A. D. Romig Jr. and J. I. Goldstein, Eds., *Microbeam Analysis-1984*

ANALYTICAL ELECTRON MICROSCOPY OF EARLY STEEL FROM THE BACQAH VALLEY, JORDAN

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The presence of a needle-like precipitate within ferrite grains of archaeological iron and steel specimens has been taken as paradigm that these precipitates are nitrides, [1-3] and the pickup of nitrogen is then accepted as strong evidence that the object has been heated in contact with an ammonia-bearing fuel such as animal dung. Because the solubility of nitrogen in iron is small ($\leq$ 0.1 wt%), very few of the bulk chemical analyses presented in these studies[1-3] demonstrate direct chemical evidence for the presence of nitrogen.

In a recent paper on early iron from Thailand,[5] the authors identified such needle-like precipitates as iron carbide (or *possibly* nitride) formed during quench-aging. Further investigation in the recent metallurgical literature reveals that this needle-form precipitate is indeed typical of quench-aged carbides; this finding brings into doubt the previous attributions of this precipitate form as nitrides in the archaeological literature. Direct microanalytical study could be important in determining whether this precipitate form is due to the presence of carbides, or nitrides, as this factor ultimately bears on the interpretation given archaeological artifacts in terms of their fabrication history. We have therefore reexamined an iron object (Sample I55)[6] from the Bacqah Valley, Jordan, which contains these needle-like precipitates and which we have previously attributed to be nitrides.

The microstructure of Sample I55 corresponds to that of a hypoeutectoid steel and is composed of pearlite, ferrite, and precipitated phases(s) of broadly varying size in the proeutectoid ferrite and in the ferritic component region of the pearlite (Fig. 1). The overall morphology is typical of that observed in a cast or seriously overheated condition. Most of the pearlite appears lamellar, but in some regions of the pearlite colonies, the cementite is spheroidized. The ferrite appears with variable morphology: massive ferrite (Fig. 1), network ferrite around prior austenite grain boundaries, and ferritic Widmanstatten plates, which appear to be the predominant form within the structure (Fig. 2). There are also three different categories of precipitated phase: small needles (Fig. 3), larger needles or plates (Fig. 1), and a more massive or blocky form which sometimes appears along prior grain boundaries (Fig. 4). The majority of the present study was concerned with the small needle-type precipitates in the ferrite.

Specimens were ion-thinned or electropolished and were examined in a Philips EM400T electron microscope at 100 kV. Bright-field (Fig. 5) and dark-field images, and selected area diffraction patterns typical of the small precipitates (Fig. 6) in the ferrite matrix were obtained. From the diffraction pattern, the orientation relation between ferrite and precipitate was determined to be

$$(001)_{\alpha} \| (125)_{p} \qquad [010]_{\alpha} \| [131]_{p} \qquad [100]_{\alpha} \| [311]_{p}$$

This orientation relationship does not match any of the published relationships for nitrides in ferrite, and is also different from the orientation relationship determined by Pitsch and Schrader[7] for cementite precipitates in ferrite. Nor is the relationship consistent with that given by Pitsch[8] for cementite and ferrite in pearlite, but it is similar in that the indices given by Pitsch for errite are found for the precipitate and vice versa. We are trying to resolve this apparent inconsistency at present.

Electron diffraction patterns were also obtained from the pearlite areas (Fig. 7), and the relation between cementite and ferrite in pearlite was determined as:

$$(100)_{c} \| (011)_{\alpha} \qquad [010]_{c} \| [211]_{\alpha} \qquad [0011]_{c} \| [111]_{\alpha}$$

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FIG. 1.--SEM image showing pearlitic and proeutectoid ferrite with large and small needle-like precipitates.

