Sample preparation for X-ray fluorescence analysis VI. Metal samples

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1. Introduction

Sample preparation methods for X-ray fluorescence analysis (XRF) featuring powder samples were discussed in the previous issues. Preparation of metal samples is introduced in this issue. XRF is superior to ICP and optical emission spectroscopy in reproducibility. However most of analysis errors in XRF can be caused by nature of sample itself and sample preparation, as in the case of powder samples discussed before. Analysis errors of metal samples come from (1) internal segregation, (2) defective surface, (3) surface roughness and uneven surface, (4) surface transformation, (5) metallurgical history, etc. Consideration of these points will provide more accurate analysis results.

2. General method of metal sample preparation for XRF

Figure 1 shows general method of metal sample preparation. Cast metal sample is cut into disk shape and surface is polished for analysis. Metal samples having internal segregation are to be drilled or milled and its metal chips are melted and molded. Also it is possible to dissolve and analyze with liquid.

3. Sampling and sample preparation for analysis

Notes for cast metal samples are discussed below. Figure 2(a) shows metal sample having cavities or gas holes, and Figure 2(b) shows normal sample surface. Having a foreign deposit or a blot on the analysis surface is not suitable for accurate analysis.

Moreover, the difference in cooling conditions during casting affects the metallurgical structure, and may lead to analytical error. For example, in the application of iron and steel, cast iron and pig iron contain high content of carbon which causes different metallurgical structure in different cooling during molding. Figure 3 shows calibration curves of silicon in cast iron, and two separate calibration lines are observed due to the difference of molds[1]. It is supposed that this phenomenon is caused by difference of cooling speed as these samples were made with different molds when casted. This phenomenon is more prominent for light elements such as carbon, magnesium, silicon, phosphorus, sulfur, etc., which are more easily affected by the surface condition.

This phenomenon is mentioned in JIS G 1256: 2013 "Iron and Steel—Method for X-ray fluorescence spectrometric method" describing that the quantification result of analysis sample whose metallurgical history is different may differ from the one obtained by using commercial standard reference meterials[2]. The same applies to copper alloys[3].

The same problem occurs with aluminum alloys as well. In case of aluminum alloy containing more than 4% of silicon, it is necessary to cool rapidly to make metal structure miniaturized (chilled) as the precipitation of silicon varies according to the cooling speed. Island shaped texture of silicon is grown when cooled slowly. Therefore, the cooling condition when sample is molded is to be standardized to rapid cooling, and then analyzed. Sometimes phosphorus or sodium compound is added to the aluminum alloy as a texture miniaturizing agent[4].

As mentioned above, it can be said that it is essential condition for accurate XRF analysis to make metal sample chilled by cooling rapidly not to produce cavity or deposition, and to pay attention to metallurgical history of analysis sample and standard sample because of its significant effect on the analysis of the molded sample. In case of problems with the analysis results,

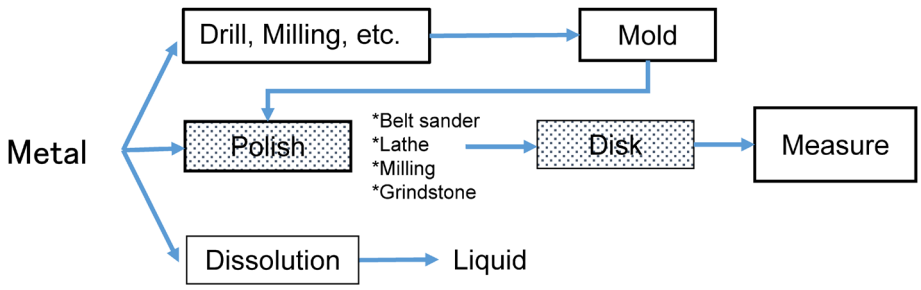

Fig. 1. Sample preparation method of metal samples.

