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CANADA

DEPARTMENT OF ENERGY, MINES AND RESOURCES

OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 72-36

IDENTIFICATION OF FERROUS ARTIFACTS RECOVERED FROM LAND OR WATER SITES

by

D. E. PARSONS AND D. A. MUNRO

PHYSICAL METALLURGY DIVISION

COPY NO. 00

AUGUST 25, 1972

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SUMMARY OF RESULTS

Metallurgical examination of 10 ferrous artifacts, 7 recovered from underwater sites, 3 recovered from land sites, identified the materials with respect to composition as charcoal iron, wrought iron or cast iron, and as to cast or wrought manufacture. The density of one land-recovered sample was determined as well as the weight loss observed after drying one of the water-recovered samples for 48 hr at 400°F. Information about water-recovered ferrous artifacts was intended to assist in the conservation of ferrous samples which are very difficult to preserve after recovery.

One sample (No. 2W) retained its form but contained only a trace of metallic iron, the metal having been completely converted to non-magnetic hydrated iron oxide (limonite). Another sample (No. 3W) was almost completely oxidized but retained areas of phosphide eutectic and graphite flakes with oxidized pearlite which identified this sample as of cast origin and pearlitic grey iron composition. Sample No. 1W was exceptional with respect to its low carbon and slag content and appeared to be a very pure form of wrought iron, manufactured using decarburized charcoal pig iron.

The remaining samples were identified as pearlitic grey cast iron or as piled, hand-forged, wrought irons. In one instance (No. 7W) a forged wrought iron spike had a carburized surface. The heads of the spikes (No. 2L and 3L) were hand forged. The wrought samples showed no evidence of mechanical rolling or of machine heading.

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*Research Scientist and **Technician, Ferrous Metals Section, Physical Metallurgy Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

INTRODUCTION

On April 19, 1972, Mr. J. H. Rick, Chief, Research Division, National Historic Sites Service, National and Historic Parks Branch, Department of Indian Affairs and Northern Development, submitted 10 ferrous artifacts for metallurgical examination to the Physical Metallurgy Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa.

Seven of the samples had been recovered from underwater sites whereas the remaining three samples had been recovered from land sites.

The covering letter from Mr. Rick stated:

"We are concerned with the conservation of ferrous artifacts in many different stages of corrosion, and as the aesthetic nature of the artifact itself must be preserved it is very often the corrosion products themselves that must be stabilized and conserved. The main problem at the moment is the conservation of ferrous artifacts from underwater sites. We feel that a more thorough knowledge of the structure and composition would assist solution of the conservation problem."

The letter requested analysis of a few representative ferrous artifacts from historic sites in Canada with respect to crystal structure and porosity, alloying components and proportions, and qualitative and quantitative determinations of foreign substances.

A subsequent letter stated:

"The world-wide field of conservation is concerned with the restoration and preservation of archeological artifacts of every material; those of metallic substances pose a wide range of problems due to their propensity to corrode under atmospheric conditions. Iron, because of its active chemical nature and, historically, its numerous combinations with other elements, has become one of the most complex and perplexing studies over many decades.

Ferrous artifacts fall generally into 4 categories with the following degree of success of conservation as shown in Table 1.

TABLE 1

Degree of Success in Conservation (Categories 1-4, Groups 1 and 2)

1.	small objects (substantial metal core)	successful
2.	small objects, (mineralized)	inconsistent results
3.	large objects (substantial metal core)	some degree of success but inconsistent and unreliable
4.	large objects (mineralized)	unsuccessful

Samples from underwater (sea) sites, Group 2, pose great problems with respect to conservation and these samples form the greater portion of samples requiring special study in comparison with samples, Group 1, recovered from land sites.

The letter further stated:

"Many years have been spent in the trial and error testing of theories and techniques on the problems presented by categories 3 and 4 without adequate success. Some scientific research has been done but it is difficult to provide controls; artifacts having the same composition, same age, and same exposure to environmental conditions (same size) are difficult to find; also, the artifact analysts are loath to allow the scientists the freedom necessary to do complete analysis of the objects as this requires partial, if not total destruction of the archeological value.

Because all other methods (non-destructive) have been tried without sufficient success, the artifacts must be analyzed and identified. From this basic information it is hoped that satisfactory methods of conservation can be developed."

Table 2 lists the 10 artifacts submitted for examination. Samples recovered from underwater sites were wet when received and were enclosed in plastic bags, whereas land-recovered samples were dry. Samples listed in Table 2 are identified with respect to report number, museum number, and description.

IDENTIFICATION OF SAMPLES

TABLE 2

Sample Identification and Description

Code No.	Size	Mfg.	Description	Museum No.	
1-W	Small	Wrought	Partially metallic	3184	Charcoal wrought iron
2-W	Small	Wrought	Completely mineralized	3189	Unidentified
3-W	Small	Cast	Completely mineralized	3760	Cast, oxidized, pearlitic grey iron
4-W	Small	Cast	Completely mineralized	3193	Cast, oxidized white iron
5-W	Large	Cast	Metallic (cannon ball) 11 lb, 15 oz		Cast, pearlitic grey iron
6-W	Large	Cast	Mineralized except for core (cannon ball) 7 lb, $\frac{1}{2}$ oz		Oxidized, cast pearlitic grey iron
7-W	-	Wrought	Spike. Metallic	2M	Surface-carburized, wrought iron
1-L	Large	Cast	Shot (2 lb, 12$\frac{1}{2}$ oz) - 16H1B2	DT5015	Cast, pearlitic grey iron
2-L	-	Wrought	Wrought iron fine grained with slag - 16H1F2	DT5044	Wrought iron
3-L	-	Wrought	Spike. Metallic - 16HE1	DT5046	Wrought iron

PROCEDURE

Attempts were made to determine the chemical composition of metallic portions of Samples 1W, 5W, 6W, 7W and of the three land-recovered Samples, 1L, 2L, 3L, by spectrochemical analysis; however, the porous nature of the metal caused unsatisfactory arcs so that it was necessary to do wet-chemical, bulk analyses. This limited the number of determinations, depending upon the quantity of drillings or millings obtainable. Electron microprobe analyses were also made on polished metallographic surfaces with 10 readings averaged to estimate the bulk composition of the oxidized metal. Samples 2W, 3W, 4W, and all except the core of Sample 6W were completely oxidized so that neither chemical nor microprobe analysis was possible.

