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UNCERTAINTY EVALUATION OF THE TGA OXIDATION DATA

Thermogravimetric analysis (TGA) involves the measurement of the changes in mass that occur when a constant heat is applied to an unknown specimen as a function of time or temperature. It is used to evaluate thermal stability, oxidative stability, composition, and estimated lifetime, among other parameters. Given that accurate TGA data is important information for lifetime and stability evaluation of parts and products, an uncertainty evaluation procedure is required to ensure the reliability of the data. In this study, the uncertainty evaluation procedure was established according to the Guide to the Expression of Uncertainty in Measurement (GUM). The mathematical expression of the relationship between the measurand and the input quantities, evaluation of the standard uncertainty of each input estimate, determination of the combined standard uncertainty, and calculation of the expanded uncertainty were performed. The biggest factor affecting the uncertainty of TGA data is the uncertainty of correction factor caused by system calibration.

Keywords: TGA; uncertainty; GUM; oxidation; system calibration

1. Introduction

Thermogravimetric analysis (TGA) involves the measurement of the changes in mass as a function of temperature or isothermally as a function of time in an atmosphere of nitrogen, oxygen, argon, helium, and air, other gases, or in a vacuum. According to international standards, thermogravimetry is defined as a method whereby the mass of substance under controlled heating or cooling conditions is recorded as a function of time or temperature [1]. Thermogravimetric analysis is an ideal compositional analysis method for detecting the content of volatile substances (moisture, solvents, etc.), polymers, carbon black, carbon fiber, ash, and fillers. Thermogravimetric analysis is used to evaluate the thermal stability, oxidative stability, composition, and estimated lifetime. The mass loss of a material is caused by evaporation, decomposition, reduction, or desorption. The mass gain of the material is caused by an oxidation reaction or adsorption. There are various standard test methods in American Society for Testing and Materials (ASTM) International and the International Organization for Standardization (ISO) for reactivity of solids and gases, evaporation of volatile and semi-volatile materials, compositional analysis of materials, and decomposi-

tion of materials [2,3]. The TGA apparatus for reactivity analysis is described in the ASTM D6558 [4]. However, there is no standard procedure for the uncertainty evaluation of TGA data in the ASTM and ISO standards.

Given that accurate TGA data is important information for the lifetime and stability evaluation of parts and products, an uncertainty evaluation procedure is required to ensure the reliability of the data. Error analysis is commonly used as a quantitative expression of the reliability of measurement. However, irrespective of the accuracy of the error evaluation and correction, the accuracy of the results is not guaranteed. The Guide to the Expression of Uncertainty in Measurement (GUM) was produced by Working Group 1 of the joint Committee for Guides in Metrology (JCGM/WG 1) [5]. The evaluation of uncertainty is roughly divided into four stages: the mathematical expression of the relationship between the measurand and the input quantities, evaluation of the standard uncertainty of each input estimate, determination of the combined standard uncertainty, and calculation of the expanded uncertainty.

In this study, the uncertainty evaluation procedure was established in accordance with the GUM to improve the reliability of the TGA data of an oxidation test.

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2. Uncertainty evaluation

2.1. Mathematically expression of relationship between measurand and input quantities

An oxidation experiment using TGA was conducted to measure the mass increase due to the reaction of the solid specimen and oxygen over time at a constant temperature, the resulting model can be expressed as follows:

$$Y(t) = \frac{\Delta M(t)}{A} f_{cal} = \Delta m(t) f_{cal} \quad (1)$$

where $Y(t)$ is the amount of oxidation per unit area over time at a constant temperature (mg/mm^2), $\Delta M(t)$ is the mass change of the specimen measured using TGA over time (mg), A is the area of the specimen (mm^2), f_{cal} is a correction factor according to the calibration of the TGA using standard mass (mg/mm^2), $\Delta m(t)$ is mass change per unit area over time (mg/mm^2) and t is time (s).

The factors influencing the uncertainty of the amount of oxidation ($Y(t)$) per unit area are the mass change amount ($\Delta M(t)$) measured using TGA with respect to time at a constant temperature, the correction factor (f_{cal}) of TGA using standard mass, and the area of the specimen (A) (mm^2).

