundary fractures (260 × magnification).

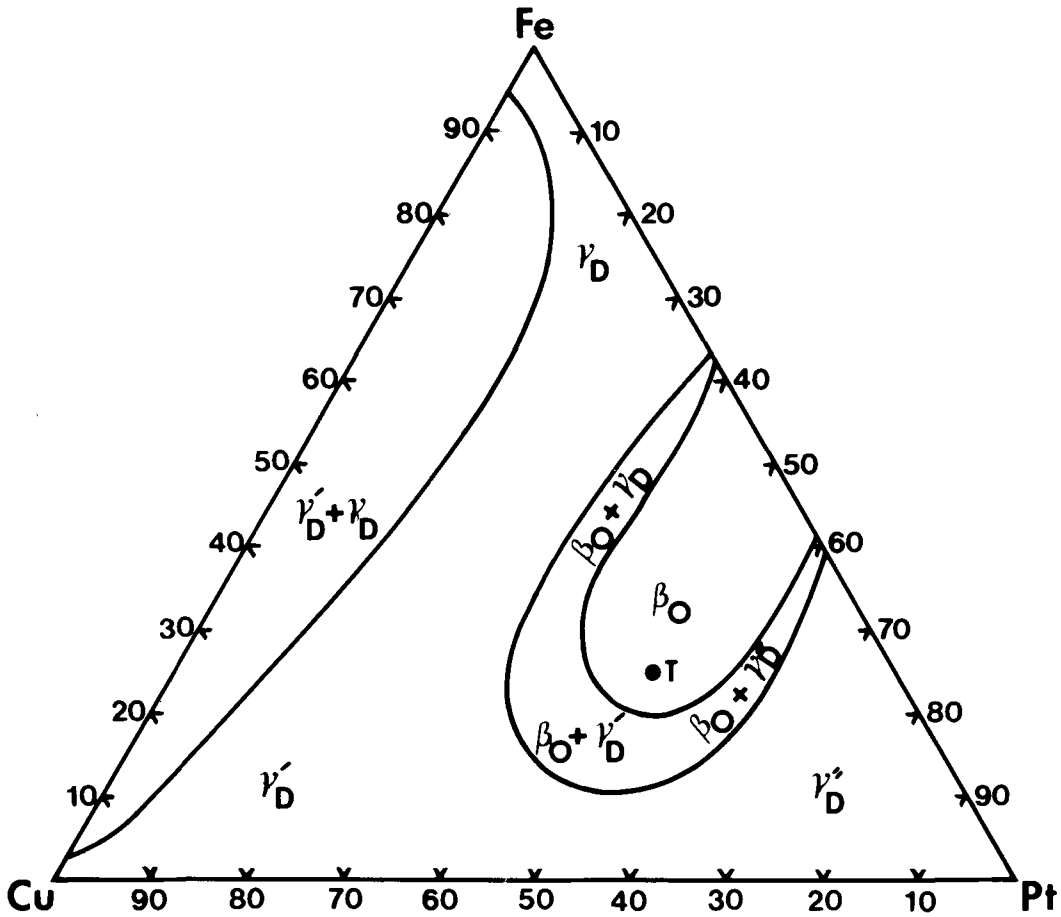


FIG. 7. Phase relations in the system Pt-Fe-Cu at 1000 °C. Figures are atomic percent metal.

Phase relations in the Pt–Fe–Cu system. From the study of the synthesized alloy compositions, isothermal sections were constructed through the Pt-Fe-Cu system at 1000 and 600 °C. Information from the previously published binary phase diagrams of the systems Pt-Fe, Pt-Cu, and Fe-Cu (Hanson and Anderko, 1958) was also employed.

