Archaeometallurgical Study at Ban Khao Din Tai Archaeological Site, Buriram Province

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Abstract: This research applied the archaeometallurgical techniques to study the slag in the ancient iron smelting furnace at Ban Khao Din Tai archaeological site, Buriram province, northeastern Thailand. In this investigation, all slag samples were examined by the scanning electron microscopy with energy dispersive x-ray spectrometry (SEM-EDX), X-ray fluorescence spectrometry (XRF), X-ray diffractometer (XRD) and optical microscope to analyze the physical and chemical properties. These iron slag likely formed under similar condition, based on the FeO-SiO2-Al2O3 ternary diagrams that they fall into hercynite region, denoting a technology producing sufficient quantities of iron, with relatively low slag melting temperatures between 1,088-1,250 °C.

บทคัดย่อ: การวิจัยทางด้านโลหกรรมโบราณของเหล็กในประเทศไทยครั้งนี้เป็นการศึกษาเทคโนโลยีด้านโลหกรรมในสมัยโบราณ ในแหล่งโบราณคดีบ้านเขาดินใต้ จังหวัดบุรีรัมย์ ภาคตะวันออกเฉียงเหนือของประเทศไทย ตัวอย่างที่นำมาวิเคราะห์เป็นกากตะกรันโลหะที่ขุดพบในแหล่งโบราณคดีนี้ การวิคราะห์ใช้เทคนิคและเครื่องมือดังต่อไปนี้ scanning electron microscopy with energy dispersive x-ray spectrometry (SEM-EDX), X-ray fluorescence spectrometry (XRF), X-ray diffractometer (XRD) ผลการศึกษากากตะกรันโลหะโดยใช้ไดอะแกรม $FeO-SiO_2-Al_2O_3$ พบว่าองค์ประกอบธาตุส่วนใหญ่อยู่ในแร่ hercynite แสดงให้เห็นประสิทธิภาพในการในการถลุงแร่เหล็กที่อยู่ในช่วงอุณหภูมิ 1,088-1,250 °C

Key words: Archaeometallurgy, scanning electron microscopy with energy dispersive x-ray spectrometry, X-ray fluorescence spectrometry, X-ray diffractometer, Ban Khao Din Tai archaeological site

1. Introduction

Ban Khao Din Tai archaeological site is one of the ancient rural sites in the region of Buriram Province, northeast Thailand (figure 1). It is located at 14°44´ N latitude and 103°08´E longitude, situated near small stream which is called Huai Ta Sek, approximately 10 km north of the Thai-Cambodian border.

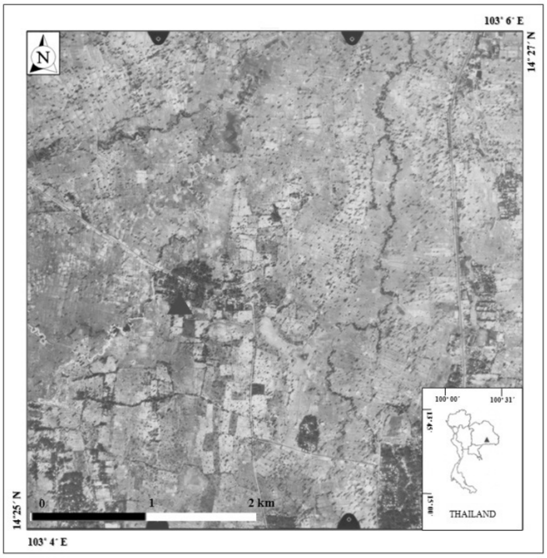


Figure 1 Aerial photograph (Department of Lands; 1991)of Ban Khao Din Tai archaeological site, Tambon Ban Kruat, Amphoe Ban Kruat, Buri Ram Province (red triangle: study area).

