Studies in Iron Manufacture Technology through Analysis of Iron Artifact in Han River Basin during the Proto-Three Kingdoms

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Abstract: The most widely excavated iron artifacts used as weapons or farm tools from central southern regions of Korea were subjects of non-metallic inclusion analysis through metallographic examination, microhardness measurement, and scanning electron microscopy with energy dispersive X-ray spectroscopy. Through metallographic interpretation and study of the analyzed results, the steel manufacturing and iron smelting using heat processing in the iron artifacts excavated from the central southern region of the ancient Korean peninsula was studied, and the analysis of the non-metallic inclusions mixed within the metallic structures was interpreted as the ternary phase diagram of the oxide to infer the type of iron ores for the iron products and the temperature of the furnace used to smelt them. Most of the ancient forged iron artifacts showed $\text{Al}_2\text{O}_3/\text{SiO}_2$ with high SiO_2 contents and relatively low Al_2O_3 contents for iron ore, indicating that for Al_2O_3 below 5%, it is presumed that magnetic iron ores were reduced to bloom iron (sponge iron) with direct-reduction process for production. The temperature for extraction of wustite for Al_2O_3 below 1% was found to be $1,020 \sim 1,050^\circ\text{C}$. Considering the oxide ternary constitutional diagram of glassy inclusions, the steel-manufacturing temperature was presumed to have been near $1,150 \sim 1,280^\circ\text{C}$ in most cases, and minimum melting temperature of casting iron part excavated in Daeseong-ri, Gyeonggi was near $1,400^\circ\text{C}$, and it is thought that hypoeutectic cast iron of about 2.3% carbon was casted and fragility of cast iron was improved by decarburizing in solid state.

Key words: Iron artifact, Iron ore, Heat treatment, Non-metallic inclusions, Ternary phase diagram of the oxide

1. INTRODUCTION

Archaeologically, there are many theories on iron artifact of the Korean Peninsula but it is a common theory that it had started to be brought from north in around the fourth century BC, to Han River basin in the third century BC and to Nakdong River area in the south in around the first century BC (Kim, 1986). Considering the fact that wrought iron and cast iron were produced as in the iron manufacture technology in China, it is known that the iron had been introduced into the Korean Peninsula through the mass migration of the group who developed iron manufacture technology in China.

In addition, it is the prevalent view of archaeologists or historians that the Korean Peninsula accepted iron manufacture technology from China, developed it in their way and spread it to Japan.

In this study, microstructure was investigated targeted at iron artifacts of Proto-Three Kingdoms that had been excavated from Han River basin and metallographic interpretation and research have been done on steel manufacture and manufacturing technology that uses heat treatment of iron artifacts excavated through an analysis of microhardness measurement and nonmetallic inclusions. And also, I tried to study the temperature of iron manufacture.

Also, I tried to study the temperature of iron manufacture in which materials for iron artifacts was smelted by reinterpreting the analyzed non-metallic inclusions in microstructure to ternary phase diagram. By doing so, I tried to study steel manufacture, iron artifact and manufacturing technology through iron manufacturing technology and heat treatment in Han River basin where the politics and economy was developed and there were a lot of exchanges with other regions with Han River as the center as the central zone in Proto-Three Kingdoms.

2. IRON OBJECTS FOR STUDY

In this study, the iron artifacts in Table 1 that were excavated from 3 sites in Yeongjong-do in Incheon, Garak-dong in Seoul, Daesung-ri in Gyeonggi, near the Han River basin in 3-4 century, archaeologically the Proto-Three Kingdoms, are targeted.

Table 1 classified sites, indicated the quantity and EDS analysis of the targeted artifacts of each site as well as collected specimen, and compared the types of artifacts by categorizing the purpose of artifacts and use.