METALLOGRAPHIC EXAMINATION

The appearance of the microstructures, illustrated, identified all sample materials with respect to material, cast or wrought manufacture, and heat treatment, except for Samples 2W and 4W containing traces of ferrite but otherwise did not contain residual metallic phases.

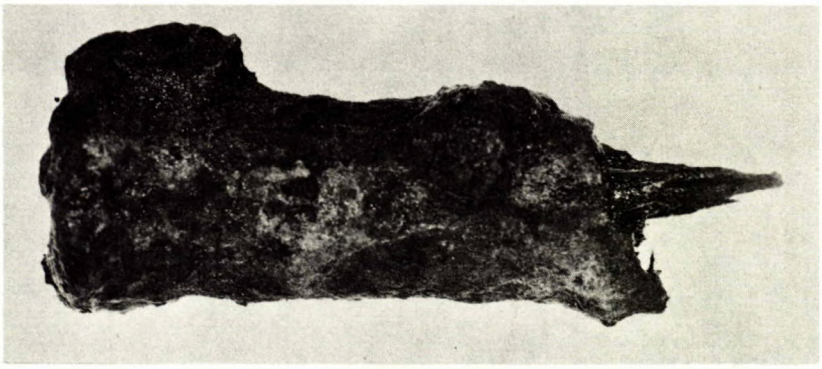
Figure 1, Sample 1W, No. 3184, illustrates part of an oxidized wrought component resembling a spike. recovered underwater, which was manufactured from a very pure decarburized charcoal wrought iron having polygonal ferrite grains and having a very low content of carbon and slag.

Figure 2, Sample 2W, No. 3189, illustrates an aggregate of iron oxides, predominantly non-magnetic, hydrated, iron oxide which retain form but contain only a minor trace of metallic iron, as shown in Figure 2(c). No identification was made of this converted heterogeneous sample.

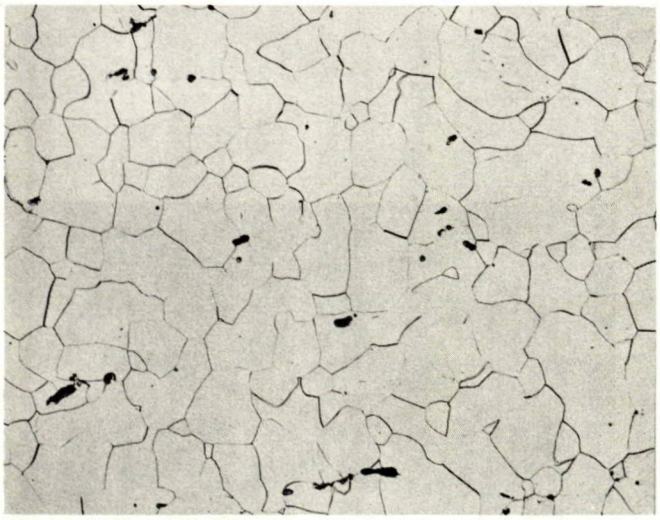
Figure 3, Sample 3W, No. 3760, underwater, illustrates the oxidized remnant of a pearlitic grey iron in which graphite flakes, steadite and oxidized pearlite lamellae are still visible.

Figure 4, Sample 4W, No. 3193, underwater, illustrates the oxidized remains of a cast white iron component having a dendritic, chilled, cast pattern. An oxidized surface, chilled zone, without any phosphide or grey iron flakes was observed. Columnar crystals and dendrites indicated a cast origin of manufacture. Traces of residual core metal consisted of ferrite and oxidized pearlite having the appearance illustrated in Figure 4(c).

(a)

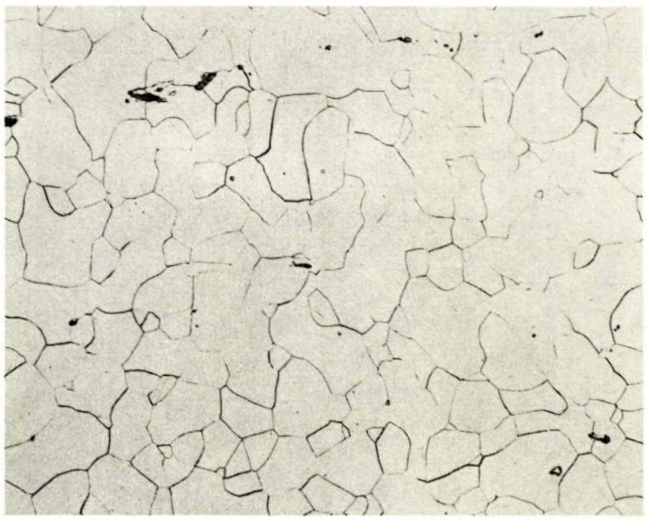


As Received



X100 - etched 2% nital

(b) Longitudinal Section at Centre Edge of Remaining Metallic Core.



