

An analysis method for oxygen impurity in magnesium and its alloys

— International standardization activity in parallel with R&D —

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A simple and reliable analysis method has been developed to measure oxygen impurity in magnesium (Mg) and its alloys. Instead of directly analyzing oxygen impurity of an analyte, a multi-step heating-up method has been invented, in which oxide, compound of oxygen impurity with metals, is first separated from an analyte and then oxygen content analysis is carried out. The oxygen analysis of the oxide has been performed by Inert Gas Fusion-Infrared Absorptiometry widely used as a method for oxygen analysis in metals. We verified that analysis with adequate accuracy can be achieved with temperature calibration of each equipment. In parallel with R&D of the analysis method, we performed international standardization activity. It has been shown that consistent data can be obtained both in Japan and Korea through our technical assistance to Korea, and a proposal to the ISO technical committee for Mg and its alloys has been submitted smoothly.

Keywords :Magnesium, magnesium alloy, oxygen analysis, inert gas fusion-infrared absorptiometry analysis, multistep heating procedure, international standardization

1 Introduction

Magnesium (Mg) is a light metal with specific gravity 1.8 g/cm³, which is one-fourth of iron (SG 7.8 g/cm³) and two-thirds of aluminum (SG 2.7 g/cm³). It is expected to have a major effect in reducing carbon dioxide when used in transportation machineries such as automobiles. The carbon dioxide emitted annually by the transportation machineries in Japan is estimated to be about 250 million ton, and 55 % thereof is dominated by private automobiles.^[1] If the weight of the automobile is cut down to three quarters by reducing the weight of various structural members, the fuel consumption is expected to improve about 20 %, and the carbon dioxide emission can be reduced to 27.5 million ton (= 250 million ton x 0.55 x 0.2) for private automobiles alone.

The researches for the use of Mg material that is excellent for reducing the environmental load have been done as major national policies in Europe and the United States. Some of the well-known projects are the “EUCAR Project” of EU, the “SFB390 Project” of Germany, and the “USCAR Project” of the US. However, the use of Mg per automobile is only 6 kg even in Europe as of 2005, and the use in Japan is much lower at 2 kg.^[2]

Mg has high oxygen affinity, and it is known that the oxygen impurities present as oxides (nonmetal inclusions) cause adverse effects on mechanical properties such as strength and fatigue life.^{[3][4]} These prevent increase in the Mg use in

various structural components such as those for automobiles. The industrial oxygen analysis method has not yet been established for Mg, and the evaluation is currently done by methods that are neither precise nor accurate, such as microscopic observation of casting surface of the sample or visual inspection of oxides from the CT scan image. This is a barrier against building the recycling system, and it makes increasing the Mg use in products more difficult.

In Mg with high oxygen affinity, the oxidation of surface tends to occur readily in the process of fabricating or being used as the structural component. Therefore, in the recycling of reuse parts and scraps produced in component fabrication process as raw material, monitoring of oxygen content and the oxide removal process based on the evaluation results are essential. However, the lack of the oxygen analysis method that can be employed at production fields is an obstacle to promoting the recycling practice.

Japan has an advantage in the manufacturing technology of Mg materials and components, and particularly in both the melting and casting under oxygen shielded condition and the injection molding in semi-molten state. In these fabrication technologies, in principle, the increase in oxygen content during the process does not occur, and the components manufactured thereby are known to have low oxygen content.^[5] In the international market for Mg, Japan can be positioned as the “raw-material-importing and products-exporting country.” In Korea, which is positioned similarly, there are

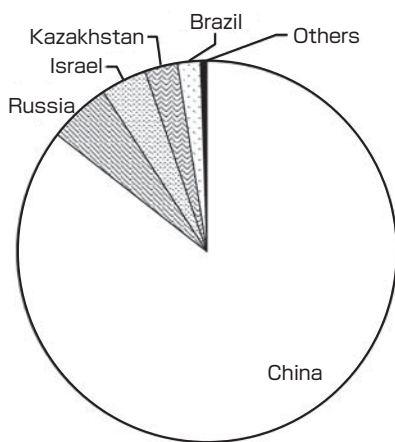
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several large companies that manufacture basic materials such as sheets by twin-roll and rods by extrusion.

On the other hand, as shown in Fig. 1, about 85 % of the world share for Mg metal is dominated by the Chinese heat refined metal. Although China is currently positioned as the “raw-material-exporting country,” it is expected to put more effort in the manufacture of alloys and components^[2] in the future. Currently, the major East Asian countries are entering the global market in various ways, and one of the characteristics of the Mg material industry is that although these three countries are rivals, there is potential for getting together to build a cooperative and collaborative relationship.

From the perspective of environment protection, there is no question that the use of Mg material should be expanded. The prevalence of the oxygen analysis method is expected to facilitate the verification of quality and reliability of the materials and components and eventually leading to the improvement thereof. At the same time, it is possible to appeal the excellence of the products of Japan, which has an advantage in Mg components manufacturing technology. Therefore we began to develop an easy yet highly reliable oxygen analysis method that can be used for process management at manufacturing plants. In this study, disseminating research results to industry was built into its objectives from the beginning. At the start of the R&D project, we set the final goal to proposing a developed method as an international standard. It was expected that the international standard would serve as a yardstick for product properties in the global market. In this paper, we will present the development of the element technologies of the oxygen analysis method, the process in which the reliability of the method was verified, and the background to international cooperation for the proposal of the standard.



Source: "Mineral Commodity Summaries, January 2011," US Geological Survey

Fig. 1 Share of international market of magnesium metal

2 Element technologies and remaining issues for international standardization

2.1 Development of the basic technology

In standardizing the analysis method of industrial materials, versatility is a factor to be considered in addition to a stand point only from analysis technology. For example, radio activation analysis that is known as the analysis method for oxygen is excellent in terms of the accuracy of results, but the use of nuclear reactors and accelerators for activation is strictly regulated, and hence this method cannot be used for routine on-site analysis. Also, the wet chemical analysis, which was mainstream in the past, tends to be avoided because the analysis personnel must be highly skilled, and such method is adopted in a standard only when no other instrumental analysis is available.

Under these circumstances, inert gas fusion infrared absorptiometry (IGF-IRA) is generally employed as the industrial measurement method of oxygen content in metals.^[6] The oxygen analysis by IGF-IRA is used widely in industries including iron and steel, and there are many commercially available automated devices. There are also many companies that can contract the oxygen analysis. From these points, this method is considered to be promising one for the standardization of oxygen analysis for Mg.