3. ANALYTICAL METHOD

3.1. Microstructure investigation

In general, it requires careful attention to collect metal that is

In order to have such functions, iron should have proper composition and viscosity. Composition of iron depends on the method of work and raw material of iron manufacture, steel manufacture or type of flux and wall furnace, and FeO-CaO-(MgO)-SiO₂ is the main constituent in basic process and FeO-MnO-(MgO)-SiO₂ in acid process. It is possible to assume the temperature of the furnace by substituting the analyzed data with FeO-CaO-SiO₂ (FCS) constitutional diagram in and FeO-Al₂O₃-SiO₂ (FAS) constitutional diagram in Figure 1 considering the fayalite (Fe₂SiO₄) slag case of ancient iron manufacturing furnace where the smelting temperature was low in the proper slag area as the main constituent of excavated slag

from ancient iron manufacturing furnace is FeO, CaO, SiO₂, Al₂O₃. In Figure 1 of FCS, it is known that as compounds of calcium, CaO lowers viscosity of oxide with high viscosity such as SiO₂, Al₂O₃ of slag, and as a flux that increases fluidity of it so that slag can be effused well, it has been working since the ancient times by charging into furnace along with ore. This FCS elementary system is the main oxide in nonmetallic inclusions and as Al₂O₃, neutral oxide, plays an important role in slag, we can assume the temperature of furnace from nonmetallic inclusions that have low Al₂O₃ or no Al₂O₃. In addition, in case of now CaO or no CaO in nonmetallic inclusions, the temperature of furnace can be assumed through FAS constitutional diagram

Table 2. Result of analysis on SEM-EDS in Figure 2D (wt%) and temperature of ternary phase diagram (°C).

Point	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	FeO	FAS	FCS
a	-	13.20	17.20	12.87	2.47	14.50	39.77	1,200	1,240

Figure 2. Microstructure and analysis of iron artifact excavated from the 2nd site of house in Daesung-ri site (Yang and Kim, 2011). (A) Sampling position. (B) Overall view of microstructure. (C) Spheroidal cementite. (D) The SEM image of the iron artifact of 2nd site of house.

in Figure 1.

I normalized by 100% three oxides that consist of ternary phase diagram in order to substitute with nonmetallic oxide in ancient iron artifacts, FCS and FAS constitutional diagrams show different temperatures even in the same slag due to the difference in composition. In such case of singular slag such as glassy, the main components of two constitutional diagrams were used to assume temperature. The temperature of singular glassy slag was assumed as the maximum smelting temperature at the time of smelting.

4. RESULT AND CONSIDERATION

4.1. Iron objects from Daesung-ri, Gapyeong

In Daesung-ri site in Gapyeong, an iron artifact, iron arrowhead, iron knife, casting and iron axe that were produced by forging in the site of house were excavated. The microstructure of artifacts varies a little but as the overheated structure of hypo-eutectoid steel that has low carbon seems to have been formed, I studied the structure and analysis on the iron artifact of 2nd site of house and casting iron axe as a representative (Yang and Kim, 2011).

Table 3. Analysis result of SEM-EDS in Figure 3D (wt%) and temperature of ternary phase diagram (°C).

Point	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	MnO	FeO	FAS	FCS
a	2.16	4.34	22.71	9.41	2.07	3.40	2.69	53.23	1,390	1,180

Figure 3. Microstructure and analysis of iron axe excavated from the 10th site of house in Daesung-ri site (Yang and Kim, 2011). (A) Sampling position. (B) Overall view of microstructure of sample. (C) Decarburized hole and Widmanstätten. (D) The SEM image of nonmetallic inclusion of (C).

I collected and observed the specimen from the same point as Figure 2A in order to analyze the structure of iron artifact excavated from the 2nd site of house in Daesung-ri. Both a and b show similar structure overall, and ferrite, the rough pure iron structure of below 0.05%C in a part as in Figure 2B, is randomly distributed, and converted structure from cementite in layer pearlite which is formed after heat treatment at low temperature than eutectoid temperature as in Figure 2C, is observed. In addition, fine nonmetallic inclusions of different sizes are located in between structures and some of them are concentrated in some part.

As in such structure, that the cementite is formed as a result from making different sizes of bloom irons through direct-reduction process to iron artifact by hot forging below eutectoid temperature is regarded as air cooling and annealing when reheated.

