METALLURGY

Destruction of the Widmanstatten Structure in Iron Meteorites by Laboratory Heat Treatment

A KNOWLEDGE of the response of iron meteorites to heat treatment is necessary for the understanding of such specimens as Kamkas[1] which appear to have suffered partial destruction of their Widmanstatten structures by cosmic heat treatment. Kasé[2] has published evidence to show that for the medium octahedrite Sacramento Mountains the nickel-rich tænite is still clearly visible after a heat treatment of 20 min at 1,000° C or 3 min at 1,200° C. Even after 4 min at 1,300° C there remains a faint trace of nickel enrichment which marks the previous location of a tænite area.

In the work recorded here more lengthy heat treatments were conducted on small ($0.5 \times 0.5 \times 1.0$ cm) fragments taken from a specimen of Canyon Diablo which is known to contain cohenite. In each case duplicate specimens were sealed in evacuated silica capsules which were heated to the maximum temperature over a period of three days and afterwards cooled to room temperature over three days. The period of holding at maximum temperature was 2 days at 1,000° C and 3 days at 1,100° C or 1,180° C. Experiments with specimens of this size do not correctly reproduce the conditions in a massive meteorite since at 1,100° C and 1,180° C it was found that all the schreibersite melted to eutectic and exuded along the original kamacite phase boundaries to produce a layer of phosphide-rich liquid on the outer surface of the specimens. At 1,000° C exudation was incomplete and the resolidification of liquid veins within the specimen produced structures similar to that illustrated by Perry[3]. With increasing temperature the phosphide eutectic, which had left the solid by way of grain boundaries in the original structure, showed an increased tendency to re-enter the solid by way of the new γ-grain boundaries which were formed by heat treatment of the kamacite. Macro- and micro-scopic observations were made on etched sections at locations away from the regions of grain boundary penetration. Macroscopic examination of the etched sections with the aid of a hand-lens revealed the recognizable remains of tænite ribbons after all heat treatments. Microscopic examination showed that the original kamacite regions had changed to a duplex arrangement of ragged ferrite and small carbide crystals. It was possible to detect the boundaries of the γ-grains from which the ferrite-carbide aggregate formed on cooling. The microstructure of the tænite regions showed a greater variation with heat treatment temperature. After the 1,000° C heat treatment the tænite still maintained a distinct boundary and was at no place crossed by the new generation of γ-grain boundaries; suggesting that the tænite had maintained its complete integrity at the heat treatment temperature. The tænite itself was characterized by a fine precipitate of non-metallics at the centre and an indistinct acicular structure at the edge.

After the 1,100° C heat treatment the tænite boundary was less sharp and was demarked by acicular (bainitic) transformation product. No precipitate was observed within the tænite and the presence of new generation γ-grain boundaries within the tænite was rare.

The 1,180° C heat treatment resulted in a coarse pattern of acicular transformation product within which the pattern of new generation γ-grain boundaries was continuous with that in the kamacite, indicating that at 1,180° C the tænite had lost its physical identity as a separate crystal but had retained a sufficiently different chemical composition to reveal itself by the production of acicular transformation product on cooling.

Less detailed examination of carbide-free specimens heated to 1,000° C and 1,100° C revealed a 'watery' appearance in the tænite without acicular transformation

product. The acicular product may thus be tentatively identified as a carbon containing bainite.

H. J. AXON

Department of Metallurgy,
University of Manchester.

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Topography of Kish Crystals and the Effect of Oxidation in Air

DETAILED studies have been reported recently on the production of etch pits in purified Ticonderoga natural graphite crystals as a result of oxidation in oxygen in the temperature range 700°–870° C[1,2]. Others have also been concerned with the effect of oxidation on the topography of natural graphite[3-6]. In this communication, the effect of oxidation on the topography of purified kish crystals is considered.

Kish is a waste product which forms on the surface of molten iron of high carbon content during the manufacture of steel. It is carbon which has been taken into solid solution with the iron and is afterwards evolved when the iron cools. Kish particles are large and flaky, resembling large particles of natural graphite. Walker and Imperial[7] have previously shown that purified kish has the same interlayer spacing as Ceylon natural graphite, indicative that it has a large crystallite size and essentially complete three-dimensional ordering.