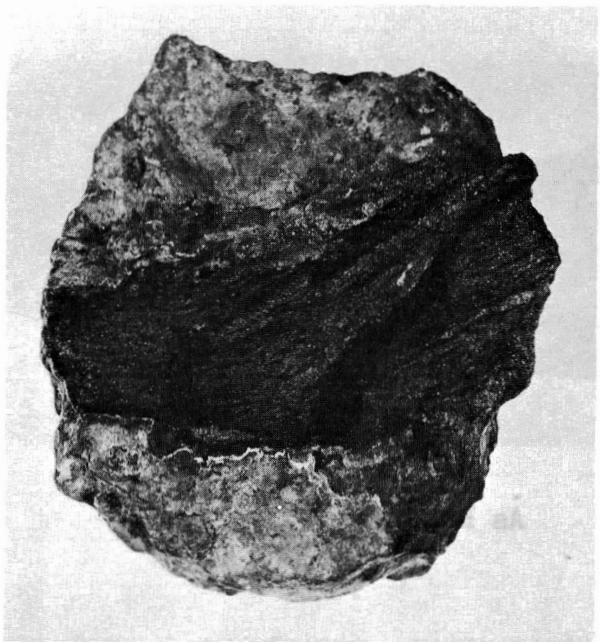
X100 - etched 2% nital

(c) Longitudinal Section at Centre of Remaining Metallic Core.

Figure 1. Sample (1W), No. 3184, Underwater Recovery.

The metal appears to be an extremely pure charcoal iron containing practically no carbon or slag. The equiaxed, polygonal, ferrite grains, observed in longitudinal sections, show that forging was done hot and finished above the recrystallization temperature.

(a)



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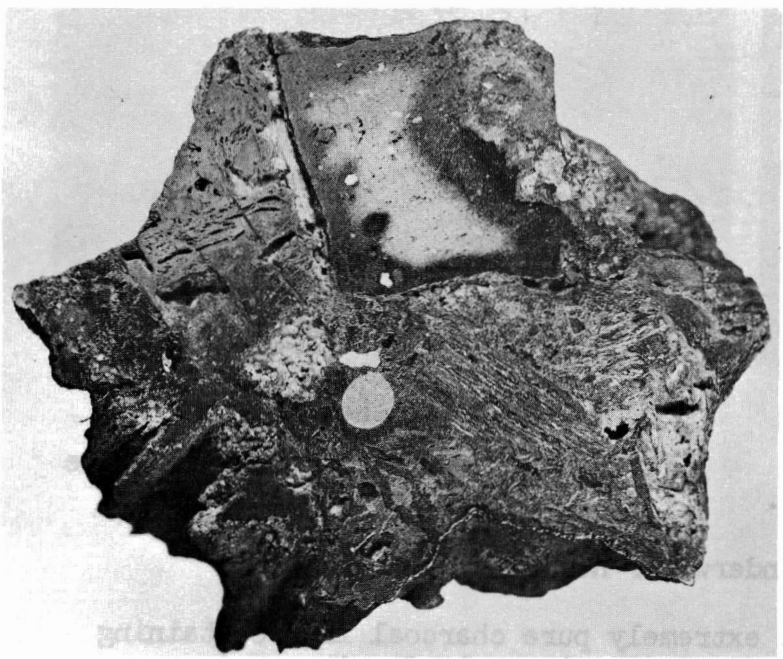
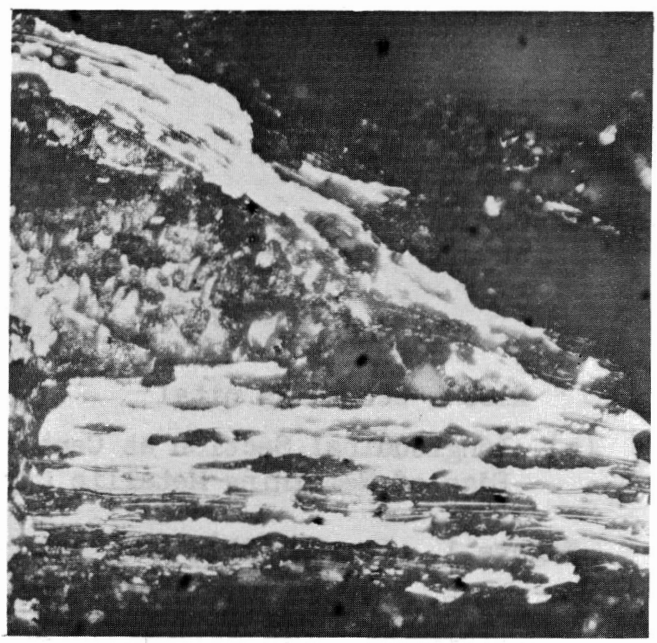


(b) X2 approx. - as polished



(c) X100 - as polished

Illustrates the only metallic trace observed in this sample.

Figure 2. Sample (2W), No. 3189, Underwater Recovery.

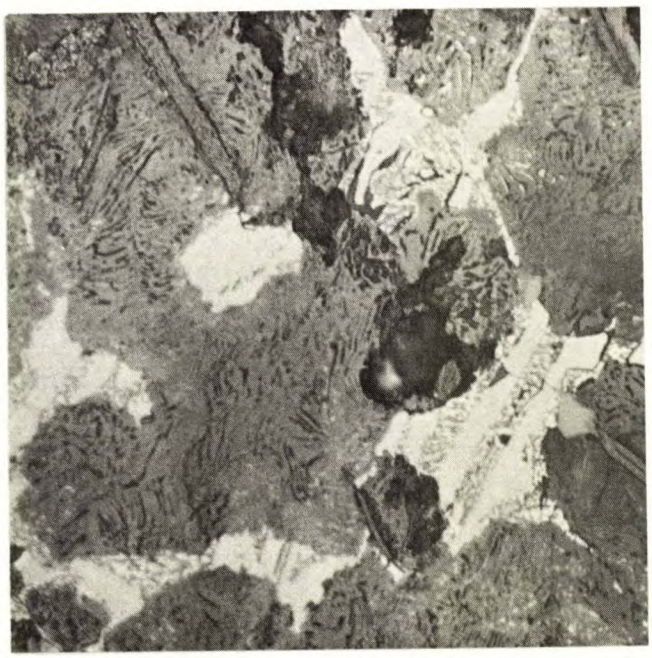
This sample was completely oxidized except for the trace of ferrite illustrated in Figure 4(c), so that no identification of the cemented composite of residual oxides was possible.