As an enlarged picture of nonmetallic inclusions of iron artifact through SEM, Figure 2D analyzed the point a as EDS and the result is illustrated in Table 2. As the result of the analysis, it is a basic slag that contains SiO_2 , CaO , K_2O , Al_2O_3 , P_2O_5 and its maximum smelting temperature is estimated at 1,240°C and P_2O_5 does not seem to have been roasted. Moreover, it is defined that they used to charge liming materials such as shells or bones to furnace as flux to work looking at the ratio of SiO_2 : CaO : Al_2O_3 .

One iron axe produced by casting was excavated from 5th and 10th site of house each in Daesung-ri, Gapyeong. The specimen of the iron axe excavated from the 10th site of house was collected from the same point as Figure 3A and observed to analyze the structure of these artifacts and they show similar aspects overall as a rough ferrite matrix structure as in Figure 3B although the entire microstructure of casting iron axe varies. The tiny pores in the microstructure are the ones that were formed upon casting and you can see corroded magnetite inside the pore wall. When casted, microstructure appears to be white cast iron or gray cast iron

depending on cooling velocity as the structure of cast iron of 2-5%C but looking at the X-ray result, tiny holes have been formed on the ferrite structure of pure iron or casting artifacts that have a lot of casting pores in iron axes excavated from Daesung-ri. As an enlarged picture of left edge of the specimen, widmanstätten structure that precipitated to lath can be seen in Figure 3C. Widmanstätten, a rough ferrite structure on the left that is close to pure iron, on the right side of microstructure, seems to have fine structure as the edge is reheated through hot forging to 900°C near the point A₃ after decarbonization and the layer cementite in pearlite is spheroidized. Considering these structures, a pore phenomenon inside, outside casting adhesive line and structure, it is regarded that carbon inside the cast iron reacted to oxygen, evaded as CO or CO₂ gas and holes were formed due to the decarbonization in process of closed heating for long time after casting.

As an enlarged picture of the big nonmetallic inclusions on the top right of Figure 3C by SEM, in Figure 3D, the point a was analyzed by EDS and the result was summarized in Table 3. According to the components found in Table 3, the point a has a lot of FeO, SiO_2 and P_2O_5 and small amount of CaO, MnO, MgO which means less reduced wüstite is being formed on the fayalite and olivine basic slag, and P_2O_5 is found high as it is not roasted. In the result of analysis through EDS, when FAS, the major element, is substituted with ternary phase diagram, the maximum smelting temperature of the basic slag oxide is assumed to be about 1,390°C.

The socket structure of iron axe excavated from the 5th site of house in Daesung-ri has tiny holes in rough ferrite grain on top and black pearlite is formed between relatively fine ferrite grains at the bottom as in Figure 4A, which is regarded as a structure that has been formed after cementite of white cast iron being reduced to pearlite due to not enough time upon decarbonization when

Figure 4. Microstructure of iron axe excavated from the 5th site of house in Daesung-ri site (Yang and Kim, 2011). (A) Overall view of microstructure of an iron axe. (B) The lower section (left) of (A).

cementite and ledeburite of white cast iron structure is decarbonized for long time. As an enlarged structure of bottom left in Figure 4A, you can observe holes formed near where carbon used to be after decarbonization in ferrite matrix in Figure 4B, and a line structure outside the ferrite grain is regarded as a line that has been formed when cementite and ledeburite were decarbonized from white cast iron structure and reduced and spread to ferrite (Yang and Kim, 2011).

4.2. Iron objects from Yeongjong-do, Incheon

As in Figure 5 and 6, I collected 1 iron sickle from the tip, 2

iron chisels from the edge and tail of iron chisel and sheel mound of the same area excavated from the layer that includes artifact in B area of Yeongjong-do site to analyze metallographically (Kim, 2011).

