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PLATINUM-GROUP MINERALS FROM ONVERWACHT. I. Pt-Fe-Cu-Ni ALLOYS*

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ABSTRACT

Ferroan platinum and two different types of Pt-Fe-Cu-Ni alloys occur in a sample from the former Onverwacht mine, Transvaal. Alloy 1 has a composition near $PtFe_{0.5}Ni_{0.25}Cu_{0.25}$ and is tetragonal, *P4/mmm, a* 2.741(3), *c* 3.644(3)Å, *D*(meas.) 14.3 g/cm^3, *D*(calc.) 15.80 g/cm^3. It may represent a copper- and nickel-rich variety of tetraferroplatinum. Should that be the case, the unit cell of type tetraferroplatinum from Mooihoek must be *a* 2.724(6), *c* 3.702(9)Å. Alloy 1 is especially characterized by perfect {001} cleavage and is very sectile. Alloy 2 has the composition $(Pt,Pd)_{1.03}Fe_{0.29}Cu_{0.29}Ni_{0.29}Sb_{0.10}$ but its X-ray powder pattern could not be indexed.

SOMMAIRE

Du platine ferrifère et deux types différents d'alliages Pt-Fe-Cu-Ni ont été trouvés dans un échantillon provenant de l'ancienne mine d'Onverwacht, au Transvaal. Le premier alliage, dont la composition est proche de $PtFe_{0.5}Ni_{0.25}Cu_{0.25}$, est quadratique, *P4/mmm, a* 2.741(3), *c* 3.644(3)Å, *D*(mes.) 14.3, *D*(calc.) 15.80. Cette composition pourrait représenter une variété de tétraferroplatine riche en cuivre et en nickel. En ce cas, la maille du tétraferroplatine type de Mooihoek devrait être *a* 2.724(6), *c* 3.702(9)Å. Le premier alliage possède deux caractères distinctifs: il est très sectile et possède un clivage parfait {001}. Le deuxième alliage répond à la formule $(Pt,Pd)_{1.03}Fe_{0.29}Cu_{0.29}Ni_{0.29}Sb_{0.10}$. Toutes les tentatives de dépouillement de son diagramme de poudre sont restées vaines.

INTRODUCTION

In 1965, a specimen (~15×20×35 mm) labelled native platinum in matrix from Onverwacht, 330, Lydenburg district, Transvaal, was purchased by W. W. P. from Ward's National Science Establishment, Inc., and given specimen No. 1949 in the Pinch Mineralogical Museum. Strictly speaking, the sample was obtained from the former platinum mine in the hortonolite–dunite body occurring on the farm Onverwacht (No. 330). The specimen had been obtained by Ward's from the collection of Mr. Aubrey Horn of Nigeria. Initial work established that the sample contained sperrylite, chromite, and silicates, but no native platinum could be found. The sample was remarkable in that it contained several clusters of a bright, highly reflecting, metallic silver-grey mineral as platelets up to about 2×2 mm. Examination of four thin plates by the precession method yielded a crystal with sufficiently sharp diffraction maxima to determine the symmetry, tetragonal with *a* 2.75, *c* 3.62Å. A Gandolfi X-ray powder-diffraction pattern was indexed on that cell. Semi-quantitative electron probe analyses gave Pt, Fe, Ni and Cu as the major elements but the total was only about 97%. Although thought to be a new mineral, further work was considered to be necessary prior to submission to the IMA Commission on New Minerals and Mineral Names. Before this was completed, however, the report of the new mineral tulameenite (Cabri *et al.* 1973) led W. W. P. and A. R. to believe that their mineral might be tulameenite because of the similarities in powder patterns and general chemistry. The sample was sent to L. J. C. to determine whether the two minerals were identical. We concluded, however, that this mineral is a variety of tetraferroplatinum.

THE ONVERWACHT PLATINUM DEPOSIT

Wagner's (1929) account of the Onverwacht deposit and its platinum minerals is the most recent except for the Genkin *et al.* (1966) discovery of the new sulfarsenide irarsite associated with ruthenian hollingworthite, and for the brief account of platinum-group minerals by Ramdohr (1969). Wagner stated that more than 60 separate occurrences of hortonolite–dunite had been discovered in the lower part of the Norite Zone of the Bushveld Igneous Complex in the Lydenburg and Rustenburg districts, but that only two were worthy of exploitation — Onverwacht No.

