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Surface chemical analysis — Analysis of metal oxide films by glow-discharge optical-emission spectrometry

Analyse chimique des surfaces — Analyse de films d'oxyde de métal par spectrométrie d'émission optique à décharge luminescente

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Foreword

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

In other circumstances, particularly when there is an urgent market requirement for such documents, a technical committee may decide to publish other types of document:

— an ISO Publicly Available Specification (ISO/PAS) represents an agreement between technical experts in an ISO working group and is accepted for publication if it is approved by more than 50 % of the members of the parent committee casting a vote;

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An ISO/PAS or ISO/TS is reviewed after three years in order to decide whether it will be confirmed for a further three years, revised to become an International Standard, or withdrawn. If the ISO/PAS or ISO/TS is confirmed, it is reviewed again after a further three years, at which time it must either be transformed into an International Standard or be withdrawn.

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ISO/TS 25138 was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 8, *Glow discharge spectroscopy*.

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Surface chemical analysis — Analysis of metal oxide films by glow-discharge optical-emission spectrometry

1 Scope

This Technical Specification describes a glow-discharge optical-emission spectrometric method for the determination of the thickness, mass per unit area and chemical composition of metal oxide films.

This method is applicable to oxide films 1 nm to 10 000 nm thick on metals. The metallic elements of the oxide can include one or more from Fe, Cr, Ni, Cu, Ti, Si, Mo, Zn, Mg, Mn and Al. Other elements that can be determined by the method are O, C, N, H, P and S.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 14284, *Steel and iron — Sampling and preparation of samples for the determination of chemical composition*

ISO 14707, *Surface chemical analysis — Glow discharge optical emission spectrometry (GD-OES) — Introduction to use*

ISO 16962:2005, *Surface chemical analysis — Analysis of zinc- and/or aluminium-based metallic coatings by glow-discharge optical-emission spectrometry*

3 Principle

The analytical method described here involves the following processes:

a) Cathodic sputtering of the surface metal oxide in a direct-current or radio-frequency glow-discharge device.

b) Excitation of the analyte atoms in the plasma formed in the glow-discharge device.

c) Spectrometric measurement of the intensities of characteristic spectral-emission lines of the analyte atoms as a function of sputtering time (depth profile).

d) Conversion of the depth profile in units of intensity versus time to mass fraction versus depth by means of calibration functions (quantification). Calibration of the system is achieved by measurements on calibration specimens of known chemical composition and measured sputtering rate.

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4 Apparatus

4.1 Glow-discharge optical-emission spectrometer

4.1.1 General

The required instrumentation includes an optical-emission spectrometer system consisting of a Grimm type[1] or similar glow-discharge source (direct-current or radio-frequency powered) and a simultaneous optical spectrometer as described in ISO 14707, capable of providing suitable spectral lines for the analyte elements.

The inner diameter of the hollow anode of the glow-discharge source shall be in the range 2 mm to 8 mm. A cooling device for thin specimens, such as a metal block with circulating cooling liquid, is also recommended, but not strictly necessary for implementation of the method.

Since the principle of determination is based on continuous sputtering of the surface metal oxide, the spectrometer shall be equipped with a digital readout system for time-resolved measurement of the emission intensities. A system capable of a data acquisition speed of at least 500 measurements/second per spectral channel is recommended, but, for a large number of applications, speeds of $>$ 50 measurements/second per spectral channel are acceptable.

4.1.2 Selection of spectral lines

For each analyte to be determined, there exist a number of spectral lines which can be used. Suitable lines shall be selected on the basis of several factors, including the spectral range of the spectrometer used, the analyte mass fraction range, the sensitivity of the spectral lines and any spectral interference from other elements present in the test specimens. For applications where several of the analytes of interest are major elements in the specimens, special attention shall be paid to the occurrence of self-absorption of certain highly sensitive spectral lines (so-called resonance lines). Self-absorption causes non-linear calibration curves at high analyte mass fraction levels, and strongly self-absorbed lines should therefore be avoided for the determination of major elements. Suggestions concerning suitable spectral lines are given in Annex B. Spectral lines other than those listed may be used, so long as they have favourable characteristics.