The result of the analysis on the structure of iron sickle excavated from sheel mound, the overall structure was similar and ferrite and pearlite were formed in matrix. As in Figure 7A, carbon on iron sickle tip is about 0.7%, which is almost the same as that of eutectoid steel, considering the fact that martensite and troostite, microstructures, are observed together, it seems that martensite was formed first by quenching, reheated at 300–400°C and cooled in air. As in this structural aspect, it is regarded that

Figure 5. Sampling position (Kim, 2011).

Figure 6. Sampling position (Kim, 2011).

Table 4. Analysis result of SEM-EDS in Figure 7B (wt%) and temperature of ternary phase diagram (°C).

Point	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	FeO	FAS	FCS
1	2.08	4.92	37.27	2.78	1.61	34.61	16.73	1,550	1,350
2	-	1.55	10.08	-	1.36	13.89	73.12	1,100	1,290
3	2.01	5.10	35.79	3.7	2.06	33.54	17.80	1,590	1,330
4	1.91	3.55	29.52	2.51	1.18	24.78	36.55	1,300	1,150

Figure 7. Microstructure of iron sickle excavated from sheel mound in B area of Yeongjong-do site (Kim, 2011). (A) Martensite located tip. (B) The SEM image of tip.

they released martensite brittleness through softening that reheats it and relatively slowly cools in air after quenching in order to prevent the edge of iron sickle from break due to martensite.

Figure 7B is a picture of nonmetallic inclusions on the iron

sickle tip taken with SEM, black part near nonmetallic inclusions is coagulated after nonmetallic inclusions are melted and the hole was formed by the difference between matrix structure and contraction rates or by wandering oxygen that is formed by

Table 5. Analysis result of SEM-EDS in Figure 8C (wt%) and temperature of ternary phase diagram (°C).

Point	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	FeO	FAS	FCS
1	1.52	4.53	30.06	4.12	21.32	38.45	1,280	1,500
2	1.48	3.41	20.14	2.29	12.45	60.23	1,150	1,250
3	1.35	0.46	0.79	-	-	97.40	1,050	1,250

Table 6. Analysis result of SEM-EDS in Figure 8D (wt%) and temperature of ternary phase diagram (°C).

Point	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	FeO	FAS	FCS
1	1.37	3.85	36.57	2.74	3.22	16.85	35.40	1,430	1,150
2	-	1.53	11.39	-	0.65	3.02	83.41	1,100	1,320
3	-	1.54	14.03	-	1.08	5.36	77.99	1,110	1,300

Figure 8. Microstructure of iron chisel excavated from the Yeongjong-do site (Kim, 2011). (A) Martensite located edge. (B) Widmanstätten located back. (C) The SEM image of edge. (D) The SEM image of back.

reduction of FeO in nonmetallic inclusions. The marked part is what I analyzed through EDS and Table 4 is the result of the analysis. In Table 4, all parts except the point 2 are basic slag mixed with fayalite and olivine, seeing that SiO_2 and Al_2O_3 are very small in the point 2, crystallization temperature to wüstite seems to be $1,100^\circ\text{C}$ and the maximum smelting temperature of basic slag seems to be $1,350^\circ\text{C}$. In addition, seeing that the construction rates of all four points are similar, compounds of calcium that have a lot of Ca seems to have been put as a flux on purpose.

As in Figure 6, I collected specimen from the edge and tail of iron chisel and analyzed that martensite, a quenching structure formed upon quenching after carburizing, was observed on the iron chisel edge as in Figure 8A and small amount of ferrite was formed on the specimen matrix at the iron chisel tail as in Figure 8B. Seeing that carbon at the tail is below 0.3% and widmanstätten structure was formed after partially being overheated and cooled

in air, it seems that the point A₃ reached around 900°C . As such, it was defined that heat treatment was partially done on the part for quenching the iron chisel blade.

