A metallographic and microprobe study of the Brenham pallasite

H. J. AXON AND E. D. YARDLEY

Metallurgy Department, The University, Manchester 13

SUMMARY. A metallographic study has been made of the macroscopic and microscopic features of the Brenham pallasite. The microprobe has been used to investigate the condition of kamacite interfaces with second kamacite grains, olivine, schreibersite, troilite, and taenite and of taenite interfaces with olivine. The results indicate that grain-boundary migration of nickel may be important in these structures.

THE structure of the metallic phase in the Brenham pallasite has recently been reported by Massalski and Park (1964) who conclude that the conditions of cooling in the later stages of the formation of the kamacite–taenite structure were similar to, but probably rather more rapid than, the conditions that applied at the similar stage in the formation of octahedrites. Goldstein and Short (1967), however, have proposed that the metal in Brenham shows a particularly slow cooling rate. Wahl (1965) has discussed the general question of pallasite structures and has proposed that they formed in low-gravitation environments at the centres of parent bodies. The present study was conducted on a slice measuring $10 \times 7 \times 0.7$ cm obtained as specimen 10·184 from Ward's Natural Science Foundation. The specimen was sectioned for microscopic and electron microprobe examination and a sample of metal free from sulphide and phosphide was analysed by wet chemical methods and gave a bulk analysis of 11·18 % nickel, in reasonable agreement with the values of 10·98 % reported by Lovering, Nichiporuk, Chodos, and Brown (1957) and 11·1±0·5 % reported by Wasson and Kimberlin (1967).

Specimens for microscopic examination were polished on $1\,\mu$ diamond paste and etched in 2 % Nital. Microhardness measurements were made with the Reichert microhardness indenter using a load of 30 g. Microprobe analyses for nickel were made with an A.E.I. microprobe analyser S.E.M. 2 using homogenized Fe–Ni calibration alloys. The microprobe analyses of the metallic and phosphide structures were conducted on samples that were polished but not etched. Analyses of silicate and metal–silicate interface structures were conducted on samples coated with a thin conducting layer of aluminium and in these instances the calibration alloys were similarly coated. No silicate or phosphide standards were available so the iron–nickel calibration alloys were used to obtain approximate nickel values for these phases.

The *macrostructure* consisted of rounded crystals of olivine enclosed by a continuous network of nickel–iron and troilite, with smaller amounts of phosphide. Terrestrial corrosion was present at many phase-interfaces and in the present work all

studies of interface compositions were done on carefully selected areas where the amount of corrosion was small.

The olivine occurred chiefly as single rounded forms with vestigal crystal faces, but occasionally clusters of olivine crystals were observed. In any cluster the olivine crystals showed straight edges when they were in contact with each other or were separated by thin layers of troilite, but they presented rounded surfaces of contact to the nickel–iron. The olivine was never observed as angular fragments although it was often cracked and the cracks were usually penetrated by troilite veins. Under polarized light the olivine crystals appeared perfect apart from the cracking. The olivine is the hardest phase in the Brenham structure and microprobe point analyses of aluminium-coated specimens showed that it was free of nickel and homogeneous with respect to iron and it contained approximately 8 % iron by weight.

The olivine was embedded in a complete network of 'nickel–iron plus troilite' but the metal was found chiefly in the larger volumes between olivine crystals and the network was completed by troilite, which occupied the smaller volumes and filled the cracks in the structure. The over-all macrostructure is thus consistent with an original aggregate of solid silicate and molten sulphide, which was later penetrated by an injection of molten metal, which displaced sulphide from the larger intersilicate volumes but was not able to penetrate the smaller veins and cracks. Of course, it is not necessary that the structure was actually produced by this mechanism and the controlling factor may be the relative surface energies at the metal, sulphide, and silicate interfaces.

Microstructure. The nickel–iron when etched in 2 % Nital revealed kamacite, taenite, and plessite, but, by contrast with octahedrites of similar nickel content, the bulk of the kamacite in Brenham occurs as a contour band around the olivine and troilite, presumably because these interfaces acted as nucleation sites for the solid state γ to α transformation. However, two variants of this general pattern were observed: firstly, within the largest metal areas the kamacite formed an incomplete Widmanstätten band structure as a form of comb plessite, and secondly, a nickel-rich taenite layer occasionally came into immediate contact with the olivine without the intervention of kamacite. This taenite–olivine juxtaposition will be considered in detail later.

The study of interface relationships on the chunky, non-lamellar structures of pallasites is less easy than in octahedrites, where it is possible to determine the dip of the interface below the surface of section; spurious results can easily arise if the interface dips at a very small angle. However, this situation is revealed by a rapid change in the position of the interface as the surface of section is polished away, and this test was employed to eliminate such cases from the present work.

The kamacite, when etched, showed sub-grain boundaries and unaltered Neumann lines; it was the softest phase present but microhardness values were variable and there was usually a decrease in the microhardness of kamacite in the vicinity of olivine or massive phosphide bodies.