4.1.3 Selection of glow-discharge source type

4.1.3.1 Anode size

Most GD-OES instruments on the market are delivered with options to use various anode diameters, 2 mm, 4 mm and 8 mm being the most common. Some older instruments have one anode only, usually 8 mm, while the most commonly used anode in modern instruments is 4 mm. A larger anode requires larger specimens and higher power during analysis; therefore the specimen is heated to a greater extent. On the other hand, a larger anode gives rise to a plasma of larger volume that emits more light, resulting in lower detection limits (i.e. higher analytical sensitivity). In a large number of applications, the 4 mm anode is a good compromise. However, in surface analysis applications it is rather common to encounter problems of overheating of the specimens due to e.g. surface layers of poor heat conductivity and/or very thin specimens. In such cases, the smaller 2 mm anode is preferable, even if there is some loss of analytical sensitivity.

4.1.3.2 Type of power supply

The glow-discharge source can be either a type powered by a direct-current (DC) power supply or a radio-frequency (RF) type. The most important difference is that the RF type can sputter both conductive and non-conductive specimens; hence this is the only type that can be used for e.g. polymer coatings and insulating oxide layers. On the other hand, it is technically simpler to measure and control the electrical source parameters (voltage, current, power) of a DC type. Several commercially available GD-OES systems can be delivered with the option to switch between DC and RF operation, but RF-only systems are becoming increasingly common. In short, there are a very large number of applications where DC or RF sources can be used and several where only an RF source can be used.

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4.1.3.3 Mode of operation

Both DC and RF sources can be operated in several different modes with respect to the control of the electrical parameters (current, voltage, power) and the pressure. There are several reasons for this:

— "historical" reasons (older instruments have simpler but functional power supplies, while the technology has evolved so newer models have more precise and easier-to-operate source control);

— different manufacturers have chosen different solutions for source control;

— there are some application-related issues where a particular mode of operation is to be preferred.

This Technical Specification gives instructions for optimizing the source parameters based on several available modes of operation. The most important reason for this is to make these instructions comprehensive so as to include several types of instrument. In most applications, there is no major difference between these modes in terms of analytical performance, but there are other differences in terms of practicality and ease of operation. For instance, a system equipped with active pressure regulation will automatically be adjusted to the same electrical source parameters every time a particular analytical method is used. Without this technology, some manual adjustment of the pressure to achieve the desired electrical source parameters is normally required.

NOTE It should be noted in this context that what is known as the emission yield[2][3] forms the basis for calibration and quantification as described in this Technical Specification. The emission yield has been found to vary with the current, the voltage and, to a lesser extent, the pressure[8]. It is impossible in practice to maintain all three parameters constant for all test specimens, due to variations in the electrical characteristics of different materials. In several instrument types, the electrical source parameters (the plasma impedance) can therefore be maintained constant by means of automatic systems that vary the pressure during analysis. Alternatively, there exist methods to correct for impedance variations by means of empirically derived functions[8], and this type of correction is implemented in the software of commercially available GD-OES systems.

5 Adjusting the glow-discharge spectrometer system settings

5.1 General

Follow the manufacturer's instructions or locally documented procedures for preparing the instrument for use.

For the optical system, the most important preparation step is to check that the entrance slit to the spectrometer is correctly adjusted, following the procedure given by the instrument manufacturer. This ensures that the emission intensities are measured on the peaks of the spectral lines for optimum signal-to-background ratio. For further information, see ISO 14707.

The most important step in developing a method for a particular application is to optimize the parameters of the glow-discharge source. The source parameters shall be chosen to achieve three aims:

a) adequate sputtering of the test specimen, to reduce the analysis time without overheating the specimen;

b) good crater shape, for good depth resolution;

c) constant excitation conditions in calibration and analysis, for optimum accuracy.

Trade-offs are often necessary among the three specified aims. More detailed instructions on how to adjust the source parameters are given in the following subclauses.