As in Table 5 that analyzed the marked part in Figure 8C, seeing that there were a lot of SiO_2 and MgO was found, it seems that the basic slag of wüstite formed on fayalite and olivine had the maximum smelting temperature of $1,250^\circ\text{C}$ and the bead type wüstite crystallization temperature of the point 3 is about $1,050^\circ\text{C}$. Table 6 is the result of the analysis from the position of Figure 8D, which is a basic slag that has less reduced white wüstite on the background of fayalite and olivine, and the oxide of this part seems to have the maximum smelting temperature of around $1,320^\circ\text{C}$. Also, seeing that CaO is relatively higher than SiO_2 , it seems that compounds of calcium such as shells were added as a flux upon smelting.

Figure 9. Microstructure of nail excavated from Garak 1st lake basin. (A) Sampling position. (B) Overall view microstructure of sample of nail. (C) Widmanstätten located upper section of sample. (D) Carburized network cementite.

Table 7. Analysis result of SEM-EDS in Figure 10 (wt%) and temperature of ternary phase diagram (°C).

Point	Na ₂ O	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	FeO	FAS	FCS
A	0.54	2.94	20.26	1.07	1.47	7.94	65.78	1,150	1,250

Figure 10. The SEM image of nail.

4.3. Iron objects from Garak-dong, Seoul

In the site of Garak-dong, I collected and observed specimen from the same position as Figure 9A in order to analyze the structure of nails excavated from Garak 1st lake basin. As in Figure 9B, what was observed was widmanstätten structure, ferrite structure of lath cooled in air after being overheated hypo-eutectoid steel, on top and under that part, carburizing structure formed overall. As in the enlarged picture of the top part of Figure 9B, a widmanstätten structure that is closer to pure iron due to incomplete carburizing compared to the bottom is observed, and in Figure 9D which is an enlarged picture of bottom right of Figure 9B, ferrite of fine lath becomes pearlite in widmanstätten structure of carburized lath and widmanstätten structure coexists in network form as rough ferrite does not be carburized. It seems that the hardness in some structures of white many-sided traits is 301.5~309.0Hv, which is higher than that of normal pearlite structure, as the amount of cementite got piled up in pearlite of layer upon carburizing.

Figure 10 illustrates the SEM layer of nonmetallic inclusions of lower top that has below 0.2%C of carbon in Figure 9B, the result of the analysis was summarized in Table 7. Light gray bead type part in Figure 10 is wüstite, the indicator microstructure of iron artifact formed by the method of reduction iron manufacture, and darker gray part of the point A is a glassy basic slag which has incompletely reduced FeO as the major element and small amount of SiO₂, CaO, K₂O, Al₂O₃ in it and its maximum smelting temperature seems to be about 1,250°C. The black arrow seems

to be either the hole formed when smelting nonmetallic inclusions were coagulated and contracted in process of nails being hot forged or the volume of oxygen left from FeO when wüstite in the glassy nonmetallic inclusions were reduced and transferred to microstructure.

Figure 11A is the whole structured specimen that was collected and observed from the central part of clamp excavated from the 2nd lake basin in Garak, and it is closer to pure iron below 0.05%C. Figure 11B is an enlarged picture of the bottom part of the specimen, pearlite is observed formed on the grain boundary of ferrite as small amount of carbon increased upon carburizing due to hot working. In addition, seeing that black bead type of nonmetallic inclusions are scattered throughout the specimen in Figure 11B, it is regarded that slags are not removed and mixed as not enough forging work is done for sponge-iron or bloom iron reduced by direct-reduction process. In this structure, clamp was made without any special work or heat treatment from bloom iron formed by solid reduction at low temperature on the surface in process of making clamp by forging. Seeing that the structures of clamps excavated from the site in Garak-dong are all overheated widmanstätten ones and partially carburized, carburizing seems to have been naturally done in process of hot forging in a furnace.

