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Archaeometallurgical Studies of Ancient Iron Smelting Slags from Ban Khao Din Tai Archaeological Site, Northeastern Thailand

[1]Theeraporn Chuenpee, [1]Krit Won-In, [2]Surapol Natapintu and [3]Isao Takashima
[1]Department of Earth Sciences, Faculty of Graduate School, Kasetsart University, Bangkok, 10900, Thailand
[2]Department of Archaeology, Faculty of Archaeology, Silpakorn University, Bangkok, 10200, Thailand
[3]Mining Museum, Faculty of Engineering and Resources Science, Akita University, Japan

Abstract: Archaeological excavations at Ban Khao Din Tai archaeological site have revealed a substantial number of iron slags. Studying these iron slags was important because of their archaeological and technological interests. In this study selected five iron slags for the archaeometallurgical studies, energy dispersive X-ray fluorescence spectrometry was used to determine the bulk chemical composition. Optical microscopy and scanning electron microscopy were used to identify the mineralogical and micro-structural composition. Furthermore, X-ray powder diffraction was used to confirm the mineralogical composition. The archaeometallurgical studies suggest that Ban Khao Din Tai slag evidence is entirely consistent with the expect waste product of the bloomery iron-making process or direct smelting process. All samples were produced in a very similar manner in terms of the methodological approach to the technology and the ingredients used. Iron, silica and alumina oxide are the main compounds in most iron slags and no flux was used in this operation but the processes could benefit from the self-fluxing of used material ore. Fayalite is dominant component of all samples and the presence of fayalite might be preliminarily indicate a relatively high operating temperature of exceed 1, 100°C.

Key words: Archaeological excavation, iron slag, archaeometallurgical study, bloomery iron-making process, direct smelting process

INTRODUCTION

Ban Khao Din Tai archaeological site is one of the ancient rural sites in the region of Buriram Province, northeastern Thailand (Fig. 1). It is located at 14°44'N latitude and 103°08'E longitude, approximately 10 km north of the Thai-Cambodian border. 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 1989-1992, 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 and his colleagues. 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 research intensively on metallurgy in this site. While the excavation was undertaken in 2007 by the team of Living Angkor Road Project as mentioned. From the excavation, archaeometallurgical evidence relating to iron metallurgy was found that is tuyère, smelting furnace fragments, potsherds, baked sediment and charcoal as well as a large number of smelting slags.

The examination of macroscopic features and chemical, mineralogical and micro-structural compositions of smelting slags can give the answers to many questions about archaeology and history of technology (Tylecote, 1962). The aim of this study was to examine macroscopic features and the chemical, mineralogical and micro-structural compositions of iron smelting slags found in Ban Khao Din Tai archaeological site dating from the Dvaravati Period (the 8th-10th century A.D).

MATERIALS AND METHODS

Materials: In this study, five iron slags found at Ban Khao Din Tai archaeological site were chosen for the analysis, both macro- and microscopically.

Methods: Macroscopic descriptions and dimensions were preliminarily recorded of all samples prior to further analyses in order to identify possible patterning in terms

Corresponding Author: Theeraporn Chuenpee, Department of Earth Sciences, Faculty of Graduate School, Kasetsart University, Bangkok, 10900, Thailand

