



## 2. Sample preparation

### 2.1. Ferroalloy

Ferroalloy is an iron alloy with other elements and is one of the materials used in the steelmaking process. The steel's properties such as strength, toughness, heat resistance and corrosion are improved by adding specific elements to the steel. It is also used for the purposes of desulfurization and deoxidation in the refining process. Ferrosilicon which is one of the ferroalloys is an iron alloy with silicon and the concentration range of silicon can vary by as much as 15–90%.

Because ferrosilicon is a metal, without oxidization agent it forms an alloy with the platinum crucible during the fusion process and causes irreversible damage. The fusion bead preparation procedure of ferrosilicon is shown in Fig. 1.

4.0000 g of lithium tetraborate is transferred to the platinum crucible and spread on the bottom of the crucible in advance. 0.1000 g of sample dried at 105°C for 2 hours and 1.8000 g of mixed oxidizing agent ( $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{KNO}_3 = 1:1:1$ ) are mixed well and

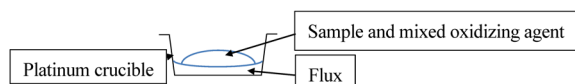


Fig. 2. Sample setting for ferrosilicon fusion bead.

placed onto the flux. Platinum crucible with the powders is shown in Fig. 2. In this case, it is recommended that the flux is in powder instead of a granular form to avoid the mixture of sample and oxidizing agent coming in contact with the platinum crucible.

A platinum crucible is placed in the electric furnace and the sample is oxidized at 500°C for 1 hour, at 550°C for 30 min. and at 600°C for 30 min. successively. After oxidation, the fusion bead is fused at 1200°C for 7 min. (stationary for 2 min. and swinging for 5 min.) and cooled for 5 min. (passive for 2 min. and active for 3 min.) with the fusion machine<sup>(2)</sup>.

It is also possible to prepare fusion beads for ferromanganese, silicomanganese and graphite spheroidizing agent (magnesium ferrosilicon) used in ductile iron with this procedure.

### 2.2. Copper ore (Sulfide)

Copper ore is a raw material for copper and contains sulfides such as chalcopyrite ( $\text{CuFeS}_2$ ) and chalcocite ( $\text{Cu}_2\text{S}$ ). It is possible to oxidize the sample using oxidizing agent such as nitric acid followed by drying prior to fusion. However, it is easier to perform oxidization during the pre-heating stage prior to fusion. The fusion bead preparation procedure for copper ores is shown in Fig. 3.

0.2000 g of dried sample at 105°C for 2 hours and 4.0000 g of mixed flux (lithium tetraborate:lithium