The site was originally surveyed by the Fine Arts Department in 1987, the project found numerous slag heaps on the surface of the mould. In 1989 to1992, a joint project entitled "An archaeological study of the iron-smelting and salt-making industries in the northeast of Thailand", was repeatedly surveyed at the site by Prof. Eiji Nitta, Prof. Srisakra Vallibhotama, Dr. Pornchai Suchitta and Mr. Chalit Chaikanchit. Until 2005, a team of Living Angkor Road Project was repeatedly surveyed. Though a previous archaeological survey before 2007 confirmed the metallurgical evidence in the vicinity of present Ban Ban Khao Din Tai, there was no excavation ever conducted to research intensively on metallurgy in this area. This excavation was divided into two pits, that is, the first pit on the centre of the mound and the second on the west slope of mound. From the excavation, archaeological evidence relating to probably iron metallurgy, include smelting slags, tuyère, smelting furnace fragments, potsherds, baked sediment and charcoal.

2. Materials and methods

Five slag samples from the archaeological site were selected from the ancient iron smelting furnace. The samples were prepared to the physical and chemical analysis. This research selected the optical microscope, scanning electron microscopy with energy dispersive x-ray spectrometry (SEM-EDS) and X-ray diffraction (XRD) were selected to this research.

2.1 Reflected light microscopy

The preparation of the specimen is most important. Although in the past few decades, there has been increasing automation of the grinding, polishing and finishing of the sample, there still is considerable skill and experience needed in selecting the procedures that are best suited for particular sample types. Polished sections are very convenient because they can be use for both reflected light microscopy and scanning electron microscopy with energy dispersive x-ray fluorescence analysis. The samples were examined at magnifications between 4, 10, 40 and 100 times in Olympus BX41 microscope with 6V-30 watt power supply, Kohler Illumination light paths for transmitted light path. Phase identifications were achieved with standard mineralogy textbooks but with an understanding of the anthropogenic phases produced rapidly at high temperatures during metallurgical processes.

2.2 X-ray diffraction (XRD)

X-ray diffraction analysis can tell us the identity and distribution of minerals in metal slags. Minerals present in metal slags are often good indicators of gas atmosphere in furnace, cooling rate of slag and homogeneity of slag. If there is un-decomposed charge trapped in slag, more information about ore and flux can be learnt. Crystalline phase was identified by powder x-ray diffraction. The XRD experiments were performed on a Bruker D8-advance diffractometer. The x-ray source is a 2.2 kW Cu-anode long fine focus ceramic X-ray tube. The running conditions for the x-ray tube are 40 kV and 40 mA, the power supply controls these with a stability of better than 0.01% for the high voltage and 10% of the variation of the supply for the current. x-ray powder diffraction patterns were recorded in the range between 10 and 70 degree.

2.3 Scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDS)

SEM-EDS was principally applied to this study for multiple purposes, namely the identification of phases, the chemical compositional spot analysis of each phase. The significant efficiency which is allows the mentioned tasks to be achieved is that SEM-EDS is a qualitatively and quantitatively chemical analyzer and the analyst can control a sharp focused beam to analyze very specific area or spot inside a sample in contrast to XRF which provides only the chemical composition of the whole sample. Thus, it benefits in terms of providing an identification or confirmation of phases or inclusions using a spot analysis together with a back scattered electron imaging. An area analysis can provide a bulk chemical composition in which it is very good for the complicated sample, especially ones with many areas or phases. Morphology and elemental compositions of all slag samples were determined by JEOL JSM-5900 microscope with Oxford energy dispersive x-ray fluorescence spectroscopy, with Probe current up to uA, optimized resolution ~5 nm, vacuum ~1 Pa, beam energy up to 30 keV.

3. Results of chemical compositional and Microscopic analysis

Macroscopically, five slag samples as A0538, A0539, A0540, A0541 and A0542 obviously different in their inner and outer morphologies. Two major types of slag were identified and labeled as either lumpy or flattened shape. Firstly, lumpy slag samples (figure 2A) appear the partially dense and porous, except for sample A0541, it consists of a large number of porosities. The size of samples ranging from 5 to 8 cm. Luster of the samples ranges from glassy to matte and textures include frothy, glassy, smooth and vesicular. Secondly, flattened shape slag samples (figure 2B) are usually flat. The thickness ranges from approximately 1 to 1.5 cm. They contain minor amounts of porosity and signs of flow on one or more surfaces typical of tapped slags, which is typically associated with a smelting process.