Both the early and more recent (Cabri and Feather, 1975) studies of the Pt-Fe system, confirm the existence of order-disorder transformations in this system centred on the stoichiometric compounds Fe_3Pt and $FePt_3$. The precise compositional ranges, the critical temperatures and the phase relations involving Fe_3Pt, $FePt_3$, and FePt are still incompletely resolved but the majority of authors agree that in the region which is based on the compound FePt, there exists a very narrow two-phase field of cubic plus tetragonal phases. Similar ambiguities also exist in the Pt-Cu binary system where ordering reactions produce Cu_3Pt, PtCu, and $CuPt_3$ stoichiometric compounds in the solid state. In the Fe-Cu binary system, no order-disorder reactions take place and at low temperatures there exists a broad miscibility gap between Fe and Cu.

Fig. 7 shows the isothermal section determined at 1000 °C. The different phases in the ternary system have been designated as follows:

Disordered f.c.c. (Pt-rich)	γ''_D-phase
Ordered f.c.t.	β_O-phase
Disordered f.c.c. (Cu-rich)	γ'_D-phase
Disordered f.c.c. (Fe-rich)	γ_D-phase

The rather complex nomenclature of the disordered f.c.c. alloys is necessary because different parts of a single-phase field are separated by a two-phase region. Thus, phases with identical crystal structures, but very different compositions, may exist together at a certain temperature. In ternary systems, it is necessary to label different