The settings of the high voltage for the detectors depend on the source parameters, but the procedure is the same for all modes of operation of the source. This procedure is therefore only described for the first mode of operation.

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Similarly, the steps to adjust and optimize the source settings in terms of signal stability and sputter crater shape are also similar in principle for all modes of operation. Therefore, these procedures are only described in detail for the first mode of operation.

5.2 Setting the parameters of a DC source

5.2.1 Constant applied current and voltage

5.2.1.1 General

The two control parameters are the applied current and the applied voltage. Set the power supply for the glow-discharge source to constant-current/constant-voltage operation. Then set the current and voltage to the typical values recommended by the manufacturer. If no recommended values are available, set the voltage to 700 V and the current to a value in the range 5 mA to 10 mA for a 2 mm or 2,5 mm anode, 15 mA to 30 mA for a 4 mm anode or 40 mA to 100 mA for a 7 mm or 8 mm anode. If no previous knowledge of the optimum current is available, it is recommended to start with a value somewhere in the middle of the recommended range.

5.2.1.2 Setting the high voltage of the detectors

Select test specimens with surface layers of all types to be determined. For all test specimens, run the source while observing the output signals from the detectors for the analyte atoms. Adjust the high voltage of the detectors in such a way that sufficient sensitivity is ensured at the lowest analyte mass fraction without saturation of the detector system at the highest analyte mass fraction.

5.2.1.3 Adjusting the source parameters

For each type of test specimen, carry out a full depth profile measurement, sputtering it in the glow discharge for a sufficiently long time to remove the metal oxide completely and continue well into the base material. By observing the emission intensities as a function of sputtering time (often referred to as the qualitative depth profile), verify that the selected source settings give stable emission signals throughout the depth profile and into the substrate. If this is found not to be the case, reduce one of the control parameters by a small amount and sputter through the metal oxide again. If the stability is still unsatisfactory, reduce the other control parameter by a small amount and repeat the measurements. If found necessary, repeat this procedure for a number of control parameter combinations until stable emission conditions are obtained.

NOTE Unstable emission signals could indicate thermal instability in the specimen surface layers; specimen cooling is beneficial in this regard.

5.2.1.4 Optimizing the crater shape

If a suitable profilometer device is available, adopt the following procedure. Sputter a specimen with a metal oxide typical of the test specimens to be analysed to a depth of about 10 µm to 20 µm, but still inside the metal oxide. If no such specimen is available, use a brass specimen. Measure the crater shape by means of the profilometer device. Repeat this procedure a few times using slightly different values of one of the control parameters. Select the conditions that give an optimally flat-bottomed crater. These conditions are then used during calibration and analysis.

5.2.2 Constant applied current and pressure

The two control parameters are the applied current and the pressure. Set the power supply for the glow-discharge source to constant-current operation. Then set the current to a typical value recommended by the manufacturer. If no recommended values are available, set the current to a value in the range 5 mA to 10 mA for a 2 mm or 2,5 mm anode, 15 mA to 30 mA for a 4 mm anode or 40 mA to 100 mA for a 7 mm or 8 mm anode. If no previous knowledge of the optimum current is available, it is recommended to start with a value somewhere in the middle of the recommended range. Sputter a typical coated test specimen, and adjust the pressure until a voltage of approximately 700 V is attained in the metal oxide.

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Set the high voltage of the detectors as described in 5.2.1.2.

Adjust the discharge parameters as described in 5.2.1.3, adjusting first the current and, if necessary, the pressure.

Optimize the crater shape as described in 5.2.1.4 by adjusting the pressure. These conditions are then used during calibration and analysis.

NOTE Before sputtering a new specimen type, make a test run in order to ensure that the voltage has not changed by more than 5 % from the previously selected value. If this is the case, readjust the pressure until the correct value is attained.