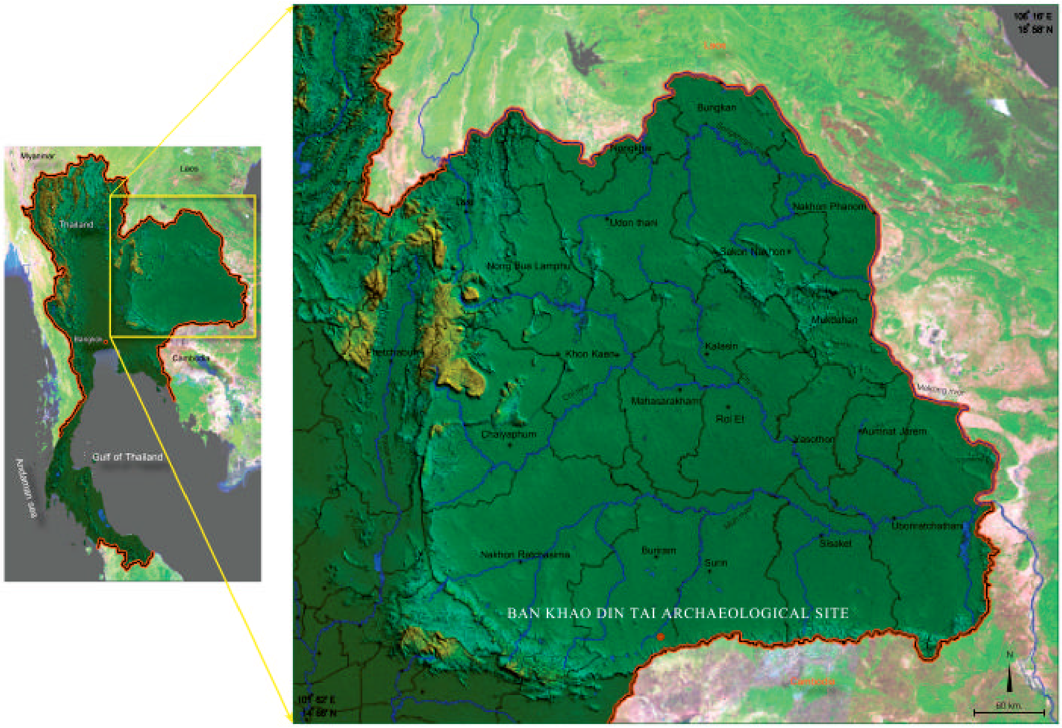

Fig. 1: Digital elevation model (DEM) showing location of the study site where situated in the lower part of Northeastern Thailand

of shape and size of slag, flow structures, plant impressions and so on. Microscopically, to determine the bulk chemical composition of the samples, energy dispersive X-ray fluorescence spectrometer (ED-XRF) was used. The mineralogy and micro-structure of the samples were studied by both optical microscopy (in reflected plane-polarized light) and scanning electron microscopy. In addition, the mineralogy of the samples was also confirmed by X-ray powder diffraction (XRD).

For ED-XRF and XRD study, the samples were perfectly cleaned and finely powdered in an electric agate mortar and pestle into the grain size of around 37 μm in order to avoid any imbrications in the obtained results. Compressed pellets of slag powders were analyzed for bulk chemical composition by energy dispersive X-ray fluorescence spectrometer using a Seiko SEA-2010 instrument. Other portions of the same slag powders were used for the X-ray powder diffraction analysis made on a Bruker-D8 diffractometer with $CuK_{\alpha 1}$ radiation, over the range 10-70° two-theta.

For optical microscopy and SEM study, the samples were prepared as resin-mounted polished section. The samples were cut to a size of about 1 cm^2, embedded in resin and ground using tungsten carbide grits (grade 200, 320, 800 and 1,000). Final polishing was performed by polished with 3 and 1 μm aluminum oxide paste. Thereafter, they were examined at magnifications between 4, 10, 40 and 100 times under an Olympus BX41 polarizing microscope in reflected plane-polarized light. The same polished sections were then coated with carbon, studied under a JEOL JSM-5900 scanning electron microscope with Oxford energy dispersive X-ray fluorescence spectroscopy. The SEM was used for micro-photographs in back-scattered electrons (BSE).

RESULTS

Two types of slag from Ban Khao Din Tai archaeological site were identified macroscopically and labeled as either platy or lumpy according to their general morphology (Fig. 2). Firstly, platy slags are usually flat. The thickness ranges from approximately 1-1.5 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. Secondly, lumpy slags appear the partially dense and porous, except for sample A0541 which consists of a large number of porosity. All the slags were dark reddish-or orange-brown, the size of samples ranging from 5-8 cm and luster of the samples ranges from glassy to matte and textures include frothy, glassy, smooth and vesicular.

