J. S. PARK, D. VOYAKIN

CAST IRON TECHNOLOGY AT MEDIEVAL TALGAR IN KAZAKHSTAN

I. Introduction

The recent excavation of the medieval Talgar site in the Republic of Kazakhstan has recovered numerous iron artifacts of historical importance along with other cultural remains [1]. As opposed to those which, on typological grounds, have been the subject of substantial interest, iron artifacts have drawn little attention and remained unexplored at least in technical terms. This is a great loss considering the importance of metallurgy evident in the excavation context and the crucial information hidden in their microstructure regarding the technical environment established in the region. The iron artifacts from Talgar have special historical significance in view of its unique geographical location connecting East and West and the fundamental difference in the nature of early iron industry between the two worlds. The difference arose primarily from the early production of cast iron in the East at around mid-1st millennium BC as opposed to the West where no cast iron was deliberately produced in large scale until around the AD 14th century [2, 3]. It is expected, therefore, that the iron artifacts from Talgar provide a unique opportunity to characterize the related technical status established under strong influences coming from both East and West. At the moment little information, whether documentary or archaeological, is known of the technical aspects of Talgar iron, not to mention the total ignorance of its role in the diffusion of cast iron technology. As an initial step to solve this problem, the present study has chosen some of the cast iron artifacts as of first importance and examined their metallurgical microstructure.

The Talgar area is approximately 25 km to the east of Almaty, the largest citiy in the Republic of Kazakhstan, and has long been one of the major settlements in southeastern Kazakhstan called the Semirechye (the Seven Rivers) region (Fig. 1). This region is bounded by the Zailiisky Alatau Mountains to the South, the Dzunghar Alatau Mountains to the Northeast and the Balkhash Desert to the West. Located at the crossroads between the desert-oasis region of Central Asia proper and the semi-arid and desert areas of Mongolia and western China, the Semirechye region played an important role in the establishment and operation of a branch of the Great Silk Road from ca. 130 BC through AD 14th-15th century. Medieval Talgar is one of the steppe towns and cities that had been developed along the Great Silk Route in Semirechye from the AD 8th to the 13th century. Talgar faced the Mongol invasion at the beginning of the AD 13th century. [1]

II. Microstructure Examination

The present work has examined a total of 8 cast iron artifacts including 5 cauldrons, 1 plow and 2 others with unknown purposes. For microstructure examination, a small specimen was taken from each of the artifacts and was prepared following standard metallographic procedures of grinding and polishing. The solution made in the ratio of 2 ml nitric acid and 98 ml methanol was used for etching the polished specimen surfaces, which were then examined morphologically under the optical microscope and scanning electron microscope (SEM). Their chemical information was estimated using the energy dispersive x-ray spectrometer (EDS) equipped with the SEM. All chemical composition is given in mass % in this work.

Fig. 2a shows a number of pieces broken off from a cast iron cauldron, one of the 5 cauldrons that were examined and reported in this work. They were all found broken in excavation and the pieces from each are currently stored in a separate container at the Institute of Archaeology in Almaty. The ruler in Fig. 2a, 30.5 cm in length, allows the approximate size of fragments to be estimated. Fig. 2b, an optical micrograph taken from one of them, shows that the microstructure consists of large dark areas in the light background. These morphological characteristics, typical of white cast iron, are mostly established in the solidification of molten cast iron during casting. In solidification, the large dark areas, called dendrite, are formed first at relatively higher temperatures than the background, called eutectic. This eutectic is seen to be a mixed structure of a number of tiny dark spots embedded in the bright matrix. The dark spots in eutectic are identical in nature to dendrites except