5.3 Setting the discharge parameters of an RF source

5.3.1 Constant applied power and pressure

The two control parameters are the applied power and the pressure. First set the applied power and adjust the source pressure to the values suggested by the manufacturer. If recommended values are not available, set the applied power and pressure to somewhere in the middle of the ranges commonly used for depth profiling of metal specimens. Measure the penetration rate (i.e. depth per unit time) on an iron or steel specimen, adjusting the power to give a penetration rate of about 2 µm/min to 3 µm/min.

Set the high voltage of the detectors as described in 5.2.1.2.

Adjust the discharge parameters as described in 5.2.1.3, adjusting first the applied power and, if necessary, the pressure.

Optimize the crater shape as described in 5.2.1.4 by adjusting the pressure.

Remeasure the penetration rate on the iron or steel specimen and adjust the applied power, if necessary, to return to about 2 µm/min to 3 µm/min. Repeat the cycle of power and pressure adjustment until no significant change is noted in the penetration rate or crater shape. Note the power and pressure used in units provided for the instrument type. These conditions are then used during calibration and analysis.

5.3.2 Constant applied power and DC bias voltage

The two control parameters are the applied power and the DC bias voltage. First set the applied power and adjust the source pressure to attain a DC bias typical of the values suggested by the manufacturer. If recommended values are not available, set the applied power and DC bias voltage to somewhere in the middle of the range commonly used for depth profiling of metal specimens. On instruments equipped with active pressure control, this can be achieved automatically. Measure the penetration rate (i.e. depth per unit time) on an iron or steel specimen, adjusting the power to give a penetration rate of about 2 µm/min to 3 µm/min.

Set the high voltage of the detectors as described in 5.2.1.2.

Adjust the discharge parameters as described in 5.2.1.3, adjusting first the applied power and, if necessary, the DC bias voltage.

Optimize the crater shape as described in 5.2.1.4 by adjusting the DC bias voltage.

Remeasure the penetration rate on the iron or steel specimen and adjust the applied power, if necessary, to return to about 2 µm/min to 3 µm/min. Repeat the cycle of power and DC bias voltage adjustment until no significant change is noted in the penetration rate or in the crater shape. If this is not the case, readjust the DC bias voltage until the correct value is attained. Note the power and DC bias voltage used in units provided for the instrument. These conditions are then used during calibration and analysis.

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5.3.3 Constant effective power and RF voltage

The two control parameters are the effective power and the RF voltage. Constant effective power is defined here as the applied power minus the reflected power and the "blind power" measured with the specimen in place but without plasma (vacuum conditions). The RF voltage is defined here as the RMS voltage at the coupling electrode.

Set the power supply for the glow-discharge source to constant effective power/constant RF voltage operation. First set the power to a typical value recommended by the manufacturer. If no recommended values are available, set the RF voltage to 700 V and the power to a value in the range 10 W to 15 W for a 4 mm anode, to give an example. If no previous knowledge of the optimum power is available, it is recommended to start with a value somewhere in the middle of the recommended range.

Set the high voltage of the detectors as described in 5.2.1.2.

Adjust the discharge parameters as described in 5.2.1.3, adjusting first the effective power and, if necessary, the RF voltage.

Optimize the crater shape as described in 5.2.1.4 by adjusting the RF voltage. Select the conditions that give an optimally flat-bottomed crater. These conditions are then used during calibration and analysis.

5.4 Minimum performance requirements

5.4.1 General

It is desirable for the instrument to conform to the performance specifications given in 5.4.2 and 5.4.3 below.

NOTE Setting up for analysis commonly requires an iterative approach to the adjustment of the various instrumental parameters described in this Technical Specification.

5.4.2 Minimum repeatability

The following test shall be performed in order to check that the instrument is functioning properly in terms of repeatability.

Perform 10 measurements of the emission intensity on a homogeneous bulk specimen with a content of the analyte exceeding a mass fraction of 1 %. The glow-discharge conditions shall be those selected for analysis. These measurements shall be performed using a discharge stabilization time (often referred to as "preburn") of at least 60 s and a data acquisition time in the range 5 s to 20 s. Each measurement shall be located on a newly prepared surface of the specimen. Calculate the relative standard deviation of the 10 measurements. The relative standard deviation shall conform to any requirements and/or specifications relevant to the intended use.

