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Glassification of Electric Arc Furnace Dust by Using Fly Ash or Bagasse Ash

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Abstract

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Electric arc furnace (EAF) dusts contain significant quantities of iron and zinc found almost entirely as iron oxide, zinc oxide and zinc ferrite. The dust has been classified as a hazardous waste due to the relative high lead, cadmium and hexavalent chromium contents. An option for treating EAF dust with an economic and uncomplicated process is by using ashes. Silica in ashes has the ability to incorporate a variety of elements in a nonleachable form in the dust. In this study, the EAF dust was mixed with fly ash or bagasse ash in several ratios. All mixed samples were heated to 1500°C in the muffle furnace and held for 120 minutes and then were examined by XRD and SEM-EDS. It was found that all mixed samples are incorporated into an amorphous glassy structure. In silica-based glassy structures with silica levels of more than 50 wt%, iron and zinc in the EAF dust are incorporated as zinc ferrite in the form of spherical particles on glassy structures.

Key words : EAF dust, Zinc ferrite, Fly ash, Bagasse ash, Treatment

Introduction

Electric arc furnaces (EAFs) are the principal means of recycling steel scrap. Steel scrap includes a large amount of steel that has been protected against corrosion by coating it with a thin layer of zinc. The coating process is known as galvanising. When the galvanised steel is melted in the EAF, the zinc, together with a number of other volatile elements such as lead and cadmium, is vaporised. In a typical EAF steelmaking operation, the high temperatures and turbulence of the melt cause 1 to 2 % of the charge to be vaporised. The vapours react with oxygen and condense on particles that are carried out of the bath by the furnace off-gases. The particles are filtered from the gases in the baghouses of the plant and there are collected as dust. The principal components of EAF dust are zinc and iron compounds. Most of the zinc is found either as zinc oxide (ZnO) or zinc ferrite ($ZnO.Fe_2O_3$). The remaining iron exists in the form of magnetite (Fe_3O_4). These dusts also contain lead, cadmium, chromium and nickel in the form of oxides. Halides are present as sodium chloride (NaCl) and potassium chloride (KCl) in small but significant amounts.(1, 2) Around 3,000,000 tonnes of EAF dust are generated worldwide every year.(3)

The alternatives presently available to steelmakers to dispose of EAF dust include:

1) ship to hazardous waste landfills,
2) ship to an off-site processor,
3) process on-site themselves or via a contractor, or
4) stabilise/glassify and dispose of or sell the product.

These alternatives are becoming increasingly restrictive and expensive because of the limited number of domestic off-site processors. Due to the high metal content of lead, cadmium and chromium, EAF dust is classified as a hazardous waste and the disposal of it in landfills without stabilising is illegal in most countries. The stabilising and dispose of option may become increasingly available, but the legal viability of this option is not yet fully clarified. Currently, the cost for landfill disposal after stabilising is around US$ 250/tonne of dust and is continuing to rise.(2, 4, 5, 6)

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Therefore, landfill disposal of EAF dust will not be available in the very near future because of environmental concerns and the very high dumping cost. The need for treatment of EAF dust has became essential and creates two important opportunities. Firstly, significant and valuable quantities of zinc which vary up to 30% by weight, and iron which is about 40% by weight, can be recovered from EAF dust and returned to the economic cycle. This latter point is particularly important for countries that are importers of zinc and iron, such as Thailand.

Secondly, this hazardous waste can be rendered innocuous and the products allowed to safely re-enter the environmental cycle. The existing processes for treating EAF dust from carbon steelmaking can be classified into either pyrometallurgical or hydrometallurgical processes that produce either zinc oxide or metallic zinc. In pyrometallurgical treatment processes, high temperatures are used and the recovery of zinc products has been low. There are numerous technologies available for the pyrometallurgical treatment of EAF dust, but most of them are still based on carbothermic processes that produce carbon dioxide and carbon monoxide which pass to the environment. Hydrometallurgical processes use leaching methods as the main extraction process. They have high operating costs and use large amounts of chemical reagents for treating liquid wastes that are in the form of acid or alkaline solutions. A major problem with hydrometallurgical processes is that they can only recover the zinc from zinc oxide in EAF dust. Zinc ferrite, which can vary up to 60% in EAF dust, is insoluble except for the case of leaching in hot strong acid and thus zinc recovery from zinc ferrite is usually low.

