The Influence of Phosphorus on the $\gamma \rightarrow \alpha + \gamma$-Transformation in Metallic Meteorites with Special Reference to the Plessite Formation*

By

G. Dörfler

From the Analytical Institute of the University of Vienna

With 12 Figures

(Received March 23, 1967)

Die Bildung von Plessit, einer innigen Mischung von α- und γ-Phasen in metallischen Meteoriten, wird auf der Grundlage der neuen Theorie von *Massalski* und Mitarb. betrachtet. Auch wenn man diese Theorie akzeptiert, kann sie die Unterschiede in der Korngröße, welche im Plessitfeld vorhanden sind, nicht erklären. Durch quantitative metallographische Untersuchungen mittels der Elektronen-Mikrosonde und durch theoretische Berechnungen (aus experimentellen metallurgischen Befunden) wird gezeigt, daß der P- und C-Gehalt den normalen $\gamma \rightarrow \alpha + \gamma$-Übergang so stark beeinflußt, daß in allen Diskussionen des Ni/Fe-Diagramms der analytische Ni-Gehalt durch einen $[\mathrm{Ni}]_{\mathrm{eff}}$-Wert zu ersetzen ist, welcher den Einfluß der Ni-, P- und C-Konzentration enthält.

The formation of plessite, an intimate mixture of α- and γ-phases in metallic meteorites, is discussed in the light of the new theory of *Massalski* et al. (1966). Accepting this theory in general, it is shown that the differences of the grain size of the plessite-fields present need an explanation, which cannot be given by this model. By quantitative metallographic work, using an electron microprobe analyzer, and by theoretical calculations, based on metallurgical experiments, it can be shown that phosphorus and carbon exert a very great influence on the normal $\gamma \rightarrow \alpha + \gamma$ transformation in meteorites. This means, that for all considerations based on the Fe/Ni-diagram, the chemically analyzed Ni-content should be replaced by a $[\mathrm{Ni}]_{\mathrm{eff}}$-value, which can be calculated from the Ni-, P-, and C-concentrations.

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* This paper has been dedicated to Professor Dr. *Friedrich Wessely* on the occasion of his 70th anniversary.

1. Introduction

The *Widmanstätten* structure, appearing in most metallic meteorites, has been the subject of several extensive papers (*Wood* 1964, *Goldstein* 1964). Recently also a discussion of several possible mechanisms which can cause the formation of plessite—a mixture of α- and γ-phase, created by decomposition of the supersaturated γ-phase—has been published (*Massalski* et al. 1966).

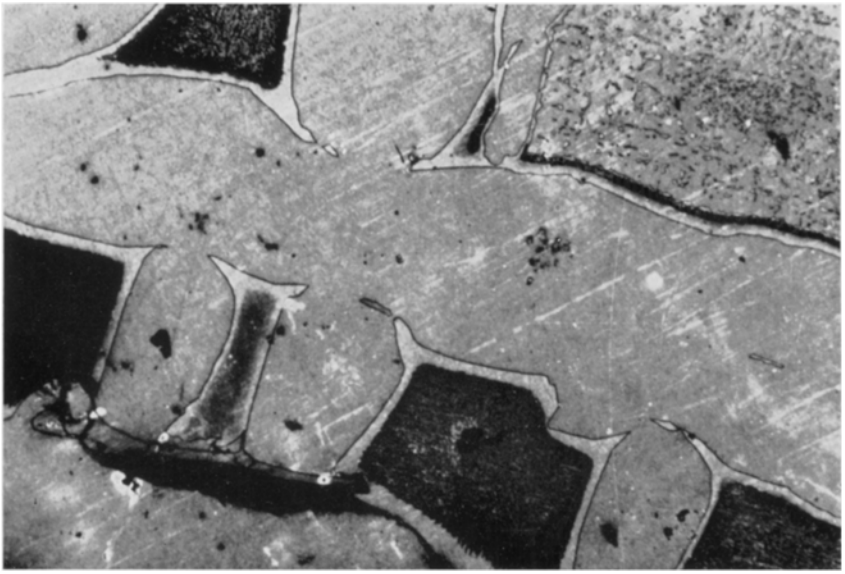

Fig. 1. Plessite-fields of different type in Siderophyte STEINBACH (250 ×)

These so-called plessite regions of iron- and stony-iron meteorites always consist of a mixture of α- and γ-phase, their grain size ranging from several microns (e.g. up to appr. 20 μm in the Toluca meteorite) to a sub-microscopically fine pattern. A typical arrangement of plessite-regions of various texture is shown in Fig. 1.