The kish used in this investigation was purified by boiling alternately in hydrochloric acid and hydrofluoric acid (or in some cases just boiling in hydrochloric acid), followed by repeated washings in distilled water, and drying in a vacuum oven. Its structure has been further studied by transmission electron diffraction, using 50-kV electrons having a beam width of 10μ. The diffraction pattern (Fig. 1) is characteristic of a material of large crystallite size and a high degree of preferred crystallite orientation (essentially a mosaic single crystal).

The basal plane (000l) surfaces of the kish were studied by light microscopy. Typical micrographs of the unoxidized kish are shown in Figs. 2 and 3. In Fig. 2, the twin planes are readily distinguished as the striations running parallel to one another or intersecting at 60° (ref. 8). The presence of impurities on the basal plane, following treatment with hydrochloric acid only, is clearly in evidence. On a very significant portion of the surface, large hexag-
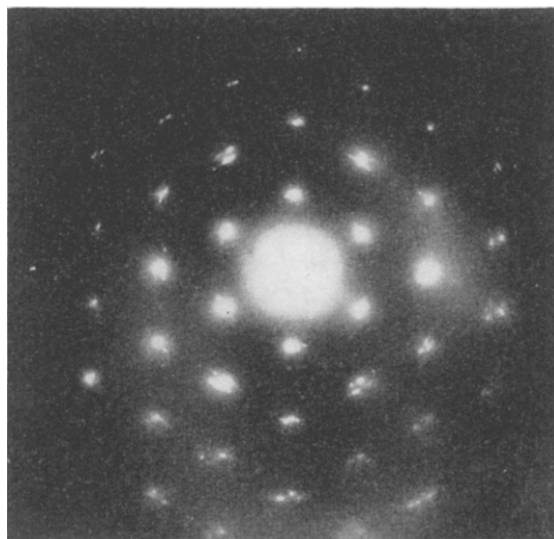

Fig. 1.   Transmission electron diffraction pattern of purified kish

Fig. 2. Basal plane (000*l*) surface of kish purified in hydrochloric acid. Twin bands run parallel or intersect at 60°. (× *c*. 200)

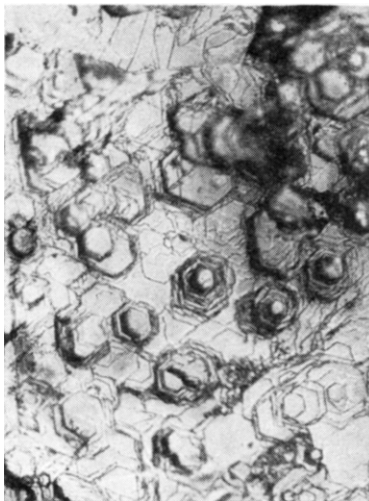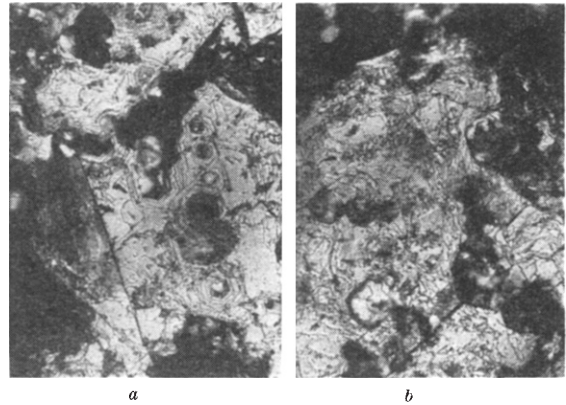Fig. 3. Basal plane surface of purified kish showing large hexagonal stepped growth features. (× *c*. 200)

Fig. 4. Development of hexagonal pits upon air oxidation of purified kish at 850° C. (× *c*. 200)