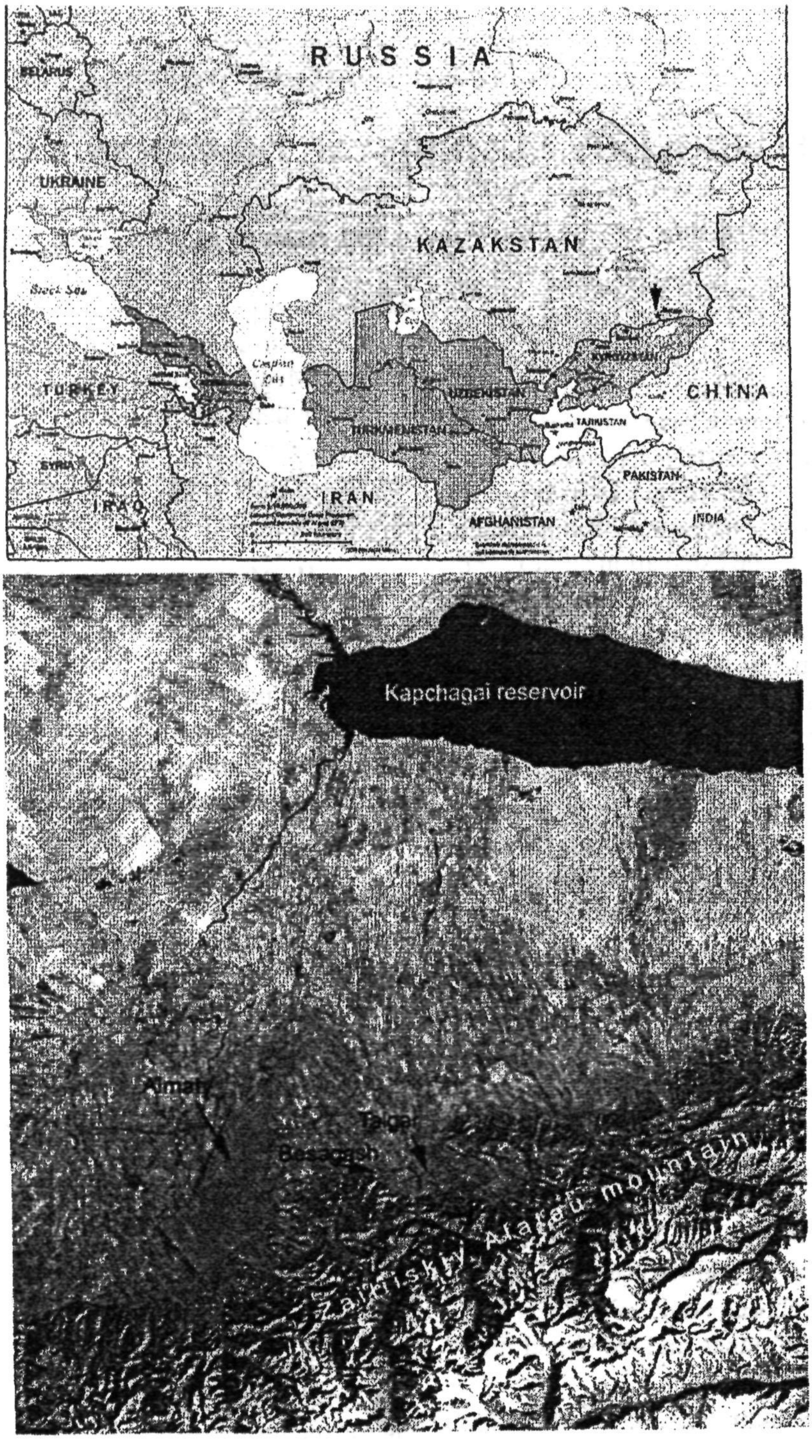

Fig. 1. The outline map of the region surrounding the Republic of Kazakhstan (top) and the local physical map of the southeastern Kazakhstan (bottom)

for the fine scale, and have less C than the matrix, called cementite, whose C content is 6.67%. The presence of dendrites in Fig. 2b, therefore, places the average C content of the structure somewhat below that of eutectic, which is 4.3%. Fig. 2c, an EDS spectrum containing peaks only at iron (Fe) and carbon (C), indicates that the structure in Fig. 2b has no other elements in such an amount as to be detected. The peak at gold (Au) in this spectrum, and also in those following, results from a thin Au layer coated on the specimen surface for the SEM examination, and has nothing to do with the original artifact.