In Brenham the amount of comb plessite is small and the kamacite usually occurs as a contour band around the olivine. Thus the most characteristic position for taenite

is as a rim separating the kamacite from the plessite fields. In this position taenite showed a maximum nickel content of about 45 % in contact with kamacite with a steep concentration gradient inward toward the plessite. Within any one field the high-nickel taenite graded through a range of fine acicular, martensitic plessites to coarse spindle-like or globular forms of plessite. Microhardness values were also variable in taenite but usually reached a maximum away from the kamacite–taenite interface, apparently at the visibly acicular, martensitic region of plessite. The taenite itself sometimes showed a dark etching rim and when, occasionally, cracks were present they ran through the darkened taenite rather than through the martensitic portion of the plessite.

The phosphide in Brenham was encountered in three forms: as rhabdites, as massive bodies of schreibersite, and as small irregular schreibersite bodies. The rhabdites were distributed non-uniformly within the kamacite and ranged in size from $4 \times 4 \times 25 \mu$ downward. The massive schreibersite bodies, which in general were harder, more extensively cracked, and contained less nickel than the smaller ones, occurred at the silicate or troilite interfaces. The smaller phosphides were always observed within the metal, either wholly within the kamacite or at kamacite–taenite interfaces. Of these latter phosphide bodies some appear to have been still in the process of formation at the interface while others apparently formed at an earlier interface position and were left behind as the kamacite–taenite interface moved. Reed (1965) has indicated that phosphorus tends to concentrate in the kamacite while nickel concentrates in taenite, and the precipitation of phosphide may be assisted by this juxtaposition of elements. However, the phosphorus content of kamacite is small and the growth of interface precipitates of phosphide may be further assisted by the enhanced diffusion of the constituent elements along the region of disorder at the moving kamacite–taenite interface.

The aspects of structure that have been considered so far could usually be studied without the intervention of terrestrial corrosion. However, the troilite was heavily infested with corrosion product and, in particular, the kamacite–troilite interfaces were so heavily contaminated that only one example was found in a condition suitable for study. Corrosion was often encountered at kamacite–olivine interfaces but microprobe investigation showed that this corrosion vein could contain appreciable quantities of sulphur and, moreover, occasional fragments of unaltered troilite were encountered, so that it is possible that the original structure involved a layer of troilite between the olivine and the kamacite. Troilite certainly tended to occupy the narrower spaces in the structure but it was found also as nodules in contact with olivine and projecting into the metal. The microhardness of this troilite was about the same as the hardest taenite but it was heavily cracked and sometimes showed twins when examined in polarized light. Pentlandite was present in some of the larger areas of cracked and corroded troilite as an unambiguous secondary alteration product and small quantities of metallic copper were also encountered at one place in a heavily altered area of troilite. It is possible that the copper also was formed as a secondary alteration product of copper-bearing sulphides, but from the material available in the present study it is not possible to be certain about this.

Microprobe analyses. It has already been noted that the olivine of Brenham is free from nickel and is homogeneous with respect to iron content. However, neither the kamacite nor the taenite is homogeneous with respect to nickel. The nickel content of
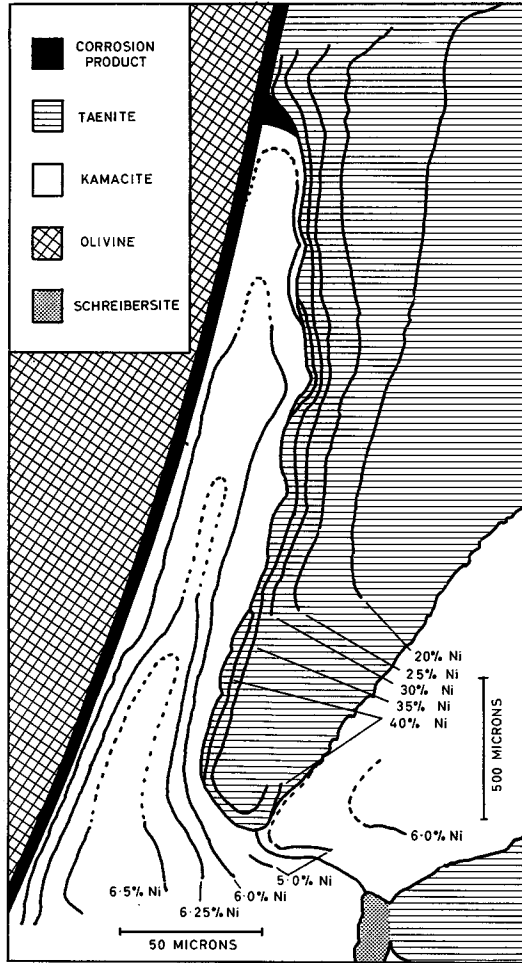

FIG. 1. Contours of Ni content near various inter-phase boundaries in the Brenham pallasite.

kamacite at locations well away from phase interfaces appears to reach a maximum value approaching 7 % but the nickel content of the kamacite decreases where it comes into contact with olivine, massive schreibersite, or troilite. A smaller decrease of nickel content is encountered where kamacite comes into contact with taenite.

There appears to be a significant decrease of nickel content at the grain boundary between two kamacite grains, particularly when the high nickel phases taenite and schreibersite are present further along the boundary as is shown in fig. 1.