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whittle the sample with drill, milling machine, etc. and re-mold it to prepare new analysis sample in accordance with the scheme in Fig. 1. Make the metallurgical history and sample chilling condition of the analysis samples consistent to that of the standard samples as much as possible.

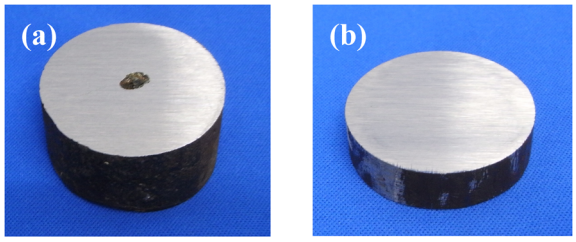


Fig. 2. Examples of metal sample surface after grinding. (a) With cavity, (b) Without cavity.

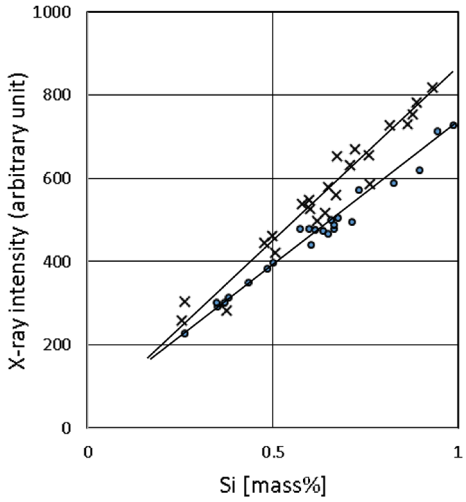


Fig. 3. Example of silicon analysis of cast iron. ● Chilled pig iron, × Sand molded pig iron.

4. Surface treatment of metal sample

4.1. Roughness of surface and surface grinding

XRF analysis is affected by the surface condition. Accurate quantitative analysis requires grinding of the analysis surface of the metal sample to make the surface flat and with consistent roughness. Roughness of the analysis surface affects the X-ray intensities. Figure 4 shows different sample surfaces due to different grinding conditions. (A) is coarse, and (B) is fine. X-ray intensity of (B) is stronger than (A) from the diagram, and it can be said that the light element X-ray intensity for which analysis depth is shallow is more sensitive to surface roughness.

Table 1 shows change of the X-ray intensities of the same steel sample (JSS654-11) ground by belt sander with different abrasive grit size. Higher X-ray intensity is obtained by using smaller the grit size belt sanders in general.

Table 2 is a summary of the relationship of surface finish, X-ray intensities and analysis precision of Cu X-ray intensities of copper alloy. The finer the surface roughness, the stronger the X-ray intensities, and the precision with same finish is better than with different treatment.

It can be said that maintaining a constant surface roughness for both standard sample and analysis sample is the key point of good analysis. Table 3 is a summary of typical grinding methods for various metal samples.

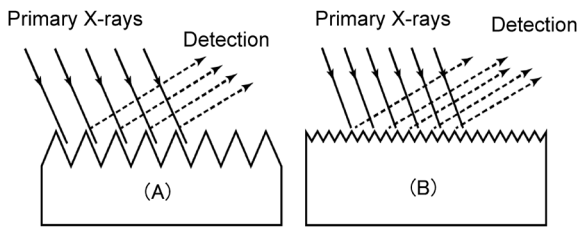
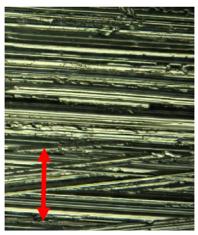
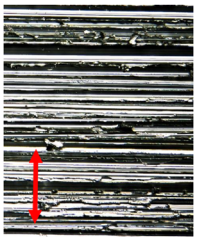
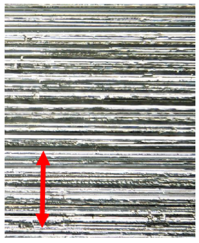


Fig. 4. Pattern diagram of roughness of metal surface and X-ray intensities.