Many EAF dust treatment processes in past decades have been investigated, but a process that is sufficiently attractive economically, technically and environmentally has not eventuated.

Ashes such as fly ash or bagasse ash contain about 50-60 wt% of silica (SiO_2)$^{(7, 8)}$ that could be used to mix with EAF dust to incorporate iron and/or zinc in the dust in the silica structure. The objectives of the research were to examine the microstructure of EAF dust treated by ashes and to establish the total iron/zinc content for a silica glass, which possesses substantial crystallinity after cooling.

Materials and Experimental Procedures

For the experimental work, sample of EAF dust was obtained from one of the steelmaking mills in Thailand. Fly ash and bagasse ash were obtained from Mae Moh Electricity Generating Authority of Thailand (EGAT) and one of the sugar industries in Thailand, respectively. EAF dust and ash were mixed into the ratio as shown in Table 1 for the total weight of 5 grams. In all tests, sodium carbonate (Na_2CO_3) at 2 wt% was included in order to lower the melting point. All samples were placed in alumina crucibles and heated to 1500°C in the muffle furnace and held for 120 mins. Air cooling was employed after the time. Microstructures of treated EAF dust by ashes were examined under Scanning Electron Microscope equipped with Energy Dispersive Spectrometer (SEM-EDS). X-ray diffraction analysis of the raw materials and solidified samples was carried out to determine possible mineral phases presented, the peaks from the spectra were analyzed using a search and match program with respect to the JPCDS index.

Table 1. Mixing ratio of EAF dust : Ash (by weight)

Item No.	**EAF dust : Fly Ash**	**Item No.**	**EAF dust : Bagasse Ash**
E1FA4	1:4	E1BA4	1:4
E1FA2	1:2	E1BA2	1:2
E1FA1	1:1	E1BA1	1:1
E2FA1	2:1	E2BA1	2:1
E4FA1	4:1	E4BA1	4:1

Results and Discussions

Chemical Composition

EAF dust sample was analyzed by EDS (averaged from four 5x5 μm points) as presented in Table 2. The major elements in the dust are iron and zinc, which constitute around 50 wt%. In addition, the dust contains significant quantities of alkaline elements, such as potassium, and halide, such as chlorine.

Table 2. Elemental composition of EAF dust

Element	Concentration (wt%)
Iron (Fe)	27.33
Zinc (Zn)	28.98
Manganese (Mn)	2.74
Calcium (Ca)	2.25
Chlorine (Cl)	3.22
Silicon (Si)	1.51
Potassium (K)	15.49
Oxygen (O)	18.48

For ashes, the major element found from both ashes is silicon (Si) for about 21 wt% and 31 wt% from fly ash and bagasse ash, respectively. In addition, the ashes also contain aluminum (Al), calcium (Ca), potassium (K) as shown in Table 3 (obtained by EDS and averaged from four 5x5 μm points).

Table 3. Elemental composition of ashes

Element	Fly ash (wt%)	Bagasse ash (wt%)
Silicon (Si)	21.01	31.23
Aluminium (Al)	15.85	7.74
Calcium (Ca)	5.02	6.15
Potassium (K)	2.59	1.53
Sulphur (S)	1.20	-
Magnesium (Mg)	1.87	3.92
Oxygen (O)	52.46	49.43

Phase Analysis

XRD analysis of the dust showed that the dominant phase was a spinel group presented as zinc ferrite ($ZnO.Fe_2O_3$). Zinc was also presented as zinc oxide (ZnO). Chlorine was also detected in the dust as potassium chloride (KCl). The analysis of ashes by XRD showed that both kinds of ashes revealed silica (SiO_2). Table 4 shows mineral phases presented in EAF dust and ashes.