(a)

As Received

X100 - as polished

(b) Illustrates the residual steadite (iron phosphide eutectic phase) and graphite flakes indicative of a grey cast iron.



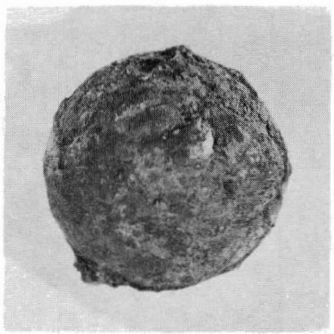
X500 - as polished

(c) Illustrates the oxidized pearlite matrix with steadite and graphite flakes.

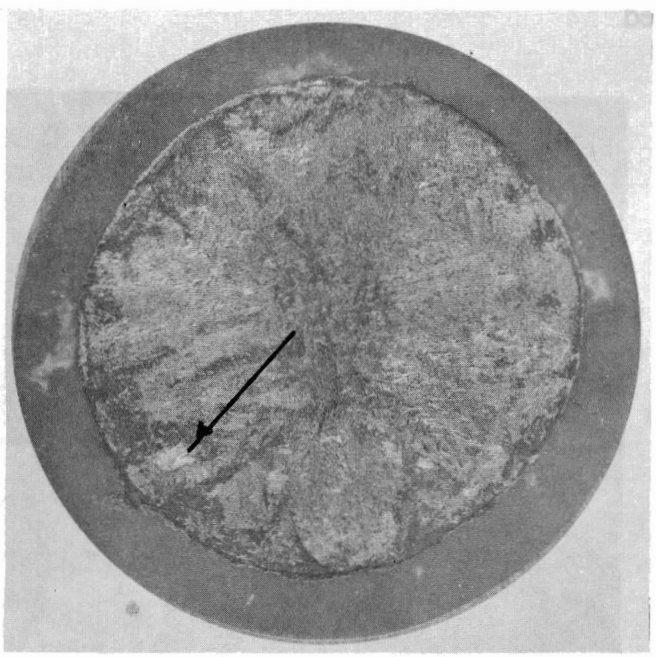
Figure 3. Sample (3W), No. 3760, Underwater Recovery.

This sample retains the form of a pearlitic grey iron except that the pearlite matrix is completely oxidized.

(a)

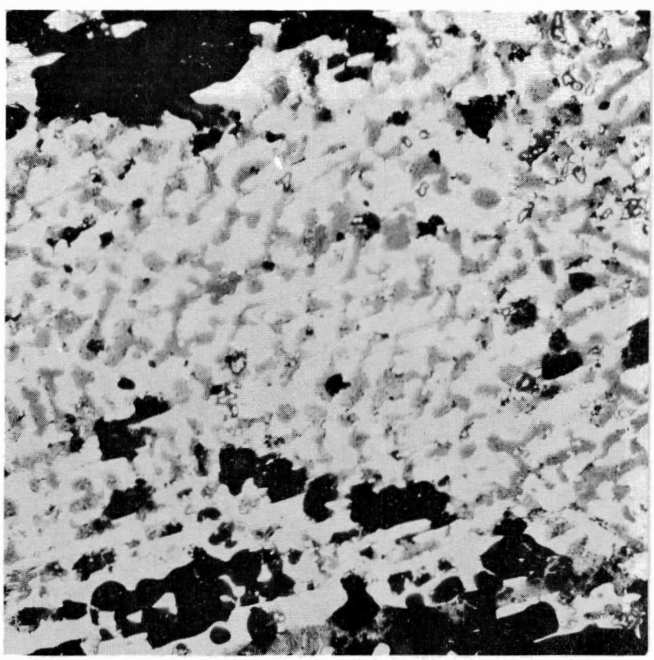


As Received



X3 approx. - as polished

(b) The sample is completely oxidized except for the small metallic (ferrite) area illustrated.

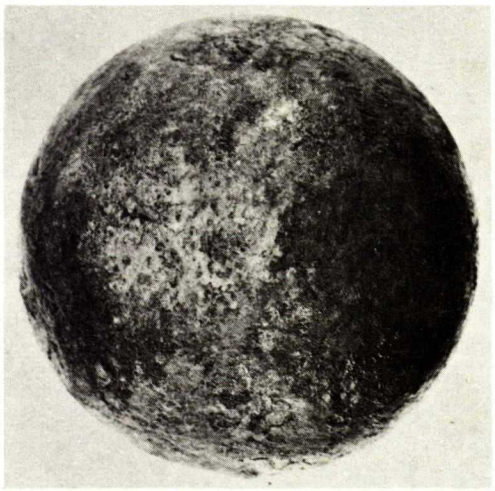


X100 - as polished

(c) Illustrates the core microstructure of ferrite and oxidized pearlite in a dendritic pattern within cast columnar crystals.

Figure 4. Sample (4W), No. 3193, Underwater Recovery "Shot"

This sample was completely oxidized except for the small metallic portion illustrated in Figure 4(b), arrow, and in Figure 4(c). The sample was of as cast manufacture, having columnar crystals with a dendritic arrangement of the ferrite oxidized pearlite microstructure suggestive of the core of a cast white iron composition. A chilled surface area is visible. No residual graphite or steadite was observed.