Figure 2 shows the schematic of the measurement principle of IGF-IRA method. The sample is placed in a graphite crucible in an inert gas flow such as helium, and heated by applying a current in the crucible. The oxygen in the sample is reduced by reaction with the carbon in the crucible material, and the carbon monoxide formed by the reduction reaction is extracted eventually. The carbon monoxide concentration in the helium flow is measured and accumulated by the infrared absorption detector to determine the oxygen content in the sample. The analysis is done by the reduction reaction of the sample by carbon, and this is the same reaction used in refining iron from iron ore. This derives from the fact that IGF-IRA method was originated and developed in the iron and steel industry.

It is expected to respond quickly to the demand for oxygen analysis in Mg, if the measurement of oxygen in Mg is enabled using an established method. However, in general, the IGF-IRA method has not been considered applicable to

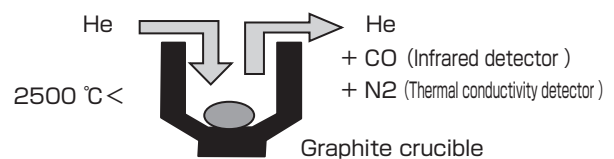


Fig. 2 Conceptual diagram of the inert gas fusion method

the oxygen analysis in Mg, because Mg has a low boiling point and high oxygen affinity.

Figure 3 shows the result of monitoring the extracted amount of carbon monoxide (or the temperature-increased inert gas fusion profile) when the magnesium oxide was placed in the graphite crucible with increase in the applied power. Although the carbon monoxide extraction started at around 2,400 W, the temperature of the graphite crucible corresponding to the applied power was estimated to be about 2,000 °C, being much higher than the boiling point of Mg, 1,090 °C. It implies that before the magnesium oxide in Mg starts to react with carbon, the matrix material Mg begins to boil at lower temperature. When the sample boils, the molten sample in the crucible causes boiling out due to the force of generated Mg vapor and eventually makes the analysis impossible.

To solve this issue, we adopted the “multistep temperature increase method” where the oxide included in the sample is separated and followed by the oxygen analysis. This method is inspired by the refining method of iron and Mg.

As mentioned earlier, the IGF-IRA method uses the reduction reaction of the sample by carbon. This is an irreversible reaction where the gaseous reaction product, carbon dioxide or carbon monoxide, desorbs from the reaction system. It can be considered that oxygen analysis corresponds to obtaining the gas phase product (carbon monoxide), contrary to obtaining the liquid phase one (metal) in iron refining.

In the Pidgeon method, which is the major thermal refining method for Mg, the raw material of magnesium oxide ore is mixed and heated with the powder of iron-silicon alloy (ferrosilicon). When the oxygen in magnesium oxide transfers to the ferrosilicon, the metalized Mg evaporates and desorbs from the reaction system. This reaction is not associated with reverse reaction, where the oxygen transfers to the ferrosilicon, and resulting in the collection of the evaporated Mg by coagulation in the low temperature area. In other words, the metal Mg is refined from the gas phase

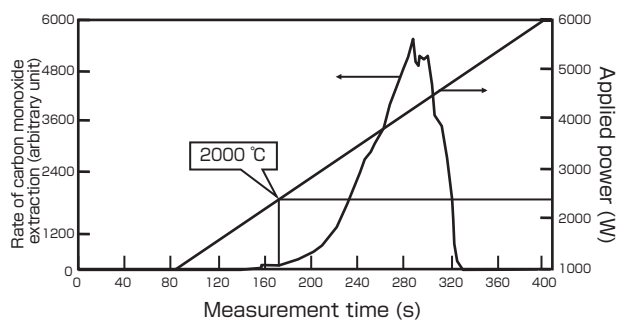


Fig.3 Temperature-increase inert gas fusion profile of magnesium oxide

product of the irreversible reaction. Therefore, we reached a conclusion that analysis of the residual liquid phase, in which the oxygen was remaining, provides the oxygen content.

When certain metal with higher boiling point than Mg is mixed with the Mg sample as the oxygen receptor, the oxygen would remain in the metal even after Mg evaporated from the sample. The oxygen that desorbed from the Mg sample could be measured as the oxygen in the receptor metal.

At the beginning of the research, we believed that it was necessary to transfer the oxygen of the oxide in the Mg sample to the receptor by redox reaction, and that a metal with strong oxygen affinity like aluminum was considered as a receptor candidate. However, we eventually came across an idea that the magnesium oxide, which is the primary oxide in the sample, can be directly transferred to the receptor. Consequently, tin (Sn) was selected as the candidate of oxygen receptor metal. Since Sn has a low melting point of 232 °C but has a high boiling point of 2,602 °C, it mixes with the molten Mg in a liquid state, and the oxide was expected to be received into it easily. Also, Sn is often used as the metal bath material in the inert gas fusion process and has advantages of low oxygen content as well as ready availability. On the other hand, aluminum is not usually used as the metal bath material, and specimen of low oxygen content is not readily available.

Figure 4 shows the conceptual diagram of the newly developed analysis method in which Sn is used as the oxygen receptor metal. After 0.3 g of Mg was melted with 0.5 g of Sn at about 900 °C, the temperature was increased gradually to 2,000 °C in more than 1,000 seconds. The residue found at the bottom of the crucible was slightly less than 0.5 g. As the vapor pressure of Sn at 2,000 °C was a few kPa, it is considered that Sn evaporated resulting in the weight loss from the original amount. This temperature also surpassed the boiling point of Mg, and it is inferred that Mg was almost thoroughly evaporated off. The appropriate heating condition for separating Mg from a receptor was determined through weight measurement of the eutectic material with systematic changes in temperature increasing rate and heating duration.