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330 and Mooihoek No. 147. The nearby platinum-bearing Driekop deposit was considered by Wagner to be a different type of deposit. Wagner described the hortonolite–dunite deposits as follows: "In these, where platinum-bearing, that metal occurs in pipe or parsnip-shaped segregations and smaller veins and lenses as a primary constituent of hortonolite–dunite and rocks associated with it". Wagner also reported that, in dunite deposits of the Lydenburg district, most of the platinum was present in the metallic state as nuggets, irregular grains, and well-formed crystals predominantly of cubic habit and up to 1 mm across. Pt-Fe alloys and sperrylite were also reported to occur and the suggestion was made that other platinum alloys should be present, especially below the water table. The platinum content of the Onverwacht hortonolite–dunite ranged from nil to 65.65 oz/short ton and the orebody was referred to by Wagner as "amazing". Further details may be found in Wagner's book.

PROCEDURES

Thin slices (1 to 2 mm) were cut from the sample with a 0.3 mm diamond wafering blade. These slices and some of the cleavage fragments, detached with tweezers and a scalpel, were mounted in cold-setting plastic, polished on lead laps, and studied by ore microscopy. Reflectivity and micro-indentation hardness measurements were made as described previously (Cabri *et al.* 1977a). Cleavage fragments, as well as grains extracted from polished sections, were X-rayed with Gandolfi cameras and, when possible, by the precession method. Film-shrinkage corrections were applied and the unit-cell parameters for the indexed powder patterns were refined by the least-squares computer program PARAM (Stewart *et al.* 1972). Compositions were determined with a Materials Analysis Company model 400 electron probe at 25kV, a specimen current of about 0.03 microamperes, and using as X-ray lines and (standards): Pt$L\alpha$, Fe$K\alpha$, Cu$K\alpha$ (synthetic $PtFe_{0.84}Cu_{0.16}$, Pt_2Fe, $PtFe_{0.64}Cu_{0.36}$); Pd$L\alpha$, Ni$K\alpha$, and Sb$L\alpha$ (pure metals). Corrections were applied using a slightly modified version of the EMPADR VII computer program of Rucklidge & Gasparrini (1969).

MINERALOGY OF THE SAMPLE

About one-third of the sample consists of chromite with the remainder being mainly coarse-grained, dark greenish brown silicates with crystals up to about 4 mm. In contrast to the abundant coarse inclusions of Pt alloys readily visible in the silicate matrix, the chromite contains few scattered inclusions of silvery Pt alloys. It may well be, as suggested by Genkin *et al.* (1966) for their Onverwacht sample, that this sample represents material from the 250′ level where high Pt concentrations occurred at the contact with tabular masses of chromite. The Pt-alloy inclusions in the silicate portions may be divided into two groups macroscopically: (1) clusters of a very bright alloy with perfect cleavage and, (2) concentrations of a less bright alloy, up to 4 mm, showing no visible cleavage.

The platinum-group minerals found in the specimen include Pt-Fe and Pt-Fe-Cu-Ni(Sb) alloys, which are the subject of this paper, as well as platarsite (Cabri *et al.* 1977a), genkinite (Cabri *et al.* 1977b), sperrylite, stibiopalladinite, ruthenarsenite, mertieite II, and some as yet unidentified minerals. One Pt-Fe alloy was determined to be ferroan platinum and the Pt-Fe-Cu-Ni alloys may be classified into two types on the basis of their compositions and symmetry. These alloys are described separately.