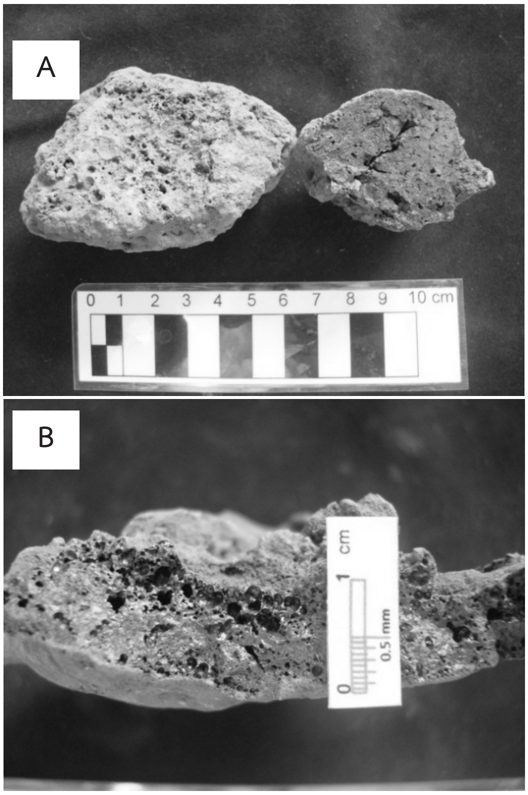


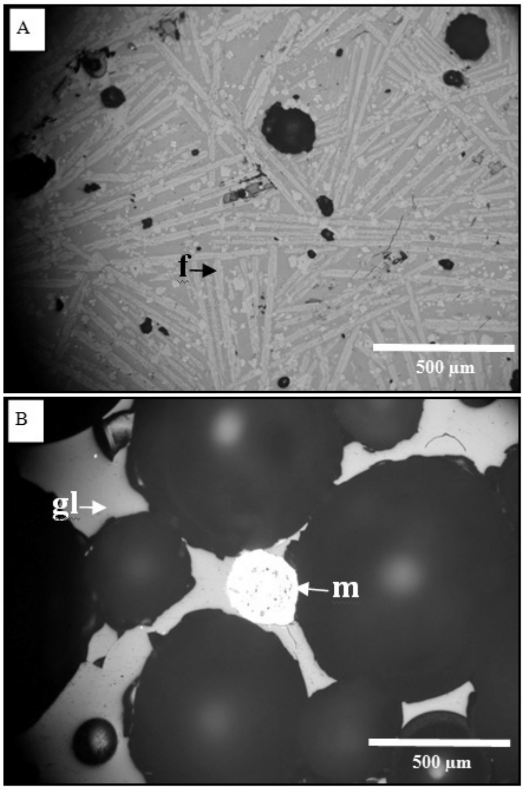
Figure 2 (A) Macroscopic of block to lump slag (sample A0538). (B) Macroscopic of flattened shape slag (sample A0539).

The bulk chemistry for five samples is given in table 1. The samples relatively contain the highest FeO (45.10-52.25 wt.%), SiO_2 (26.23-33.97 wt.%) and Al_2O_3 (11.58-12.70 wt.%) concentrations with lesser amounts (<2 wt.%) of K_2O, CaO, TiO_2, V_2O_5, Cr_2O_3, MnO, ZrO_2, SrO in sample A0540 and CdO in sample A0539. Due to the relative high content of Al_2O_3 related with abundant hercynites being seen in all slags.

Microscopically, the mineralogy of the samples obtained by x-ray diffraction, optical microscope and scanning electron microscope analyses is given in table 2, and appendix d to f. Slag samples from Ban Khao Din Tai consist of various phases including fayalite, hercynite, quartz, metallic phase in a glassy matrix. Fayalites were commonly found as very fine- to fine-skeletal laths crystals (figure 3A). The laths up to several millimeters in length are very abundant. The following ranges in elements of fayalite were found (by EDS spot analyses, see appendix d): 52.46-58.83 wt.% O, 23.19-29.82 wt.% Fe, 16.21-17.84 wt.% Si with a trace of 1.760 wt.% Al in sample A0542. Regarding the shapes of the fayalites in slags, that can be informative in terms of the smelting process, and exists in all samples, they show the very fine- to fine-skeletal laths crystals. It is assumed that they could have been produced by either being tapping out of furnace or dripped down into a cold slag pit.