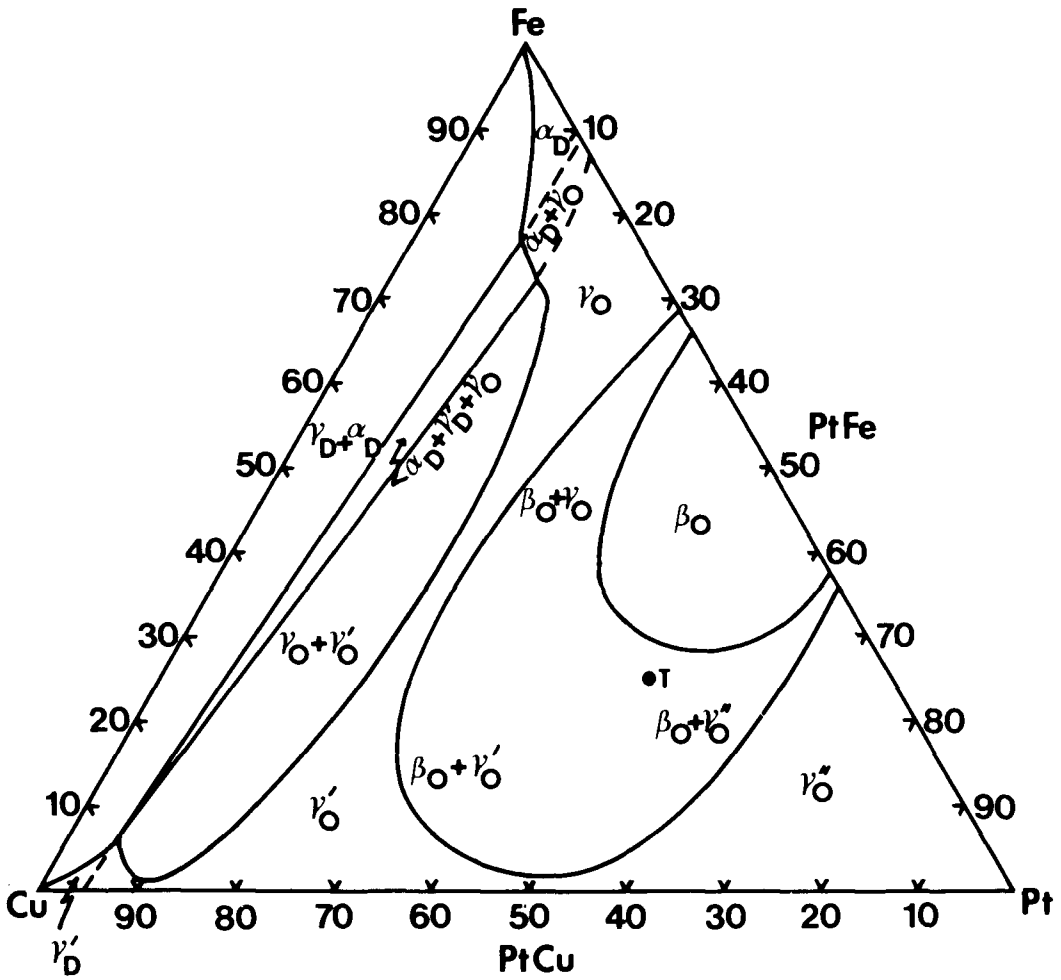


FIG. 8. Phase relations in the system Pt–Fe–Cu at 600 °C. Figures are in atomic percent metal.

parts of a single phase field in some way which allows a meaningful discussion of phase assemblages. Therefore, in Fig. 7 the field labelled γ_D, γ'_D, γ''_D is continuous; yet, for example, alloys in the two-phase field near the Fe–Cu edge of the diagram are made-up of two distinct phases of very different composition but identical crystal structure.

Previous investigations of the Pt–Fe binary system have confirmed that below 1300 °C, there exists a broad single-phase region of ordered tetragonal structure which is based on the compound PtFe. In the present investigation, it was found that at 1000 °C and by addition of Cu this region extends towards the interior part of the system and reaches approximately 50 at. % Pt, 30 at. % Fe, and 20 at. % Cu. The variation of Pt content in the β_O-phase is 38–58 at. %. At the exact composition of 50 at. % Pt, 25 at. % Fe, and 25 at. % Cu, there exists the ternary compound (tulameenite) which forms a continuous region of solid-solution with the binary compound FePt. The ordered tetragonal β_O-phase is separated from the γ_D, γ'_D, and γ''_D single-phase regions by a wide two-phase field of the disordered f.c.c. phase and ordered tetragonal phase. Between the single phase fields of γ'_D and γ_D there exists a two-phase field of Cu- and Fe-rich phases ($\gamma'_D + \gamma_D$). Apart from the β_O-phase and these two-phase fields at 1000 °C, all other alloys were single phase f.c.c. solid-solutions of Pt, Fe, and Cu.

Fig. 8 shows the isothermal section determined at 600 °C. The phases present in addition to those

observed in the experiments quenched from 1000 °C are as follows:

Ordered f.c.c. (Fe-rich)	γ_O
Ordered f.c.c. (Cu-rich)	γ'_O
Ordered f.c.c. (Pt-rich)	γ''_O
Disordered f.c.c. (Fe-rich)	α_D

As can be seen from fig. 8, the β_O-phase field boundaries change so that this phase can accommodate less Cu and slightly more Fe than at 1000 °C. The two-phase field surrounding the β_O phase ($\beta_O+\gamma_O$, $\beta_O+\gamma'_O$, $\beta_O+\gamma''_O$) increases considerably in area, partly as a result of this. The other major changes which occur on cooling to 600 °C are on the Fe–Cu side of the ternary as seen from fig. 8.

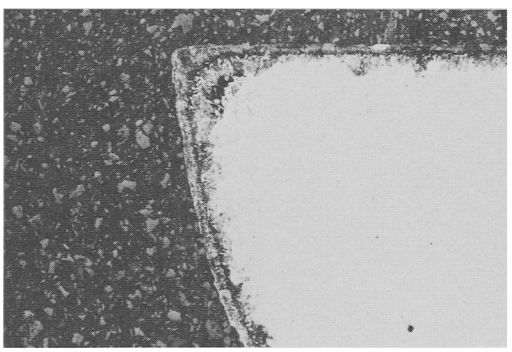
The compound Pt_2FeCu which is stable as a stoichiometric phase at 1000 °C decomposes on slow cooling and by 600 °C lies in the $\beta_O+\gamma''_O$ region of the two-phase field. This breakdown takes place slowly and in an unusual manner, whereby only the outer margins of the grains take on the two-phase composition, the core remaining homogeneous. This can be clearly observed in polished section as shown in figs. 9 and 10.