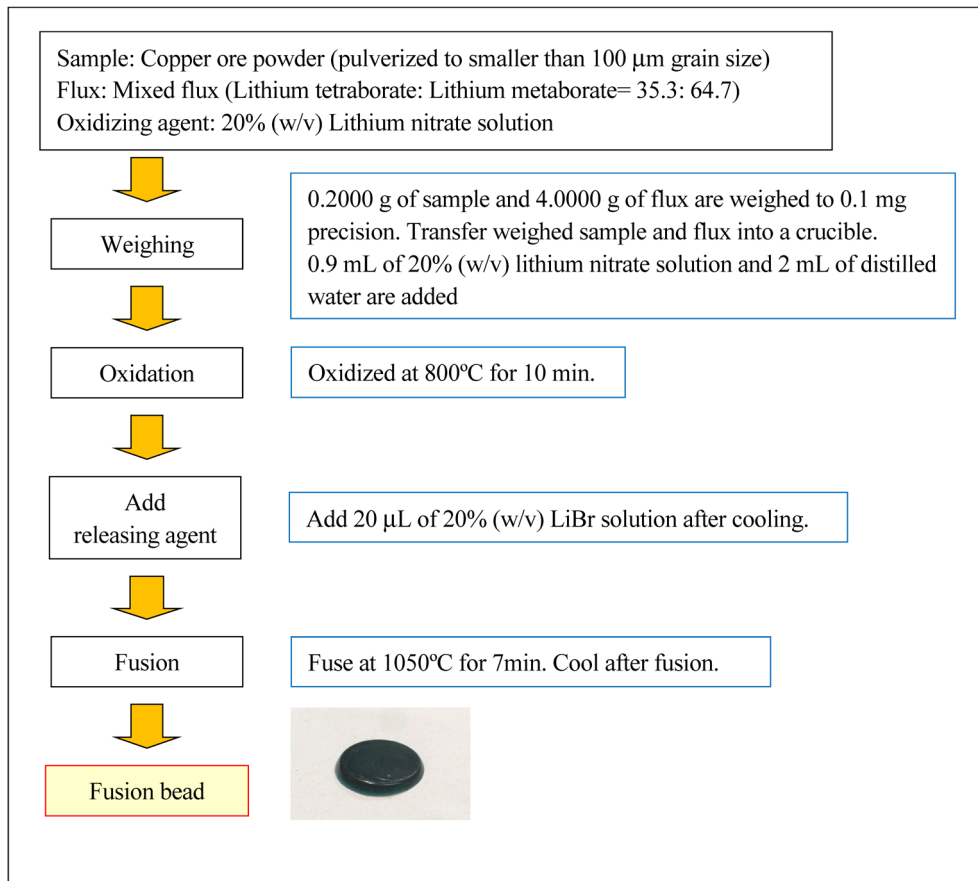


Fig. 3. Fusion bead preparation procedure for copper ores.

metaborate=35.3:64.7) are mixed well. After mixing, it is transferred to a platinum crucible, 0.9 mL of 20% (w/v) lithium nitrate solution and 2 mL of distilled water are added such that sample is completely immersed.

It is heated at 800°C for 10 min. in the fusion machine to oxidize the sulfur in the sample and then cooled. After cooling, 20 µL of 20% (w/v) lithium bromide solution is added, fused at 1050°C for 7 min (stationary for 2 min. and swinging for 5 min.). Finally perform cooling for 5 min. (passive cooling 2 min. and active cooling 3 min.) to obtain a fusion bead<sup>(3)</sup>.

### 2.3. Silicon carbide

Silicon carbide has high hardness property next to diamond and boron carbide, and is superior in wear resistance. It begins to oxidize at over 800°C in the atmosphere, but silicon carbide forms a passivation layer of silicon dioxide on the surface, which acts as a barrier to prevent further oxidation. It also has good chemical stability and thermal conductivity. That is why it is used in many materials such as abrasion materials, cutting tools, heat resistance parts, fireproof materials, heating element and substrate for semiconductors.

It is difficult to pulverize these powders finely with typical vessels due to high hardness and wear resistance of silicon carbide. Analysis error increases

due to the influence of the grain size and mineralogical effects and the contamination from a vessel increases. It takes a long time for the oxidation reaction in the general procedure of ceramics fusion bead due to heat resistance, oxidation resistance and chemical stability. The fusion bead procedure described in JIS R2011 Annex 3 (Methods for X-ray fluorescence spectrometric analysis of refractory which contains carbon and silicon carbide) is shown in Fig. 4<sup>(4)</sup>.

0.3000 g of dried sample at 105°C for 2 hours and 3.0000 g of lithium tetraborate are mixed well. After charging them into the platinum crucible, heated at 840°C for 30 hours to oxidize gently and warmed up to 1150°C at the end. Once cooled, it is added to 50 µL of 50% (w/v) lithium iodide solution as a releasing agent, fused at 1150°C for 5 min. (stationary for 2 min. and swinging for 3 min.) and cooled for 5 min. (passive for 2 min. and active for 3 min.)

However, in this procedure it takes more than 30 hours to prepare the bead because no acid and oxidizing agent are used. The procedure which can prepare the bead more quickly with oxidizing agent is shown in Fig. 5.

4.0000 g of lithium tetraborate is transferred to the platinum crucible and spread on the bottom of the crucible in advance. 0.2000 g of dried sample at 105°C for 2 hours and 4.0000 g of oxidizing agents (lithium

