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DETECTION OF IRON CARBIDE STRUCTURE IN THE OXIDE REMAINS OF ANCIENT STEEL

BY R. KNOX

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INTRODUCTION

The poor oxidation resistance of iron and steel hinders efforts of archaeologists to date the beginnings of iron smelting and the discovery of the "steeling" process that may have marked the opening of the Iron Age. Many ancient iron objects that have been brought to light appear to consist entirely of oxide. In such cases metallographic methods of study would seem to be incapable of determining the structure and composition of the original metal. That this is not necessarily true was shown when the oxide remains of an iron weapon from Hasanlu, Iran were recently examined metallographically.

The corrosion products of severely weathered iron meteorites sometimes contain recognizable traces of the original metallic structure (Buddhue, 1957); it is, therefore, reasonable to suppose that oxides produced by rusting of steel artifacts might also harbour relics of the original microstructure of the steel. Pearlite is a common constituent of steel which might plausibly be expected to leave traces or pseudomorphs of its microstructure in oxide. Pearlite has a fine lamellar structure and is found in all carbon steels that have been cooled in air from above approximately 725°C. It consists of alternate parallel plates of iron and iron carbide (cementite) which are visible microscopically on a polished and etched surface. The percentage of microstructural area, exclusive of nonmetallic inclusions, occupied by pearlite varies from zero in iron with less than 0.04% carbon to 100 when the carbon content is about 0.80% (eutectoid composition). If the carbon is higher, nodules or networks of "free cementite" appear in the microstructure in addition to the cementite bound up in the pearlite. One should therefore search for traces of these "free cementite" structures and/or those of pearlite in attempting to identify completely oxidized artifacts suspected to have been made of steel. It should be noted, however, that steels quenched in water from somewhat above 725°C have a very different, extremely hard and brittle microstructure called martensite, in which most, if not all, of the carbide is retained in solid solution and therefore microscopically invisible unless the steel has been tempered by reheating to several hundred degrees centigrade (a treatment that produces high mechanical strength). Because of its chemical homogeneity, in contrast to the heterogeneity of the much softer pearlite, it seems unlikely that martensite could leave structural relics in its oxide remains, although any carbide nodules left undissolved in the matrix before quenching might do so, in which case they, too, would be visible.

With these thoughts in mind, the remains of a steel (or iron) bladed bronze dagger (University Museum Cat. No. 60-20-185) found in the ruins of the sacked town of Hasanlu, Iran, which was excavated in 1959 (Dyson, 1960), were examined. Radiocarbon dating of material from the site indicates that the dagger dates from about 800 B.C. (Stuckenrath, 1963). The microscopic investigation was included in the programme of the Applied Science Centre for Archaeology of the University Museum.

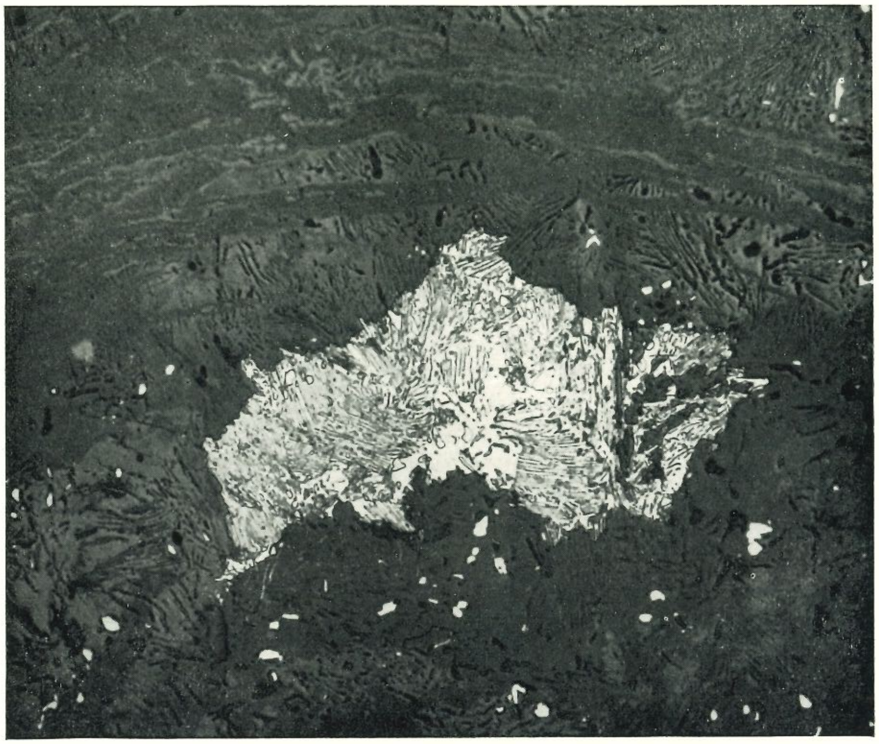

FIG. 1. Hasanlu Dagger Magnification: 500x

Pearlite and nodular carbide in iron, surrounded by pseudomorphic pearlite and carbides in matrix of iron oxide.