Results of interface nickel contents measured by microprobe traces are collected in table I. Kamacite–taenite values are for uncorroded interfaces. In other instances a small amount of corrosion product is present; a maximum thickness of 4μ corrosion product was accepted in the present work and only one kamacite–troilite interface fulfilled this requirement.

In one field of view examples of olivine–taenite, olivine–kamacite, kamacite–taenite, and kamacite–kamacite interfaces were all encountered together without extensive corrosion and detailed microprobe point analyses within this area have been used to plot contour lines of nickel content on the microstructure in the way shown in fig. 1.

TABLE I. *Nickel contents of the metal in the Brenham pallasite measured by the micro-probe method. Col. 1 Bulk nickel content of the kamacite. Col. 2 Nickel content at the interface with olivine (Ol); troilite (Tro); taenite (Tae); or massive schreibersite (Sch) at which the kamacite had nucleated. Col. 3 Interface depletion of nickel. Col. 4 The maximum content of nickel in the second phase in contact with kamacite or, last line, olivine. Col. 5 Width of the depleted zone in μ*

1 Ni % bulk	2 Ni % at interface with	3 Ni %	4 Ni % in second phase	5 Width μ	1 Ni % bulk	2 Ni % at interface with	3 Ni %	4 Ni % in second phase	5 Width μ
6·6	Ol 4·2	2·4	—	150	6·3	Tae 5·2	1·1	42*	50
6·7	Ol 4·1	2·6	—	150	6·9	Tae 5·7	1·2	39	50
6·3	Sch 3·8	2·5	38	~150	6·5	Tae 5·3	1·2	47†	50
6·8	Sch 3·3	3·5	35	~150	6·4	Tae 5·3	1·1	46	50
6·6	Sch 4·2	2·4	38	~150	6·8	Tae 5·8	1·0	44	50
6·5	Sch 4·2	2·3	39	~150	6·7	Tae 5·4	1·3	39	50
6·5	Sch 3·8	2·7	40	~150	olivine	—	—	42*	—
6·4	Tro 4·1	2·3	—	150					

* In plessite 17 % Ni.   † In plessite 16 % Ni.

Discussion. The recent work of Wood (1964), Goldstein and Ogilvie (1964), and Goldstein (1965) has produced a good understanding of the way in which plates of Widmanstätten kamacite form in octahedrites. According to these workers the kamacite nucleates when the parent γ is undercooled to the extent of about 100 °C. The first, high-temperature, crop of kamacite is relatively poor in nickel and on further cooling more nickel-rich kamacite grows at the expense of taenite by the lattice diffusion of iron and nickel perpendicularly across the plane interface. Goldstein (1965) has shown how the variation of nickel content within the kamacite and at kamacite–taenite interfaces may be related to the binary iron–nickel equilibrium diagram.

However, in the pallasites the distribution and mode of growth of the kamacite is controlled by the distribution of olivine within the structure. Thus, in the pallasites, the kamacite nucleates at the olivine interface with probably less undercooling than would be required of Widmanstätten kamacite. The primary contour bands of kamacite in pallasites are thus analogous to the swathing kamacite that is found around sulphide and other inclusions in octahedrites.

From table I it may be seen that kamacite in contact with olivine has an apparent nickel content of about 4 %, and essentially similar values are encountered at interfaces where kamacite comes into contact with massive schreibersite and also, perhaps, with troilite. The value of 4 % nickel corresponds approximately to the kamacite that would first form from a parent γ of 11·2 % nickel in the absence of undercooling and provided that the binary iron–nickel equilibrium diagram is applicable. The situation is in fact complicated by the presence of phosphorus in the system and, furthermore, in each case in Brenham the curve of nickel content with distance is steeply convex to the non-metallic surface, whereas, by analogy with Goldstein's observations on the octahedrites, a flat concave relationship would be expected if the effect were entirely due to the incomplete homogenization of the successive crops of kamacite. Furthermore, it is very surprising to find kamacite of essentially the same nickel content in contact with the olivine, which contains no nickel, and the schreibersite, which is rich in nickel. The shape of the nickel concentration curve suggests that nickel has diffused, from the kamacite, equally into both the olivine and the massive schreibersite, but, in view of the absence of nickel in the olivine, it is more probable that the movement of nickel has taken place not by diffusion through the lattices but by migration along the olivine–metal interface towards the schreibersite. A similar grain-boundary diffusion of nickel along the kamacite–kamacite interfaces is suggested to explain the observations of fig. 1.

The presence of high-nickel zoned taenite in contact with silicates has been noted in chondrites by Wood (1967), who suggested the possibility of nickel diffusion through the solid silicate lattice. However, the alternative possibility exists of nickel diffusing along the metal–silicate interface to build up the high nickel content in the taenite. The plot of nickel concentration in the kamacite of fig. 1 is entirely consistent with such a phase boundary diffusion process. Unfortunately in the present work the situation is complicated by the presence of small amounts of terrestrial corrosion at the metal–silicate interface, but it would be worth while to investigate any similar area encountered in a pallasite that was free of corrosion.

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