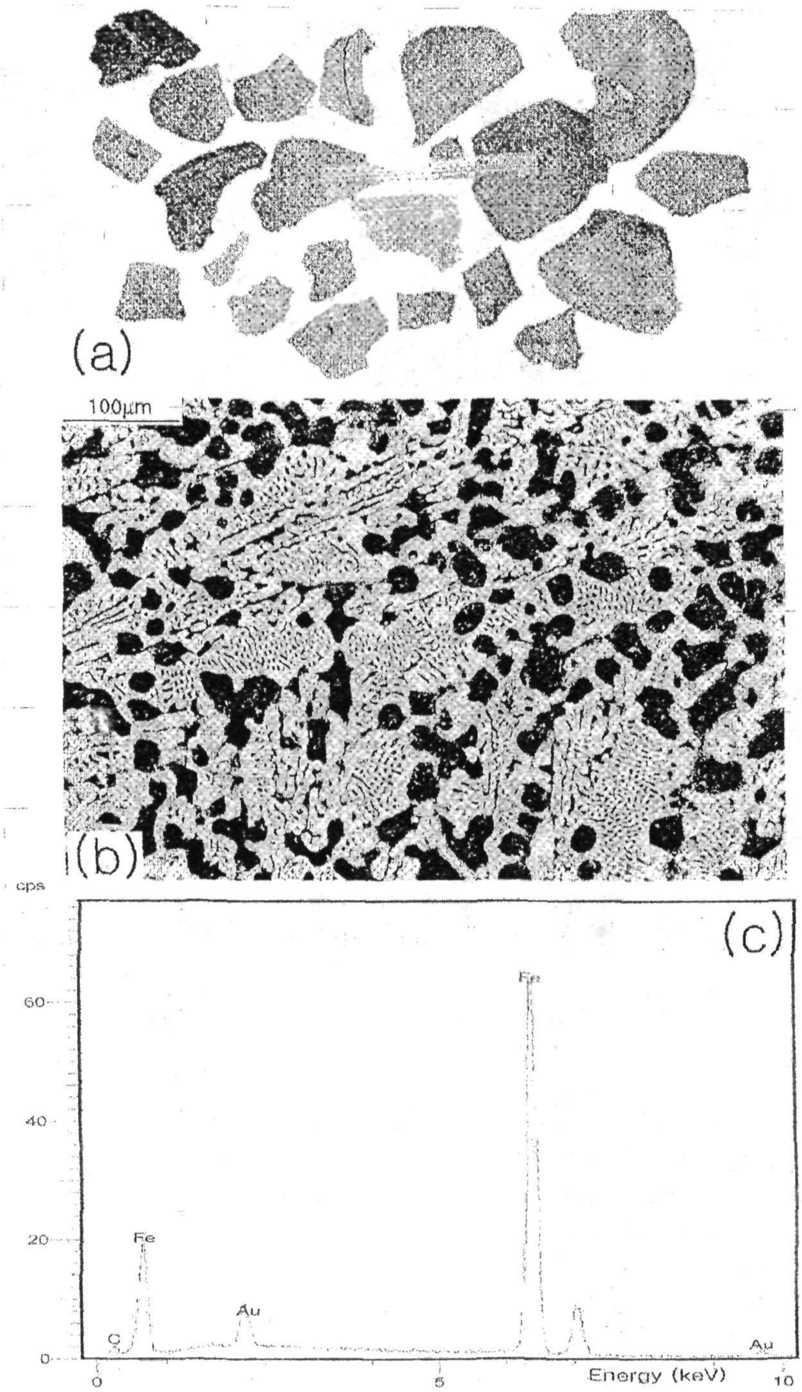

Fig. 2. Cast iron cauldron from the medieval Talgar site in Kazakhstan.
(a) Pieces from the broken cauldron (ruler at the center 30.5 cm),
(b) Optical micrograph showing microstructure of (a), EDS spectrum taken from (b)

Fig. 3a through 3d, optical micrographs from the other 4 cauldrons, illustrate microstructures that are almost identical in nature. They are, however, clearly distinguished from that in Fig. 2b at least in 2 respects, i.e., the substantial increase in the fraction of large dark areas, i.e., dendrites, and the absence of such fine eutectic structures as observed in Fig. 2b. These two differences are intimately related and both serve as unmistakable signs of the reduced C content in the latter cauldrons. The reduced C in cast iron has a significant practical implication because it raises the melting point of cast iron, and thereby requires