Massalski et al. (1966) point out that the formation of these different types of plessite is caused by at least three mechanisms which partly compete with and partly supplement each other. While cooling from a temperature at which the whole metallic meteorite is in the f.c.c. (face centered cubic) state (γ-phase) to lower temperatures, where the duplex field is reached, the normal *Widmanstätten* pattern appears by the growth of α-phase b.c.c. (body centered cubic) along the (111)-planes of the taenite (γ-phase). The Ni/Fe-equilibrium diagram, which describes this process, is given in Fig. 2. The remaining taenite-lamellae subsequently

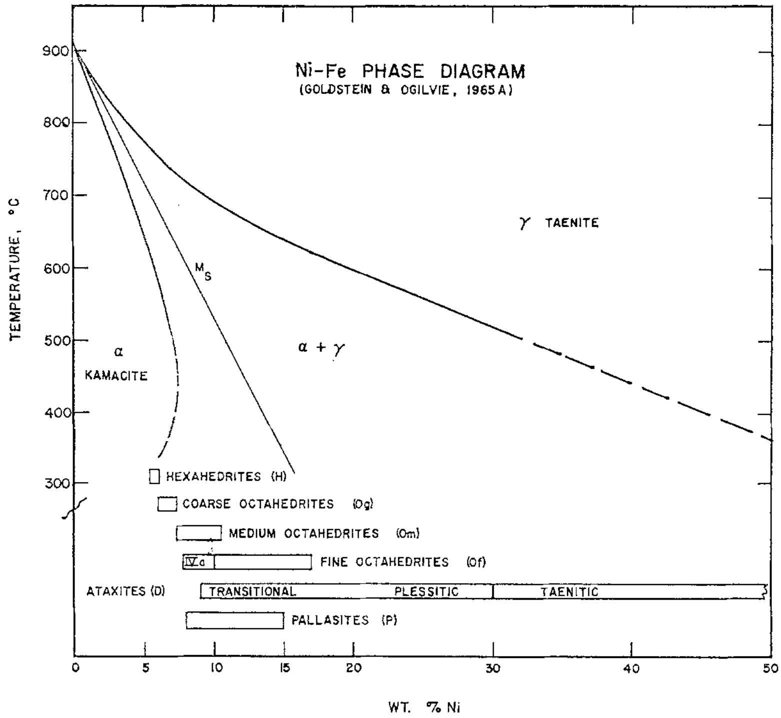

Fig. 2. Ni-Fe Phase Diagram (*Goldstein* 1966)

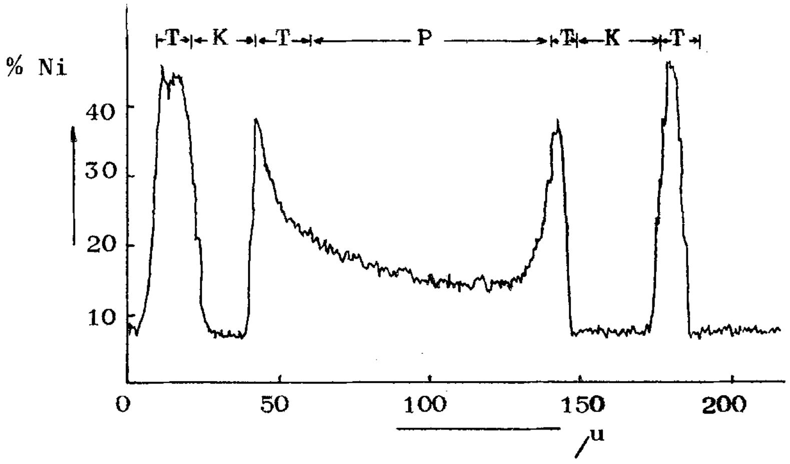

Fig. 3. Ni-concentration diagram across the *Widmanstätten* pattern shown in Fig. 7 (T = taenite: K = kamacite; P = plessite)

become inhomogeneous because the solid-state diffusion in the γ-phase cannot be maintained down to very low temperatures (appr. 400° C) so

