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Characterization of iron slag of Kakching, Manipur by X-ray and optical spectroscopy

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The mineral and elemental constitutional analysis of the slag obtained from Kakching area of Thoubal district, Manipur have been carried out. The techniques used for characterization are X-ray fluorescence (XRF), X-ray diffraction (XRD), Fourier transform infrared (FTIR) and optical microscopy. The age of the slag is determined to be 400 AD by thermoluminescence dating technique.

Keywords: Slag, Thermoluminescence, Spectroscopy, Fourier transform infrared spectroscopy

1 Introduction

Characterization of iron and its slag obtained from various parts of India is well documented[1-3]. The chronology of early age iron smelting technologies are also documented[4,5]. The Dhatwa iron was found to be produced through small crucible type furnace where limonite type ore was reduced. The slag obtained from such sites was found to be fayalite[6-8] (SiO_3 Fe). The characterization of iron slag obtained from the Kakching area of Thoubal district in Manipur has been studied in the present paper. The slag obtained from the area has been characterized by X-ray fluorescence, X-ray diffraction, Fourier transform infrared spectroscopy and optical microscopy and the dating of the slag was carried out using thermoluminescence dating technique[9-11].

2 Experimental Details

Recently, our team has undertaken an excavation of some ancient iron-smelting site of Kakching in Thoubal District, Manipur in November 2008 for providing a chronology of iron smelting in North East India. The site locally known as Tumu Ching is famous for ancient iron smelting and full of slags[12]. It lies about 70 km south - east of Imphal, the capital city of Manipur and is just about 40 km away from the Indo-Myanmar border. During excavation just below the surface, two large pieces of slag that formed the ancient furnace could be found (Fig. 1). A layer of sediment of a few mm thickness was attached to one such piece; quartz sample extracted from the adhered sediment has been dated by the thermoluminescence (TL) dating technique[13].

Fig. 1 — A sample of slag that formed a part of the furnace

The slag obtained from this area was powdered and sieved through to 300 mesh size and then, was subjected to X-ray fluorescence (XRF), X-ray diffraction (XRD) and FTIR analysis. The XRF analysis was performed with IQ^+ software for semi-quantitative determination of elemental composition as presented in Table 1. Similarly, the powder was analyzed for its constituent phases by X-ray diffraction. Figure 2 shows the phases present in the sample. Fourier transform infrared (FTIR) spectrum was measured with the help of Perkin-Elmer Spectrometer (Spectrum GX Model) and has been shown in Fig. 3. Petrography investigation was also carried out with an optical microscope to supplement the data from XRD.

Table 1 — XRF analysis of Kakching slag

Sl. No.	Name of compound	Concentration (%)
1	CO_2	6.52
2	Na_2O	0.152
3	MgO	0.915
4	Al_2O_3	8.98
5	SiO_2	51.7
6	P_2O_5	2.02
7	SO_3	0.207
8	Cl	0.0891
9	K_2O	3.07
10	CaO	4.38
11	TiO_2	0.348
12	Cr_2O_3	0.0193
13	MnO	0.139
14	Fe_2O_3	21.4
15	SrO	0.0105
16	ZrO_2	0.00933
17	BaO	0.0212