As an SEM of nonmetallic inclusions of clamp excavated from the 2nd lake in Garak-dong, Figure 11C summarizes the result of the EDS analysis on marked part. According to the result of the analysis that relatively small amount of SiO₂ and high FeO in four parts, it is estimated that incompletely reduced Fe is the main element and the maximum smelting temperature of a glassy basic slag that has small amount of P₂O₅, CaO, K₂O, Al₂O₃ is 1,310°C, and light gray B and D has bead type wüstite that has FeO as the main element and the crystallization temperature of 1,050°C. Seeing that P₂O₅ is analyzed to be high in this basic slag, it is assumed that raw stone was charged to furnace without roasting. An analysis of a clamp excavated from the Garak 1st Lake in the site of Garak-dong showed that its structure is similar to nonmetallic inclusions of clamp excavated from the Garak 2nd Lake, and a basic slag that has wüstite with incompletely reduced FeO as the major element and small amount of SiO₂, P₂O₅, CaO, K₂O was found.

I collected specimen from the back edge, edge and socket and observed them as in Figure 12 to analyze structure of iron knife excavated from the Garak 2nd Lake, and found that back edge and edge had overall similar microstructure with minor differences. Also, martensite, a structure for quenching, was formed in general as in Figure 14A, pearlite colony was formed

in part as in Figure 14B, and dark gray nonmetallic inclusions that looked like glassy was mixed. Pearlite colony formed on the martensite of iron knife was resulted from the quenching process of hypo-eutectoid steel below 0.6%, such structure was formed by quenching at higher temperature than critical temperature of iron knife and by cooling at lower temperature than critical cooling rate and was spit transformation. As a microstructure of specimen on socket part of iron knife, Figure 14C has small amount of pearlite between rough ferrites and there are great and small nonmetallic inclusions scattered in part. Thus, seeing that there is a lot of carbon in the edge of iron knife and that there is martensite on the edge and back edge while no martensite was found on socket, it is regarded that the edge was quenched in

furnace after carburizing and partial heat treatment was done for sockets not quenched.

As enlarged by SEM, Figure 14D is a picture of nonmetallic inclusions of specimen on the back edge of iron knife excavated from the Garak 2nd Lake, and Table 9 is the result of the analysis on nonmetallic inclusions by EDS. As in Table 9, the maximum smelting temperature of a basic slag that has FeO and SiO₂ as the major elements is estimated at 1,250 °C. In addition, although it has over 5% of CaO, iron is reduced and CaO looks like a lot and it has relatively smaller amount than SiO₂, so it is difficult to say that a component whose major element is Ca was put as a flux on purpose.

As in Figure 13, I collected specimen of iron spear from fleet,

Table 8. Analysis result of SEM-EDS in Figure 11C (wt%) and temperature of ternary phase diagram (°C).

Point	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	MnO	FeO	FAS	FCS
A	-	-	11.91	3.30	-	0.46	1.00	83.09	-	1,300
B	-	-	7.88	2.11	-	0.27	0.89	88.62	-	1,350
C	0.36	0.66	10.98	6.70	0.31	1.65	0.46	78.59	1,050	1,310
D	-	0.46	6.87	4.36	0.20	1.20	0.40	86.20	1,050	1,360

Figure 11. Microstructure of clamp excavated from the 2nd lake basin in Garak site. (A) Overall view of microstructure of sample of clamp. (B) Nonmetallic inclusion of the left side. (C) The SEM image of nonmetallic inclusion.

edge and the center of the body and observed them. Although the whole structures of all specimens vary, it is uneven as overheated

Figure 12. Sampling position.

structures of widmanstätten and pearlite are mixed. As in Figure 15A, the whole structure of edge specimen is relatively even, the

Figure 13. Sampling position.

Table 9. Analysis result of SEM-EDS in Figure 14D (wt%) and temperature of ternary phase diagram (°C).

Point	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	FeO	FAS	FCS
A	1.72	1.75	42.14	2.58	6.78	0.26	44.78	1,500	1,250
B	1.70	2.00	41.40	2.52	6.89	0.38	45.11	1,450	1,180

Figure 14. Microstructure of iron knife excavated from the Garak 2nd lake. (A) Martensite located edge. (B) Pearlite colony located back edge. (C) Ferrite of iron knife socket. (D) The SEM image of the back edge of iron knife.

amount of carbon is close to 0.7%, of eutectoid steel, and network widmanstätten is formed on the matrix of pearlite. Figure 15B is a microstructure of body centered specimen which is similar to edge one, glassy nonmetallic inclusions are mixed.