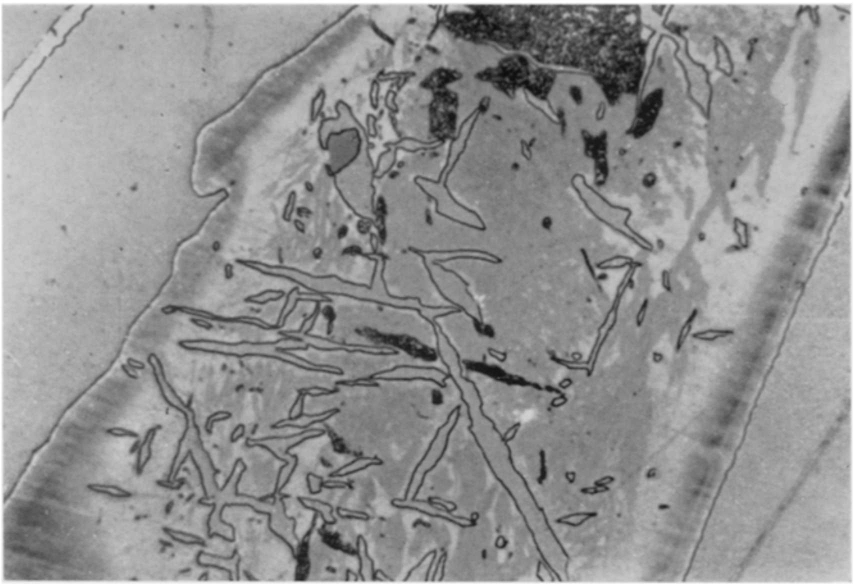

Fig. 4. Type-I-plessite of the meteorite TOLUCA (500 ×)

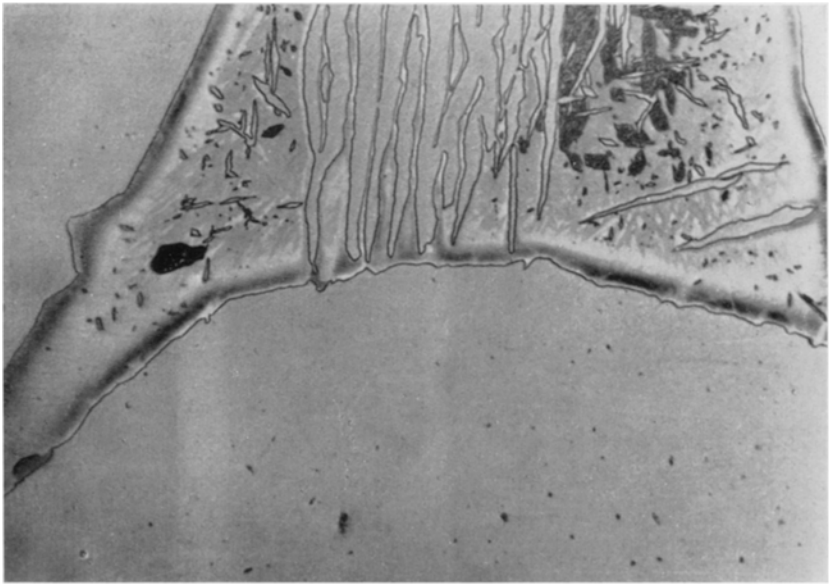

Fig. 5. Type-I-plessite of the meteorite TOLUCA (250 ×)

that equilibrium conditions only exist at the α/γ-grain boundaries. These facts cause a Ni-concentration gradient across a taenite-lamella as shown

