

CCQM-K67 and P108

SURFACE ANALYSIS MEASUREMENT OF THE COMPOSITION OF Fe-Ni ALLOY FILMS

A Key Comparison of the Consultative Committee on Amount of Substance

Draft B – Report of the Results

Kyung Joong KIM Division of Industrial Metrology Korea Research Institute of Standards and Science, 1 Doryong, Yuseong, Daejeon 305-600, Korea

Participants: Thomas WIRTH, Vasile-Dan HODOROABA, Thomas GROSS and Wolfgang UNGER (BAM, Germany); Werner JORDAAN, Martin VAN STADEN and Sara PRINS (NMISA, South Africa); Jeong Won KIM and Dae Won MOON (KRISS, Korea) Hai WANG and Xiaoping SONG (NIM, China); Lulu ZHANG, Toshiyuki FUJIMOTO, and Isao KOJIMA (NMIJ, Japan)

CCQM-K67 Key Comparison and P108 Pilot Study Measurement of Composition of Fe-Ni Alloy Films

Kyung Joong KIM Division of Industrial Metrology Korea Research Institute of Standards and Science, Yuseong, Daejeon 305-600, Korea [email: kjkim@kriss.re.kr]

Participants in K67

- 1) Thomas WIRTH and Wolfgang UNGER, Bundesanstalt fuer Materialforschung und pruefung (BAM), D-12200 Berlin, Germany
- 2) Werner JORDAAN, Martin VAN STADEN and Sara PRINS, National Metrology Institute of South Africa, Surface and Microanalysis (NMISA), Private Bag X34, Lynnwood Ridge, Pretoria 0040, South Africa
- 3) Kyung Joong KIM, Jeong Won KIM and Dae Won MOON, Korea Research Institute of Standards and Science (KRISS), Doryong-1, Yuseong, Daejeon 305-600, Korea.
- 4) Hai WANG and Xiaoping SONG, Chemical Metrology & Analytical Science Division, National Institute of Metrology (NIM), No. 18, Bei Sanhuan Donglu, Chaoyang District, Beijing 100013, P. R. China
- 5) Lulu ZHANG, Toshiyuki FUJIMOTO, and Isao KOJIMA, Materials Characterization Division, National Metrology Institute of Japan, (NMIJ), AIST, AIST Tsukuba Central 5, Higashi 1-1, Tsukuba, Ibaraki 305-8565, Japan.

Participants in P108

- 1) Vasile-Dan HODOROABA, Bundesanstalt fuer Materialforschung und pruefung (BAM), D-12200 Berlin, Germany
- 2) Thomas GROSS and Wolfgang UNGER, Bundesanstalt fuer Materialforschung und pruefung (BAM), D-12200 Berlin, Germany

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Abstract

CCQM K67 key comparison and P108 pilot study on quantitative analysis of alloy films has been completed in the Surface Analysis Working Group (SAWG) of the Consultative Committee for Amount of Substance (CCQM). The aim of this key comparison and pilot study is to compare the equivalence in the measurement capability of National Metrology Institutes (NMIs) and Designated Institutes (DIs) for the composition of thin alloy films expressed in atomic percent. In this study, a Fe-Ni alloy film with a certified composition was available to be used as a reference specimen to determine the relative sensitivity factors (RSFs) of Fe and Ni to improve the equivalence in the measurement of composition if required. The composition of the reference specimen was certified by inductively coupled plasma mass spectrometry (ICP-MS) with isotope dilution method. The in-depth and lateral homogeneities of composition were confirmed by secondary ion mass spectrometry (SIMS) using C₆₀ primary ions. Five laboratories participated in the key comparison as shown above. Four of the laboratories used x-ray photoelectron spectroscopy (XPS) and one laboratory used Auger electron spectroscopy (AES). One laboratory participated in the parallel P108 pilot study using electron probe micro analysis (EPMA) and XPS.