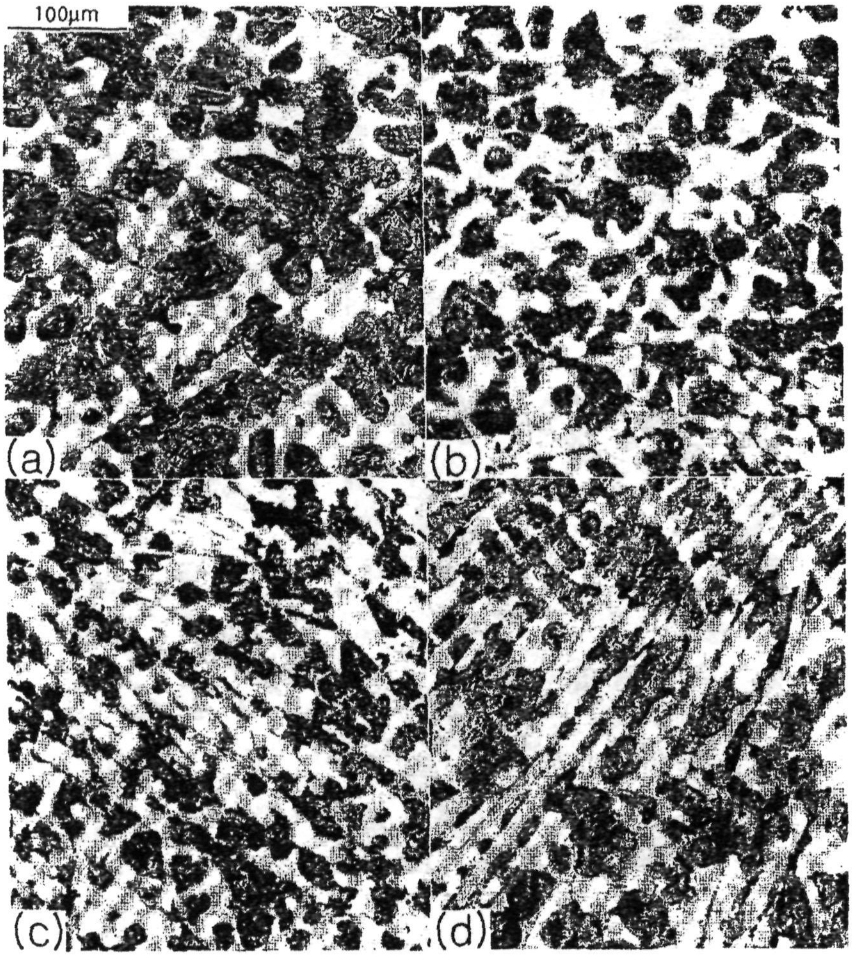

Fig. 3. Optical micrographs showing microstructure of 4 cast iron cauldrons excavated from the medieval Talgar site in Kazakhstan

higher heating temperatures in casting. Fig. 4a through 4d are presented to illustrate another aspect that is unique and common to the latter low C cauldrons. Fig. 4a, an optical micrograph from the same specimen as Fig. 3a, shows, at the area noted, one of the particles observed only in the low C cauldrons but not in the high C cauldron of Fig. 2a. Fig. 4b, a SEM micrograph magnifying the near central region of Fig. 4a, is another attempt to view the particle. The character of this particle is revealed in Fig. 4c, an EDS spectrum from it, which shows 2 major peaks at S and Mn in addition to Fe and C. The particle is, in fact, a sulfide containing Fe and Mn. The presence of these particles implies that the level of S and Mn in cast iron is not negligible. Fig. 4d, a spectrum from another such particle, contains major peaks only at S and Fe with the one at Mn being greatly reduced. It is apparent that the Mn content is not enough to take part in every sulfide formation.

The foregoing results drawn from examining microstructure are supported by the quantitative chemical analysis on C and S using the C/S determinator, whose result is summarized in Table 1. The artifact #1 contains 4.00%C and 0.015%S whereas the other 4 have 2.95%C and 0.230%S on the average. It is of special significance to see that the amount of S in the lower C artifacts, #2 through #5, is more than an order of magnitude greater than that in the higher C artifact, #1.