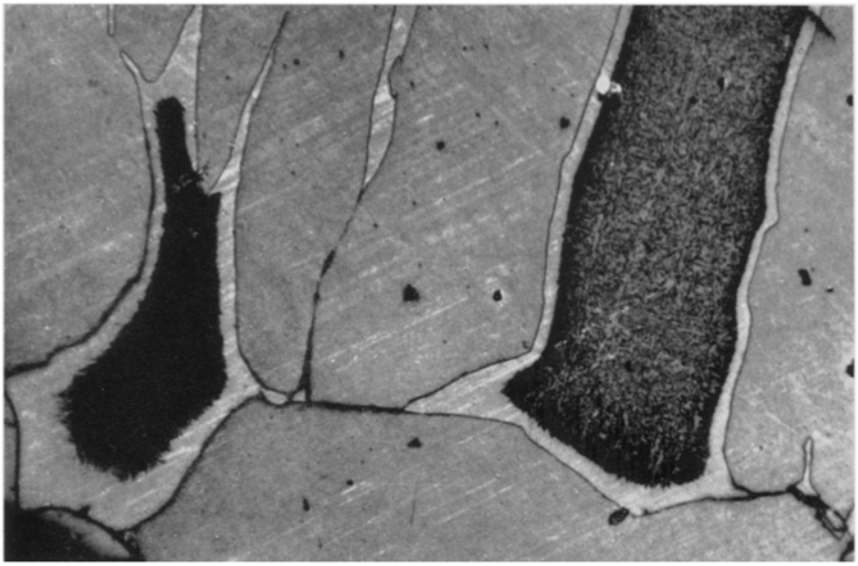

Fig. 6. Two plessite-fields of different grain-size in the meteorite STEINBACH (250 ×)

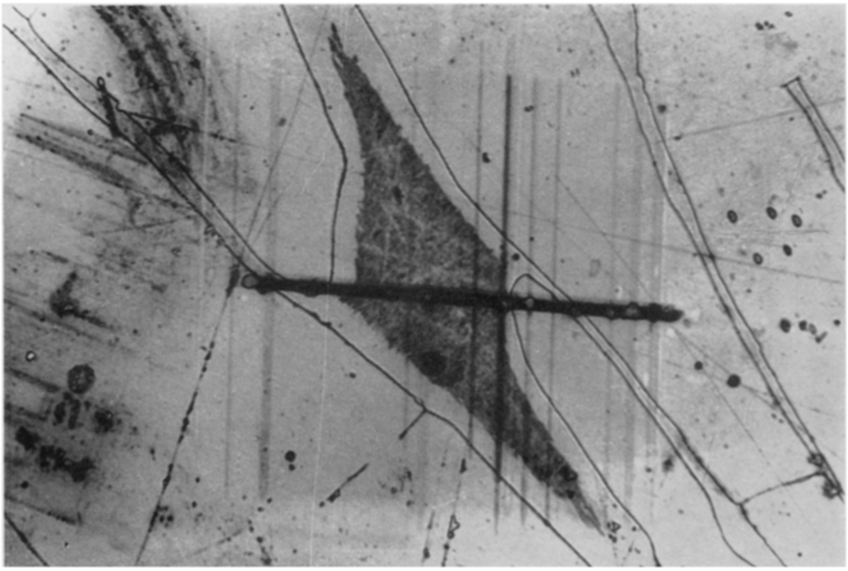

Fig. 7. Type-II-plessite in the meteorite STEINBACH (250 ×)

in Fig. 3—the typical, so called "M-profile". If these γ-bands are large enough (appr. more than 10 μm) their nonequilibrium state causes a decomposition into plessite. How this can be accomplished is suggested by *Massalski* et al. (1966) as follows:

"Type-I-plessite"

This "normal" plessite is formed by the $\gamma \rightarrow \alpha + \gamma$ reaction mentioned earlier. The reaction mechanism implies a crystallographic relationship between the γ-matrix and the α-precipitates. The α-particles are embedded in a single-crystal matrix of the taenite.

Examples are shown in Figs. 1, 4, 5, 6. The coarseness of this plessite depends on the temperature of its formation.

"Type-II-plessite"

Besides the normal decomposition as it occurs by the formation of type-I-plessite, the possibility of a martensitic transformation ($\gamma \rightarrow \alpha_2$) also exists. The resulting α_2-phase will have the same composition as the taenite-region from which it has been formed.

An example is given in Fig. 7.

"Type-III-plessite"

If the M_s-temperature (temperature of martensite formation) is sufficiently high (above 350° C) the reaction $\alpha_2 \rightarrow \alpha + \gamma$ will take place. Due to the fact that the martensitic phase is b.c.c. and strained, the diffusion rates are probably several hundred times faster than in the taenite-phase from which the α_2-phase was formed. The arrangement of the α- and γ-particles should be distinctly different from type-I- and type-II-plessite, because the $\alpha_2 \rightarrow \alpha + \gamma$ process is an eutectoid reaction.

