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Electron microanalysis of metallic meteorites

Part 1—Phosphides and sulfides

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Abstract—The composition of phosphide and sulphide precipitates in the Canyon Diablo, Breccia and Grant meteorites were examined with the electron microanalyzer. The phosphides had a composition of 15.5 wt% P, between 20 and 46 wt% Ni, 0.1 wt% Co with Fe as the remaining constituent. The sulfide precipitates had a composition of stoichiometric FeS with no solubility for Ni. The regions of swathing kamacite around the phosphide particles had a Ni depletion of from 0.5 to 2 wt%.

Excluding the massive phosphides, which are unrelated to the kamacite structure, it is concluded that the schreibersite nucleated within the supersaturated kamacite in the temperature range from 700 to 500°C while rhabdite formed between 500 and 400°C. The variation in the composition of the phosphides is due to the limited diffusion of Ni from kamacite to the phosphide at lower temperatures.

The very large troilite particles are formed directly from the molten state. However, sulfides also precipitate from the solid state below the eutectic temperature and grow with the rejection of both iron and nickel into the region surrounding the particle, called swathing kamacite.

I. INTRODUCTION

METEORIC structures have fascinated investigators since the early 1800's and a large number of studies have been conducted to determine their composition, structure, and the thermal history by which they formed. The purpose of this study was to determine the composition of meteoric phosphides and sulfides and from such data, to establish the method by which these structures might have formed.

The determination of the chemical composition of these minerals has unfortunately been hampered to date because the chemical techniques used required a relatively large amount of material for analysis. With the advent of the electron microanalyzer, it is now possible to determine with a high degree of accuracy not only the average particle composition but also compositional variations within the individual particles.

It has been demonstrated (CASTAING, 1952) that the electron microanalyzer can measure the composition of an extremely small volume of material. Essentially the technique employs an electron optical system that focuses an electron beam on the surface of the specimen to be examined. The size of the irradiated area is of the order of 1 μ in diameter. The depth of penetration of the electrons is of the same order of magnitude so that the X-ray spectrum which results originates from a few millionths of a microgram of material. The subsequent analysis of the X-ray spectrum allows one to determine the chemical composition for elements in the periodic table from sodium through uranium.

Since the introduction of this instrument, several studies have been published

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on the compositions of the metallic phases in meteorites (WITTRY, 1957; YAVNEL *et al.* 1958; MARINGER *et al.* 1959; FELLER-KNIEMAYER and UHLIG, 1961). However, only a very limited amount of work has been published on the composition of metallic phosphides (ADLER and DWORNIK, 1961) and no systematic studies on sulfides have been made using the electron microanalyzer.

II. PHOSPHIDES AND SULFIDES

A. Phosphides

Phosphorus is usually found segregated into a mineral known as schreibersite. This mineral is a phosphide of iron, nickel, and cobalt whose stoichiometric composition corresponds to the formula $(\text{Fe-Ni-Co})_3\text{P}$. In general the composition of the mineral fluctuates between the following limits; iron from 50 to 70 wt.%, nickel from 35 to 16 wt.%, phosphorus from 15.5 to 16 wt% and cobalt less than 1 wt.%. Another form of phosphide with the same stoichiometric composition, called rhabdite, is also very abundant. It exists as minute inclusions, observed in cross section in the form of squares or rhombi, scattered through the main mass of a meteorite.

The formation of schreibersite has been discussed by only a few investigators (HENDERSON and PERRY, 1958; Vogel, 1958). It has been suggested (HENDERSON and PERRY, 1958) that the phosphide existed as essentially an iron phosphide (Fe_3P) at high temperatures. That is, they suggest that after the iron-nickel alloy has solidified, the phosphide which is still in the liquid state, contains much less than 15 wt. % Ni. As the metallic meteorite continues to cool, the phosphide solidifies. After solidification, nickel from the γ phase diffuses into the phosphide replacing the iron which in turn migrates to the zone surrounding the phosphide. This nickel poor zone would be in the γ phase at high temperatures and would transform to α (swathing kamacite) at lower temperatures.