Table 4. The compounds in EAF dust and ashes (in order of a main phase, respectively)

Raw Material	Compound
EAF dust	ZnO Fe_2O_3 ZnO KCl
Fly ash	SiO_2 Al_2SiO_5
Bagasse ash	SiO_2

From the results in Tables 2-4, the common compounds could be estimated in wt% as shown in Table 5. It was found that amounts of about 70 wt.% Fe_2O_3 and ZnO were obtained in the dust. Silica (SiO_2) could be found as 50 wt% and 75 wt% in fly ash and bagasse ash, respectively.

Table 5. Estimated concentration of common compounds in EAF dust and ashes used in this study.

Raw material	Compound	Aproximated concentration (wt%)
EAF dust	Fe_2O_3	37
	ZnO	35
Fly ash	SiO_2	50 (Amorphous)
Bagasses ash	SiO_2	75 (Crystalline)

Compounds of the treated dust

From Tables 1-5, an estimated concentration of main compounds in EAF dust and ashes could be calculated and shown in Tables 6-7.

Table 6. Estimated concentration of the main compounds in EAF dust treated by fly ash

Item No.	EAF dust : Fly ash ratio	Aproximated Concentration (wt%)		
		Fe_2O_3	ZnO	SiO_2
E1FA4	1:4	8	8	40
E1FA2	1:2	12	12	33
E1FA1	1:1	18	18	25
E2FA1	2:1	25	25	17
E4FA1	4:1	30	30	10

Table 7. Estimated concentration of the main compounds in EAF dust treated by bagasse ash

Item No.	EAF dust : Bagasse ash ratio	Aproximated Concentration (wt%)		
		Fe_2O_3	ZnO	SiO_2
E1BA4	1:4	8	8	60
E1BA2	1:2	12	12	50
E1BA1	1:1	18	18	38
E2BA1	2:1	25	25	25
E4BA1	4:1	30	30	15

XRD analysis was also used to determine the solidified samples treated by ashes. Spinel phases of iron, zinc and aluminum were identified by XRD and the amounts of crystalline spinels vary directly with the amounts of EAF dust in the mixture solidified samples. In addition, analysis samples by EDS indicated the high percentage of silicon and oxygen which implied that silica formed as an amorphous glassy structure and could not be found as XRD patterns. Table 8 presents phases obtained from solidified mixed samples (EAF dust + ashes) at 1500°C, 120 mins, obtained by XRD analysis.

Table 8. Phases of EAF dust after treatment by ashes at 1500^{o}C for 120 mins

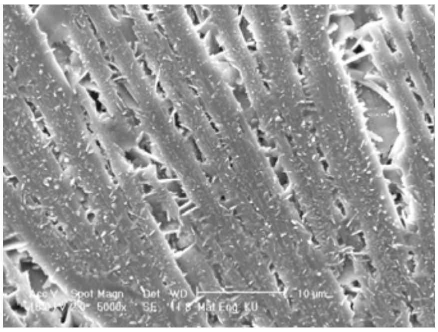
Item No.	Compound
E1FA4	(Ca,Na) $(Al,Si)_2$ Si_2O_8 $(Zn_{0.399}Fe_{0.159}Al_{0.082})Fe_{0.07}$ SiO_2 (Amorphous)
E1FA2	$(Zn_{0.399}Fe_{0.159}Al_{0.082})Fe_{0.07}$ SiO_2 (Amorphous)
E1FA1	$Zn(AlFe)O_4$ SiO_2 (Amorphous)
E2FA1	$(Zn_{0.399}Fe_{0.159}Al_{0.082})Fe_{0.07}$ SiO_2 (Amorphous)
E4FA1	$(Zn_{0.399}Fe_{0.159}Al_{0.082})Fe_{0.07}$ SiO_2 (Amorphous)
E1BA4	$ZnFe_2O_4$ SiO_2 (Amorphous)
E1BA2	$(Zn_{0.79}Fe_{0.167}Al_{0.042})$ SiO_2 (Amorphous)
E1BA1	$(Fe_{0.837}Al_{0.163})$ $(Fe_{0.159}Al_{1.83})$ SiO_2 (Amorphous)
E2BA1	$ZnFe_2O_4$ SiO_2 (Amorphous)
E4BA1	$(Zn_{0.79}Fe_{0.167}Al_{0.042})$ (Ca,Na) $(Al,Si)_2$ Si_2O_8 SiO_2 (Amorphous)