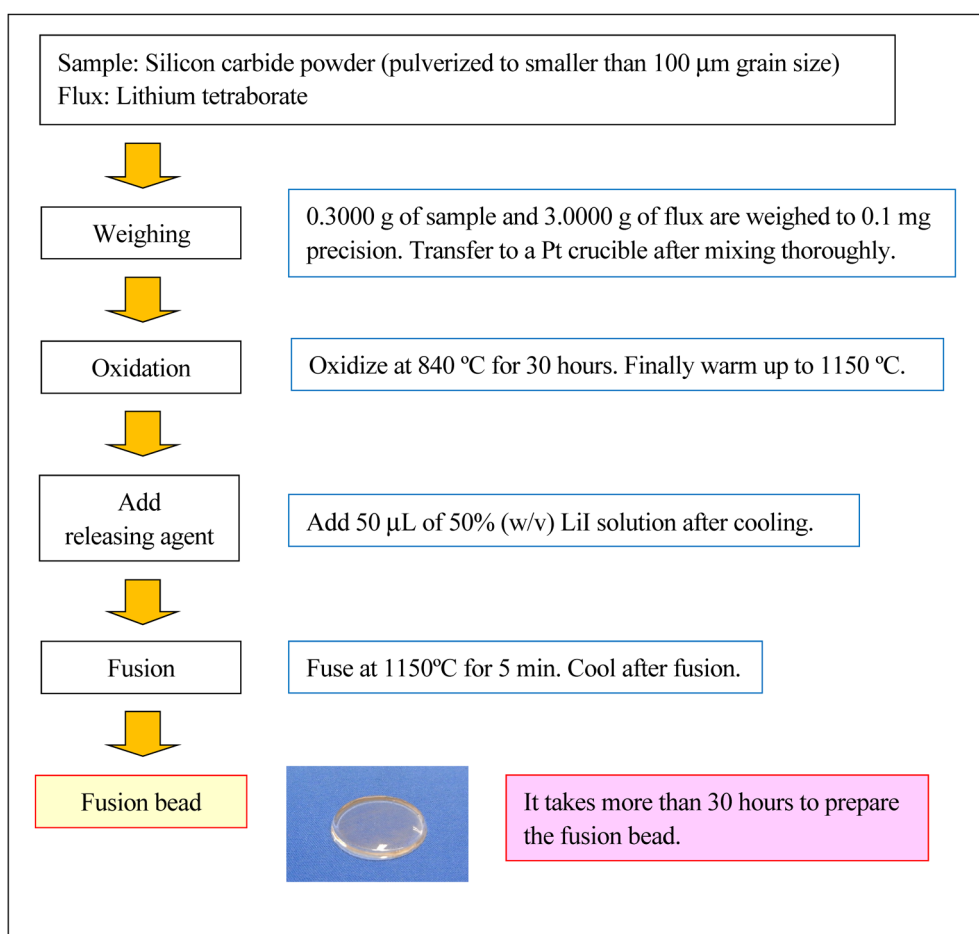


Fig. 4. The fusion bead preparation procedure of silicon carbide (JIS R2011 Annex 3).