The type-I-plessite, as well as the type-III-plessite, can undergo recrystallization and therefore coarsening, so that a distinction is not very easy (Fig. 8).

These are the probable mechanisms of plessite formation as pointed out by *Massalski*, et al. (1966). This theory seems very well to explain the occurring plessite structures. However, there remains a question, which has been previously pointed out by several authors. In most iron- and stony-iron meteorites, plessite-fields occur which are approximately of the same size but of very different grain-size. Since the distances between these structures are sometimes only some tens of microns as can be seen in Figs. 1, 8, different cooling-rates cannot be involved. Also a possible recrystallization of type-I- or type-II-plessite should have led to approximately the same grain-size in all these fields.

A further factor which can strongly influence the reaction and has received very little consideration up to now, is the influence of the minor constituents in metallic meteorites, especially of phosphides $(Fe, Ni)_3P$ and carbides (Fe_3C). In the majority of the recent papers it has been pointed out, that these minerals form only a very small portion of the metallic meteorite, and also that all theories on the formation of the *Widmanstätten* pattern and of the plessite structures make use of only the Fe—Ni diagram (Fig. 2) for their interpretation.

The present paper tries to show that this point of view seems to be an oversimplification and it has been attempted to find a correlation between the structure of the plessite and the amount of phosphide present in the encountered plessite-fields. It should be pointed out, that all conclusions which can be drawn, refer to the normal $\gamma \to \alpha + \gamma$ transformation, i.e. to the type-I-plessite.

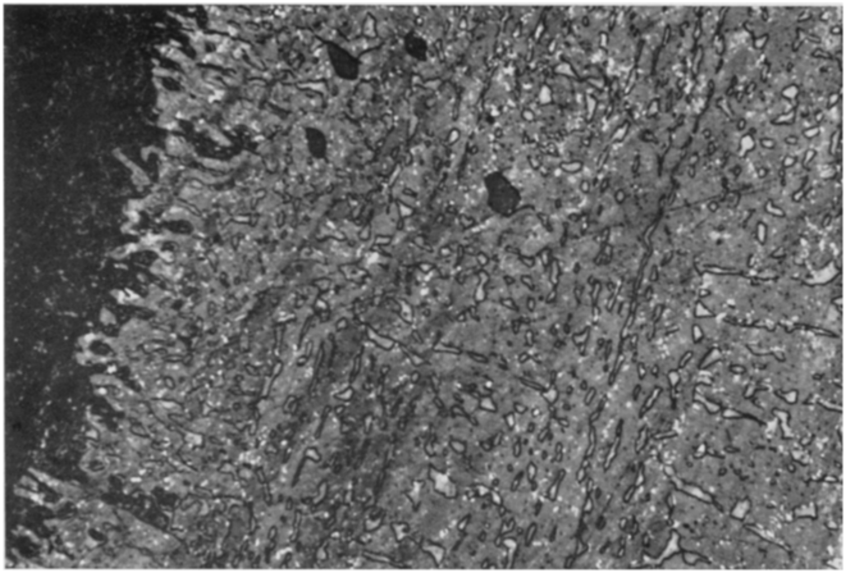

Fig. 8. Interior of a large plessite field. Mixture of dense (type II?) and coarse (recrystallized?) plessite (660 ×)

In order to determine these correlations it is necessary to measure as accurately as possible the amounts of the kamacite- (α), taenite- (γ) and schreibersite- (= phosphide) phase, respectively. For this purpose a new apparatus, working in combination with the electron-microprobe has been used.

2. Stereometric techniques (quantitative metallography)

The phase-integrator, which is a new instrument for stereometric work and which has been described in detail elsewhere (*Dörfler,* 1965), uses characteristic signals of an electron-microprobe-analyzer (especially the number of characteristic X-ray quanta per unit time) to detect the selected phases.