Fig. 5a shows the general appearance of another cast iron artifact, a plow, from the same site as the above cauldrons. Fig. 5b is an optical micrograph of its microstructure consisting mostly of eutectic. The eutectic here is of the same kind as that in Fig. 2b except that its relative fraction is increased with its scale much coarsened. Fig. 5b has 2 more structures distinctly different from eutectic in scale and gray level. The first is found at the white areas marked by dark arrows and the second at the dark areas noted

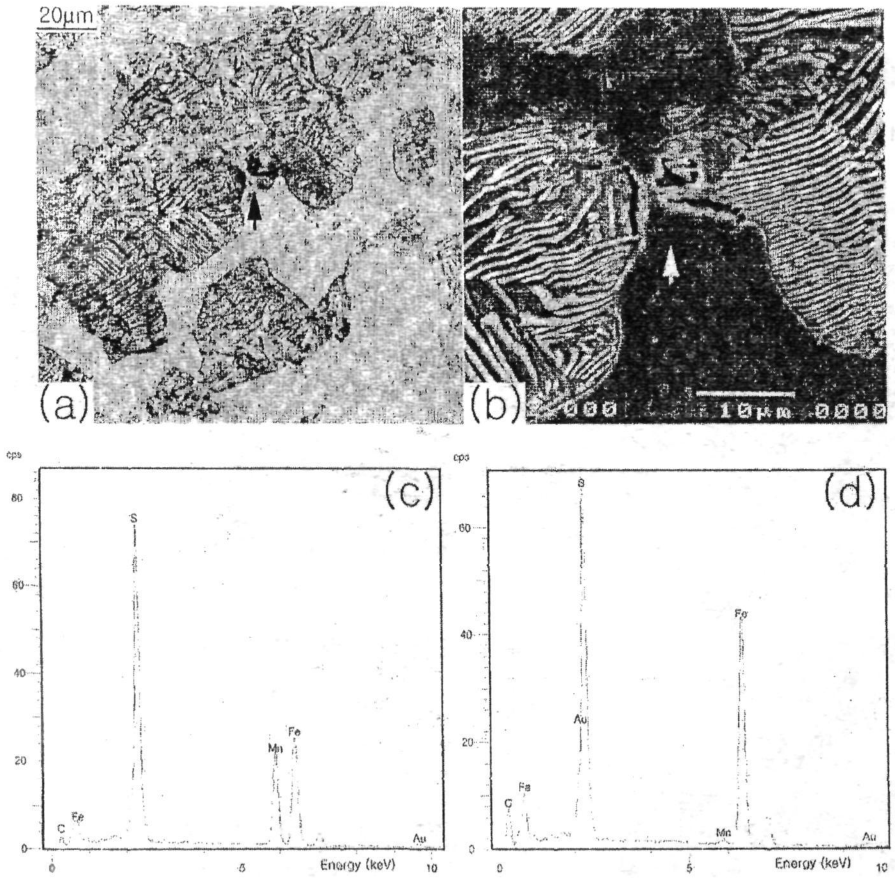

Fig. 4. Micrographs and EDS spectra showing the presence of sulfide particles.
(a) Optical micrograph showing microstructure with sulfide inclusion at the area noted,
(b) SEM micrograph magnifying the near central region noted in (a), (c) EDS spectrum from the sulfide inclusion noted in (a) and (b), EDS spectrum from another sulfide inclusion in the same samplebut not shown in (a).

by white arrows. Both hold important information. The white areas represent cementite, which is identical in nature to one of the 2 constituents of eutectic. The difference is that it exists alone and is of much larger scale. If it is recalled that cementite contains much more C than the other element of eutectic, the average C of Fig. 5b is a little higher than eutectic, i.e., 4.3%. In fact, this large scale cementite is formed only in solidification from molten iron whose C content is above 4.3%C. By contrast, the dark areas hold a unique structure that is formed in solid state. Fig. 5c, an optical micrograph, magnifies one of them near the upper central region of Fig. 5b. It has a number of dark flakes embedded in the gray background. These flakes represent graphite of almost pure C. It is impossible to form such graphite directly from molten cast irons having little or no silicon (Si), which is the case here. Instead, they can be obtained from white cast iron in a process, termed graphitization [4]. Here, white cast iron from casting is subjected to prolonged heating at elevated temperatures and is replaced by such graphitized structure as shown near the center of Fig. 5c. The plow must have been given this treatment. The coarsening of eutectic noticed in Fig. 5b by comparison to that in Fig. 2b is another effect occurring inevitably in the treatment along with graphitization. The majority of Fig. 5b still maintaining white cast iron structure, however, demonstrates that the duration and temperature of heating were far from being sufficient for the completion of such transformation. But the changes observed cannot occur inadvertently without a deliberate action requiring considerable skill, time and facilities.