Microstructure analysis

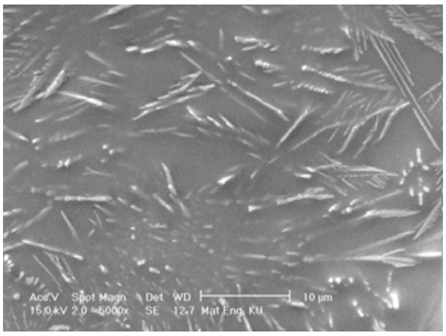
Figures 1-2 show the difference in microstructures by SEM-EDS at 1,500X and 5,000X of EAF dust reacted with ashes after solidification. Figures 1 (A) - 1 (B) show the same morphology as Figure 2 (C) which is a dendrite of iron-zinc-aluminium spinel in amorphous silica matrix. Silica was found to be around 33-40 wt% in these samples (E1FA4, E1FA2 and E1BA1).

Figures 1 (C) - 1 (H) and Figures 2 (E) - 2 (H) show the angular shaped grains of iron-zinc-aluminium spinel and zinc ferrite in amorphous silica matrix. Silica in these samples (E1FA1, E2FA1, E4FA1, E2BA1 and E4BA1) was found to be approximately 10-25 wt%. In addition, it was noticed that the density of the spinel phase varied indirectly with the amounts of silica in the samples.

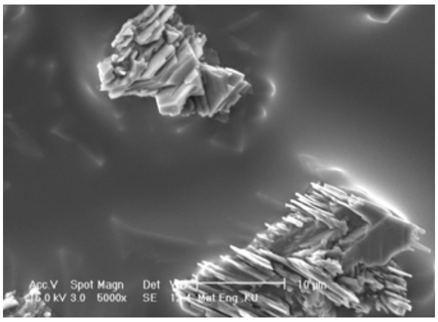
The uniform distribution of zinc ferrite and iron-zinc-aluminium spinel particles could be obtained in silica matrix in Figure 2 (A) and Figure 2 (B), respectively. In sample E1BA4 (Figure 2(A)), the mixture contained about 8 wt% of Fe2O3, 8 wt% of ZnO and 60 wt% SiO2. At this ratio, the formation of 2 μm diameter spherical zinc ferrite grains had obtained and identified by SEM. It confirmed the approximated chemical composition by EDS. Zinc ferrite is one of the main phases presented commonly in EAF dust and the spherical grain formation in the silica matrix implies the better mechanical properties in both tension and compression. However, no leaching test has been provided for any samples in this work and should be performed in further works to confirm the capability of incorporating hazardous elements in the dust.