1. Introduction

Quantitative surface analysis is one of the most important issues in the application of surface analysis techniques. Although XPS and AES are generally used for the quantitative surface compositional analysis of multi-component systems, it is typically difficult to obtain an accurate surface composition because of matrix effects. The relative sensitivity factors (RSFs) determined from pure metals are generally used for the quantification of alloy materials. However, the matrix effects due to the atomic density, the attenuation lengths of electrons and the electron backscattering factor in the matrix materials must be taken into account.[1] A calibration method using alloy reference materials is recommended for the quantitative analysis of binary alloys to compensate the matrix effects.[2-4] The ideal method for the quantification of binary alloys is to use an alloy reference sample with a closely similar composition; next best is to use a calibration curve measured using alloy reference samples with a series of different compositions spanning the unknown composition. The quantification of Fe-Ni alloy films was reported to be a good candidate as a subject for international round robin test for the quantification of alloy material because there is no severe matrix effect and sample cleaning could be achieved by inert gas ion sputtering with minimal preferential sputtering. [5]

The CCQM P98 pilot study for the measurement of composition of Fe-Ni alloy films was conducted by nine laboratories. [6] The aim of that pilot study was to find optimized conditions to improve the equivalence of measurement between NMIs. In that work it was shown that the equivalence in the quantitative analysis of Fe-Ni alloy films is efficiently improved using an alloy film as a reference material to determine the relative sensitivity factors of Fe and Ni. Linear fitting results of the quantification showed an average slope of 1.002 with a standard deviation of about 0.020. The offset value was efficiently reduced from 0.725 % to 0.105 % using the RSFs determined from the certified alloy reference film used in this report.

CCQM-K67 key comparison and P108 pilot study on the quantitative analysis of a Fe-Ni alloy film was conducted by five NMIs. As a result of P98, an alloy film was recommended

to be used as a reference specimen. This report provides the tabulated data from the participants to the key comparison K67 and pilot study P108.

2. CCQM K67

2.1. Objective

The objective of CCQM K67 key comparison and P108 pilot study is to determine the atomic fractions of a Fe-Ni alloy film and to compare the international equivalence in the measurement. The required measurand was the atomic fraction of the alloy film expressed in atomic percent. As usual in CC comparisons, there was no limitation in choosing analytical techniques for quantitative analysis.

2.2. Participation

Four NMIs and one DI participated in CCQM-K67 key comparison and one DI participated in P108 pilot study, respectively, as tabulated in Table 1.

No.	Institute	Country	Contact Person	K or P	Туре
1	BAM	Germany	T. WIRTH and W. E. S. UNGER	Κ	DI
2	NMISA	South Africa	W. JORDAAN, M. VAN STADEN and S. PRINS	Κ	NMI
3	KRISS	Korea	K. J. KIM, J. W. KIM and D. W. MOON,	Κ	NMI
4	NIM	China	H. WANG and X. P. SONG	Κ	NMI
5	NMIJ	Japan	L. ZHANG, T. FUJIMOTO and I. KOJIMA	Κ	NMI
6	BAM	Germany	Vasile-Dan HODOROABA	Р	DI
7	BAM	Germany	T. GROSS and W. E. S. UNGER	Р	DI

Table 1:	Participants	in K67	and P108
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3. The Specimens [6]

3.1. Production

The Fe51-Ni49 alloy film, which has been already used in the pilot study P98, was provided to analysts to use as a certified reference specimen to determine the relative sensitivity factors of Fe and Ni if desired. Both the certified reference and the unknown test Fe-Ni alloy films were grown by the ion beam sputter deposition system in KRISS. The target materials of Fe and Ni were co-sputtered by a 1 keV Ar^+ ion beam produced using a Kaufmann-type DC ion gun and deposited on a substrate wafer at room temperature. The films were grown on 150 mm diameter Si (100) wafers rotating with a speed of 30 revolutions per minute to improve the uniformity. The wafers were then divided into 10 mm x 10 mm specimens. The nominal composition of the reference specimen was Fe51-Ni49. The real composition of the certified reference specimen was determined by ICP-MS.

The nominal composition of the test specimen was controlled by in-situ XPS analysis to be similar to that of the certified reference specimen. However, this information was unknown to the participants. Both films were about 200 nm thick although the true thickness was not known. They were in the thickness range often used commercially but too thin for analysis by

most bulk analytical methods. The thickness of the surface oxides, which have an Fe to Ni ratio that is different from that of the alloy film below, occupy a thickness of 3 nm and this, together with any sub-surface depletion zone, have to be considered before the analysis, for instance by sputter removal.

3.2. Certification of the composition by ICP-MS

The composition of the reference Fe-Ni alloy film was certified by ICP-MS with isotope dilution method. Table 2 shows the average certified composition and the expanded uncertainty (k = 2) of the reference specimen at 95% confidence.