The correction factor, f_{cal} , is expressed by the following equation:

$$f_{cal} = \frac{M_{ref-c}}{M_{ref}} \quad (2)$$

where M_{ref-c} is the standard mass given in the calibration certificate, and M_{ref} is the standard mass measured using TGA.

2.2. Evaluation of the standard uncertainty of each input estimates

2.2.1. Uncertainty of mass change of the specimen: $u(\Delta m(t))$

The random uncertainty of the mass change of a specimen measured using TGA is type-A uncertainty. This causes variations in the repeated measurements of the measurand, and is expressed as the experimental standard deviation of the mean:

$$u(\Delta m(t)) = s(\Delta m(t)) / \sqrt{n} \quad (3)$$

2.2.2. Uncertainty of the specimen area: $u(A)$

Given that a disk-type specimen was used in this study, its area can be represented as follows:

$$A = \pi(D+b) \times (th+b) + 2 \times \frac{\pi(D+b)^2}{4} \quad (4)$$

where A is the specimen area (mm^2), D is the specimen diameter (mm), th is the specimen thickness (mm), and b (mm) is the cor-

rection value of the micrometer used. Moreover, the correction value was relatively small, and its square terms were ignored.

Therefore, the uncertainty of the specimen area can be expressed using the following equation:

$$u(A) = \sqrt{c_D^2 u^2(D) + c_{th}^2 u^2(th) + c_b^2 u^2(b)} \quad (5)$$

where $c_{xi} = \partial A / \partial xi$ is the sensitivity coefficient of each factor influencing the uncertainty, and $u(xi)$ is the uncertainty of each factor.

The uncertainties of the specimen diameter and thickness consist of the random uncertainty due to repeated measurements and the systematic uncertainty due to the resolution limit of the micrometer. In particular,

$$u(D) = u(D_r) + u(D_R) \quad (6)$$

$$u(th) = u(th_r) + u(th_R) \quad (7)$$

where $u(D_r)$ and $u(th_r)$ are the random uncertainties of the specimen diameter and thickness, and $u(D_R)$ and $u(th_R)$ are the systematic uncertainties of the specimen diameter and thickness due to the resolution limit of the micrometer.

Therefore, the uncertainty of the specimen area is given by

$$u(A) = \sqrt{\begin{aligned} &(\pi th + 2\pi b + \pi D)^2 (u^2(D_r) + u^2(D_R)) \\ &+ (\pi D + 2\pi b)^2 (u^2(th_r) + u^2(th_R)) \\ &+ (2\pi D + \pi th)^2 u^2(b) \end{aligned}} \quad (8)$$

Random type-A uncertainty of the diameter $u(D_r)$ and thickness $u(th_r)$ of the specimen using the micrometer, expressed as the experimental standard deviation of the mean:

$$u(D_r) = s(D) / \sqrt{n} \quad (9)$$

$$u(th_r) = s(th) / \sqrt{n} \quad (10)$$

The systematic type-B uncertainty (expressed as $u(D_R)$ and $u(th_R)$) of the micrometer is expressed with respect to its resolution limit. Given that the digital measuring instrument has a rectangular probability distribution, the uncertainty due to the resolution limit is expressed as

$$u(D_R) = a / \sqrt{3} \quad (11)$$

$$u(th_R) = a / \sqrt{3} \quad (12)$$

where a is 1/2 of the minimum reading of the micrometer.

The calibration certificate provides the expanded uncertainty, which was obtained using the coverage factor k . The uncertainty of the correction value is obtained by dividing the expanded uncertainty in the calibration certificate by the coverage factor k :

$$u(b) = U_b / k \quad (13)$$

where $u(b)$ is the uncertainty of the micrometer correction, and U_b is the expanded uncertainty of the micrometer.

2.2.3. Uncertainty of the correction factor: $u(f_{cal})$

The uncertainty of the correction factor f_{cal} consists of the uncertainty of the standard mass presented in the calibration certificate and the random uncertainty due to repeated measurements of standard mass. The calibration uncertainty is the value obtained by dividing the measurement uncertainty of the calibration certificate by the coverage factor k :

$$u(M_{ref-c}) = U_{ref-c}/k \quad (14)$$

where U_{ref-c} is the measurement uncertainty of the standard mass in the calibration certificate.