The ternary phase diagram of Fe-Ni-P (Vogel and BAUR, 1931) can be used as a guide in order to explain the formation of schreibersite and rhabdite in meteorites. The two incongruently melting compounds Fe_3P and Ni_3P have complete solid solubility in one another which explains how it is possible to have a varying Ni content in $(\text{Fe-Ni})_3\text{P}$.

It was shown (VOGEL, 1958) that in alloys having the same Fe, Ni, and P contents as found in hexahedrites, rhabdite needles are precipitated from solid solution below 500°C. Therefore rhabdite must have formed by a precipitation reaction and not from the molten state. Two possible methods for the formation of schreibersite were suggested by VOGEL, cooling from the melt and solid state precipitation. Several meteorite samples were heated above the eutectic temperature (1050°C) then cooled rapidly (VOGEL, 1958). The resulting eutectic structure of the schreibersite is quite similar to the structure of phosphides found in the reheated zones of meteorites. Meteorite samples were also heated to temperatures below the eutectic (900 to 700°C) and the schreibersite precipitates completely dissolved. This indicates that schreibersite probably formed by precipitation in the parent body of the meteorite. The formation of the swathing kamacite zone around the phosphide was not discussed.

It will be shown that both rhabdite and schreibersite form by precipitation in

the solid state and that the size and composition of the resulting phosphides is dependent on the nucleating temperature and the time available for the growth of these precipitates. It should also be noted that massive phosphides which show no apparent relation to the Widmanstätten pattern in octahedrites, must form directly from the liquid state.

B. Sulfides

Sulfur is found segregated into a mineral called troilite, a monosulfide of iron, its stoichiometric composition corresponding to the formula FeS. The inclusions are usually in irregular rounded forms and can reach large dimensions. Very often troilite is enclosed by a layer of schreibersite or by a region of swathing kamacite. Occasionally troilite is observed as scattered plates of lamellae with a definite cubic orientation unrelated to the octahedral pattern. These particles are called Reichenbach lamellae.

It was suggested (HENDERSON and PERRY, 1958) that molten FeS is immiscible in liquid Fe-Ni and that it would segregate from the metallic Fe-Ni as the meteorite solidifies. At a temperature of about 1000°C, the liquid FeS solidifies and forms a troilite precipitate which has no orientation relationship to the Fe-Ni matrix.

Another investigator (Vogel, 1958) also believes that troilite forms from the liquid state. The Fe-Ni solid solution forms first as the meteorite cooled from the liquid state and the remaining liquid forms a eutectic structure at about 975°C which is surrounded by solid solution Fe-Ni. The sulfide homogenizes upon cooling and assumes the rounded forms usually seen in the final structure.

As will be shown later, troilite forms not only from the melt but also by solid state precipitation. These precipitates form at a temperature above the nucleation temperature of the phosphides. As the temperature decreases, these precipitates grow because of the decreasing solubility of sulfur in the kamacite phase.

III. EXPERIMENTAL

A. Electron microanalyzer

The details and construction of various electron microanalyzers are readily available in the literature (CASTAING, 1952; WITTRY, 1957; BIRKS and BROOKS, 1957; MACRES, 1958; MULVEY, 1959; PETERSON, 1961), and will not be discussed here. The Fe, Ni, and Co radiation was measured by a North American Phillips proportional counter using a bent LiF crystal and the P and S radiation was analyzed using a bent mica crystal and a North American Phillips flow proportional counter. A helium path from exit port to counter was used to reduce the absorption of the soft X-rays.

B. Specimens and specimen preparation

Three meteorites were used in the investigation; the Grant, Canyon Diablo, and Breece. The compositions of these meteorites are given in Table 1. Each meteorite was mounted in a one-inch bakelite mount along with small pieces of pure Co, Fe and Ni which were used as standards. The sulfur standard was a sulfide of stoichiometric FeS₂ (pyrite) and the phosphorus standard was a hard brittle phosphide of stoichiometric MnP.