All samples also contain coarse-dendritic to euhedral hercynite crystals with large amounts of O (49.19-55.41 wt.%), Al (29.37-31.55 wt.%), Fe (14.48-

17.36 wt.%) and minor amounts (<1.5 wt.%) of V, Cr in sample A0539 and Ti in sample A0538. Metallic iron commonly occurs as rounded blebs or prills up to 250 μm in diameter, some metallic iron occurs as irregular in shape. By EDS spot analyses (see appendix d), the chemical component of metallic iron is 100 wt.% Fe. Quartz is rarely present as macroscopic to microscopic anhedral fractured grains with cracks of unmelted inclusions. The matrix of most samples is abundant glass, some areas of sample A0541 is only clear glass with iron prills (figure 3 C).



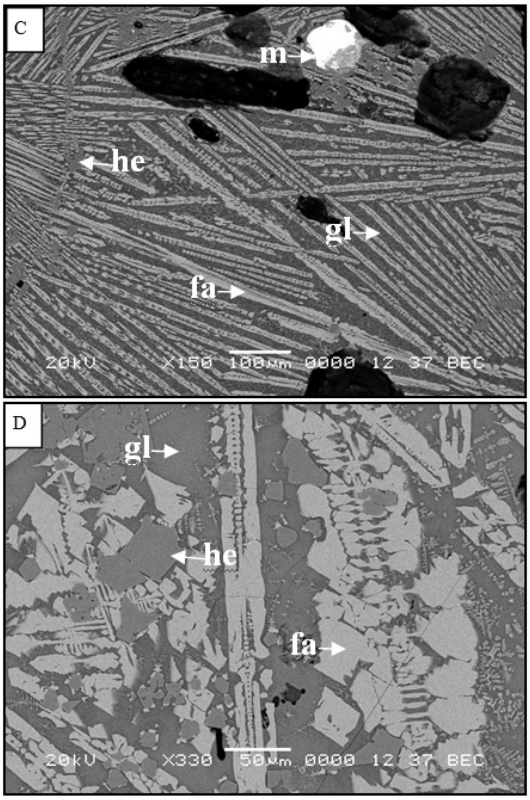


Figure 3 Reflected light microscope image (A) Skeletal fayalite laths in glassy matrix (sample A0540) (B) Iron prill in sample A0541; Scanning electron microscope image (C) Corroded iron in sample A0540 (D) Euhedral hercynite and fayalite laths in glassy matrix of sample A0538, fa-fayalite, he-her cynite, Qt-Quartz, m-metal, gl-glassy matrix.

When plotted in the FeO-SiO_2-Al_2O_3 ternary diagrams to provides insight into the evolution of the melt as phases crystallize as well as required smelting temperatures, as Khok Kroy and Ban Saitho 7 slags. All slag samples fall into hercynite region close to the optimum 1, indicating operating temperature at about 1,088-1,250 °C (figure 3), although sample A0540 plots within the little more SiO_2 region, characterized by lower operating temperature and approaching the optimum 1.

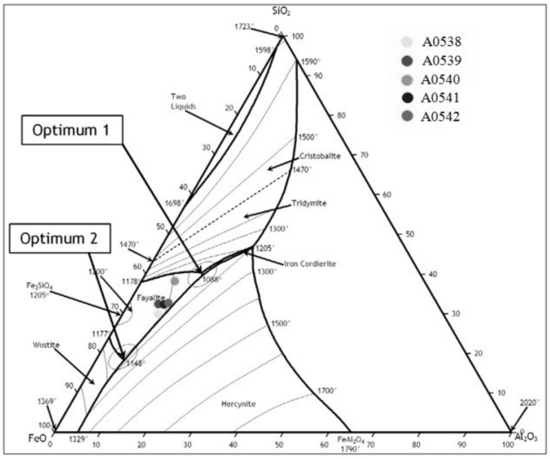


Figure 3 FeO- SiO_2-Al_2O_3 ternary diagrams, presenting the distribution of studied slags of Ban Khao Din Tai archaeological site [1].