(a) As Received, Grey Cast Iron, Metallic, 11 lb, 15 oz Cannon Ball.

X100 - 2% nital etch

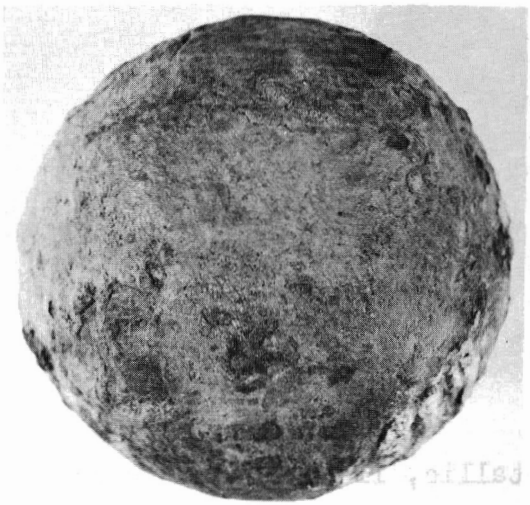
(b) Surface. Illustrates the carbide microstructure observed in the 3/8-in. thick (chilled) surface area.

X100 - 2% nital etch

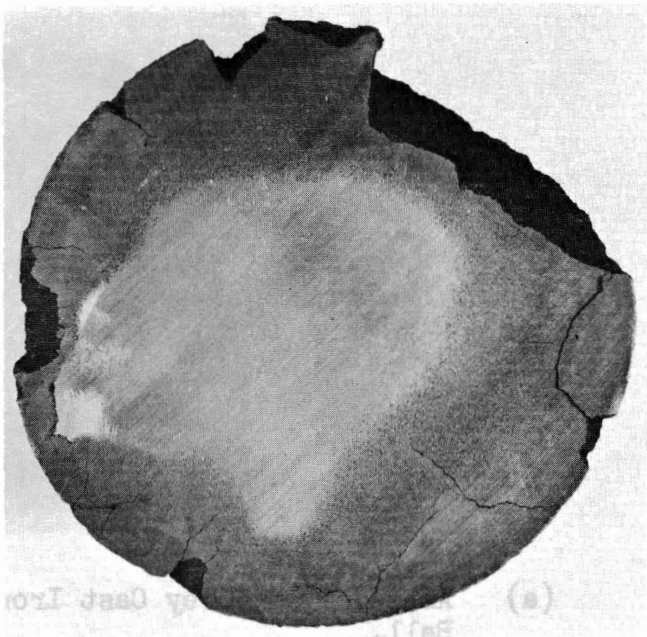
(c) Centre. Illustrates the typical microstructure of a pearlitic grey cast iron comprising a pearlite matrix, graphite flakes and steadite.

Figure 5. Sample (5W) Metallic Cannon Ball, 11 lb 15 oz, Underwater Recovery

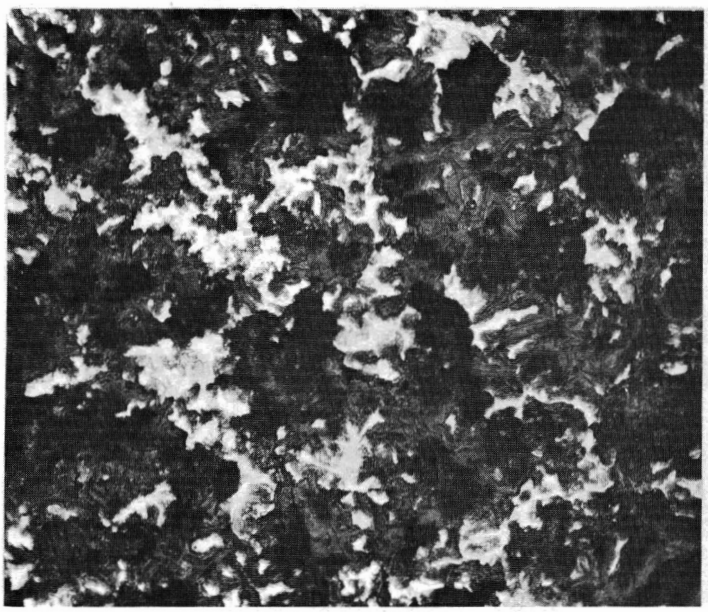
This sample was in a much better state of preservation than sample (6W); however. traces of oxidation had commenced in the pearlite adjacent to graphite flakes, such that the arc response to spectrochemical analysis was not normal.



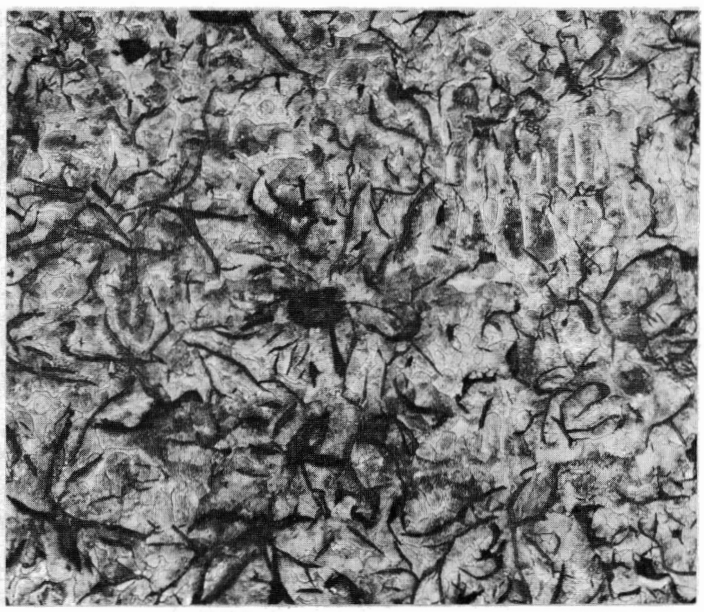
(a) As-Received, oxidized 7 lb ½ oz Cannon Ball.