Fig. 6a and 6b show 2 more cast iron artifacts from the medieval Talgar site, and Fig. 6c and 6d are optical micrographs showing their respective structure. Both micrographs consist of dark and white areas. Here, in the dark areas was consistently observed graphitized structure of exactly the same

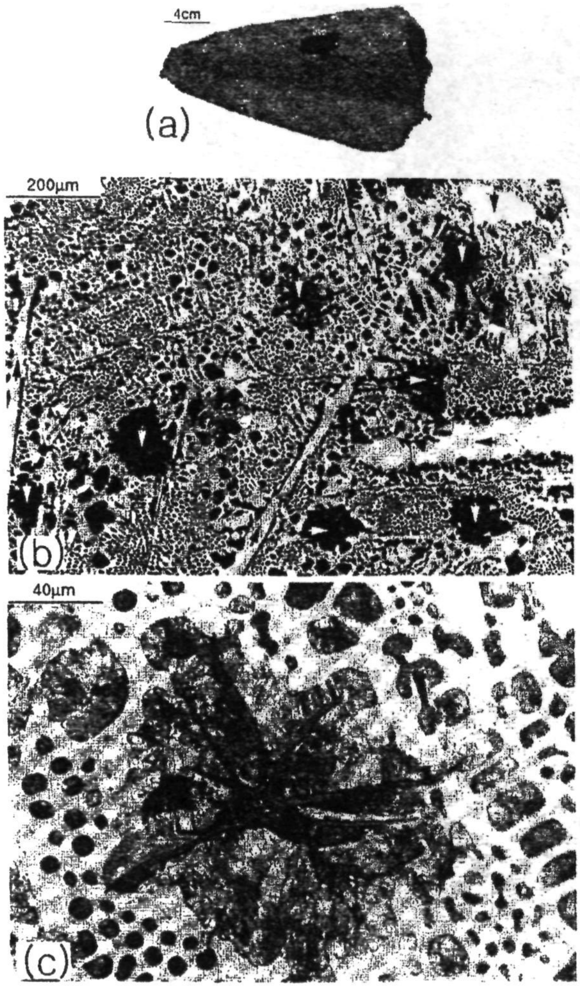

Fig. 5. Cast iron plow excavated from the medieval Talgar site in Kazakhstan. (a) General appearance, (b) Optical micrograph showing microstructure of (a), Optical micrograph magnifying upper central area of (b).

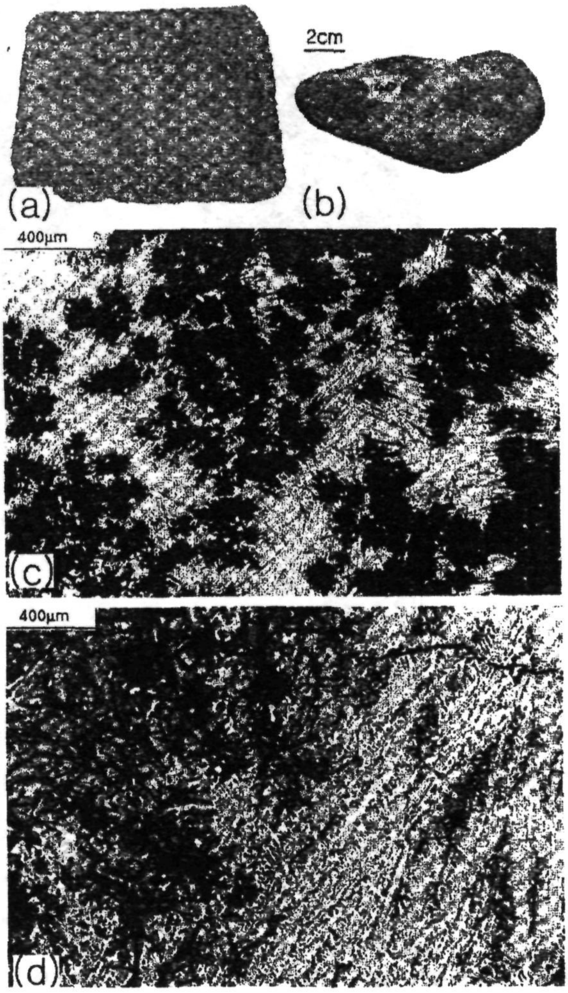

Fig. 6. Cast iron articles excavated from the medieval Talgar site in Kazakhstan, (a) and (b) General appearances, (c) Optical micrograph showing microstructure of (a), (d) Optical micrograph showing microstructure of (b).