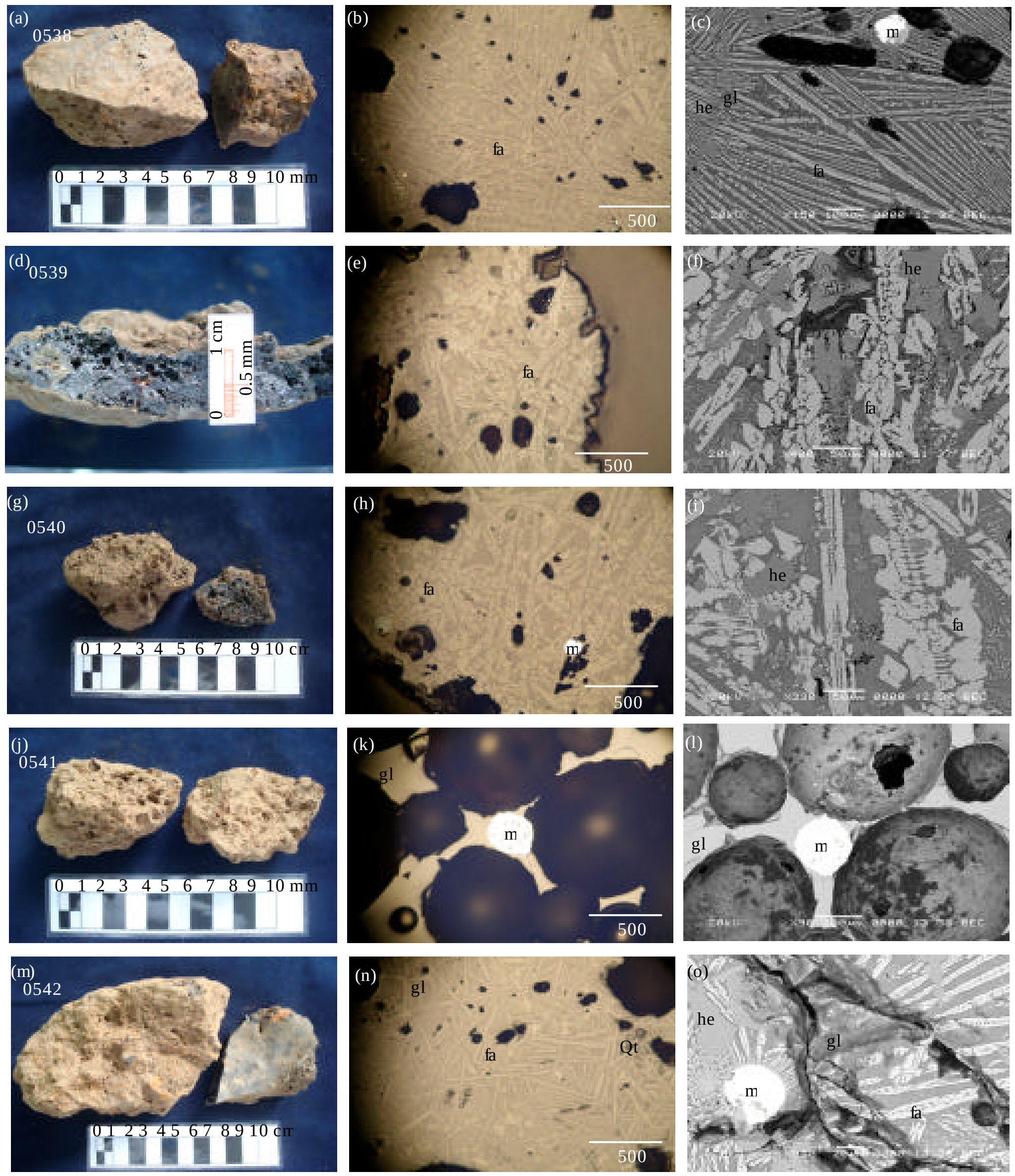

Fig. 2(a-o): Five slag samples found at the site: A0538, A0539, A0540, A0541 and A0542; Reflected light microscope images of each sample, (b, e, h, k and n), Scanning electron microscope images of each sample, (c, f, i, l and o), Abbreviations: Fa-fayalite, he-hercynite, Qt-Quartz, m-metal or iron prill, gl-glassy matrix. (a, b, c) Sample A0538: Skeletal fayalite (fa) laths, small grains of hercynite (he) and corroded iron prill (m) in glassy matrix (gl) (d, e, f). Sample A0539: skeletal fayalite (fa) laths and euhedral hercynite (he). (g, h, i) Sample A0540: Euhedral hercynite (he), skeletal fayalite (fa) laths and small grain of iron prill (m) in glassy matrix (gl). (j, k, l) Sample A0541, clear glass (gl) with iron prill (m). (m, n, o) Sample A0542: Skeletal fayalite (fa) laths, euhedral hercynite (he), iron prill (m) and Quartz (qt) in glassy matrix (gl)