The residue in the crucible was considered to be composed

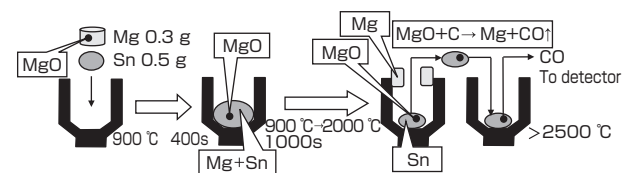


Fig. 4 Conceptual diagram of the analysis method for oxygen in magnesium by multistep temperature increase method

of Sn and magnesium oxide originally contained in the Mg sample. As shown in the profile of Fig. 3, it was expected that the oxygen could be extracted completely as carbon monoxide when heated with power of over 5,000 W. Therefore, we studied the percentage (recovery rate) of the amount of oxygen in the carbon monoxide extracted and detected against the 4 mg of oxygen predicted from the added magnesium oxide (the stoichiometric composition of oxygen in magnesium oxide is 39.7 %) when Mg was separated using the model sample where 10 mg of magnesium oxide was added to a mixture of 0.3 g Mg and 0.5 g Sn. The residue was heated at 5,000 W. In this experiment, however, the recovery rate remained at about 20 %, and much time was consumed to figure out the cause of discrepancy. Finally, we found that the Mg rebonded with the oxygen in the carbon monoxide that was produced from the residue when the crucible was heated with evaporated Mg remaining in it. We reached a simple procedure to prevent the rebonding: the residue is removed from the graphite crucible in association with the removal of the remaining Mg by opening the furnace and followed by the oxygen measurement with a new graphite crucible.

Since the reactivity between the Mg vapor and the generated carbon monoxide was unexpectedly high, we were possessed by a bias that the analysis procedure had to be done under inert gas flow in the IGF-IRA method. As a consequence, much time was wasted to find the cause of discrepancy in oxygen analysis. There was a concern that the sample may become oxidized when the residue was exposed to the atmosphere during analysis, but the effect of the oxidation was ruled out by conducting the blank test, analysis without placing the sample in the crucible.

2.2 The method of sampling

In commercial transaction, analysis values measured according to a standard are considered to be representative ones of traded merchandises. Therefore, in standardizing the analysis method, it is necessary to specify a sampling method to have the analysis value representing the characteristic of the entire sample, in conjunction with basic analysis

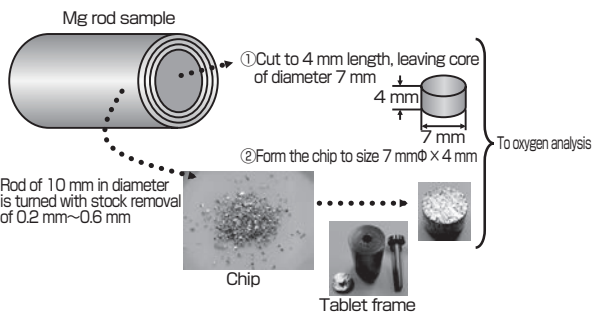


Fig. 5 Chip sampling method and creation of samples for analysis

procedures. Normally, a larger amount of sample than that actually used in the analysis is taken from several parts of the object to be measured and then these samples are mixed well to homogenize.(homogenizing process) At the beginning of this research, we tried the “chip sampling method”, which is used widely in the chemical analysis of the major component and impurities of metal, allowing homogenization of the sampled material. In this method, homogenizing process was done for the chips sampled by drilling several areas of the object to be measured.

Mg is, however, readily oxidized and the oxidation of the samples during the chip sampling procedure could not be avoided only with simple and practical oxygen shielding. Consequently, we examined the core drill sampling method which has only a small effect of oxidation, but lack of homogenization. The results of examination of the sampling methods and additional findings expected to contribute to the standardization will be described below.

2.2.1 Chip sampling method

In the ordinary chip sampling method, the sample will have a large surface area in the chip formation process. The surface oxidation of the chip cannot be avoided in materials with high oxygen affinity like that of Mg. Direct application of the chip sampling to Mg was expected to be quite difficult.

Considering these results, we attempted to apply the chip sampling with a simple oxidation resistant treatment. Figure 5 shows the schematic diagram. Using a miniature lathe placed inside a nitrogen-purged glove box, a 10 mm diameter rod was turned and its stock removal ranged 0.2~0.6 mm. The chips formed by turning were measured with a tablet frame, taken out from the glove box through a pass box, followed by forging to form tablet samples. As shown in Fig. 6, the chip sampled under nitrogen purge showed higher oxygen concentration than that of the core of the rod. The oxidation of the chips could not be avoided, the same as those

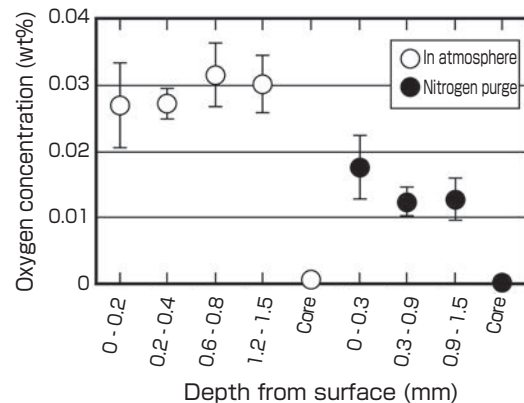


Fig. 6 Effect of surface oxidation by atmosphere during chip sampling

formed in the atmosphere, even though they were formed in the nitrogen-purged glove box.

It is inferred that such oxidation of the chip is caused by a small amount of remaining oxygen in the glove box, resulting from the purging by blowing off the oxygen with nitrogen, without vacuuming.

We reached a conclusion that the chip sampling is not appropriate for on-site analyzing with a simple procedure. To avoid the oxidation, extremely careful operation is necessary. The operation of fabricating the chips and collecting them with a tablet frame placed in the glove box was not only difficult and required skills, but also handling a lathe, which is a rotating machinery, with thick gloves is quite dangerous. Therefore, we considered that the chip sampling is inappropriate for an analysis method to be done easily on site and should not be adopted as a sampling method for a standard.

From the experimental results about chip sampling, we obtained two findings which are helpful for subsequent research. First, as seen in the measurement result of the core of the rod shown in Fig. 6, it is inferred that the effect of oxygen on the bulk surface was almost negligible in the developed analysis method. It implies that the oxidation is limited to the very thin layer on the surface despite high oxygen affinity and susceptibility to oxidation of Mg. It also implies that the effect of surface oxidation could be kept at the same level as the detection limit of the IGF-IRA method if the surface area of the sample was relatively small compared to the volume. This led to the development of the core drill method described below. Second, another finding is that oxygen content could be kept within a certain range if the chip thickness remained roughly constant. This is important for preparing samples for verification of the analysis value and for the joint analysis tests.