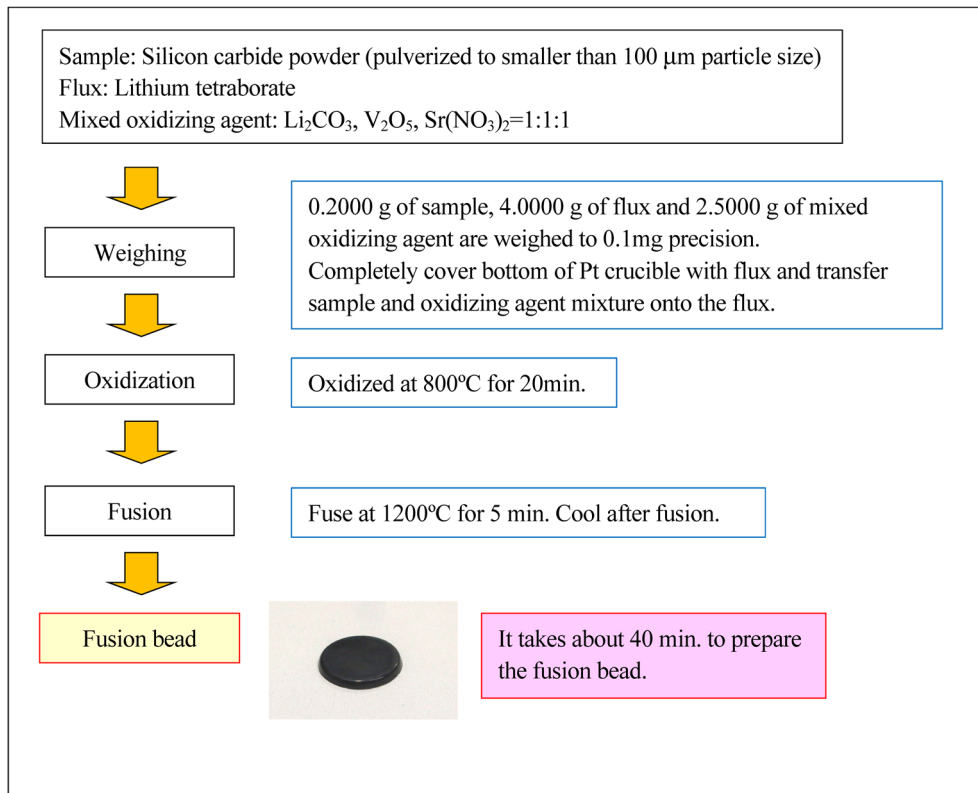


Fig. 5. Fusion bead preparation procedure of silicon carbide.

carbonate, vanadium oxide and strontium nitrate are mixed in equal amounts) are mixed well and then placed onto the flux. This mixture must not contact the crucible directly. After oxidizing at 800°C for 20 min., fuse at 1200°C for 7 min. (still 2 min. and swinging 5 min.), and then cool for 5 minutes (passive 2 min. and active 3 min.). Fusion beads can be prepared in about 40 min. with this procedure, including weighing and mixing<sup>(5)</sup>.

### 3. Analytical considerations

#### 3.1. Dilution ratio

If analysis is carried out in accordance with a specific standard method, the dilution ratio (flux weight/sample weight) should be as prescribed by the standard method. If not, the dilution ratio should be chosen based on solubility of the sample in the flux. As described in the previous article, the X-ray intensity of the fusion bead decreases with dilution. It can be expected that decreasing the dilution ratio (increasing sample ratio) improves the analytical precision.

The correlation between the dilution ratio and the X-ray intensity is shown in Fig. 6. X-ray intensity is the theoretical intensity which is calculated by FP method for 1.72 g/cm<sup>3</sup> density and 40 kV excitation voltage. The relative intensity assumes pressed pellet sample to be 100.

Table 1 shows that Ti-Kα intensity for the fusion bead with dilution ratio 10 is half of pressed sample intensity. As the wavelength of the analytical line increases, the X-ray intensity decreases due to absorption effect by the flux.

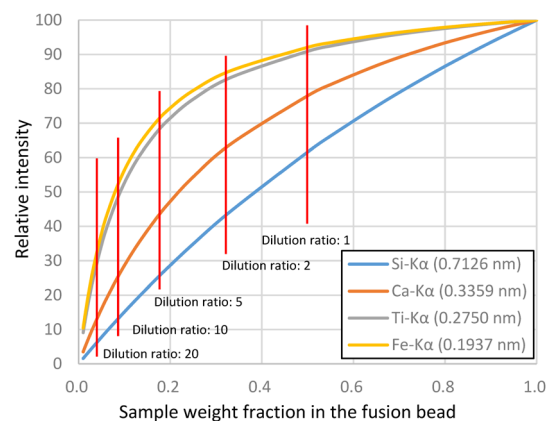


Fig. 6. Correlation between the sample weight fraction in the fusion bead and relative intensity. (Sample: Portland cement)

Table 1. Dilution ratio and relative intensity.

Dilution ratio	Relative intensity			
	Si-Kα	Ca-Kα	Ti-Kα	Fe-Kα
1	62	78	91	92
2	45	64	83	85
5	24	42	67	70
10	14	27	50	54
20	7.4	15	33	38

Relative intensity to pressed pellet sample as 100.

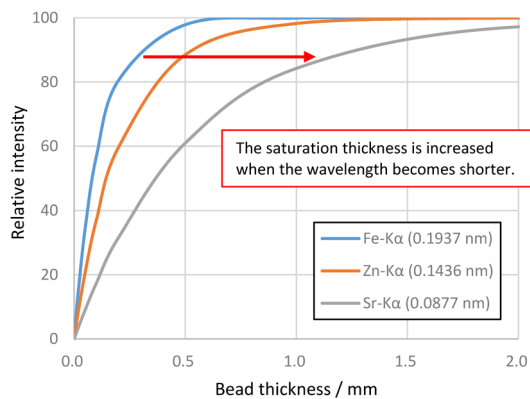


Fig. 7. Correlation between bead thickness and relative intensity.