The Ban Khao Din Tai slag evidence is entirely consistent with the expect waste product of the bloomery iron-making process according to their macroscopic, chemical compositional and microscopic information. The chemistry of the slag melt as well as the condition within the smelter determined which phase will ultimately form in the slag. Therefore, the phase as well as their chemical composition and microstructure all provide insight into the smelting condition in their furnaces.

4. Discussion and conclusion

Regarding the bulk chemical composition, all samples have very similar chemical compositions, suggests that these samples were produced in a very similar manner in terms of the methodological approach to the technology and the ingredients used. This similarity in chemical composition between the slag samples is illustrated in table 1 as mentioned above. In addition, Alumina, silica and iron oxide are the main compounds in most iron smelting slags, together they make up over 90% of the bulk weight of the samples. This indicates that all of samples are metallurgical slags produced during the bloomery iron-making process. However, low content of CaO in all samples (0.289-0.910 wt.%), suggests that no flux was used in this operation but the process could benefit from the self-fluxing of used material ore [2].

The microstructure and phase composition show that fayalite and hercynite are dominant component of all samples. As mentioned in the bulk chemical compositions, all samples have relatively low CaO content which is in good agreement with the presence of fayalite. In contrast, if the system contains relatively high CaO content, the crystal may become Kirschsteinite ($CaFeSiO_2$). Regarding the shapes of the fayalites in the samples, which can be informative in terms of the smelting process, and exists in all samples, they show the very fine- to fine-skeletal laths crystals. Technically, this very fine- to fine-skeletal laths crystals is formed when their solidification is speeded up by exposure to cooler air. This fast cooling may be due to many reasons during the processes. However, for the studied slags, it is assumed that they could have been produced by either being tapping out of furnace or dripped down into a cold slag pit [3] and the presence of fayalite might be preliminarily indicate a relatively high operating temperature of exceed 1,100 °C. In addition, the relative high content of Al_2O_3 related with abundant hercynites being seen in all slags.

All slag samples likely formed under similar condition, based on the $FeO-SiO_2-Al_2O_3$ ternary diagrams in figure 3, all slag samples fall into hercynite region, denoting a technology producing sufficient quantities of iron, with relatively low slag melting temperatures between 1,088-1,250 °C. In addition, the overall alumina to silica ratio within the slags at this site is relatively high at about 1:2, in the $FeO-SiO_2-Al_2O_3$ ternary diagrams the high alumina within the sample is apparent, in accordance with the generally dominant hercynite phase.

5. Acknowledgement

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Table 1 Bulk chemical composition (in wt%) of slags from Ban Khao Din Tai archaeological site (determined by ED-XRF method).

	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	V_2O_5	Cr_2O_3	MnO	FeO	SrO	ZrO_2	CdO
A0538	12.15	26.23	0.344	0.466	1.898	0.182	0.138	0.456	52.25	-	0.064	-
A0539	11.58	27.91	0.192	0.289	1.621	0.155	0.118	0.443	51.84	-	0.054	0.028
A0540	11.63	33.97	0.298	0.910	1.792	0.153	0.125	0.925	45.10	0.014	0.057	-
A0541	12.20	28.07	0.317	0.754	1.997	0.080	0.068	0.445	50.39	-	0.061	-
A0542	12.70	29.76	0.331	0.307	1.257	0.133	0.068	0.572	49.31	-	0.069	-
Mean	12.06	29.19	0.296	0.545	1.713	0.140	0.103	0.568	49.78	n/a	0.061	n/a

Symbols used: -, not detected; n/a, not available

Table 2 Phases in Ban Khao Din Tai archaeological site slag samples obtained by XRD analysis (% wt), optical microscope and scanning electron microscope. LAB ID.

LAB ID.			A0538	A0539	A0540	A0541	A0542
Group	Name	Ideal/range composition					
Silicates	Fayalite	Fe_2SiO_4	81.31	74.45	71.00	74.91	72.91
	Quartz low	SiO_2	-	4.200	15.85	6.760	7.650
Oxides	Hercynite	$FeAl_2O_4$	18.69	21.34	13.15	18.32	19.44
Metal	Pure metal	Fe	*	*	*	*	*
Glass			*	*	*	*	*

Symbols used: -, not detected; *, detected by optical microscope and scanning electron microscope