Figure 15C analyzed nonmetallic inclusions of specimen of iron spear tip excavated from Garak-dong on SEM by EDS, and

its results are summarized in Table 10. A in Table 10 is a fayalite basic slag where small amount of incompletely reduced SiO_2 , Al_2O_3 and CaO , K_2O are in solid solution whose maximum smelting temperature is $1,150^\circ\text{C}$ and B is less incompletely reduced wüstite whose crystallization temperature is estimated to be $1,050^\circ\text{C}$.

Table 10. Analysis result of SEM-EDS in Figure 15C (wt%) and temperature of ternary phase diagram ($^\circ\text{C}$).

Point	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	FeO	FAS	FCS
A	0.39	0.61	3.87	17.49	0.93	0.99	75.72	1,150	1,250
B	-	-	1.26	4.05	-	-	94.36	1,050	-

Table 11. Analysis result of SEM-EDS in Figure 15D (wt%) and temperature of ternary phase diagram ($^\circ\text{C}$).

Point	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	FeO	FAS	FCS
A	-	1.37	0.70	18.17	-	-	0.45	79.31	1,050	1,250
B	1.24	-	8.97	21.86	1.25	3.52	3.38	59.78	1,220	1,200

Figure 15. Microstructure of iron spear excavated from Garak site. (A) Overall view of microstructure of edge of iron spear. (B) Pearlite located the body of iron spear. (C) Nonmetallic inclusion of fleet of iron spear. (D) Nonmetallic inclusion of edge of iron spear.

Table 12. Microstructure and nonmetallic inclusions by artifact excavated in Seoul and Gyeonggi Region (decarbonization eutectoid=decarbonization hypo-eutectoid steel, carburizing eutectoid=carburizing hypo-eutectoid steel).

Site	Artifact	Century	Microstructure	Material	Form of Nonmetallic Inclusions	Al ₂ O ₃ SiO ₂	Crystallization Temperature (°C)	Maximum Smelting Temperature (°C)	Carbon (%)
Daesung-ri, Gapyeong	Iron Artifact, Iron Arrowhead, Iron Knife	2~3	Ferrite, Pearlite, Spheroidite	Hypo-Eutectoid Steel + Nonmetallic Inclusions	Wüstite, Irregular Compound, Glassy Slag	0.76	-	1240	0.03
	Ferrite, Pearlite, Magnetite, Widmanstätten		Decarbonization Eutectoid, Decarbonization Hole	Fayalite, Wüstite, Bead Type Irregular Compound, Glassy Slag	0.19	-	1390	0.02	
Yeongjong-do	Iron Sickle	4	Ferrite, Pearlite, Martensite, Troostite	Hypo-Eutectoid Steel + Nonmetallic Inclusions	Fayalite, Wüstite, Irregular Compound, Glassy Slag	0.15	1100	1350	0.7
	Ferrite, Pearlite, Martensite, Widmanstätten				0.15	1050	1320	0.3	
Garak-dong	Nail	4	Ferrite, Pearlite, Widmanstätten	Hypo-Eutectoid Steel + Nonmetallic Inclusions	Wüstite, Irregular Compound, Glassy Slag	0.15	-	1250	0.2
	Clamp				0.06	1050	1310	0.2	
	Iron Knife		Martensite, Pearlite Colony		Wüstite, Singular Compound, Glassy Slag	0.04	-	1250	0.6
	Iron Spear		Ferrite, Pearlite, Widmanstätten		Wüstite, Regular · Irregular Compound, Glassy Slag	0.26	1050	1220	0.4

Figure 15D analyzed nonmetallic inclusions of edge specimen on the position marked as SEM layer by EDS and its result of the analysis is summarized in Table 11. The light point A is incompletely reduced wüstite whose crystallization temperature is 1,050°C and the black point B is fayalite basic slag whose maximum smelting temperature seems to be 1,220°C.