NOTE Typical relative standard deviations determined in this way are 2 % or less.

5.4.3 Detection limit

5.4.3.1 General

Detection limits are instrument-dependent and matrix-dependent. Consequently, the detection limit for a given analyte cannot be uniquely determined for every available instrument or for the full range of metal oxides considered here. For the purposes of this Technical Specification, the detection limit for each analyte will be acceptable if it is equal to or less than one-fifth of the lowest expected mass fraction in the metal oxide.

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5.4.3.2 SNR method

The first method is often called the SNR (signal-to-noise ratio) method. In order to evaluate the detection limit for a given analyte, the following steps are performed.

1 Select a bulk specimen to be used as a blank. The composition of the specimen should preferably be similar, in terms of the elemental composition of the matrix, to that of the metal oxides to be analysed. Further, the specimen shall be known to contain less than 1 µg/g of the analyte.

2 Perform ten replicate burns on the blank. For each burn, acquire the emission intensity at the analytical wavelength for 10 s. These are the background emission intensity measurements. The glow-discharge conditions used should preferably be the same as those that will be used in the analysis of the coated specimens. For each measurement, the blank shall be preburned at these conditions for a sufficient length of time to achieve stable signals prior to the quantification of the emission intensity. Use an unsputtered area of the surface of the blank for each individual burn.

3 Compute the detection limit, expressed as a mass fraction, using the following equation:

$$\mathrm{DL} = \frac{3 \times \sigma}{S} \tag{1}$$

where

DL is the detection limit;

σ is the standard deviation of the background intensity measurements performed in step 2;

S is the analytical sensitivity derived from the instrument calibration, expressed in the appropriate units (the ratio of intensity to mass fraction).

If the detection limit calculated is unacceptable, the test shall be repeated. If the second value calculated is also unacceptable, then the cause shall be investigated and corrected prior to analysing specimens.

5.4.3.3 SBR-RSDB method

The second method, which does not require a blank, is often called the SBR-RSDB (signal-to-background ratio — relative standard deviation of the background) method. The method is performed as follows:

1 Select a bulk specimen which has a matrix composition that is similar to that of the metal oxides to be analysed and in which the mass fraction of the analyte is greater than 0,1 % and accurately known. If an analytical transition that is prone to self-absorption (see 4.1.2) is to be used, the mass fraction of the analyte should preferably not exceed 1 %.

2 Perform three replicate burns on the chosen specimen. For each burn, integrate the emission intensity at the analytical wavelength for 10 s. The glow-discharge conditions used should preferably be similar to those that will be used in the analysis of the coated specimens. For each measurement, the specimen shall be preburned at these conditions for a sufficient length of time to achieve stable signals prior to the quantification of the emission intensity. Use a freshly prepared area of the surface of the specimen for each individual burn. Average the three replicate emission intensities.

3 Select a peak-free region of the emission spectrum within 0,2 nm of the analytical peak. Perform ten replicate burns on the chosen specimen. For each burn, integrate the intensity at the peak-free region for 10 s. These are the measurements of the background intensity. The glow-discharge conditions and preburn shall be the same as those used in step 2. Once again, use a freshly prepared area of the surface of the specimen for each individual burn. Compute the average and the relative standard deviation of the ten replicate measurements.

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4 Calculate the detection limit using the following equation:

$$DL = \frac{3 \times \left(w_A \times \sigma_{Rel,B} / 100 \right)}{(I - I_B)/I_B} \quad (2)$$

where

DL is the detection limit;

w_A is the mass fraction of the analyte in the specimen;

$\sigma_{Rel,B}$ is the relative standard deviation of the background from step 3, expressed as a percentage;

I_B is the average background intensity from step 3;

I is the average peak intensity from step 2.

If the detection limit calculated is unacceptable, then the test shall be repeated. If the second value calculated is also unacceptable, then the cause shall be investigated and corrected prior to analysing specimens.