2.2.2 Core drill method

As mentioned in 2.2.1, the effect of surface oxidation can be suppressed by using a bulk specimen with a small surface

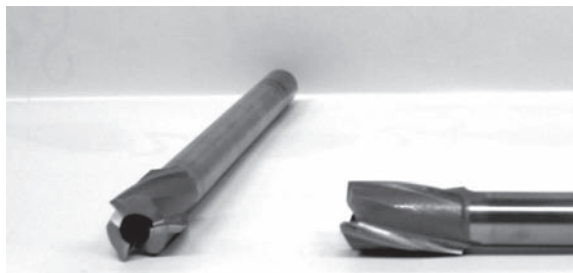


Fig. 7 Core drill for collecting sample (inner diameter 7 mm)

area against its volume. Meanwhile, the sampling method is required to be able to sample the material without bias. In addition, the specimens of a shape suitable for the analysis, have to be sampled from any part of objects which may have various configurations. Another unique requirement of the IGF-IRA method is that the specimen must be placed most certainly in the graphite crucible. In the commercially available IGF-IRA device, the graphite crucible is degassed after conducting the inert gas purge of the furnace, and the specimen is dropped by its own weight through the sample drop path of about 8 mm in diameter. That does not matter for heavy samples such as iron due to its large specific gravity. In contrast, there is the possibility that Mg, which has low specific gravity, will be lodged in the path for some reason. To fulfill these two requirements, the specimen should be made small and spherical as much as possible. However, there is a trade-off between the quantity of the specimen used and the precision of the measurement value. In the case of a spherical sample, the more time will be needed for processing, the more profound influence of oxidation is exerted on the analysis result. In our preliminary study, a cylinder specimen, which enables easy sampling, was adopted. After much trial-and-error, we chose a cylinder with a diameter of 7 mm and a length of 4 mm as the smallest size specimen while maintaining the measurement precision.

To efficiently collect the sample of this shape from the object to be measured, we prepared a custom-made core drill to core a rod of 7 mm in diameter. Using the core drill, the rods were sampled from any area of any depth in the object, and the specimens were cut out at arbitrary depth from the rod. The appearance of the core drill is shown in Fig. 7. Figure 8 shows the case where 130 specimens were cut out systematically from the extruded billet of 170 mm in diameter and 500 mm in length. It should be noted that collecting specimens for distributional analysis from such a large object could be done within two days.

3 Investigation of reliability of the method for international standardization

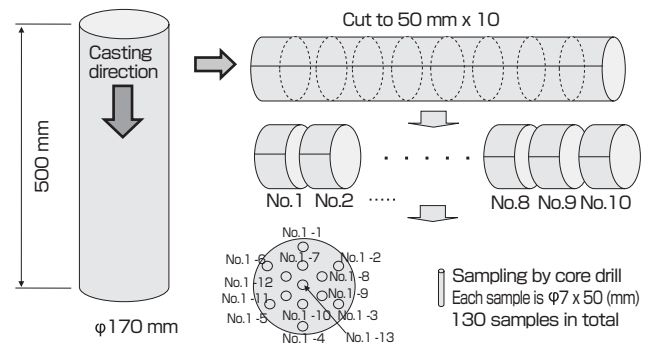


Fig. 8 Example of sample collection by core drill for the measurement of oxygen distribution in the extrusion billet

For international standardization, it is necessary to show that the method to be standardized reach a level required by experts in various countries, in addition to the establishment of the element technologies described above. Specifically, 1) an analysis value should represent the precise oxygen content of the object, 2) the range of the alloys to which the analysis method can be applied should be clear, and 3) results with a good reproducibility can be obtained by this method using a commercially available inert gas fusion device. In the following, we examine whether our proposed method meets these requirements or not.

3.1 Verification of the analysis value

When a new analysis method is developed, it is necessary to examine whether the analysis value accurately represents the content of the analyte in the measured specimen. However, the higher the novelty of developed analysis method is, the more difficult the examination is. For example, if a certified reference material with known content of the analyte is widely available, an analysis value of the new method can be verified by comparison with the certified value by analyzing the reference material. However, in an analysis method for a substance considered difficult to measure, a certified reference material does not naturally exist. In such a case, the widely used practice is to check the validity by comparing the analysis value with that obtained by another applicable measurement method, in compliance to the concept of traceability, validation, and data evaluation described in “ISO Guide 34: General requirements for the competence of reference material producers”^{Note 2)} issued by ISO.

Here, the “phenol dissolution method” was selected as a standard for comparison. This is a method for quantifying the magnesium oxide in Mg, based on the fact that magnesium oxide in Mg is insoluble in phenol while Mg reacts with phenol and generates phenoxide as it dissolves. The outline of this operation is shown in Fig. 9. This method is applicable only to chip samples which dissolve readily in phenol. In the cases where the phenol or methanol used for dissolving or dilution contains water, the generated phenoxide should

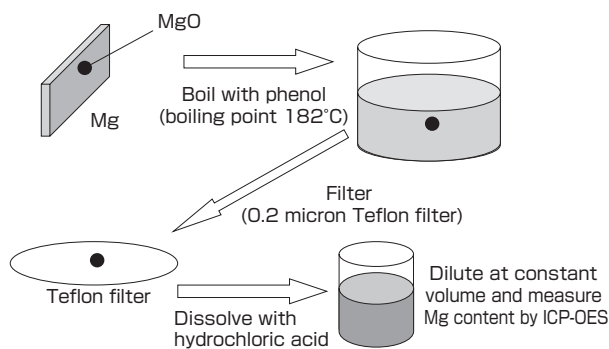


Fig. 9 Conceptual diagram of phenol dissolution method

be hydrolyzed to magnesium hydroxide. This will cause an overestimate of the oxygen content, and hence it can be asserted that the phenol dissolution method is sensitive to humidity. The phenol dissolution method is considered inappropriate as a standard analysis method to be employed at production fields of Mg components because it requires skills in complex procedures of wet analysis to eliminate the effect of humidity.

Figure 10 shows the comparison between the analysis results of various Mg materials by the IGF-IRA method and those by the phenol dissolution method. While there is a correlation between both analyses, the results of phenol dissolution method are somewhat higher than those of IGF-IRA method. This is attributed to the aforementioned moisture effect.