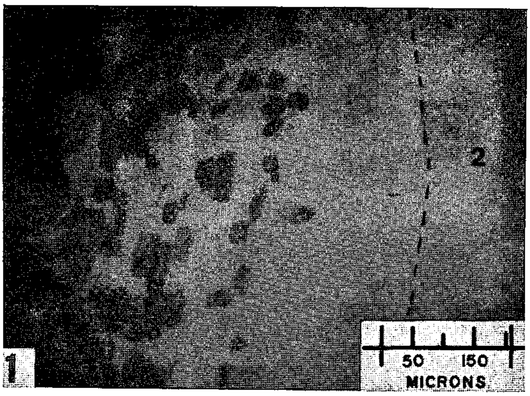
Pt-Fe alloys

Three grains of Pt-Fe alloy were analyzed (Table 1, Nos. 9-11) from three different associations. Their compositions and minor elements are typical of Pt-Fe alloys from many worldwide localities (Cabri & Feather 1975; Toma & Murphy 1977). Numbers 9 and 10 were included in silicates in contrast to No. 11 which occurred as intercumulus material in chromite. No. 9 Pt-Fe alloy appears as the matrix of a large complex grain (Fig. 1) containing intergrowths of sperrylite and stibiopalladinite as well as apparently exsolved grains of a Pt-Fe-Cu-Ni-Sb alloy (type 2). No. 10 Pt-Fe alloy (600×970 μm) contains several lamellar inclusions of genkinite (Fig. 2). No. 11 Pt-Fe alloy is inclusion-free and *f.c.c.* with *a* 3.848(3)Å. It is, therefore, ferroan platinum.

Pt-Fe-Cu-Ni alloys — alloy 1

The Pt-Fe-Cu-Ni alloys which typically show perfect cleavage have very similar compositions (Table 1, Nos. 1, 4-8) and plot in one area of the $(Pt,Pd)_2(Fe,Sb)_2 - (Pt,Pd)_2Cu_2 - (Pt,Pd)_2Ni_2$ composition diagram (Fig. 3). The six crystals analyzed were cleavage fragments detached from the hand sample under a binocular microscope. Though the compositions of all six crystals plot in a group near the hypothetical composition $Pt_2(FeNi_{0.5}Cu_{0.5})$, all are slightly Fe- and Ni-rich. $Pt_2(FeNi_{0.5}Cu_{0.5})$ plots midway between ideal tulameenite (Pt_2FeCu) and hypothetical Pt_2FeNi.

X-ray powder data (Table 2) have been indexed on a tetragonal cell, *a* 2.741(3), *c*



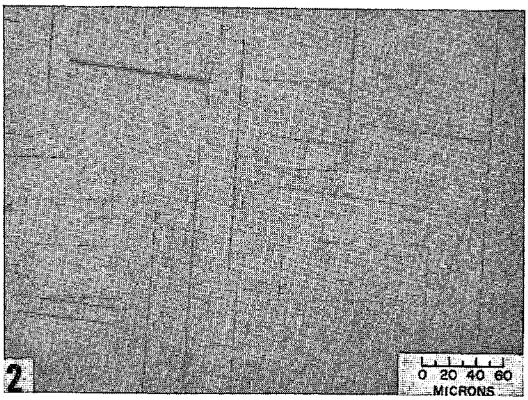


FIG. 1. Part of a Pt-Fe alloy grain (Anal. 9, Table 1), included in silicates, which contains Pt-Fe-Cu-Ni alloy 2. Scattered subhedral crystals of sperrylite (dark grey) are present in the Pt-Fe alloy.

FIG. 2. Pt-Fe alloy (Anal. No. 10, Table 1) with oriented lamellae of genkinite.

3.644(3)Å, as established from precession studies. The X-ray data correspond to space group *P4/mmm*, and for analysis No. 4 *D*(calc.)=15.80 g/cm^3 with Z=1.

In hand specimen the mineral is bright, light silver-grey. Reflectances in air on sections parallel {001} are: 470nm 61.3; 546nm 61.3; 589nm 62.2; and 650nm 63.0% (av. of 2 and 3 meas. on grains reported as analyses 5 and 6 respectively). The mineral has one perfect cleavage {001} and is very sectile, making it difficult to obtain an undeformed cleavage flake for X-ray single-crystal studies. Micro-indentations (perpendicular {001}) were perfect, with very faint parallel cracks which sometimes developed on one to three sides. VHN_{50} was 552 (498-593) and 522 (498-553) as determined from 6 and 5 measurements on grains reported as analyses 5 and 6, respectively. The mineral has a very weak attraction to pure iron foil, but is strongly attracted by a hand magnet. The measured density of 14.3 g/cm^3 (av. of 2 readings on a Berman balance) is low compared to the calculated density, possibly due to inclusions of genkinite which were observed in polished basal sections.