(b) Section illustrating Oxidized Surface and Metallic Core.



(c) X100 - 2% nital etch. Oxidized Surface with Remnants of Iron Phosphide Eutectic.



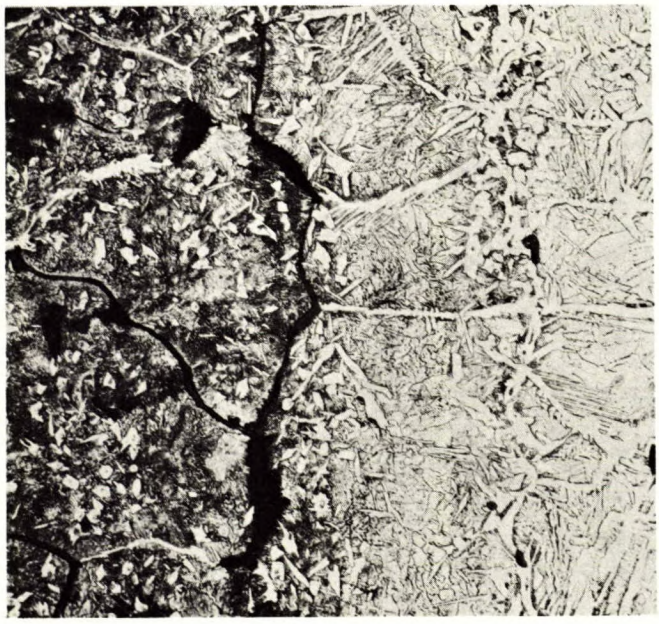
(d) X100 - 2% nital etch. Typical pearlite, graphite, steadite microstructure for pearlitic grey cast iron as observed in the core.

Oxidized except for metallic core.

Figure 6. Sample (6W), Oxidized Cannon Ball, 7 lb ½ oz, Underwater Recovery.

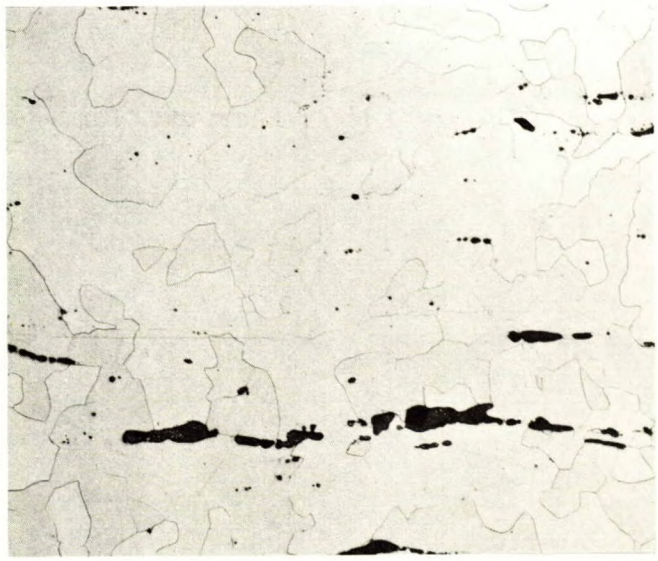
The weight of this sample decreased to 6 lb 10 oz when heated 48 hr at 400°F.

(a) As Received, Carburized, Wrought Iron Spike.



X100 - 2% nital etch.

(b) Surface. Carburized Surface of Wrought Iron Spike.

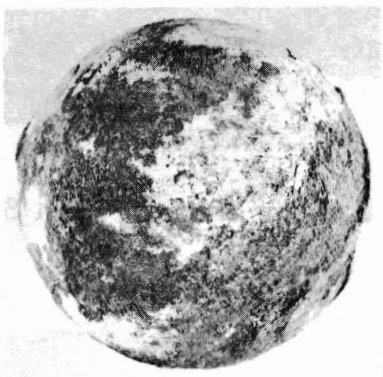


X100 - 2% nital etch.

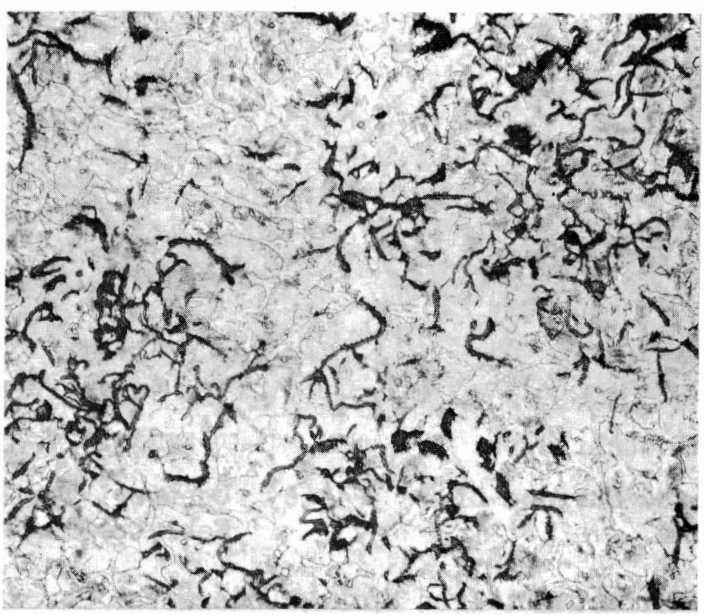
(c) Centre. Typical Wrought Iron Ferrite-Slag Microstructure.