Next, another standard for comparison was the charged particle activation analysis (CPAA). In this method, the sample is irradiated with helium atom (α particle). The oxygen in the sample is activated as the radioactive fluoride atom, and the oxygen amount in the sample is calculated from the amount of radiation of the fluoride atom. Since an accelerator is necessary in the CPAA, it cannot be used as a routine on-site analysis. It is, however, used relatively frequently in the measurement of oxygen content in Mg in the development stage of alloys, and there are many analysis laboratories experienced in this analysis. The outline of the CPAA is shown in Fig. 11 and the results in Table 1. The samples were extruded pure Mg (no.1), the tablet formed from chips of 0.2 mm thickness by turning of extruded material in the atmosphere (no.2), and the tablet from the chips which were left for 3 days in the desiccators with 100 % humidity to enhance oxidation (no.3). Sample no.1 had oxygen concentration that was close to the lower limit of the IGF-IRA, and therefore had high standard deviation against the average value, while, for samples no.1 and no.2, the analysis values agreed within the standard deviations for

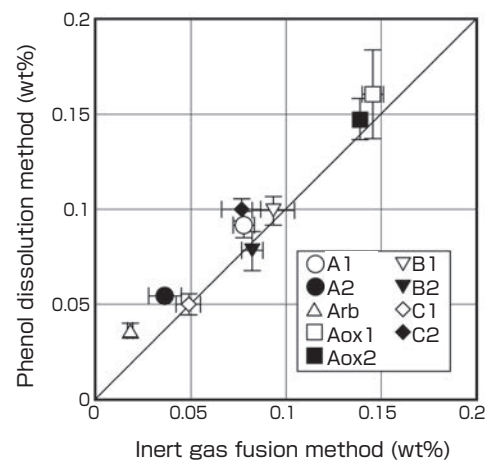


Fig. 10 Relationship between the analysis values by inert gas fusion method and phenol dissolution method

the IGF-IRA and CPAA methods. For the analysis value of sample no.3, the value for IGF-IRA was slightly lower than that from CPAA. From the analysis principle of CPAA, the cause of discrepancy was considered to be the fact that the CPAA detects every oxygen in the sample, even that in water, while the IGF-IRA measures only the oxygen in the form of stable oxides. Particularly, in sample no.3 it is inferred that a stable oxide is not formed because of incomplete oxidation by moisture and that water and hydroxides are contained. Considering these situations, it was asserted that the analysis values of the CPAA and IGF-IRA methods agree within the standard deviations for samples no.1 and no.2, which were not affected by moisture. As a result, the validity of the analysis value of IGF-IRA was considered to be confirmed.

3.2 Applicability range of IGF-IRA for Mg alloy

For Mg alloys, there are many reference materials with known alloy composition and impurity content distributed by several companies. However, there are no reference materials with certified oxygen content. Therefore, we investigated only whether there would be any problems in the measurement procedure of the IGF-IRA method using the commercial reference materials. As a result, as shown in Table 2, the procedure was applicable to most of the commercially available Mg alloys excluding some exceptional troubles in the following. For the samples containing more than 6 % aluminum, after the Mg was evaporated off from the eutectic compound, the residual Sn was found to adhere to the crucible. Furthermore, with increase in aluminum content to more than 9 %, the Sn adhered to a wide area at the bottom of the crucible. This is attributed to the fact that the aluminum tended to form carbide which has good wetness against carbon. Since the residue could be removed by the disruption of the crucible, it was recognized in this standardization that our method is commonly applicable to commercially available Mg alloys.

3.3 Applicability range of the analysis device

The analysis devices of the inert gas fusion method are

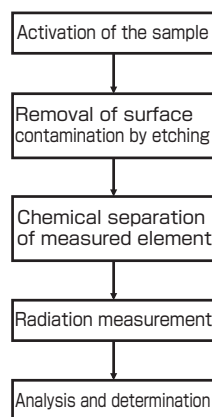


Fig. 11 Analysis flow diagram for CPAA

Table 1. Comparison of the analysis results between the inert gas fusion method and the CPAA method

Sample no.	Inert gas fusion method	CPAA method
No.1	0.0006±0.0005 (mass%)	0.0001(mass%)
No.2	0.0165±0.0023 (mass%)	0.0180(mass%)
No.3	0.0480±0.0052 (mass%)	0.0600(mass%)

Table 2. Applicability of IGF-IRA to various alloys

Name of sample	Form	Alloy composition (concentration)	Yes/no of analysis (○: yes, △: problem, X: no)
MBH C61XMgp10	Chip	—	○
MBH C61XMgp30	Chip	—	○
MBH C63XMge30	Chip	Mn(2.36 %)	○
MBH C65XMga50	Chip	Al(6.01 %),Zn(0.411 %)	△(Adhesion of molten material)
MBH C66XMgc40	Chip	Zn(6.81 %),Mn(0.166 %)	○
MBH C67XMgf30	Chip	Rare earth(2.4%),Zn(3.18 %)	○
MBH C67XMgg40	Chip	Zn(5.47 %),Th(1.85 %)	○
MBH C68XMgh40	Chip	Ag(2.05 %),Rare earth(2.4 %)	○
MBH C69XMgy4-a	Bulk	Zn(0.5 %),Mn(0.1 %),Nd(2.4 %),Gd(1.5 %)	○
HMP A-41-T05	Bulk	Al(4.1 %),Zn(0.2 %),Mn(0.4 %),Si(1.2 %)	○
HMP STD1/85	Bulk	Al(9.5 %),Si(1.1 %)	○
Commercial AZ91	Bulk	Al(approx.9 %),Zn(approx.1 %)	△(Adhesion of molten material)
Commercial AM60b	Bulk	Al(approx.6 %),Mn(approx.0.1 %)	△(Adhesion of molten material)
Commercial ZK61a	Bulk	Zn(approx.6 %),Zr(approx.0.7 %)	○
Commercial AMX602	Bulk	Al(approx.6 %),Mn(approx.0.1 %),Ca(approx.2 %)	△(Adhesion of molten material)
Commercial AZX1211	Bulk	Al(approx.12 %),Zn(approx.1 %),Ca(approx.1 %)	△(Adhesion of molten material)

Table 3. Result of the joint analysis test in Japan

Sample	Analysis lab A	Analysis lab B	Analysis lab C	Analysis lab D	Charged particle
No.1	ND	0.0014	Bumping	0.0006	0.0001
No.2	0.0015	0.0212	Bumping	0.0165	0.0180
No.3	0.0021	0.0492	Bumping	0.0480	0.0600

supplied from two companies; one in Japan and the other overseas. There are, however, various models according to their manufacturing year. In standardizing a method using an analysis device, a standard must include as many manufacturers and models of the analysis device used in industry as possible. Therefore, we called for participants in Japan to conduct joint analysis tests. For the analysis devices of the different manufacturer from that of our device, the analysis conditions such as applied power and heating time that suited the device were disclosed through cooperation from the manufacturer. Using the sample described in 3.1, we specified the heating condition according to the voltage applied to the graphite crucible.