4.4. Summary and discussion

Table 12 summarizes analyzed structure and nonmetallic inclusions of iron artifact excavated from Seoul and Gyeonggi area and it seems that partial heat treatment was done depending on the purpose of artifact or on occasion demands. Seeing that the content of Al_2O_3 is lower than SiO_2 in iron ore, it is regarded that they worked with magnetite. Also, what is noteworthy is that the structure of casting iron axe excavated from Daesung-ri, Gapyeong was decarbonized after casting of iron axe, supplemented the weakness of casting artifact that has strong brittleness and was found to be cast iron decarbonization steel with tenacity.

The result of EDS analysis showed that as wüstite was crystallized a lot, most of them except solid decarbonized iron axe excavated in Daesung-ri was made by direct-reduction process. The crystallization temperature of such wüstite was estimated to be around 1,050°C and CaO , Al_2O_3 , K_2O , MgO , P_2O_5 were in solid solution of glassy slag in fayalite and olivine of nonmetallic inclusions, its solidification temperature was about 1,250°C and varied depending on the content of FeO and CaO , Al_2O_3 .

5. CONCLUSION

I researched microstructure of iron artifact excavated from Han River basin in Proto-Three Kingdoms, measured microhardness, analyzed nonmetallic inclusions mixed in microstructure and reinterpreted the results as ternary phase diagram to study work temperature. In addition, I acquired following results of steel manufacture that uses heat treatment and manufacturing technology by metallographic interpretation.

Seeing that the portion of iron ore is $\text{Al}_2\text{O}_3/\text{SiO}_2$ regardless of region and age and the content of SiO_2 is high and Al_2O_3 is relatively low in iron artifacts of Han River basin in Proto-Three Kingdoms, it is assumed that they worked with magnetite. Also, seeing that wüstite, indicator structure of iron artifact that was formed by direct-reduction process, is crystallized in nonmetallic inclusions, it is regarded that bloom iron and sponge-iron were made through direct-reduction process and transformed to iron artifacts.

Carburizing steel that carburizes by CO , CO_2 gas that comes from charcoal when forge welding bloom iron that is close to pure iron is the steel manufacturing method, seeing that partial heat treatment was done on artifacts depending on the purpose of

artifacts as in iron chisel excavated in Yeongjong-do or iron knife excavated in Garak-dong, I was able to find the technological perception of iron artifact manufacturers in Han River basin in Proto-Three Kingdoms. Seeing that artifacts with blade were carburized, quenched and heat treated, it is judged that such heat treatment was commonly used in Han River basin in the 3rd century.

It was found that wüstite was crystallized below the temperature of 1,050°C in below 1% of Al_2O_3 and considering the ternary phase diagram of glassy nonmetallic inclusions, it is assumed that iron manufacture work was done at the temperature of around 1,250°C. With 1,400°C of the maximum smelting temperature of casting iron axe excavated in Daesung-ri, assuming its temperature in Fe-C phase diagram, it was regarded as decarbonized cast iron in which casting was done by hypoeutectic cast iron around 2.3%C, decarbonized in solid state, reduced to steel that is close to pure iron and improved brittleness of cast iron.

Structure portions of CaO and SiO_2 of both the two artifacts from Yeongjong-do were similar which was different from that mixed in iron ore, and it is judged that calcareous elements such as shells with high content of Ca were put as a flux on purpose. Moreover, seeing that P_2O_5 is high in sites, it is assumed that unroasted iron ore was charged to furnace.

Although it was meaningful to research iron manufacture and manufacturing technology of iron artifacts in Han River basin during the Proto-Three Kingdoms through this study, I think the result cannot represent the era and region as there were not enough artifacts that are difficult to collect uncorroded specimen for analyzing the number of sites. However, it is considered that the outcome of this study will contribute to more research on the differences and similarities of iron manufacturing technology system in era and region of Han River basin, and I am confident that if such researches are done a lot, it will be important data to define the development of ancient iron manufacturing technologies.

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