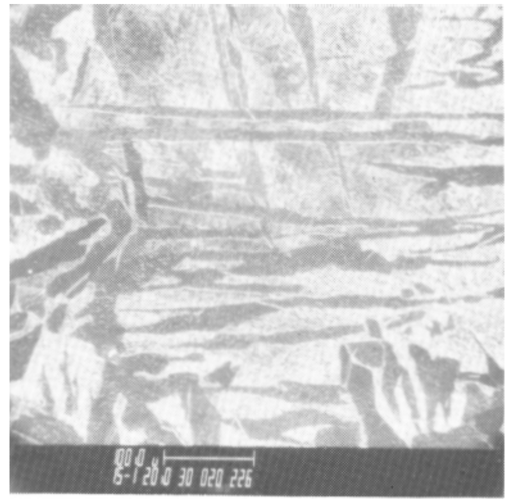

FIG. 2.--SEM image showing Widmanstatten ferrite.

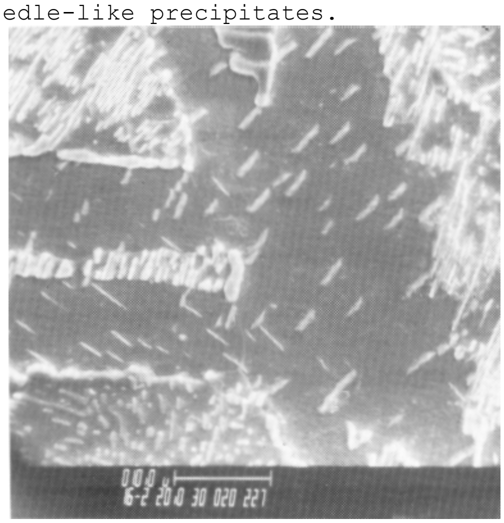

FIG. 3.--SEM image showing small needle-like precipitates in Widmanstatten ferrite and in pearlite regions.

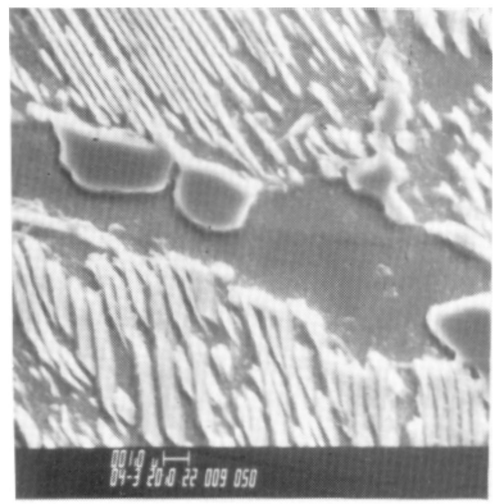

FIG. 4.--SEM image showing blocky or massive carbides.

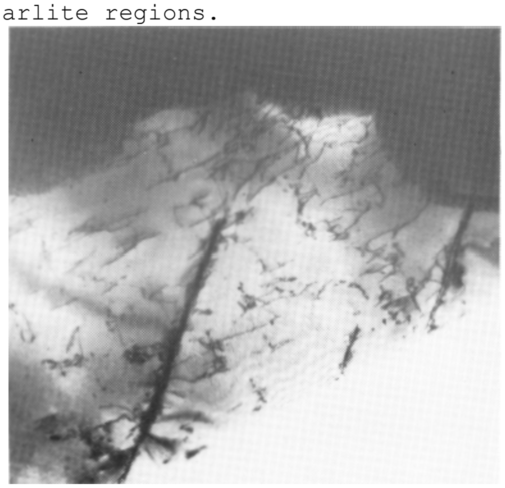

FIG. 5.--Bright-field TEM image of small needle-like precipitates in ferrite matrix.