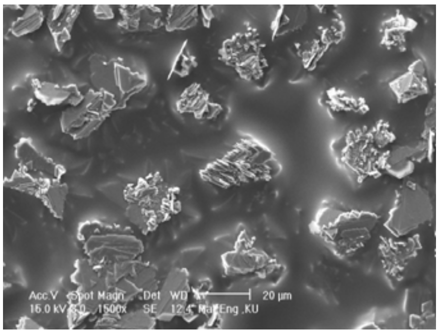
(A) E1FA4



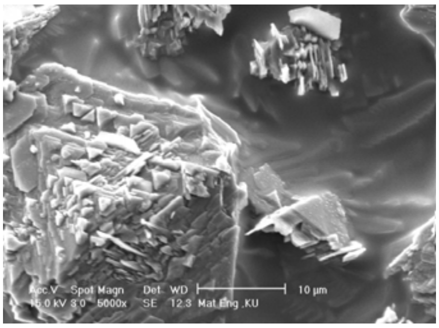
(B) E1FA2



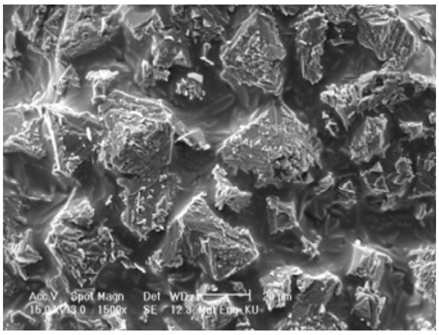
(C) E1FA1



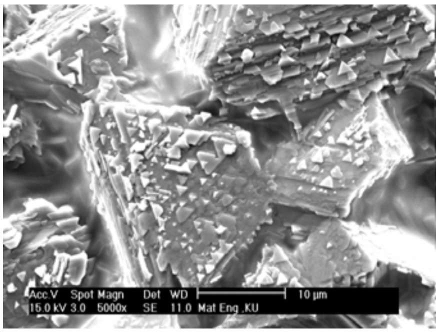
(D) E1FA1 (1500 X)



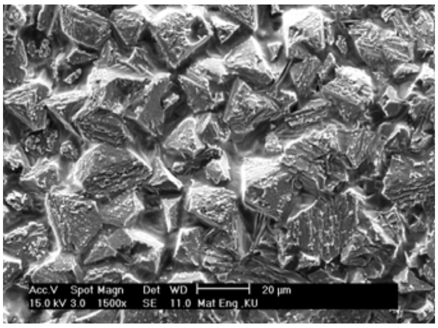
(E) E2FA1



(F) E2FA1 (1500 X)

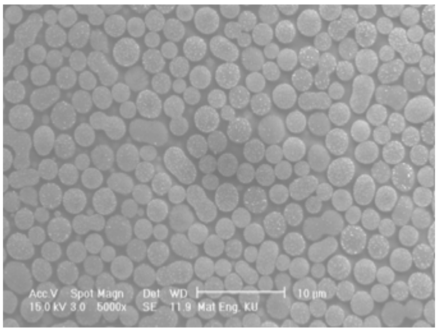


(G) E4FA1

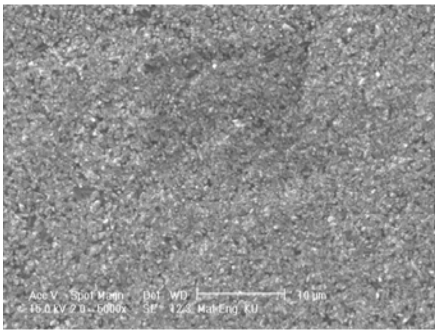


(H) E4FA1 (1500 X)

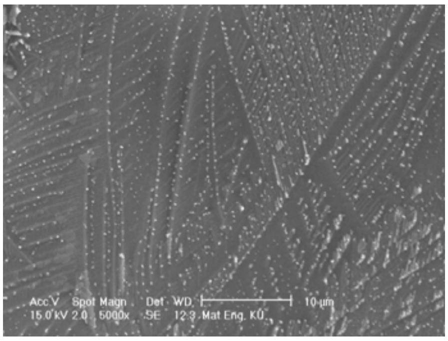
Figure(A)-(H). SEM micrographs of EAF dust treated by fly ash at difference ratio at 1500°C for 2 hours