The working-principle of the "*phase-integrator*" is shown in Fig. 9. Setting the X-ray-spectrometers of the microprobe for the appropriate element, the line-scan across two different phases in a matrix (Fig. 9 a) yields a concentration diagram as given in Fig. 9 b. The rate-meter-voltage can be easily discriminated by electronic means, which results in the selection of one phase (Fig. 9 c). This discriminated voltage, which

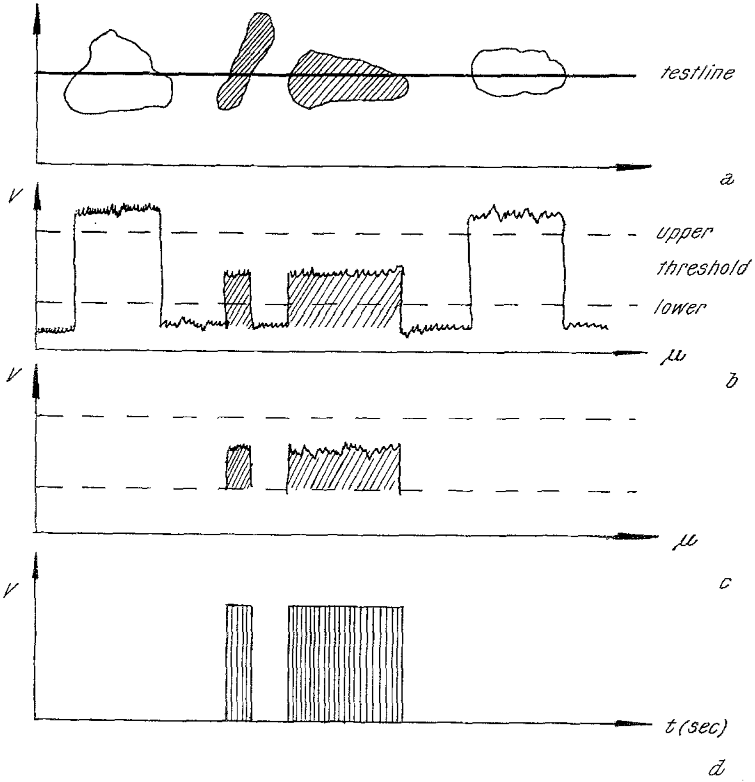

Fig. 9. Working principle of the phase-integrator

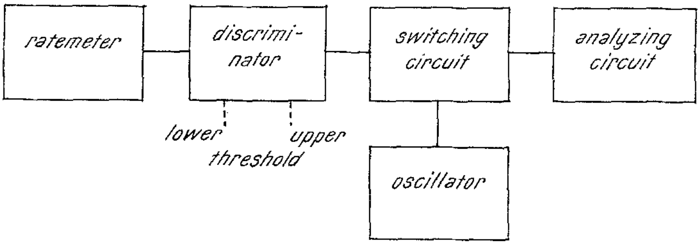

Fig. 10. Schematic diagram of the phase-integrator

corresponds to a certain concentration range of a characteristic element, opens a switching circuit through which pulses of uniform frequency can pass to a counting unit. The passage of these pulses is stopped, when the voltage at the exit of the switching circuit becomes zero (Fig. 9 d). The pulse groups coming to the counting unit, represent the intercepts of the phase encountered. The basic arrangement of the "*phase integrator*" (*PI*) is given in Fig. 10.

It is apparent, that the pulse-groups, representing the intercept-lengths, can be used to calculate all known parameters of stereology; i.e. volume-fractions, specific surface areas, and the mean diameter of a phase etc. Moreover, several units such as depicted in Fig. 10 can be operated simultanously to measure all phases present, as well as to define one phase by the presence of two elements.

The α-phase can therefore be easily selected by its Ni-content below 8%, the γ-phase by a Ni-content over 10% (or another value if required) and the phosphide by the presence of phosphorus.

The use of the microprobe has several advantages compared to the normal metallographic techniques. First of all it is known that phosphides have nearly the same appearance as carbides, and therefore, errors are easily possible. Secondly, the recognition of phosphides in dense plessite by light-microscopy is extremely difficult. Finally, the use of an automatic measuring device is very convenient and garantees accurate results.

3. Experimental Results and Discussion

The first indication of a possible influence of the phosphorus content on the grain size of plessite was given by *Axon* (1962). He found schreibersite inclusions in coarse plessite regions of the Mbosi-meteorite. *Axon* pointed out that the presence of phosphorus shifts the $\gamma/\alpha + \gamma$-phase boundary of the Ni/Fe-diagram to higher temperatures and causes in this way an earlier precipitation of the α-phase, which coarsens on the subsequent cooling. However, he was not able to explain the observed effect quantitatively.