The notable difference between the two slag types is not detected. Interestingly, analysis of each of the slags showed that it is highly homogeneous in its chemical composition, mineralogy and micro-structure. Bulk chemical compositions obtained from five slags are given in Table 1. Iron oxide (45.10-52.25 wt%), silicon oxide (26.23-33.97 wt%) and aluminium oxide (11.58-12.70 wt%) are predominant in all samples. Calcium oxide (CaO) is present in all samples in relatively low amount, with an average of 0.545 wt%. Other elements also present in lesser amounts (<2 wt%) of K_2O, TiO_2, V_2O_5, Cr_2O_3, MnO, ZrO_2, SrO in sample A0540 and CdO in sample A0539.

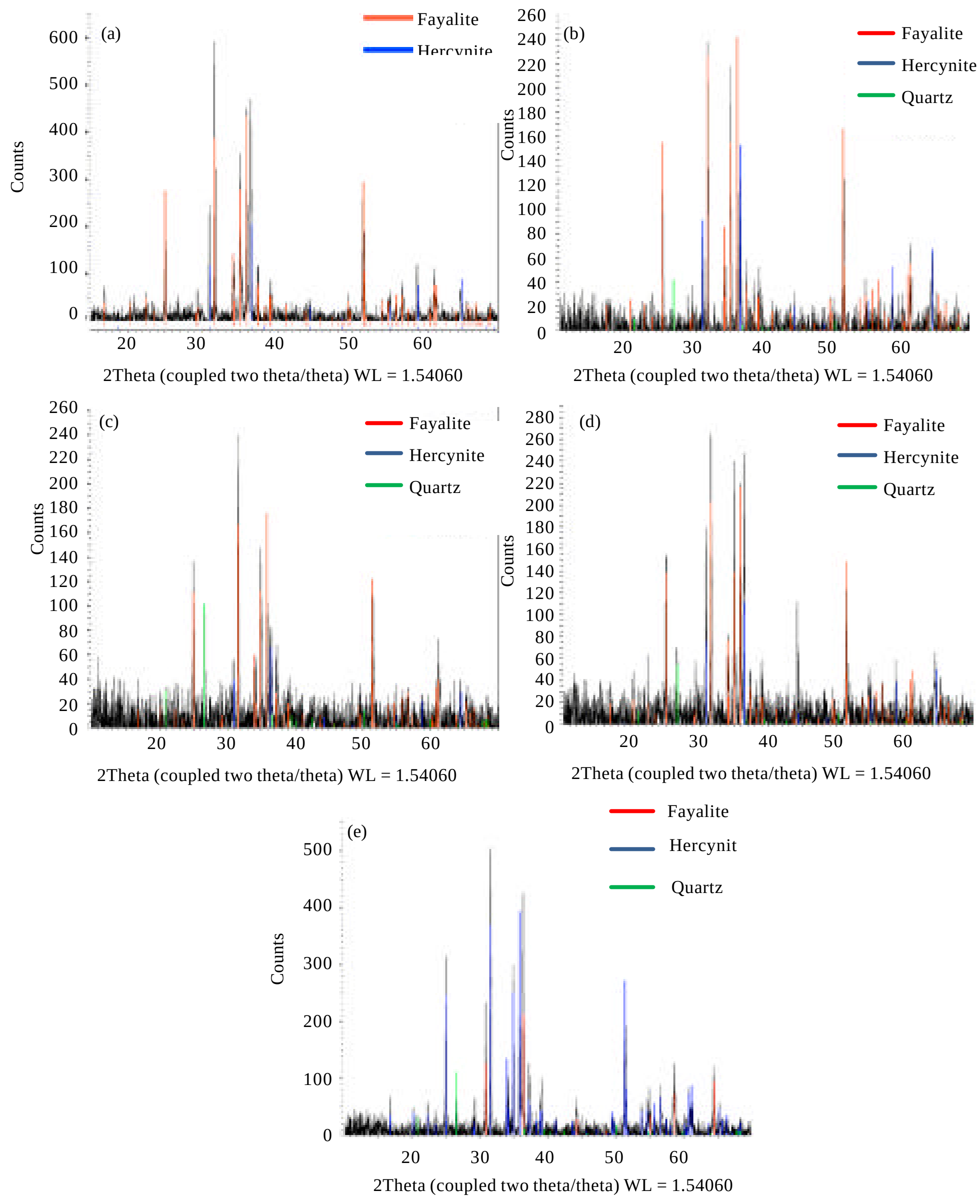

Fig. 3(a-e): XRD diffraction pattern obtained from five slag samples, (a) A0538, (b) A0539, (c) A0540, (d) A0541 and (e) A0542), confirming the formation of fayalite, hercynite and quartz. The x-axis is 2-theta and y-axis is the intensity (counts)

The mineralogy and micro-structure of the samples obtained by optical microscope and SEM analyses are given in Fig. 2. Slag samples 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.

The laths up to 500 μm in length are very abundant. The samples also contain coarse dendritic to euhedral hercynite crystals. Metallic iron commonly occurs as rounded blebs or prills up to 250 μm in diameter, some metallic iron occurs as irregular in shape. 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. Mineralogical compositions of the samples were also studied using XRD. Figure 3 shows the diffraction pattern obtained from five samples. Fayalite, hercynite and quartz were identified in almost samples, confirming the optical microscope and SEM results.

Table 1: Bulk chemical composition of slags from Ban Khao Din Tai Archaeological site (determined by ED-XRF method and data is normalized to 100%)

		wt %											
Sample ID	Slag	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	V_2O_5	Cr_2O_3	MnO	FeO	SrO	ZrO_2	CdO
A0538	L	12.15	26.23	0.344	0.466	1.898	0.182	0.138	0.456	52.25	-	0.064	-
A0539	P	11.58	27.91	0.192	0.289	1.621	0.155	0.118	0.443	51.84	-	0.054	0.028
A0540	L	11.63	33.97	0.298	0.910	1.792	0.153	0.125	0.925	45.10	0.014	0.057	-
A0541	L	12.20	28.07	0.317	0.754	1.997	0.080	0.068	0.445	50.39	-	0.061	-