Figure 7. Sample (7W), Wrought Iron Spike, Underwater Recovery.

This wrought iron sample shows evidence of carburization (blacksmith's hearth) and was manufactured by the pile and hot-forging technique.



(a) As Received, Land-Recovered, Cannon Ball.



X100 - 2% nital etch.

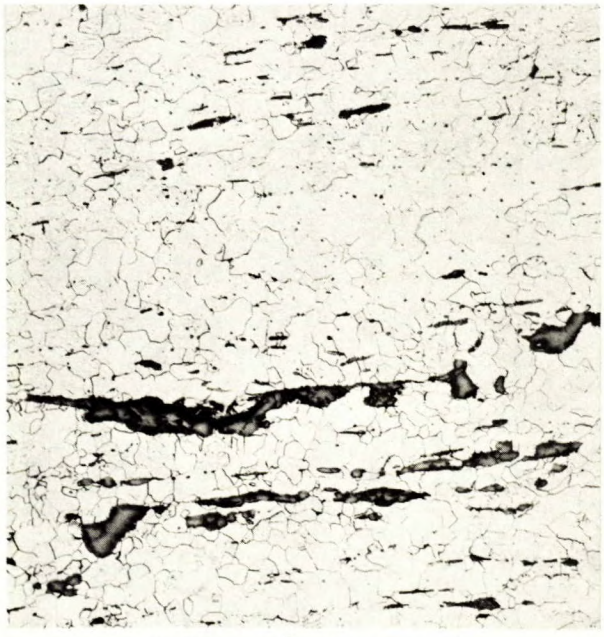
Figure 8. Sample (1L), No. 16H1B2-DT5015 Cannon Ball, Land Recovery.

Pearlitic grey cast iron.
Volume of cannon ball = 195 ml. Weight = 2 lb $12\frac{1}{2}$ oz = 1260 g
Density measured = $\frac{1260}{195}$ = 6 g/cc (Theoretical density of cast iron 7.2 g/cc)

(a) As Received, Land-Recovered Spike. (Round Head Hand Made).

X100 - 2% nital etch

(b) Longitudinal at Surface.



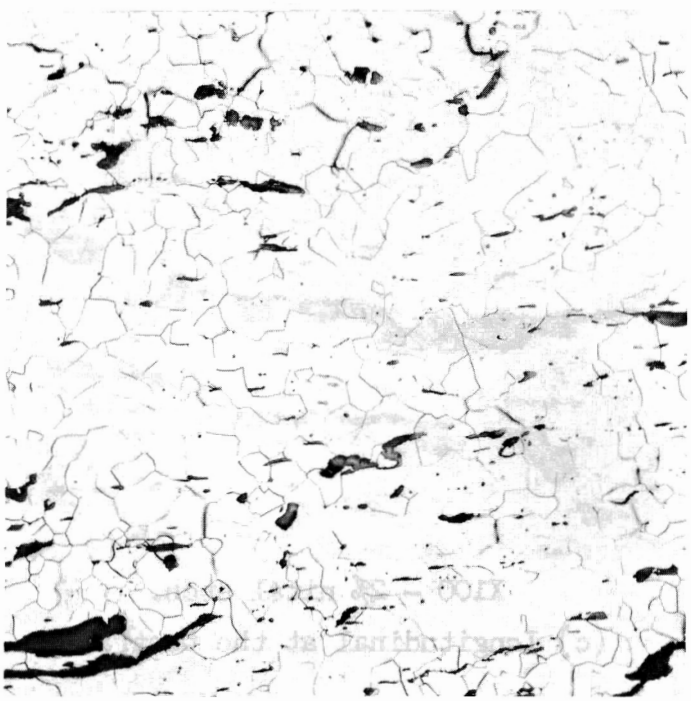
X100 - 2% nital etch.

(c) Longitudinal at the Centre.

Figure 9. Sample (2L), 16H1F2, DT5044, Spike, Land Recovery

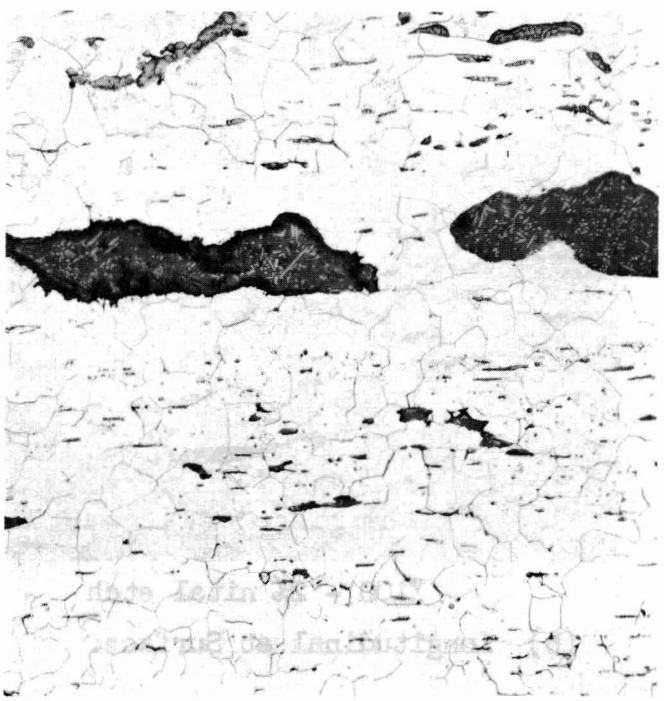
This sample is identified as piled and forged wrought iron. Traces of cold work are visible at the surface of this sample. The wrought iron spike appears to have been manufactured by forging together of separate wrought iron "piles".