Table 1. Grit size of abrasive and X-ray intensities of iron steel sample.

Element	Concentration (mass%)	Grit size of abrasive		
		80	120	240
		X-ray intensities (kcps)	X-ray intensities (kcps)	X-ray intensities (kcps)
Ni	18.80	53.183	53.931	54.567
Cr	24.74	89.410	90.446	91.023
Si	0.39	5.167	5.305	5.450
Surface roughness (Scale of arrow: 100 μm)				

4.2. Change of component and structure, and analysis position

It is necessary for samples to be cooled quickly when molded. Component for depth direction from the surface to 0.5 mm deep of the chilled sample changes significantly, and it is not suitable for analysis. This part being shown in Fig. 5(a) is generally called as "black scale" which needs to be ground down and removed. Figure 5(b) is a cross sectional illustration of cast iron. Usable depth for analysis is up to 2–3 mm, and the deeper area is not chilled. Figure 5(c) shows a ground cast iron.

The same applies to aluminum alloys having high silicon concentration. The calibration curve of the non-chilled area will be bended up as shown in Fig. 6.

Silicon in aluminum alloy having high concentration silicon mentioned above is dotted on the analysis surface as black fine grains as shown in Fig. 7. If this sample is finished by a lathe, the fine grains are peeled off from the surface and analysis results will vary after each finish. In this case, rough finish of the surface by

Table 2. X-ray intensities and analysis precision for surface treatment of copper alloy.

No.	Surface finish	Roughness μm	Intensity ratio (%)	Precision with same finish (mass%)
1	Lathe	3–4	100.00	—
2	〃	10–20	99.73	0.037
3	〃	50–100	99.62	0.034
4	Belt sander #400	5–10	99.94	0.025

Table 3. Summary of typical grinding methods for metal samples.

Sample	Classification	Grinding method	Precautions for grinding and analysis	Remarks
Iron and steel	General (No carbon analysis)	Grinding by belt sander (#60–#240) #80 alumina series belt is commonly used.	Precautions are: Dressing new belt, checking times of grinding (change of roughness), contamination from the belt, use of SiC (carborundum) series belt for aluminum analysis, alumina series for silicon analysis, contamination of phosphorus and sulfur.	Belt sander is widely used as it is handy.
	Carbon analysis sample	Grinder (white alumina series) #36–#80 is used.	Dress the stone surface to make it flat. There must be no burn on the surface. Do not wipe the surface with solvent, etc. Do not touch the surface with bare hand.	Grinder is the most suitable for grinding white cast iron.
Copper alloy	General	Finish by lathe (10 μm or less)	Apply solvent such as toluene to the tip of bite to make the finish smooth and to prevent contamination of oil. Pay attention for not leaving projection behind at the center of sample.	Suitable for grinding soft and having high viscosity sample such as zinc alloy, lead alloy, etc.
Aluminum alloy	General	Finish by lathe (10 μm or less)	Precaution same as above is necessary. Sample containing 2% or more copper or zinc is especially paid attention.	
	Silicon concentration 4% or more	Finish by file or grinder a little bit roughly	As silicon is deposited granular or like island, care must be taken not to drop the silicon more than necessity.	
Precious metal	Gold, etc.	Grinding sometimes. But generally cut surface or product itself is pressed to make analysis surface. Clean up the surface with solvent.	Thin sample might be unleveled when pressed by finger.	Effective to soft sample. Hard sample is to be ground by lathe, etc.