Since Z=1, the nearest theoretical composition is $PtFe_{0.5}Ni_{0.25}Cu_{0.25}$. The mineral is very closely related to tulameenite in composition and X-ray powder-diffraction pattern. The major differences between X-ray powder-diffraction patterns of tulameenite and this mineral are the absence of the (013) and (113) lines in tulameenite and synthetic Pt_2FeCu (Table 2 in Cabri *et al.* 1973). These two lines, however, are present on the X-ray powder-diffraction patterns of te-

TABLE 1. ELECTRON MICROPROBE ANALYSES OF Pt-Fe-Cu-Ni-Sb ALLOYS

Anal. No.	Weight percent Pt	Pd	Fe	Sb	Ni	Cu	Total	Atomic proportions Pt	Pd	Σ	Fe	Sb	Ni	Cu	Σ
Alloy 1															
1*	77.9	0.06	10.4	1.2	5.9	4.4	99.86	1.04	0.001	1.04	0.49	0.03	0.26	0.18	0.96
4*	77.5	0.09	10.6	1.8	5.9	4.0	99.89	1.04	0.002	1.03	0.49	0.04	0.26	0.16	0.95
5	78.0	0.11	10.5	1.8	5.7	4.0	100.11	1.05	0.003	1.05	0.49	0.04	0.25	0.16	0.94
6	76.0	0.10	9.6	2.7	6.0	5.3	99.70	1.01	0.002	1.01	0.45	0.06	0.26	0.22	0.99
7*	77.4	n.d.	10.4	1.6	5.4	4.5	99.3	1.05	0.00	1.05	0.49	0.03	0.24	0.19	0.95
8	78.1	0.06	10.6	1.5	5.4	4.0	99.66	1.06	0.001	1.06	0.50	0.03	0.24	0.17	0.94
Alloy 2															
2*†	74.9	0.24	6.1	4.5	6.4	6.9	99.04	1.02	0.006	1.03	0.29	0.10	0.29	0.29	0.97
Pt-Fe alloys															
9	84.4	0.10	8.8	1.4	3.9	1.4	100.00	2.50	0.005	2.51	0.91	0.07	0.38	0.13	1.49
10	84.4	0.25	10.3	0.96	2.0	1.2	99.11	2.55	0.01	2.56	1.08	0.05	0.20	0.11	1.44
11**	86.1	0.11	10.3	0.72	1.5	0.96	99.69	2.62	0.006	2.63	1.10	0.03	0.15	0.09	1.37

*Grain X-rayed. ** ferroan platinum. † The atomic proportions are calculated on the basis of Z=1 only for comparison with Alloy 1. Os,Ir,Ru,Rh sought for but not detected.

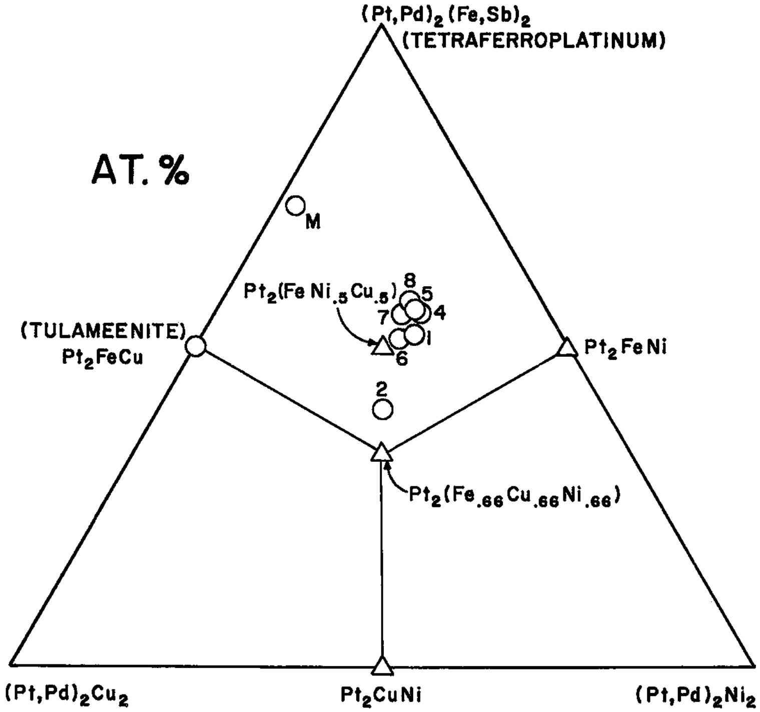


FIG. 3. Diagram showing compositions of Pt-Fe-Ni-Cu-Sb alloys. Formulae shown for tetraferroplatinum are for the doubled contents of the cell. Triangles refer to idealized compositions that are not known to exist in synthetic or natural materials. Numbers 1-8 refer to analyses listed in Table 1. M is the tetraferroplatinum from Mooihoek, Transvaal (Cabri & Feather 1975).

traferroplatinum and synthetic PtFe (Table 5 in Cabri & Feather 1975).