The results of the above experiment and the CPAA analysis described in 3.1 are shown in Table 3. Here, the values of

the device manufacturer (analysis lab B) based on their own disclosed conditions and those of AIST (analysis lab D) were not far apart from the CPAA results. There was a case where the measurement could not be done because the samples were boiled over the crucible (analysis lab C), and the case where low value was obtained because the Mg vapor was produced during the oxygen analysis of the residue due to incomplete evaporation of Mg leading to the return of the carbon monoxide to form the oxide again (analysis lab A). From these results, it was assumed that the relationship between the applied power and the graphite crucible temperature depends on the device and/or its manufacturing year. In other words, the crucible temperature rather than the applied power should be specified as the heating condition for standardization, and the method for obtaining the calibration curve for temperature versus applied power for each device must be described in the standard.

To obtain the calibration curve, the melting of the metal particles of known melting points in the graphite crucible is monitored under gradual increase in the applied power, as shown in Fig. 12. This method is widely used to measure temperatures in the graphite ohmic-heating furnace of which direct measuring of temperature inside is difficult. Figure 13(a) shows the relationship calculated from the data

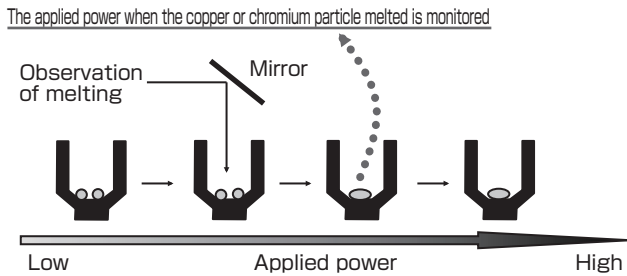


Fig. 12 Conceptual diagram of the temperature calibration of the graphite crucible

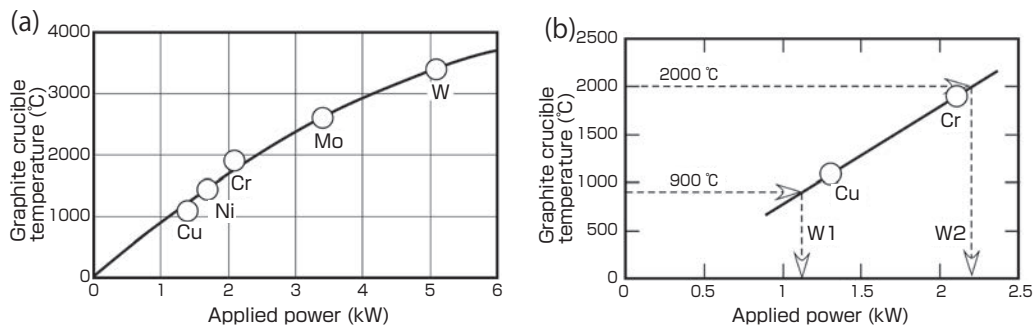


Fig. 13 Relationship of applied power and graphite crucible temperature
 (a) Calibration curve by five kinds of metal of different melting points. (b) Calibration method in the range 900 °C ~ 2,000 °C.

Table 4. Activities for international standardization

2008	2009	2010	2011	2012
April			March	
METI "Kijun Ninsho Kenkyu Kaihatsu Seido" "Standardization of Oxygen Analysis Method in Magnesium Metal and Alloy"				
	May	May	May	
	★ Explain basic concept at ISO/TC79/SC5 Tokyo meeting	★ Report progress at Berlin meeting	★ Explain outline of standard proposal at London meeting	
		Technical cooperation to Korea		
			June	
			★ Submit NWIP	
			July October	WD deliberation
				NWIP voting

of five types of metals. In general, the calibration curve exhibits curvature as shown in the figure. In the temperature range 900 °C - 2,000 °C where the Mg is evaporated off, the curvature is sufficiently small and a linear regression is applicable to the data points of the power at which the copper and chromium particles melted, as shown in figure 13(b).

4 Activities for the proposal of international standard

When proposing an international standard of analysis method, it is important to indicate the intention to propose the standard and to let it be known domestically and internationally that the proposal satisfies technological demands which are internationally-recognized, in parallel with the R&D to establish a method for increasing the technological reliability. Our efforts will be described below.

4.1 Representing preferences of industry in Japan by the Japan Magnesium Association

After establishing the elemental technologies for this analysis method, we proposed the R&D project for making the proposal of an ISO standard. To know the preferences in industry, we maintained a close relationship, from the preparatory stage of the project, with the Japan Magnesium Association (JMA), which is the industry association and

the domestic organization deliberating proposals for ISO standard. One of the authors reported the progress of our research as a member of the Analysis Committee of JMA from the early stage of development of the oxygen analysis method in FY 2006 to develop the analysis method satisfying the demands in industry. In FY 2007, a questionnaire survey was conducted on the demands of oxygen analysis among the member companies of JMA. As a result, 20 % of the companies said that the analysis method was “needed immediately,” and 50 % “needed in the future.” The survey indicated the strong demand for oxygen analysis method in industry, and a strong reason for us playing an important role in supporting the process of proposing and carrying out the R&D project.