6 Sampling

Carry out sampling in accordance with ISO 14284 and/or relevant national/international standards, as appropriate. If no such standards are available, follow the instructions from the manufacturer of the coated material or another appropriate procedure. The edges of a coated strip should preferably be avoided. The size of the test specimens taken shall be suitable for the glow-discharge source used. Typically, round or rectangular specimens with sizes (diameter, width and/or length) of 20 mm to 100 mm are suitable.

Rinse the surface of the specimen with an appropriate solvent (high-purity acetone or ethanol) to remove oils. Blow the surface dry with a stream of inert gas (argon or nitrogen) or clean, oil-free compressed air, being careful not to touch the surface with the gas delivery tube. The wetted surface may be lightly wiped with a wetted, soft, lint-free cloth or paper to facilitate the removal of oils. After wiping, flush the surface with solvent and dry as described above.

7 Calibration

7.1 General

Calibration of the system consists of determining, for each analyte and spectral line, the calibration equation as described in either Clause A.2 or Clause A.3. In order to carry out the calibration, it is necessary to know both the chemical composition and the sputtering rates (mass loss rates) of the calibration specimens. The software of all commercially available spectrometers is designed to create several dedicated calibrations for different applications. A combination of a set of spectrometer system settings and a set of calibration equations valid at these settings is usually called an analytical method.

7.2 Calibration specimens

7.2.1 General

Whenever possible, spectrometric calibration specimens issued as CRMs (certified reference materials) shall be used. Due to the quantification being based on emission yields, the calibration specimens need not be very similar to the metal oxide materials in composition but they shall have sputtering rates which are well determined and reproducible. In particular, specimens of very low melting point (Zn, Sn, Pb) are not recommended, due to difficulties in obtaining reproducible and stable sputtering rates. Furthermore, high-purity metals are not necessary in order to calibrate correctly for high mass fractions, but they are valuable for

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the determination of the spectral backgrounds. The following considerations are the most important in the selection of the calibration specimens:

a) there shall be at least five calibration specimens for each analyte, covering a range from zero to the highest mass fraction to be determined;

b) the specimens shall be homogeneous.

Based on these general requirements, the types of calibration specimen described in 7.2.2 to 7.2.13 are suggested. Additional calibration specimens of other alloy types containing the analytes may also be used.

NOTE 1 A reference material (RM) is a material, sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process.

NOTE 2 A certified reference material (CRM) is a reference material, characterized by a metrologically valid procedure for one or more specified properties, accompanied by a certificate that provides the value of the specified property, its associated uncertainty and a statement of metrological traceability. By trademark, a Standard Reference Material® (SRM®) is a CRM issued by the National Institute of Standards and Technology, Gaithersburg, MD, USA.

7.2.2 Low-alloy iron or steel specimens

Use steel specimens with iron mass fractions that are greater than 98 %. The iron mass fraction for a given specimen can be determined by subtracting the sum of the mass fractions for all other known elements from 100 %.

7.2.3 Stainless-steel specimens

Use stainless-steel specimens with nickel mass fractions in the range 10 % to 40 %, chromium mass fractions in the range 10 % to 40 %, molybdenum mass fractions in the range 0,5 % to 10 % and manganese mass fractions in the range 0,1 % to 3 %.

7.2.4 Nickel alloy specimens

Use nickel-based alloy specimens with nickel mass fractions that are greater than 50 %.

7.2.5 Copper alloy specimens

Use copper alloy specimens with copper mass fractions that are greater than 50 % and zinc mass fractions that are greater than 30 %.

7.2.6 Titanium alloy specimens

Use titanium alloy specimens with titanium mass fractions that are greater than 50 %.

7.2.7 Silicon specimens

Use a nearly pure silicon specimen, which may also be used to determine zero points for all analytes except silicon.

7.2.8 Aluminium alloy specimens

Use aluminium alloy specimens with aluminium mass fractions that are greater than 50 % and magnesium mass fractions in the range 0,1 % to 5 %.

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