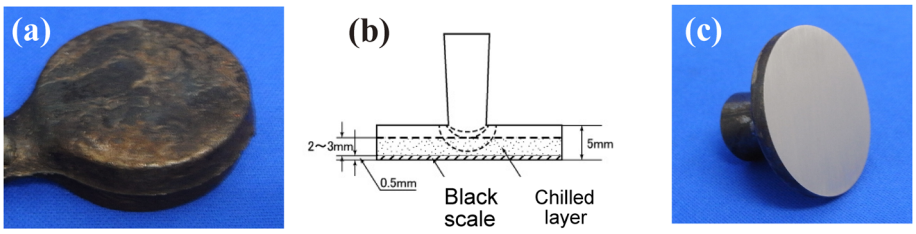


Fig. 5. Cast iron sample.
(a) Black scale, (b) Pattern diagram, (c) Ground cast iron sample.

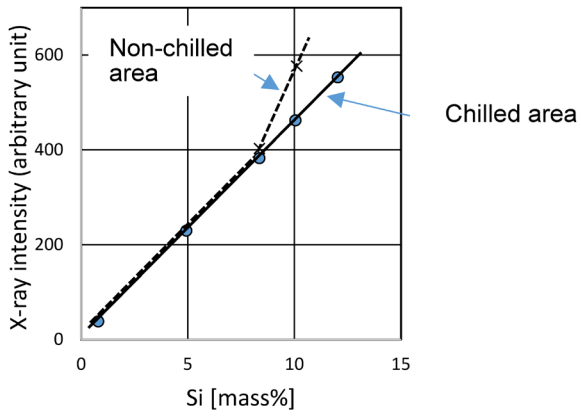


Fig. 6. Calibration curve of silicon in aluminum alloy.

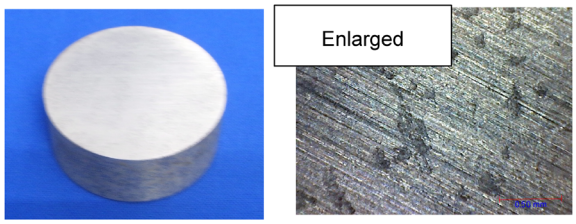


Fig. 7. Surface of aluminum alloy.
(Sample MBH 55XG28J2: Si 17 mass% included)

a file will actually improve accuracy of calibration and reproducibility of analysis results.

4.3. Contamination

It is well known that when belt sanders are used, silicon contamination occurs from SiC type and aluminum contamination from alumina type grinding belt. Quantification of trace sulfur is affected if sulfone type hardener is contained in the binder of abrasive. Grinding by grinder or file is effective for ultra-trace sulfur analysis without contamination.

4.4. Storage of sample and time of surface renewal

Storage of metal samples is simple. However, the change of the surface condition, for example (1) oxidization of the surface, (2) adhesion or adsorption of contamination to the surface, etc., begins immediately after the grinding and continues over time. Storing samples in a desiccator, etc. will be effective to keep the X-ray intensities stable for certain period of time.

Dust (silicon, etc.) and gas (sulfur, etc.) in the air atmosphere may adhere to the sample surface and negatively affect analysis results. Iron and steel samples may rust in high humidity. Change due to repeat of X-ray exposure for long term may occur as well.

In general re-grinding is recommended when surface color changes.

5. Summary

Sample preparation methods and precautions of metal samples for the XRF analysis were discussed. It was described that analysis results are affected by the segregation in the sample, difference of metallurgical structure, surface contamination and roughness of sample, surface grinding, changing of surface properties (oxidization). Specific treatment is required in particular cases such as high silicon analysis in aluminum alloy which requires rough finish of the surface rather than finest finish which is the conventional method. There are a large variety of metal samples and various sample preparation methods to meet them from the point of workability and precision required. We hope that this report will contribute to more accurate analysis results.

References

(1) T. Matsumura, T. Goto and K. Narita: *Iron & Steel*, **58** (1972), 2049–2059 (in Japanese).
(2) JIS G 1256: 2013 Iron and Steel—Method for X-ray fluorescence spectrometric analysis.
(3) JIS H 1292: 2005 Method for XRF fluorescence spectrometric analysis of copper alloys.
(4) Rigaku Corporation: *Guide book for XRF analysis*, *5th edition* (2008) (in Japanese).