The random type-A uncertainty of the standard mass is expressed as the experimental standard deviation of the mean:

$$u(M_{ref}) = s(M_{ref})/\sqrt{n} \quad (15)$$

The uncertainty due to the correction factor $u(f_{cal})'$ can be evaluated using the following equation:

$$u(f_{cal})' = \sqrt{c_{M_{ref-c}}^2 u^2(M_{ref-c}) + c_{M_{ref}}^2 u^2(M_{ref})} \quad (16)$$

where $c_{xi} = \partial f_{cal}/\partial x_i$ is the sensitivity coefficient of each factor influencing the uncertainty, and $u(x_i)$ is the uncertainty of each factor.

The uncertainty of the correction factor should be greater than that calculated above by a factor of 10 considering the buoyance effect at the high oxidation temperature. In particular,

$$u(f_{cal}) = 10 \times u(f_{cal})' \quad (17)$$

2.3. Determination of the combined standard uncertainty u_c

Combined standard uncertainty was calculated using the previously evaluated standard uncertainty. In particular, the combined standard uncertainty was calculated as the standard uncertainties of the specimen mass, specimen area, and correction factor, as follows:

$$u_c = \sqrt{c_{m(t)}^2 u^2(M(t)) + c_A^2 u^2(A) + c_{f_{cal}(T)}^2 u^2(f_{cal})} \quad (18)$$

where

$$c_{m(t)} = \frac{\partial}{\partial m} \left(\frac{M(t)}{A} f_{cal} \right) = \frac{1}{A} f_{cal} \quad (19)$$

$$c_A = \frac{\partial}{\partial A} \left(\frac{M(t)}{A} f_{cal} \right) = -\frac{M(t)}{A^2} f_{cal} = -\frac{m(t)}{A} \times f_{cal} \quad (20)$$

$$c_{cal(T)} = \frac{\partial}{\partial f_{cal}} \left(\frac{M(t)}{A} f_{cal} \right) = \frac{M(t)}{A} = m(t) \quad (21)$$

Therefore, the combined standard uncertainty is given by

$$u_c = \sqrt{\left(\frac{1}{A} f_{cal} \right)^2 u^2(M(t)) + \left(-\frac{m(t)}{A} \times f_{cal} \right)^2 u^2(A) + m(t)^2 u^2(f_{cal})} \quad (22)$$

2.4. Calculation of expanded uncertainty U

The expanded uncertainty U is obtained by multiplying the combined standard uncertainty u_c by a coverage factor k [5]:

$$U = k u_c \quad (23)$$

If the effective degrees of freedom (DOF) ν_{eff} is significantly high, the following can be carried out:

- Adopt $k = 2$ and assume that $U = 2u_c$ defines an interval with a confidence level of approximately 95%. Otherwise, for more critical applications:
- Adopt $k = 3$ and assume that $U = 3u_c$ defines an interval with a confidence level of approximately 99%.

2.4.1. Effective DOF calculation

The effective DOF is calculated using the Welch–Satterthwaite formula [6-8]:

$$\begin{aligned} \nu_{eff} &\approx \frac{u_c^4(y)}{\sum_{i=1}^N \frac{[c_i u(x_i)]^4}{\nu_i}} \\ &= \frac{u_c^4}{\frac{c_{m(t)}^4 u^4(m(t))}{\nu_{m(t)}} + \frac{c_A^4 u^4(A)}{\nu_A} + \frac{c_{f_{cal}}^4 u^4(f_{cal})}{\nu_{f_{cal}}}} \end{aligned} \quad (24)$$

2.4.2. Determination of expanded uncertainty (U)

The expanded uncertainty U is obtained by multiplying the combined standard uncertainty u_c by the coverage factor k :

$$U = k \times u_c \quad (25)$$

3. Conclusion

The uncertainty evaluation procedure was established in accordance with the GUM to improve the reliability of the measurement data of an oxidation test conducted on Zircaloy-4 using TGA, and to evaluate the uncertainty. The study can be summarized as follows:

- (1) The uncertainty consists of the uncertainties of the measurement value of the mass gain due to oxidation, measurement of the specimen area and correction factor.
- (2) System correction was conducted using the standard mass, and the uncertainty of the correction factor should be greater than the calculated uncertainty by a factor of 10 considering the buoyance effect at the high oxidation temperature.
- (3) The biggest factor affecting the uncertainty of TGA data is the uncertainty caused by system calibration.

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