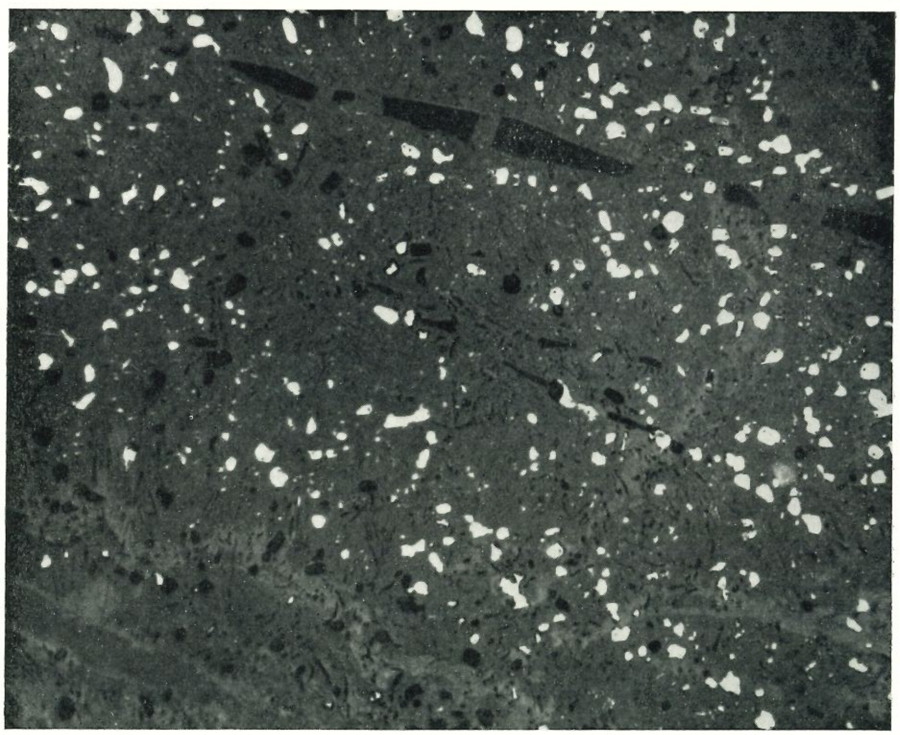

FIG. 2. Hasanlu Dagger Magnification 500x

The white particles are unaltered iron carbide; the black material consists of the carbonaceous residue of corroded carbide and some stringers of slag.

TECHNIQUE

What remained of the Hasanlu blade consisted of a hard, dark grey, highly magnetic mass of oxide with a lenticular cross section and a deep longitudinal furrow-like crack; the latter was probably produced by volume change during corrosion. A specimen section was cut transversely from the blade with a diamond impregnated cutting wheel, mounted and polished.

Microscopic examination of the polished oxide in reflected light revealed a few irregular particles of surviving metal (Fig. 1) approximately 150 microns long, and numerous white nodules (Fig. 2) a few microns in diameter. Present also in the microstructure of the oxide were many black nodules of the same size and shape as the white ones, a few nodules which were partly black and partly white, a dark fine lamellar constituent, and some elongated slag particles.

Etching in a 2% solution of nitric acid in alcohol (Nital) revealed pearlite and nodular carbides within the metal particles (Fig. 1). It is evident from the carbide structure in the metal that the white nodules in the surrounding oxide are simply particles of nodular carbide which have survived the rusting process, while the dark nodules are relics or pseudomorphs of carbides which have been reduced by corrosion to a dark carbonaceous material—probably an intimate mixture of oxide and amorphous carbon. Similarly, the lamellar structure in the oxide is evidently a pseudomorph of the pearlite originally present in the metal.

CONCLUSION AND DISCUSSION

The presence of nodular carbides in both the metal particles and the oxide, and of pearlite in the metal particles indicate that the original object was steel. The foregoing observations show that it may sometimes be possible to demonstrate by metallographic methods that an ancient article was made of steel, although nothing apparently remains of it but rust. Fortunately, the artifact examined contained some small surviving particles of metal and carbides, but this might not often be the case. However, even without the particles of uncorroded metal, the presence of carbonaceous pseudomorphs in the oxides afforded sufficient evidence of the ancestry of the corrosion products.