nature as that in Fig. 5b whereas in the white areas eutectic of white cast iron surviving the transformation. These unique morphological characteristics indicate that, after they had been shaped by casting, the 2 artifacts were given the similar thermal treatment. The C content in both is estimated from their microstructure to be near eutectic, 4.3%. Another thing to be noticed in Fig. 6d is the dark crack running horizontally in the white region from the upper right edge to the left, which stops upon impinging the dark area. This suggests that the graphitized structure is more resistant to the formation of cracks, and improves the critical weakness of white cast iron, i.e., the extreme brittleness in as-cast conditions. It is this brittle nature that makes white cast iron totally unsuitable for use in impact situations, not to mention its inability to be forged, and thereby restricts its application. In fact, the heating treatment had long been practiced in cast iron industry until quite recently in an effort to make it malleable and even fit for forging [4].

III. Discussion

The material evidence from the Talgar site makes it clear that cast iron was an important element in the local iron industry during the medieval period. The major advantage of cast iron lies in its low melting point arising from its high C content, which makes it fit for mass production not only in smelting but also in casting. Its use in as-smelted or as-cast states, however, is very limited due to the extreme brittleness inherent to it. Ironically this problem comes from the high C content, the very character that makes it useful. And solutions have traditionally been sought

Table 1. **Carbon and sulfur content of the cast iron cauldrons excavated from the medieval Talgar site in the Republic of Kazakhstan**

#	Artifact ID	C [mass%]	S [mass%]
1	T6	4.00	0.015
2	T7	2.88	0.270
3	T41	3.03	0.220
4	T42	3.03	0.220
5	T53	2.87	0.210

Measurements were made using the LECO C/S determinator.
All the data are the average of 2 or 3 separate measurements.

in processes involving the control of C, which can proceed in 2 directions. Either carbon atoms are rearranged to transform as-cast structure into different one that is less brittle or some of them are removed to make iron and steel from cast iron.

The brittle nature of white cast iron arises primarily from one of its constituents, cementite, which remains extremely brittle even at elevated temperatures. One way to lessen this brittleness is to reduce the fraction of cementite, which is achieved in graphitization. This process involves no change in the total amount of C, but only the rearrangement of C atoms, which precipitates graphite in the iron-rich matrix of great malleability. If the transformation rate is to be practical, temperatures of approximately 800°C or above are required along with the oxygen content strictly restricted in the reaction atmosphere. The evidence of graphitization observed in the Talgar artifacts demonstrates that the contemporary ironworkers were well aware of its beneficial effect and also the technical aspects involved. The introduction of this treatment would substantially expand the use of cast iron and thereby require more cast iron to be smelted. Besides, a little modification of it could remove C atoms from cast iron, inspiring another technique that has far reaching significance as follows.

The removal of C from cast iron is in principle equivalent to making the most important material in iron industry, steel [5]. It is known that the early production of cast iron in the East at around the mid-1st millennium BC led to the invention of various steel making processes involving cast iron [2, 6]. According to the Chinese texts quoted by Needham [2], steel was produced either by the direct decarburization of cast iron in solid or liquid state or by heating cast iron and wrought iron together to average their C content. In his recent metallurgical work on iron artifacts, Park has discovered material evidence of some of these ancient processes practiced in Korea no later than the AD 7th century [7, 8]. The present results strongly suggest that steel could be produced from cast iron in Talgar using a process similar to graphitization but with a little modification for more oxygen in the reaction atmosphere. This corresponds to steel making from cast iron by direct decarburization, which, according to both documentary and material evidence, was frequently accompanied by forging in an effort to enhance the reaction rate.