Figs. 5*a* and *b*. Coalescence of pits during a more advanced stage of air oxidation of kish purified in hydrochloric acid at 850° C. (× *c*. 150)
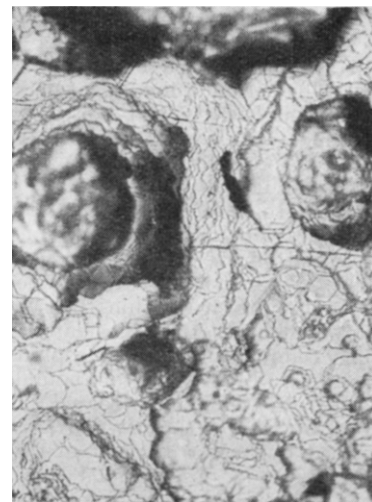

Fig. 6. Roughly hexagonal holes produced by rapid attack of air at 850° C on hexagonal stepped growths of purified kish. (× *c*. 200)

onal stepped growth features are in evidence (Fig. 3). It is suggested that the growth steps within these features arise from a piling-up of a large number of clockwise and counterclockwise spiral growth steps of molecular dimensions[9,10] (the spirals being invisible on our photographs). A substantial concentration of impurity nucleating centres from which such screw dislocations and spiral growth of graphite could occur might well be expected, considering the origin of kish.

Kish crystals were oxidized in air (1 atm.) at 850° C. Fig. 4 shows the development of a large number of hexagonal pits oriented parallel to each other and parallel to the twin lines, as previously discussed[1]. Figs. 5*a* and *b* show the results of coalescence of pits during a more advanced stage of oxidation. The shapes of the holes are reminiscent of those suggested by Ubbelohde, when considering defects in graphite[11].

In general, it is found that the large, hexagonal stepped growths are attacked at an enhanced rate. Fig. 6 shows the result of exposure of such growths to air at 850° C for only about 5 min. Large, roughly hexagonal holes are produced, in contrast to the relatively minor attack on other portions of the surface. However, it is not possible to decide on the basis of this result whether the presence of dislocations or the possible concentration of impurities at dislocations is of primary importance in the production of pits in the basal plane. As discussed previously[2], uncertainty will remain until oxidation studies are carried out on ultra-high purity graphite of known dislocation content.

P. L. WALKER, JUN.
B. C. BANERJEE

Fuel Technology Department,
The Pennsylvania State University,
University Park, Pennsylvania.

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CHEMISTRY

Reaction of Platinum and Boron under Pressure

DURING some high-temperature–high-pressure experiments involving boron, a new phase appeared in the X-ray diffraction patterns of the samples. This phase was traced to the reaction of boron and the platinum foil used to encapsulate the sample between the chromo carbide pistons of a Griggs and Kennedy simple squeezer[1]. Since platinum foil is a standard technique of sample enclosure for this type of experiment, it was decided to investigate the $P-T$ phase diagram of this reaction so that it would not cause difficulty when encountered again.

At about the time this work was finished two papers came to our attention bearing on this problem and have prompted us to publish our results. The first was a paper by Jamieson and Lawson[2] in which they referred to the formation of a new phase from boron at 600° C and
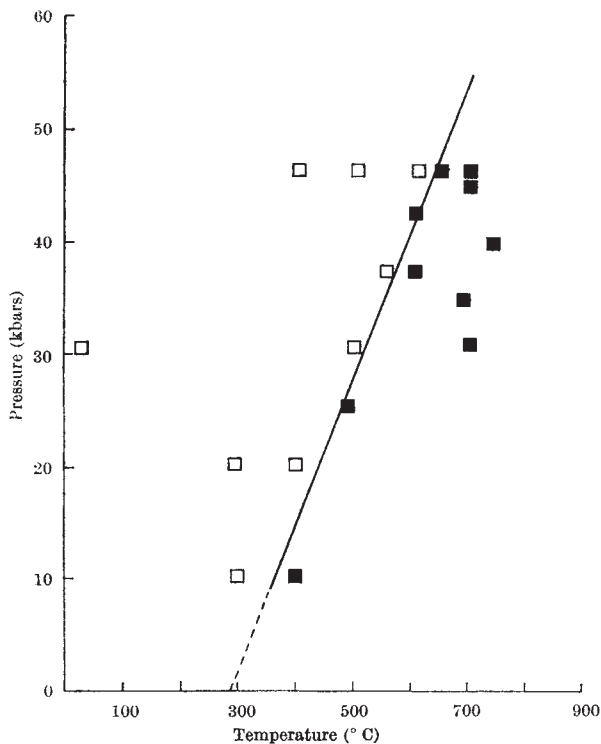