4.2 Preliminary activities at the ISO technical committee and cooperation with Korea

For three years from the beginning of FY 2008, we conducted the R&D project for submitting the draft standard of oxygen impurity analysis, under “Kijun Ninsho Kenkyu Kaihatsu Seido” of the Ministry of Economy, Trade and Industry (METI). During this R&D project, we started activities at the ISO technical committee ISO/TC79/SC5^{Note 3)} for Mg in advance before the submission of draft. The activities are summarized in Table 4. First, in the meeting held in Tokyo May 2009, the basic concept of this analysis method was introduced as the “Future Proposal to SC5,” and the plan of the ISO standardization proposal using this method was announced. In the meeting held in Berlin May 2010, we reported the progress of the development including the sampling method and the comparison with the result of CPAA. At that meeting, there was a report from Korea that said that the analysis cannot be done well under our measuring conditions introduced in Tokyo 2009. There is a big Korean firm that engages in both the iron and steel manufacturing and Mg components production, and they have deep understanding of the IGF-IRA method frequently used in the iron and steel industry. In addition, major Mg products in Korea are basic materials such as plates rather than components with specific functions. Under these circumstances, they have high demand for quality assurance such as suppressing oxygen content. This seems to be the most likely reason why Korea showed strong interest in the oxygen analysis method and conducted additional testing voluntarily. Recently Korea has occupied a position as a Mg basic material supplier and is enhancing its influence in SC5. It was expected that forming a technological alliance with Korea would be advantageous for the prospective standardization proposal process. Fortunately, at that point we knew the fact that the “applied power – graphite crucible temperature” relationship depends on the device and/or its manufacturing year as mentioned in 3.3, enabling to point out the cause of the problem mentioned above and solution thereof. In February 2011, a mission from the JMA visited Korea and obtained information that Korea was able to obtain stable analysis value by conducting the

temperature calibration we suggested and good agreement with the result of CPAA using their original samples. In the ISO/TC79/SC5 meeting in London May 2011, we reported the method for temperature calibration of the graphite crucible and our technological cooperation with Korea. The secretary of SC5 commented, “The new proposal is well considered and we welcome it.”

The early indication of intention to propose a draft standard and giving update of the development status at the ISO technical committee provide a better atmosphere to have constructive discussions. We believe a good impression that the “standardization will go smoothly without major friction” was given to the secretariat and P member countries.^{Note 4)} The draft of the analysis method including the calibration of the graphite crucible temperature was proposed at the ISO/TC79/SC5 on June 2011 after the deliberation by the Standardization Committee of the JMA, and is currently on three-month ballot as a new work item proposal (NWIP).

5 Future prospect

In most standardization of analysis and evaluation methods, they are standardized based on established ones and from time to time, if necessary, differences of measuring conditions are reconciled among countries involved in the standardization. Meanwhile our case is perceived as rare because, we started from the development of basics of our method and eventually led to the proposal of standard to disseminate the method to industry. The dissemination and wide use of the frontier technology for analysis and evaluation is a dream of the researchers and engineers who are involved in the development of the measurement analysis technology. We believe standardization is essential in disseminating the frontier technology.

This analysis method is being applied as the product management technology for heat resistant and fire-retardant magnesium in the project of “Development of Heat Resistant Components of Power Train by Casting of Heat Resistant and Fire-retardant Magnesium” in “Senryakuteki Kiban Gijutu Kodoka Shien Jigyo” (Support Industry Project), METI. To solve the issue of rendering Mg fire retardant, which is a major problem in using the Mg in transportation machineries, an alloy doped with calcium has been developed by AIST.^[7] In regard to the improvement of the heat resistance of Mg components to use at high temperature, it is widely known that the addition of rare earth elements or silicon is effective. However, all of these additive metals have high oxygen affinity and are accompanied with the increase in oxides in the alloys. Moreover, although casting is a cost-efficient method for the components manufacturing, the reuse of runner and head, which are wastes in the casting process, as feed stock for casting is essential to prevent cost increase. The reuse of the recycled material in casting

may also cause oxide increase in components. The analysis method for measuring the oxygen content of the materials during the plant processes is highly in-demand as a process management and quality control technology. The Support Industry Project has a purpose to support the product development by companies and our analysis method is expected to disseminate into industry and to become popular. Currently, we are engaging in R&D that aims to sophisticate the method as a quality control technology.

Acknowledgement

Part of this research was conducted under the project of “Standardization of the Oxygen Analysis Method for Magnesium Metal and Alloy,” sponsored by METI and NEDO. We express our thanks to the members of the execution committee of the project and the Japan Magnesium Association that cooperated in carrying out the project.

Notes

Note 1) The temperature of the graphite crucible during the application of 2,400 W is estimated to be about 2,000 °C from the comparison with Fig. 13(a).

Note 2) Under the assumption that an analysis method as a standard for comparison is greatly different in principle from the analysis method to be standardized, the validity of analysis value by the latter can be assessed by a comparison between them. This is based on the fact that even if both methods have errors from the true value respectively, there is little possibility that the effects of their errors have the same trend. Consequently it can be considered that the effects of the errors are small and that the analysis value is close to the true value when both methods provide similar results. (Corresponding JIS Standard is “JIS Q 0034: 2001 General requirements for the competence of reference material producer”)

Note 3) ISO standardization proposal is discussed in the technical committee (TC) for the corresponding technology or the subordinate subcommittees (SC). ISO/TC79/SC5 means the subcommittee no.5 of technical committee no.79, and its name is “Magnesium and alloys of cast or wrought magnesium.” The name of TC79 is “Light metals and its alloys.”

Note 4) The countries that participate in the TC and SC of ISO are divided into the P (participating) members that are responsible for actively participating in the committee such as voting for the standard proposal and the O (observer) members. There are nine P members of ISO/TC79/SC5: Japan, China, Korea, Germany, UK, Italy, Russia, Spain, and Romania. China is the secretariat.

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Authors

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Joined the National Industrial Research Institute of Nagoya, Agency of Industrial Science and Technology in 1983, and engaged in the R&D for chemical analysis method of fine ceramics. After reorganization to AIST, also engaged in the research for industrial standard. In the drafting and revision of JIS R1603, R1616, was in charge of the development of the analysis method for oxygen, nitrogen, and carbon impurities in the powder of fine ceramics material. Currently, senior researcher of the Inhomogeneity Analysis Research Group, Research Institute of Instrumentation Frontier. In this research, worked on the development of the analysis method and ISO draft preparation in the research under the Standard Certification R&D Project, METI, and also worked in the preliminary activities for the standard proposal through participation in the ISO/TC79/SC5 meetings.



Wataru KANEMATSU

Joined the National Industrial Research Institute of Nagoya, Agency of Industrial Science and Technology in 1984, and engaged in research on the mechanical properties and machining damage of structural ceramics. After reorganization to AIST, also engaged in the research for industrial standard. Worked as the chief of committee for drafting JIS R1674, convener of ISO/TC206 (fine ceramics) /WG31, and project leader of ISO/TC206/WG36. Currently, leader of the Inhomogeneity Analysis Research Group, Research Institute of Instrumentation Frontier. In this research, worked on the coordination of the research under the Standard Certification R&D Project, METI as well as the ISO proposal drafting.