Some recent papers [*Goldstein* and *Ogilvie* (1964); *Reed* (1965)] which were concerned with growth-mechanism of phosphides used the Fe—N—P phase diagram, which was established by *Vogel* and *Bauer* in 1931, although it was pointed out that all conclusions drawn from this diagram can only have a qualitative nature.

However, there are some papers which show the influence of phosphorus on the position of the $\gamma/\alpha + \gamma$-phase-boundary (A_3-point), measured by dilatometry in steel- and pure iron samples (*Roques* et al., 1956; *Roquet* 1951). The results of these measurements are shown in Fig. 11. It can be seen that the influence of phosphorus is exactly the same on pure iron as well as on steel, i.e. the raising of the A_3-temperature. The lower

A_3-temperatures of the steel-samples can be explained by the influence of carbon and nickel. Since it does not seem that nickel influences the general relationship (dependence of A_3-temperature on the P-content), it is assumed that increasing the Ni-content only decreases the A_3-temperature, which can be estimated from the Ni/Fe-diagram (Fig. 2). These estimated values are also shown in Fig. 11 (dotted lines), and demonstrate the relationship for two alloys (or plessite-fields) with average Ni-contents of 10% and 15% respectively.

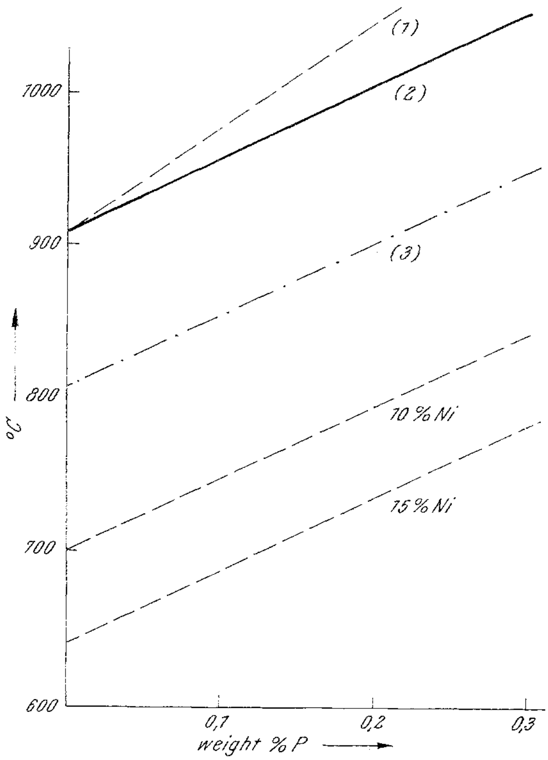

Fig. 11. Influence of phosphorus on the $\gamma \to \alpha + \gamma$ transformation

(1) = *Vogel* and *Bauer* (1931)
(2) = *P. Roquet* et al. (1951)
(3) = *C. Roques* et al. (1957)

This influence can be interpreted as follows: The addition of phosphorus acts in the same way as if the structure contained less nickel. According to the lever-rule, more α-phase will be precipitated. In addition to this, the reaction starts earlier and therefore causes a coarser structure. There must be a clear relationship between the γ/α-ratio and the phosphide content of a certain plessite field, all given in volume- or weight-fractions. For the theoretical calculation of the $\gamma/\alpha + \gamma$ vs. P-curve the lowest equilibrium temperature for the formation of the *Widmanstätten* pattern was assumed to be 500° C. The dashed line in Fig. 12 shows the calculated relationship. It was computed for an average Ni-content of 15% in the encountered plessite-field. The curve starts with the theoretical $\gamma/\alpha + \gamma$-value of a 15% Ni-alloy. An addition of a certain amount of phosphorus gives a higher A_3-temperature, thus representing a hypothetical alloy with a lower Ni-content. This corrected Ni-value could be designated as $[\mathrm{Ni}]_{\mathrm{effective}}$. For this $[\mathrm{Ni}]_{\mathrm{eff}}$ the new $\gamma/\alpha + \gamma$ ratio can be calculated from the Fe/N-diagram (Fig. 2).