Table 2. Saturation thickness for different analytical lines. (Unit: mm)

Analytical line	Saturation thickness
Fe-K $\alpha$	0.65
Zn-K $\alpha$	1.15
Sr-K $\alpha$	2.80

### 3.2. Selecting the analytical line

Bead thickness can influence X-ray intensity for analytical lines with shorter wavelengths since the fusion bead is composed of light elements such as lithium, boron and oxygen. The correlation between bead thickness and relative K-line intensity for Fe, Zn and Sr is shown in Fig. 7. The thickness where X-ray intensity saturates is shown in Table 2. X-ray intensity is the theoretical intensity and is calculated by FP method for 1.72 g/cm<sup>3</sup> density and 40 kV excitation voltage.

Defining saturation thickness as being over 99% of relative intensity, saturation occurs at 0.65 mm for Fe-K $\alpha$ , 1.15 mm for Zn-K $\alpha$  and 2.8 mm for Sr-K $\alpha$ . Thickness of fusion beads depend on sample and flux amount as well as shape of the platinum crucible, but typically is a few millimeters in most cases. Therefore, when selecting analytical lines having shorter wavelengths than the Zn-K $\alpha$ , it is necessary to prepare fusion beads with consistent thickness. It should be noted that thickness can vary depending on the degree of damage to the platinum crucible and amount of releasing agent added.

If fusion bead thickness is less than saturation thickness and it is not possible to prepare fusion beads with consistent thickness, analytical line with longer wavelength should be selected. As an example, the correlation between fusion bead thickness and X-ray intensity for zirconium oxide sample (dilution ratio 10) is shown in Fig. 8.

The saturation thickness for Zr-K $\alpha$  is about 3.8 mm whereas Zr-L $\alpha$  saturate at about 30  $\mu$ m. As described above, it is desirable to select Zr-L $\alpha$  when the fusion beads cannot be prepared with constant thickness. However, because X-ray intensity for L-line of the

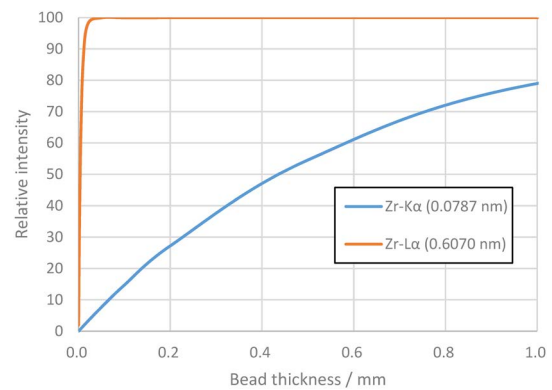


Fig. 8. Correlation between bead thickness and relative intensity (Zr-K $\alpha$  and Zr-L $\alpha$ ).

fusion bead is lower than K line, the measurement time has to be adjusted to obtain required analytical precision. In addition, it should be noted that surface contamination and deliquescent of the fusion bead has a larger influence on X-ray intensities of longer analytical line wavelengths.

### 4. Summary

Fusion bead method allows accurate analysis by reducing matrix effects due to dilution and eliminating errors caused by inhomogeneity such as grain-size and mineralogical effects and therefore has been commonly applied for oxides samples such as refractories and cement raw materials.

By using preparation methods described in this article, it is possible to rapidly fuse non-oxides such as ferroalloys, sulfides and carbides which have previously been considered to be difficult to analyze by fusion bead method.

Fusion preparation methods described here are significantly simpler compared to conventional methods using acids. However, irreversible damage to the platinum crucible can occur if sample is insufficiently oxidized due to coarse grain size and comes in contact with the platinum crucible during the fusion process. In such case, recasting of the crucible may be required. It is therefore important to prepare samples carefully. Nevertheless, analytical accuracy can be improved for a variety of samples broadening possible applications by the fusion bead method.

### References

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- (5) M. Watanabe, Y. Yamada, H. Inoue and Y. Kataoka: *Adv. in X-ray Chem. Anal. Japan*, **44** (2013), 253–259.