The increased demand for cast iron by the invention of such processes as graphitization and steel making would necessarily call for its mass production. In technical sense, smelting of cast iron is far more effective in such large scale production than any others, but not without difficulties, especially in the great demand for fuel. The significantly varying C and S contents summarized in Table 1 suggests how the local cast iron industry confronted this problem. It is of particular importance to notice that the decrease in C content by more than 1% is accompanied by the increase in S by more than an order of magnitude. This change consistently found in the latter 4 cauldrons, in contrast to the first caldron and the 3 articles in Fig. 5a, 6a and 6b, cannot be accidental, but serves as a sure sign of technical transition. The motivation of this transition may be found from the high S content observed only in the lower C cauldrons. The S level in cast iron is generally determined by the amount of S in fuel supplied for smelting. And the big increase in S is frequently caused by using fossil fuels, like coal, which is high in S [5]. This effect is not readily obtained with charcoal from wood. It may be concluded, therefore, that Talgar experienced a noticeable transition in cast iron technology during the medieval period owing to the beginning of the use of coal as fuel in smelting. It is interesting to note that this transition reduced the C content by more than 1%, which corresponds approximately to 100°C increase in the smelting temperature, another indication of different fuel.

IV. Conclusion

The present study has examined microstructure of the 8 cast iron artifacts from medieval Talgar, Kazakhstan, and established that the local cast iron technology may be characterized by 2 aspects; the practice of an advanced thermal treatment for graphitization of white cast iron, and the technical transition initiated by the beginning of the use of fossil coal as apparent in the remarkable change in the C and S content of cast iron alloys. The practice of graphitization treatment means that the local ironworkers were well aware of the physical and chemical properties of cast iron and knew how to control them. It must have expanded the use of cast iron and, as a result, increased the demand for cast iron. Besides, it could hardly be practiced alone without inspiring other more important processes such as steel making from cast iron although solid material evidence is yet to be discovered. The demand for more cast iron apparently drove the technical innovation based on the use of coal in smelting. It may, therefore, be concluded that the cast iron technology at medieval Talgar had reached a highly advanced state and evolved into a new stage during the medieval period.

Future studies are encouraged to trace the route followed in the achievement of such an advanced technical status in Talgar as well as her role in the flow of the related technical ideas via the Great Silk Road passing through her. The results may explain how the early cast iron technology established in the East had influenced its appearance in the West after nearly 2 millennia.

REFERENCES

[1] C. Chang, P. A. Tourtellotte, K. M. Baipakov, F. P. Grigoriev, The Evolution of Steppe Communities from the Bronze Age through Medieval Periods in Southeastern Kazakhstan (Zhetysu), The Kazakh-American Talgar Project 1994-2001, Sweet Briar, Almaty Kazakhstan, 2002.

[2] J. Needham, The Evolution of Iron and Steel Technology in East and Southeast Asia, in: T. A. Wertime, J. D. Muhly (Eds.), The Coming of the Age of Iron, Yale University Press, New Haven and London, 1980, pp. 507-541.

[3] R. Maddin, The History of the Evolution and Development of Metal, Proceedings of the Forum for the Fourth International Conference on the Beginning of the Use of Metals and Alloys (BUMA-IV), Shimane Japan, 1996, pp. 1-7.

[4] W.F. Smith, Structures and Properties of Engineering Alloys, McGraw-Hill Book Company, New York NY, 1981.

[5] W. Rostoker, B. Bronson, Pre-Industrial Iron Its Technology and Ethnology, Archaeomaterials Monograph, No. 1., Philadelphia, 1990.

[6] D. Wagner, Iron and Steel in Ancient China, E. J. Brill, Leiden·New York·Koln, 1996.

[7] J. S. Park, Steel making in the ancient Korean Kingdom of Koguryo, Materials Characterization, 54 (2005) 409-416.

[8] J. S. Park, M. Hall, The Use of White Cast Iron in Ancient Korea, in press at IAMS.

Резюме

Шойынның құрамы мен оның микроқұрылымы зерттелген. Жұмыстың нәтижелері шойынды дайындау технологиясы, шамамен екі мыңжылдықтан кейін, Батыста жаңа технологиялардың пайда болуына қалай әсер еткенін түсіндіруге септігін тигізеді.

Резюме

Статья посвящена исследованиям состава чугуна, его микроструктур. Результаты работ могут объяснить то, как технология изготовления чугуна могла повлиять на появление новых технологий на Западе, спустя около 2 тысячелетий.