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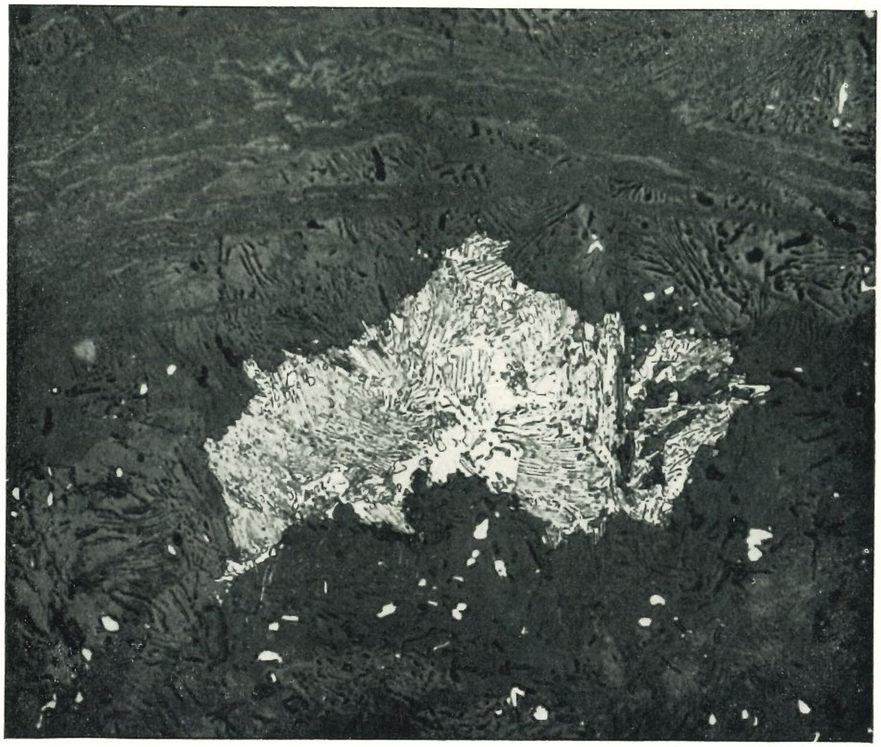

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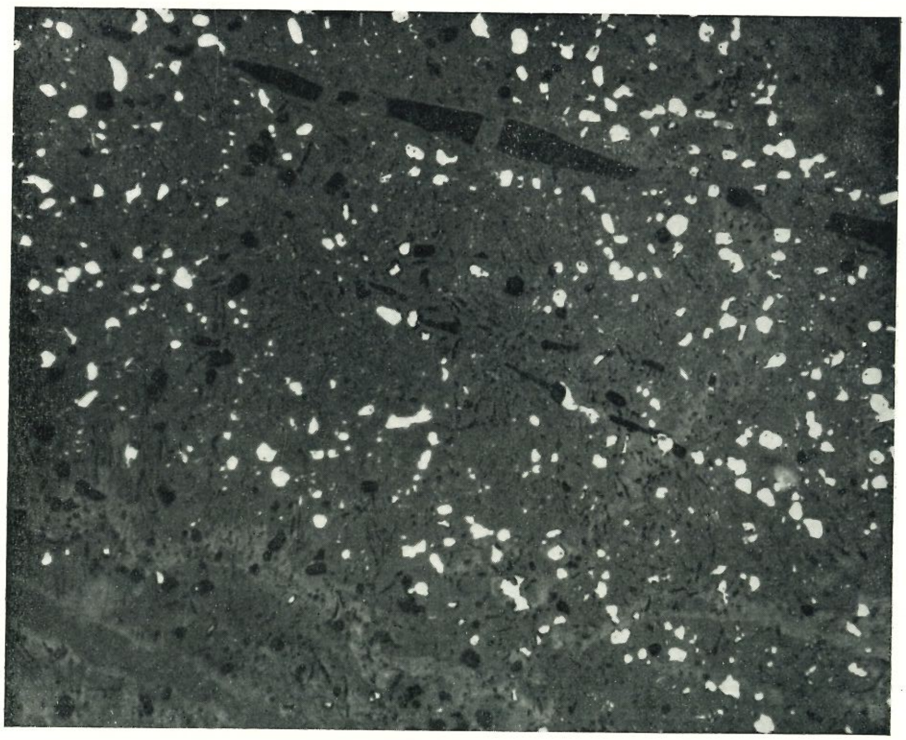

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