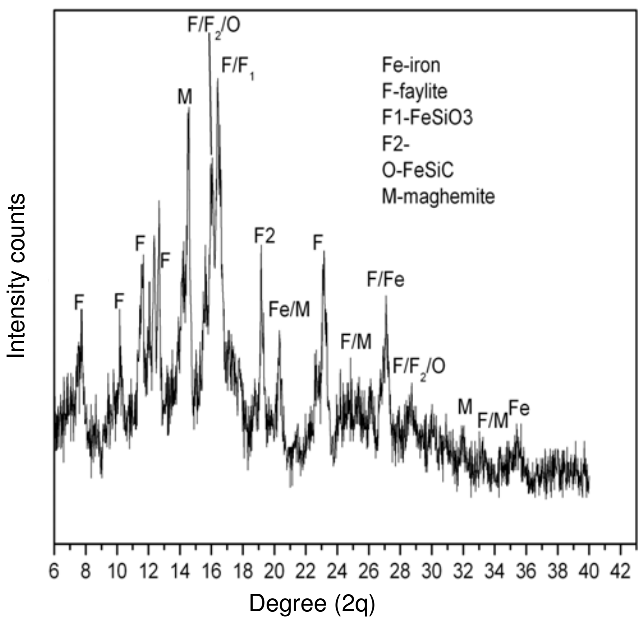

Fig. 2 — X ray diffraction pattern of Kakching slag sample: Fe-Iron card no – 6-696; F-Fayalite card no – 34-178; F1-$FeSiO^{3-}$card no – 12-284; F2- $FeSiO_4$ card no – 22-118; O-$FeSi^{C-}$ card no – 26-798; M-Maghemite$^-$card no – 39-1346

The slag collected from the iron smelting place was washed with water in a tub to remove the outer soil from the slag. It was washed again with water in another tub to extract the soil which was not exposed to sunlight. The soil so extracted was treated with 30% hydrogen peroxide (H_2O_2) to remove organic materials contained in the soil, 10% HCl to remove carbonates. Finally, the soil was treated with dilute HF for about 30 min and then with conc HF for another about 40 min to extract quartz contents.

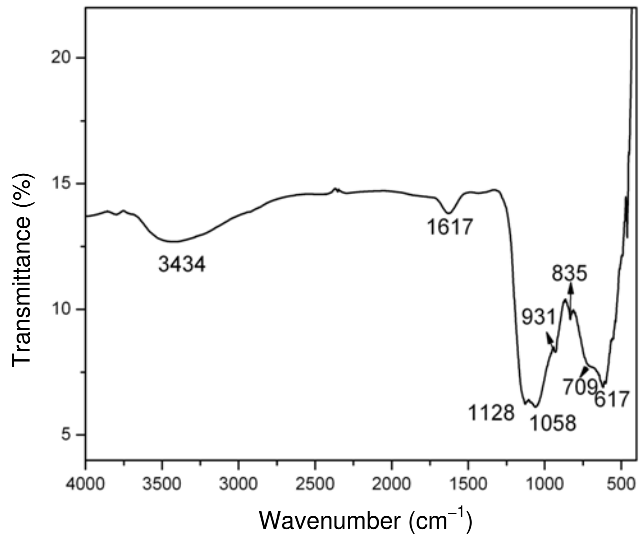

Fig. 3 — FTIR spectra of Kakching slag sample

Thermoluminescence (TL) measurements of the samples were carried out by the Risø TL/OSL (Model TL/OSL-DA-15*)* reader using internal Sr/Y-90 beta source in flowing of N_2 atmosphere. Detection filter was the combination of Schott UG-11 and BG-39 filters. The Risø TL/OSL reader is a commercial system which is used globally for dating and dosimetry[14]. The heating rate used was 5°C/s, with the final temperature set to 575°C. The natural thermoluminescence (NTL) glow curves as well as N+β_i (natural with laboratory dose) glow curves were recorded after glowing out the sample up to 175°C to remove unwanted lower temperature glow peaks[13].

3 Results and Discussion

XRF analysis shows high content of silica and iron oxide present in the slag. X-ray diffraction revealed the presence of fayalite (Fe SiO_3) as major phase. Wustite and metallic iron were also found to be present in small amount in the slag. The phosphorous content has been found to be more compared to the conventional iron produced in India. The presence of Fe_2O_3 and also Fe_3O_4 were also recorded. In ancient times, high amount of P (0.05 to 0.5 wt%) has been reported[3] to be present in the iron implements. This has been attributed to iron production using Indian bloomer furnaces where limestone was not used. However, our studies revealed the phosphorous amount to be higher in Kakching slag, which indirectly hints about the use of limestone during the production of iron as the dephosphorisation efficiency of fayalite/wustite/phosphate slag is, generally, lower that of iron bearing slag.