A0542	P	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

-: Not detected, n/a: Not available, P: Platy slag, L: Lumpy slag

DISCUSSION

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, mineralogical and micro-structural information. Macroscopically, there were two samples (A0539 and A0542) of slag displaying flow structures, this phenomenon was probably the result of slag being tapped from the furnace. While the three others (A0538, A0540 and A0541) were probably the result of drips solidifying inside the furnace rather than the result of slag being tapped from the furnace (Iles and Martinon-Torres, 2009).

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. In addition, Iron, silica and alumina 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 the samples are metallurgical slags produced during the bloomery iron-making process (Bani-Hani *et al*., 2012). 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 (Selskiene, 2007).

The micro-structure and phase composition show that fayalite is dominant component of all samples (Sheikh *et al*., 2010). As mentioned in the bulk chemical compositions, all samples have relatively low CaO content, which is in good agreement with the presence of fayalite (Eliyahu-Behar *et al*., 2012). 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. In addition, the relative high content of Al_2O_3 related with abundant hercynites being seen in all slags (Muralha *et al*., 2011).

CONCLUSION

The overall features of analyzed samples indicate that all of samples are metallurgical slags produced during the bloomery iron-making process or direct smelting process. 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. Iron, silica and alumina oxide are the main compounds in most iron smelting slags and no flux was used in this operation but the processes could benefit from the self-fluxing of used material ore. Fayalite is a dominant component of all samples, regarding the shapes of the fayalites, it is assumed that they could have been produced by either being tapping out of furnace or dripped down into a cold slag pit and the presence of fayalite might be preliminarily indicate a relatively high operating temperature of exceed 1, 100°C.

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