(a) As Received, Land-Recovered Spike. (Square head, hand made).



X100 - 2% nital etch.

(b) Longitudinal at Surface.



X100 - 2% nital etch.

(c) Longitudinal at Centre.

Figure 10. Sample (3L), 16HE1, DT5046, Spike, Land Recovered.

The results of chemical analyses are listed in Table 3.

TABLE 3

Chemical and Microprobe Analyses of Artifacts

(Per Cent)

Sample	C	Mn	Si	S	P	Remarks
1W**		≥0.02	≥0.02			
2W						
3W**						
4W						
5W*	3.83	0.33	0.62	0.098	0.96	Pearlitic grey iron, Type "A"
6W	3.50	0.30	1.60	0.080	0.95	Pearlitic grey iron, Type "A"
7W**		≥0.02	≥0.02			
1L	3.16	0.34	1.26	0.15	1.36	Pearlitic grey iron, Type "A"
2L**		≥0.02	≥0.02			
3L**		≥0.02	≥0.02			

W - water recovered

L - land recovered

* Has carbide chill surface 3/8 in. thick rather than martensitic, possibly for increased shock resistance.

**Average of 10 electron microprobe analyses (matrix).

Sample 2W, despite retention of some form of agglomerated metallic particles, had been completely oxidized to form hydrated iron oxide so that identification by examination of metallic iron was not possible.

Sample 1W, as illustrated in Figure 1, was distinctive in the purity of its wrought iron and in having a low-carbon content and almost complete absence of slag and inclusions. This sample was of wrought origin and appeared to be a charcoal iron of high purity. The surface of this sample was heavily oxidized.

Sample 3W, though completely oxidized, with respect to its pearlite matrix, retained the phosphide eutectic and graphite flakes typical of grey cast iron.

Sample 4W, also completely oxidized except for trace quantities of ferrite, appeared to be of cast origin having a surface chill with dendrites of ferrite and oxidized pearlite visible within columnar cast samples. The lack of graphite flakes and the presence of the chill indicate that this "shot" sample was cast white iron having a relatively low carbon content.

Samples 5W and 6W were typical high-phosphorus grey cast irons having a chilled iron surface and core containing well-distributed flake graphite. Sample 6W was dried 48 hr at 400°F; loss of water resulted in a weight change from 7 lb 1 oz to 6 lb 10 oz for a weight loss of approximately 6% at 400°F. The appearance of sample 6W, Figure 6, which was completely oxidized except for the core, is illustrative of the difficulty of preservation of this type of sea-recovered cannonball. Sample 5W, Figure 5, was in a much better state of preservation but did show evidence of oxidation adjacent to graphite flakes and developed a larger than normal arc area during attempts at spectrochemical analysis. The enlarged arc area was indicative of increased porosity in comparison with modern, commercial, cast cannon balls of the same composition and microstructure.

Sample 7W was of wrought (hand-forged) manufacture and had a carburized surface probably indicative of reheating in a blacksmith's forge. The wrought iron comprised "piles" of different composition which had been forged together except in one location where a lamination was visible at the forge-weld interface.

Sample 1L was manufactured as a cast, pearlitic grey iron and, despite storage on land, had a density of only 6 g/cc in comparison with the theoretical density of 7.2 g/cc approximately. The departure from theoretical weight was attributed to superficial oxidation and to the presence of shrinkage in the casting rather than to internal oxidation of the type observed in samples 5W and 6W.

Sample 2L was a "piled" hand-forged wrought iron spike having a blacksmith-type round head. There was no evidence of machine rolling or of machine heading during manufacture.

Sample 3L resembled sample 2L, and appeared to be of hand-forged manufacture using "piled" wrought iron (the separate "piles" were visible in

transverse sections) and having a blacksmith-type rectangular head. There was no evidence in any of the wrought samples of machine rolling or machine heading; all samples appeared to have been manufactured by forging.

CONCLUSIONS

(1) Except for Sample No. 2W, the ferrous artifacts were identified as of hand-forged wrought iron or of cast pearlitic grey iron origin. Sample 2W retained form but contained no metallic iron.

(2) Sample IW appeared to be an exceptionally pure wrought iron having a low carbon and slag content, typical of wrought iron of the decarburized, charcoal iron type.

(3) Samples 2W and 4W were almost completely oxidized, the form of the phosphide eutectic and the presence of graphite flakes resulting in positive identification of Sample 3W as a cast pearlitic grey iron, whereas identification of Sample 4W was positive with respect to manufacture by casting and the presence of a surface chill - the absence of graphite and the apparent dendritic microstructure of ferrite and oxidized pearlite being suggestive of a white iron composition for "shot" manufacture.

(4) The cannonball samples were of cast pearlitic grey iron manufacture. Sample 6W was completely oxidized except for the core region which was only partially oxidized.

(5) The "spikes" were of hand-forged (blacksmith) manufacture, Sample 7W showing evidence of surface carburization, possibly indicative of hearth-reheating. The irregular appearance and large size of the slag particles indicate forging rather than machine rolling. No evidence of machine heading was observed, the two spikes having typical hand-forged round or rectangular (off-centre) heads.

(6) Recommendations concerning preservation of ferrous artifacts are not attempted in this report pending the results of cooperative investigations done by national museums with input from corrosion and corrosion-protection companies.

(7) The chemical analysis is indicative of the use of high-strength pearlitic grey cast iron with a chilled surface composed of carbide rather than martensite. The silicon contents were held low with relatively high-phosphorus contents.

ACKNOWLEDGEMENT

The assistance of Dr. R. Packwood, Metal Physics Section, in obtaining electron microprobe analyses of the samples and of Dr. G. Biefer, Corrosion Section, concerning recommendations about the preservation of ferrous artifacts is gratefully acknowledged.