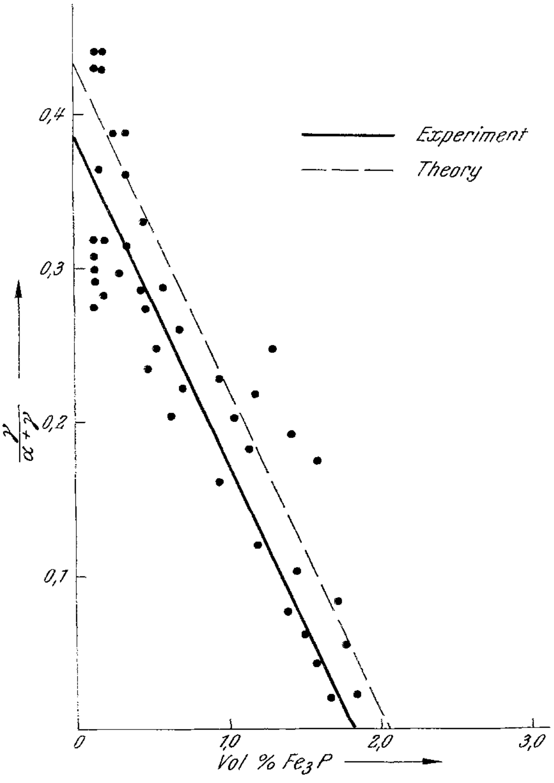

Fig. 12. Relationship between the $\gamma/\alpha + \gamma$-ratio and the amount of phosphides present in a plessite field

Using the phase integrator, 40 measurements of the α-, γ-, and phosphide-fractions of several regions in the meteorites Toluca and Steinbach have been made. The values obtained are given in Fig. 12.

It is apparent that there is a clear correlation between the $\gamma/\alpha + \gamma$ ratio and the phosphide content of a certain plessite-field. The dependence seems to be exactly the same as that of the theoretically calculated curve, the parallel shift only being caused by the assumed average Ni-content of the hypothetical alloy.

Conclusions

From the experimental results it can be concluded that the formation of type-I-plessite is strongly influenced by the presence of phosphorus. The phosphorus being in solid-solution at the time of the α-precipitation causes this reaction to start at higher temperatures. This results in a considerable change of the γ/α-ratio and in the coarsening of the kamacite grains. The temperature of the first nucleation of the α-phase can be changed by the P-content as much as 50—100° C. If one bears in mind that the meteorite Toluca cooled with a rate of $1.6^\circ/10^6$ years (*Goldstein* and *Short,* 1966), this means that the α-phase had several million years to coarsen. This effect was further enhanced by the fact that the Fe/Ni-interdiffusion coefficient varies approximately by a factor of 100 for a temperature change of 100° C (*Goldstein* and *Ogilvie,* 1965). It can therefore be explained, why the different plessite-fields in the same meteorite can have such different grain size.

The volume-fraction of the second minor constituent of metallic meteorites, cohenite (Fe_3C), which can also exact a strong influence on the $\gamma \rightarrow \alpha + \gamma$ reaction, has not been measured. Its influence on the kamacite-nucleation must be approximately the same as that of the phosphorus. Measurements on Fe—C-alloys and steels are well known in literature. Carbon lowers the A_3-temperature and therefore shows the opposite effects than does phosphorus.

The best way to compute the effective "activity" of the Ni present, while influenced by P and C, is perhaps the definition of a $[Ni]_{eff}$-value as it has been done in this paper for the calculation of the P-influence on the $\gamma/\alpha + \gamma$ ratio.

Since all these conclusions have been drawn for the normal $\gamma \rightarrow \alpha + \gamma$ reaction, which does not only control the type-I-plessite formation, but the formation of the *Widmanstätten* pattern as a whole, these relationships should also be applicable to the growth mechanism of this structure. Concerning the computer programs of *Goldstein* and *Short* (1966) and of *Wood* (1964), this means that the chemically analyzed bulk Ni-content should be corrected by the factors involved by P and C to give $[Ni]_{eff}$.

It should be kept in mind that these elements were in solid solution when the first precipitation of kamazite plates took place and therefore they strongly influenced this precipitation. A more detailed account of these problems will be given in a later paper.

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The research reported in this document has been sponsored
by the

United States Government

under Contract 61 (052)-948