Tetraferroplatinum reported by Cabri & Feather is also plotted in Figure 3. In comparison, the Pt-Fe-Ni-Cu alloy from Onverwacht seems to be a more copper- and nickel-rich variety of tetraferroplatinum. If so, then tetraferroplatinum should be considered to also have a smaller unit cell. Synthetic PtFe and the Mooihoek tetraferroplatinum were re-indexed on the smaller unit cell and gave a 2.724(2), c 3.722(6)Å, and *a* 2.724(6), *c* 3.702(9)Å*, respectively. The tulameenite pattern may also be satisfactorily re-indexed on the smaller unit cell, except possibly for the 0.9433Å *d*-value, but there are no supporting single-crystal data.

The most Cu-rich Pt-alloy analyzed in the sample was considered to be a separate type. However, this grain, whose bulk composition plots near the center of Figure 3, may be a mixture of two or more alloys that cannot be distinguished optically under oil immersion with a 100× objective. Such complications suggest that more detailed work, especially synthetic, needs to be done in the PtFe-PtCu-PtNi system. Further discussion of this mixture is deferred until the component parts are resolved.

Pt-Fe-Cu-Ni alloys — alloy 2

The large Pt-Fe alloy grain (Anal. 9, Table 1) in silicates (Fig. 1) contains another alloy which is grey and has lower reflectivity in polished section. This grey mineral is also weakly to moderately anisotropic and its composition is given in Table 1 as analysis No. 2. Reflectances in air are 470nm 62.2, 61.4; 546nm 61.9, 61.4; 589nm 63.0, 62.4; and 650nm 63.1, 62.6% (mean of 4 meas.). Micro-indentations formed a series of sub-parallel cracks on one side of the imprint, and VHN_{50} was 552 (536-566) for 5 measurements. This alloy has Fe=Cu=Ni in atomic proportions and the relatively high Sb content has been arbitrarily assigned to Fe for plotting purposes in Figure 3.

*Except that the line at 1.068Å, intensity ½, cannot be indexed on the smaller cell and may be extraneous.

TABLE 2. X-RAY POWDER DATA FOR Pt-Fe-Cu-Ni ALLOY 1

I	d_{meas}	hkl	d_{calc}	I	d_{meas}	hkl	d_{calc}
6	3.621	0 0 1	3.644	2	1.224	1 2 0	1.225
4	2.741	0 1 0	2.741	½	1.215	0 0 3	1.215
10	2.188	0 1 1	2.190	9	1.162	1 2 1	1.162
5	1.939	1 1 0	1.938	7	1.110	0 1 3	1.110
7	1.820	0 0 2	1.822	8	1.096	0 2 2	1.095
3B	1.707	1 1 1	1.711	5B	1.029	1 1 3	1.029
4	1.516	0 1 2	1.517	6B	1.017	1 2 2	1.017
5	1.370	0 2 0	1.370	3B	0.9707	2 2 0	0.9691
7	1.327	1 1 2	1.327	1B	0.9383	2 2 1	0.9365
3	1.282	0 2 1	1.282	½	0.9148	0 3 0	0.9137
				5B	0.9106	0 0 4	0.9110

Grain No.1, 114.6mm Gandolfi camera, Co/Fe radiation, λ=1.7889

TABLE 3. X-RAY POWDER DATA FOR Pt-Fe-Cu-Ni ALLOY 2

I	d_{meas}	I	d_{meas}
1	2.754	½	1.518
½	2.446	2	1.347
10	2.212	2	1.328
3	1.953	2	1.168
3	1.931	2	1.153
½	1.812	3	1.101
½	1.718		

Co/Fe radiation, λ=1.7889, 57.3mm Gandolfi camera.

This mineral gives an apparently unique powder pattern which has not been indexed (Table 3). It is not known whether Sb is essential to the structure nor whether the mineral occurs over a range of compositions.

Preservation of the Samples

The remainder of the original hand specimen (No. 1949) is preserved in the Pinch Mineralogical Museum. Polished sections containing alloy 1 are preserved in the U.S. National Museum, Smithsonian Institution, Washington, D.C. (No. 136552) and the Royal Ontario Museum, Toronto (No. M34692).

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