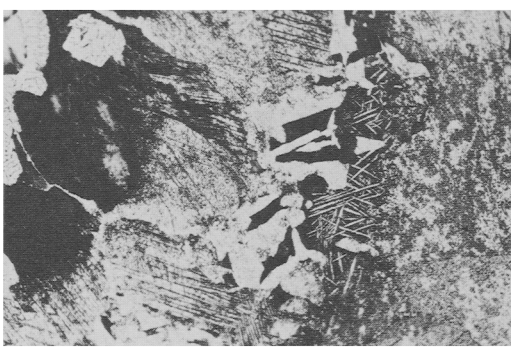
Discussion. This study of the crystal structure, phase transformations, and phase relations of synthetic tulameenite shows that it undergoes an ordering transformation at *c.*1178 °C. Above this temperature, the composition Pt_2FeCu has a nonquenchable structure which is presumed to be disordered face-centred cubic. Below the critical temperature, an ordered face-centred tetragonal structure is observed. Comparisons of measured and calculated electron density distributions show that the ordering reaction produces a layered structure cell in which Pt and Fe/Cu atoms alternately occupy layers parallel to {001}.

The ordering transformation which occurs below 1178 °C requires growth of ordered tetragonal domains in the isotropic matrix of high-temperature Pt_2FeCu. This produces stresses which are partly relieved by the formation of twin-related order domains, deformation twins and also by grain boundary fracture.

The study of phase relations in the system Pt–Fe–Cu shows that complete solid solution occurs between Pt_2FeCu and PtFe at 1000 °C (and above) along with substantial Pt/Fe substitution. However, on cooling to 600 °C the boundaries of this solid solution field change so that stoichiometric Pt_2FeCu lies just outside this field in a two-phase region. The breakdown of stoichiometric Pt_2FeCu appears to take place slowly and to occur in the region of grain margins.

Comparison of the experimental results with data for tulameenite (Cabri *et al.*, 1973; Shahmiri *et al.*, 1980) suggests certain conclusions regarding the mode of formation of this mineral. Compositions of tulameenite (fig. 1) extend from Pt_2FeCu towards the Pt–Fe join in the ternary diagram as would be expected from the phase relations at high temperature. The natural occurrence of phases with compositions of essentially Pt_2FeCu composition may reflect their metastable preservation due to the slowness of the decomposition reaction (as observed in the experimental work). The relatively rare occurrence of tulameenite compared with the Pt–Fe alloy phases may also be due in part to the breakdown reaction. Of course, the role of the minor amounts of Ir, Ni, Sb, Pd, Rh, Os, and Ru reported to occur in tulameenite (Cabri *et al.*, 1973; Bowles, 1981) is unknown but they are unlikely to have a very great effect on phase relations, although they could further stabilize stoichiometric Pt_2FeCu.





FIGS. 9 and 10. FIG. 9 (*left*). Photomicrograph of a lightly etched section of Pt_2FeCu showing decomposition along the grain margin with the appearance of the γ''_O phase (16 × magnification). FIG. 10 (*right*). Photomicrograph of an etched section of Pt_2FeCu showing in greater detail the decomposition along grain margins to form the γ''_O phase (160 × magnification).

Tulameenite is invariably penetrated by thin veinlets of silicates or other associated gangue minerals in a manner not observed in other naturally occurring platinum group metal alloys. This material could well be introduced as a result of grain boundary fracture occurring after the tulameenite has passed through the ordering temperature at 1178 °C which, as noted above, introduces stresses in the material which result in twinning and in such fracturing. This explanation for the veining of tulameenite by silicates lends strong support to the view that this mineral, and the closely associated Pt–Fe phases with which it occurs, formed by crystallization from a magma at high temperatures (for tulameenite > 1178 °C) and not by later processes at lower temperatures.

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