Discussion with Reviewers

1 Overall

Comment (Masahiro Okaji, AIST, currently at Chino Corporation)

This research clearly aims for industrial application from the beginning and engages in R&D toward the standardization as an outlet, and I think it is appropriate as a *Synthesiology* paper.

2 International situation

Comment (Yasuo Hasegawa, Energy Technology Research Institute, AIST)

You discuss the situation of Japan, China, and Korea in “1 Introduction,” but I think it will become easier to understand the situation of the industry if you add a graph of the share of raw material production and goods production by countries.

Answer (Wataru Kanematsu)

I added the pie chart of the production of magnesium metal by countries based on the report by the US Geological Survey, as Fig. 1 in chapter 1. I also corrected the figures for the world share based on this (95 % → 85 %). For goods production, the market scale is small compared to other non-iron metal products, and the statistics of the industrial organizations do not have magnesium as an independent survey subject.

3 Process of selecting the IGF-IRA method

Comment (Masahiro Okaji)

Please describe the process of choosing the IGF-IRA method among several oxygen analysis methods, from the scenario-driven standpoint.

You start with the inert gas fusion infrared absorptiometry (IGF-IRA) in 2.1. I think it will be logically easier to understand if you start with the comparison of the phenol dissolution method and CPAA method described in 3.1, and show why the IGF-IRA is more appropriate for standardization. Please reconsider the line of reasoning.

Answer (Akira Tsuge)

For the process of choosing the IGF-IRA method, I added the sentences describing the problems of the analyses using activation or wet operation, and the fact that IGF-IRA method is used widely in industry and therefore appropriate for standardization at the beginning of “2.1 Development of the basic technology” to clarify the reason for the appropriateness of standardizing IGF-IRA.

4 Process of the selection of sampling method

Comment (Masahiro Okaji)

As is the case with the preceding discussion, for the sampling method, I think the reasoning is natural and easier to understand if you describe the comparison of the two methods (chip sampling and core drill methods) in the beginning.

Answer (Akira Tsuge)

I added the description at the beginning of “2.2 On the sampling method” and at the beginning of “2.2.1 Chip sampling.” I clarified the process by explaining the fact that the effect of surface oxidation in the material with high oxygen affinity like magnesium cannot be avoided in general chip sampling method, and therefore the core drill sampling that has small effect on oxidation was chosen although homogenizing process cannot be done.

5 Justification of agreement with CPAA method

Comment 1 (Masahiro Okaji)

In the last paragraph of 3.1, you explained the justification of agreement between this method and the charged particle method. However, there are assumptions in the description of the cause of discrepancy of the data, and I think a more objective explanation

is required here. For example, in the later paragraph, it is written, “Sample no.3 ... probably contained moisture and hydroxides.” Is this the result of measuring the concentration of moisture and oxides? Also, for the degree of agreement, can you say it is satisfactory in the comparison with the requirement level of uncertainty?

Answer 1 (Akira Tsuge)

The moisture and hydroxides were not measured. These are error factors caused by the assumption that the sample no.3 used in this experiment is a sample oxidized by increasing the humidity of the chips.

For the requirement level of uncertainty, the analysis value of the oxygen in metal by the IGF-IRA method is allowed to have about 2 %~10 % fluctuation by relative standard deviation (this depends on the amount of sample used). This relatively low precision is attributed to the fact that there are many cases where the oxygen analysis value in metal is used for the detection of failures associated with the increase of an order of magnitude in the analysis value in daily product process management. In this sense, this method is considered to fulfill the required standard for uncertainty for use at production sites.

Comment 2 (Yasuo Hasegawa)

You compared the two different analysis methods in chapter 3, and discussed the cause of discrepancy with this analysis method. If you can assume a definite reason, shouldn't you verify whether the degree of agreement improves when the cause of discrepancy is eliminated? If not, I think you can just say that the results agree within the margin of error.

Answer 2 (Akira Tsuge)

Since analysis results for the sample no.3 did not agree within the margin of error, we investigated the cause of discrepancy. In the comparison among the analysis methods with different analysis principle, investigating the differences originating from the analysis principle is necessary even if the result agrees within the error range; in inert gas fusion method, oxygen contained as oxide in the sample is analyzed, whereas oxygen of any form in the sample is done so in CPAA method. In this case, the difference exceeded the error range in sample no.3.

6 Validity of the result of the joint analysis experiment

Comment (Masahiro Okaji)

In 3.3, you mentioned that as the result of the joint analysis experiment by AIST and three other institutions, AIST and one institution were able to have measured values. However, you did not show the data so the reader cannot examine the validity. I think you have to demonstrate how the consistency is improved by knowing the relationship of the “applied power – graphite crucible temperature” using experimental data.

Answer (Akira Tsuge)

The results of the joint test in Japan were summarized in Table 3. I also added the explanation of each analysis value and the reason for ND (not detected).

7 International standardization

Comment 1 (Yasuo Hasegawa)

I think the process for international standardization is informative for people involved in such a project. I think it will help such efforts if you show the process in a chronological table.

Answer 1 (Wataru Kanematsu)

The efforts for international standardization are described in chapter 4 in chronological order. For a better understanding, I organized the contents in Table 4.

Comment 2 (Masahiro Okaji)

In 4.2, the position of Korea is unclear in the ISO standard proposal. Since international cooperation is important,

please describe in detail the background and the process to standardization, such as: “Did Korea participate in response to the request for cooperation from Japan, or did they voluntarily raise their hand?”

Answer 2 (Wataru Kanematsu)

Since there is a big Korean firm that engages in both the iron and steel manufacturing and Mg components production, Korean delegations were highly interested in the oxygen analysis from the beginning. Therefore, the check of our measurement procedure was done voluntarily rather than by request from Japan. I added the explanation of the background of their active cooperation in our activities, with some possible implications.

Comment 3 (Yasuo Hasegawa)

What is the role of Korea in SC5? Also, did the positive evaluation by Korea affect the discussions at the technical committee?

Answer 3 (Wataru Kanematsu)

As mentioned in chapter 1, Korea is solidifying its position as a basic material supplier in the world market of magnesium. Therefore, Korea has a great influence as a P-member in SC5. We believe that the P-members other than Japan and Korea were favorably impressed with the fact that Korea verified the accuracy of the analysis method to be proposed to ISO. Some sentences were added to clarify this point.