Fig. 1. Phase diagram for the reaction B + Pt→PtB. White squares indicate no reaction; black squares indicate the formation of platinum boride

Table 1. COMPARISON OF X-RAY DATA FOR PLATINUM BORIDE

h k l	Aronsson d	Aronsson I	Jamieson d	Jamieson I	Whitney and Giese d	Whitney and Giese I	d, calc.
100	2·903	st	2·896	st	2·906	6	2·908
101	2·360	v st	2·364	v st	2·370	10	2·364
002	2·025	m	2·041	m	2·049	2	2·029
102	1·663	st }	1·671	st	1·675	8 {	1·664
110	1·676	st }					1·679
200	1·453	w	1·450	w	1·451	1	1·454
201	1·368	st	1·367	st	1·367	5	1·369
112	1·291	st+	1·293	st+	1·296	6	1·294
103	1·225	m+	1·232	m+	1·234	4	1·227
202	1·180	m	1·182	m	1·184	1	1·182
210			1·097	v w	1·096	1/2	1·099
211			1·063	m	1·059	4	1·061
203			0·9940	w	0·9928	2	0·9904
212					0·9661	2	0·9665
302					0·8735	4	0·8747
213					0·8540	4	0·8530
220					0·8373	1/2	0·8395
303					0·7889	3	0·7879

40 kilobars (kb). No mention was made of platinum and, in reply to a letter of ours, Prof. Jamieson confirmed our suspicion that platinum foil was in contact with the boron. He was also kind enough to send us X-ray photographs of his samples. It will be seen that this new phase lies just to the right of the boundary between boron and platinum and platinum boride (Fig. 1).

A recent paper by Aronsson *et al.*[3] has allowed us to identify the platinum boride as PtB (space group $P\bar{6}_3/mmc$, $a = 3·36$ Å, $c = 4·06$ Å), and to confirm the identity of Jamieson's material with our platinum boride. There are a few weak X-ray diffraction lines not due to PtB which can be attributed to B_2O_3 and the original boron.

The slope of the curve shown in Fig. 1 was found to have a value of $dP/dT = 133$ bars degree^{-1}. It is of interest to note that Strong and Bundy[4] found the value of dP/dT for the melting point of platinum to be 140 bars degree^{-1}.

The X-ray diffraction results are listed in Table 1. We are grateful to Prof. Jamieson for permission to examine his films and publish the results.

E. DOW WHITNEY
ROSSMAN F. GIESE, JUN.

Basic Research Branch,
The Carborundum Co.,
Niagara Falls, New York.

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Electrical Storage and Hydrogen Transfer between Electrodes of Palladium and Palladium Alloys

ELECTRODES of palladium and palladium alloys can absorb large volumes of hydrogen. In general, the solid hydrides retain excellent electrical conductivity and are not severely embrittled or disrupted. For pure palladium, and for many alloys, the relationships between electrode potential E (with respect to a hydrogen reference electrode in the same solution) and hydrogen content (written here. Fig. 1, as the ratio, H/Me, of hydrogen atoms to the total number of metal atoms) exhibit 'plateau' regions—over which α- and β-phase hydrides co-exist—where E is relatively invariant ($E_{\alpha,\beta}$). Over such 'plateau' regions, hydrogen transfer should, in principle, occur at a constant rate when connexion is made between an alloy and palladium or between two alloys. However, polarization[1] would be expected to occur rapidly if the diffusion of hydrogen within the electrodes were not sufficiently fast for the concentration of hydrogen at the surfaces to be continuously representative of the ranges of H/Me corresponding to the plateaux. The following experiments serve to illustrate what may be observed in practice.

The $E - $H/Me relationships, at 25° C, for palladium and two selected alloys[1-3] are shown in Fig. 1, where full lines indicate relationships which apply when hydrogen