The FTIR spectra of the slag revealed the presence of Si-O band around 1090 cm^{-1}. Sowmaya[15] has observed that the Si-O band shifts to higher wave number side as the silica content in Indian iron slag increases. The band at 612 cm^{-1} can be identified for Fe_2O_3. The band at 707 cm^{-1} can be related to Ca-O stretching mode. Most of the hydroxide minerals show IR bands in the wave number range 400-1200 cm^{-1}. Thus, band around 820 (cm^{-1}) may be attributed to FeOOH phase. This data supplements the phases identified from XRD data. Further, investigation was carried out with the optical microscope and the phases identified from these can be enumerated as some silicate (major), iron oxide (minor) glassy matter and specs of pure iron. Pure iron was also found to be present as separate phase in the slag from XRD data.

The XRF analysis indicates the presence of Al, Mg, Mn S and P to be quite high in the slag. Fayalite can absorb oxides of manganese, magnesium and aluminum present in the gangue. The two major reactions obtained during reduction of hematite (Fe_2O_3) are[10]:

$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$ (Endothermic)
$Fe_3O_4 + 3CO \rightarrow 2Fe + 3CO_2$ (Exothermic)

Study of the ancient iron smelting furnace slag has shown that silica being the major gangue material forms fayalite (Fe_2SiO_4) which has a melting point of 1205°C with a FeO-Fe_2SiO_4, eutectic melting point of 1177°C. This means that the smelting furnace should be operated in the temperature range 1250-1300°C and at this temperature range low carbon, δ-ferrite is produced having a melting point above 1410°C. Thus, in this case the gangue material separates out as molten fayalite slag and red hot solid sponge having low C can still be produced. Broomgoen and Tholander[7] have studied the constitution of iron smelting furnace slag and the environmental conditions inside the smelting furnace and they have concluded that although due to the formation of iron rich ($2FeO.SiO_2$) slag much iron is lost, the high oxygen activity of the slag acts as a controlling parameter in lowering the carbon content of the metal. The chemical reactions which is taking place:

$FeO + C \rightarrow Fe + CO$ (Endothermic)
or
$Fe_3C + FeO \rightarrow 4Fe + CO$ (Endothermic)

Thus, the tribes present in the area of Kakching were using charcoal from the native sources for this iron ore smelting. The optically stimulated luminescence (OSL) and TL dating carried out on this sample gave the age to be 1600 ± 80 years[11]. Like carbon dating, TL dating has been widely accepted by the geologists, mineralogists and archaeologists throughout the globe. Accordingly, the dating of iron bearing slag was found to be around 400 AD.

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References

1 Piccardo P, Ienco M G, Balasubramaniam R & Dillman P, *Curr Sci*, 87 (2004) 650.
2 Dillman P & Balasubramaniam R, *Bull Mater Sci*, 24 (2001) 317.
3 Balasubramaniam R, *NML Tech J*, 37 (1995) 123.
4 Godfrey-Smith D I & Casey J L, *J Archaeo Sci*, 30 (2003) 1037.
5 Rao D V, Sasisekaran B, Satyamurti T, *et al*., *Sangam: Numismatics and Cultural History* (New Era Publications), 2006, pp 146-154.
6 Hegde K T M, *Indian J Hist Sci*, 16 (1981) 189.
7 Broomgoen S & Tholander E, *Scam J Metal*, 15 (1986) 151.
8 Prakash B & Igaki K, *Indian J Hist Sci*, 19 (1984) 172.
9 Aitken M J, *Thermoluminescence Dating* (Academic Press, London), 1985, pp 1-353.
10 Prakash B, *Indian J Hist Sci*, 26 (1991) 351.
11 Sheikh R, Nabadwip Singh S, Basanta Singh Th & Gartia R K, *Sanatan*, 19 (2009) 3.
12 Gourachandra M, *Traditional iron smelting and forging in Manipur* (Peoples Museum Publications, Kakching, Manipur), 1997, pp 1-37.
13 Gautier A, *Quat Sci Rev*, 20 (2001) 973.
14 Lars Bøtter-Jensen, *Radiat Meas*, 27 (1997) 749.
15 Sowmya T & Sankaranarayanan S R, *Spectroscopic analysis of slags-preliminary observations* (VII International Conference on Molten Slags, Fluxes and Salts, The South African Institute of Mining and Metallurgy, South Africa) January 2004, pp 693-697.