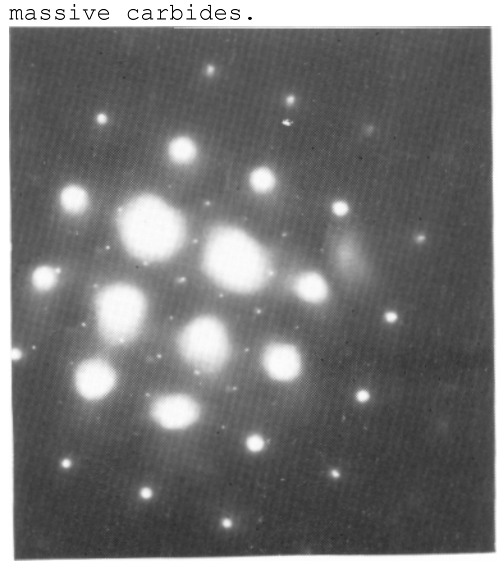

FIG. 6.--Selected area diffraction pattern of region from Fig. 5.

This present result, obtained in a hypoeutectoid steel, coincides with that given by Bagaryatskii[8] but obtained on a hypereutectoid steel.

Electron energy loss spectra for these precipitates were obtained by means of a GATAN Electron Energy Loss Spectrometer attached to the Philips EM400T. In all, seven or eight spectra were obtained from precipitates of different sizes and shapes. The results were similar and a typical spectrum obtained from one single precipitate is shown in Fig. 8; there is a carbon loss peak in the region of 286 eV, but no evidence for the presence of nitrogen was found.

Last, and in cognizance of its insensitivity to small volume fractions of a second phase below about 1%, x-ray diffraction spectra were obtained on a Philips APD3600; all peaks prove to be from metallic iron and cementite and no evidence for the presence of nitrides was found

Within the range of our observations--from microstructural studies, from electron diffraction study to determine crystallographic relationships, and from direct microanalytical examination using EELS--all evidence indicates the needle-like precipitates to be carbides. Based on the microstructure of the steel, it appears that during cooling from the austenitic region the specimen underwent a Widmanstatten transformation under relatively large undercooling conditions, i.e., roughly estimated to be an undercooling of about 200 C. The ferrite that formed (both proeutectoid and within the pearlite structure) is therefore supersaturated with respect to carbon. Following the Widmanstatten transformation, the carbide precipitation process intervenes not only in the Widmanstatten ferrite but also in the ferritic portion of the pearlite structure.

It therefore appears that microstructural studies alone are not sufficient to identify the precipitate and that microanalytical techniques open a new scale of examination that can be helpful in the interpretation of the fabrication history of archaeological artifacts.

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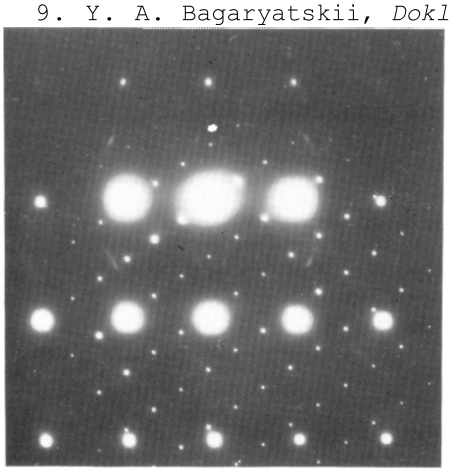

FIG. 7.--Selected area diffraction pattern free from pearlite region.

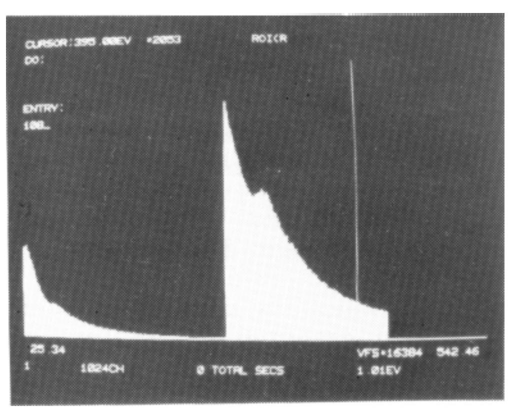

FIG. 8.--EELS spectra obtained from small needle-like preciptate