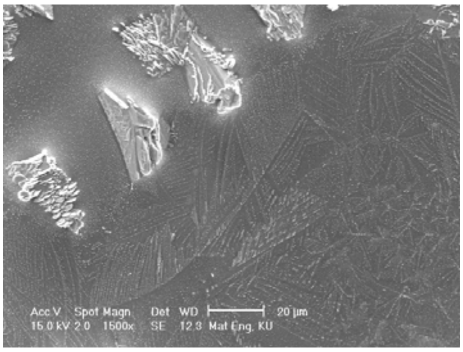
(A) E1BA4



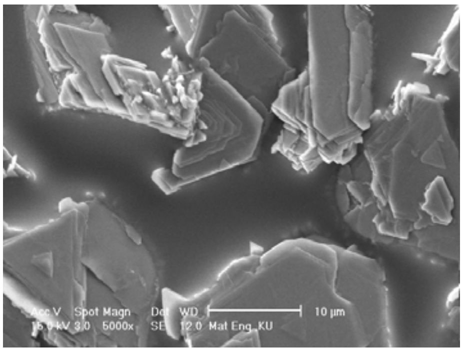
(B) E1BA2



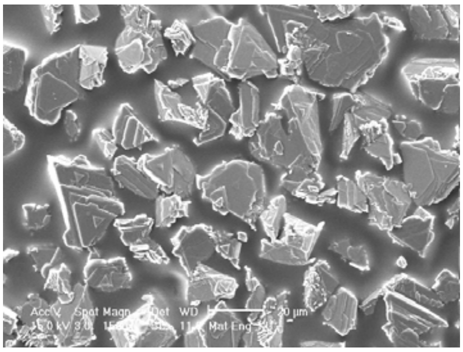
(C) E1BA1



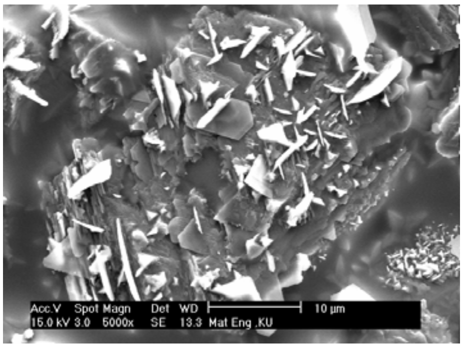
(D) E1BA1 (1500 X)



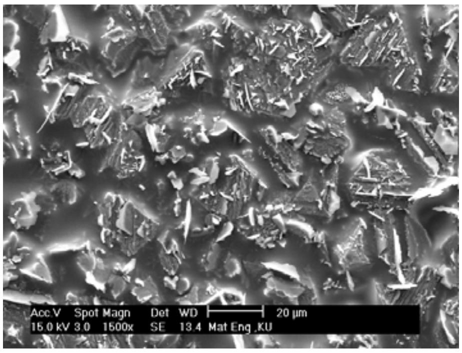
(E) E2BA1



(F) E2BA1 (1500X)



(G) E4BA1



(H) E4BA1 (1500 X)

Figure2 (A)-(H). SEM micrographs of EAF dust treated by bagasse ash at difference ratio at 1500°C for 2 hours

Conclusions

1. The main phases found in EAF dust are zinc ferrite ($ZnO.Fe2O3$), zinc oxide (ZnO), and potassium chloride (KCl).

2. The main phase found in fly ash and bagasse ash is silica ($SiO2$). In fly ash, silica presented at about 50 wt% in the form of amorphous whereas 75 wt% in the form of crystalline for bagasse ash.

3. For the tests, every ratio of EAF dust : ash (1:4, 1:2, 1:1, 2:1 and 4:1) could form glassy structure.

4. A glassy structure matrix containing more than 50 wt% silica results in a uniform distribution of spherical zinc ferrite grains in iron and zinc in the EAF dust to be.

5. A glassy structure matrix containing less than 50 wt% silica resulted in the formation of an iron-zinc-aluminium spinel phase. The density of the spinel phase varied indirectly with the amount of silica in the samples.

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