Nominal	Mass of specimen	Determined mol amount		Composition	
Composition	(g)	Fe (µmol)	Ni (µmol)	Fe (at. %)	Ni (at. %)
Fe51-Ni49	0.01666 0.01586 0.01869	0.1616 0.1717 0.1991	0.1582 0.1684 0.1933	50.53 50.48 50.74	49.47 49.52 49.26
	E	xpanded unce	Average rtainty (k = 2)	50.58 2.84	49.42 2.84

Table 2: The average composition and expanded uncertainty of the reference specimen.

3.3. In-depth and lateral uniformity of composition

The studies on the in-depth and lateral homogeneity by SIMS depth profiling using a C_{60}^{+} ion source showed that the composition of the Fe-Ni alloy films were homogeneous with depth and sample position.

4. Measurement procedures of the participants

In CCQM-K67, four NMIs and one DI used XPS and AES to measure the composition of the test alloy sample, respectively. One participant in P108 used EPMA (EDX) and XPS. All participants in K67 and P108 used the reference specimen to determine the RSFs of Fe and Ni, or in case of EPMA, to calibrate the quantification algorithm. All participants submitted reports with the atomic composition of Fe and the expanded uncertainty at 95% confidence level.

The RSFs of Fe (S_{Fe}) and Ni (S_{Ni}) were determined from XPS or AES spectra of the delivered reference sample by the following equation.

Where C_{Fe}^{ref} is the certified atomic fraction of Fe, I_{Fe}^{ref} and I_{Ni}^{ref} are intensities of Fe and Ni from the XPS or AES spectra of the reference sample.

The atomic fraction of Fe (C_{Fe}^{test}) of the test specimen was determined from the XPS or AES spectra of the test sample by the following equation.

$$X_{Fe}^{test} = \frac{I_{Fe}^{test} / S_{Fe}}{(I_{Ni}^{test} / S_{Ni} + I_{Fe}^{test} / S_{Fe})}$$
(2)

Here, X_{Fe}^{test} is the atomic fraction of Fe, I_{Fe}^{test} and I_{Ni}^{test} are intensities of Fe and Ni from the XPS or AES spectra of the test sample.

1) BAM measured their data using a Scanning Auger Nanoprobe model 700 from ULVAC-PHI. A beam energy of 5 keV was used with 20 nA current, rastered over an area 20 µm x

20 μ m. The intensities of the Auger transitions Fe MVV and Ni MVV were observed and 5 spectra were measured for each sample. To remove the surface oxides and contamination, the film surface was sputtered by 5 keV/5 μ A Ar⁺ ions (beam raster: 0.8 mm x 0.8 mm) for 30 seconds. Before starting the first analysis run, the surface was further sputtered for 30 seconds as well as additionally after each measured spectra for 1 second. The angle between ion beam and surface normal was 60°. The RSFs and atomic fraction of Fe were determined from equations (1) and (2).

2) NMISA used XPS with a Physical Electronics Quantum 2000 Scanning ESCA involving monochromatic Al K α X-rays. The XPS instruments energy scale was calibrated by analyzing a pure copper sample. Spectra of three binding energy ranges (940–925 eV, 620-520 eV and 90–60 eV) were acquired using multiple pass energies. From the data, the binding energy scale is checked for linearity and offset. The nominal values are 933 eV, 568 eV and 75 eV for the 2p3/2, LMM and 3p peaks, respectively. The transmission is calibrated by determining the coefficients *a* and *b* for a SCA analyzer:

where A is the peak area, E_P is the pass energy and R is the retard ratio.

After removing the samples from their respective holders, they were rapidly loaded into the system. The system was allowed to pump down to 6.7×10^{-9} mbar or less. The distance between the analyser and each sample was optimized and five analysis points per sample, close to the centre of each sample, were selected. The samples were sputtered for 1 min with Ar⁺ at 2 keV over an area of 1 mm x 1 mm prior to analysis. The XPS peak areas were selected on a consistent basis, as with the reference materials, using an iterated Shirley background. The atomic fraction of Fe was calculated by equation (2).

The RSF of Ni, relative to that of Fe (which was chosen as 1), was determined by analyzing the reference specimen supplied by KRISS. Due to peak overlaps it was decided that the 3p peaks of Ni and Fe should be used for all calibration and sample analyses. The RSFs were calculated from equation (1).

3) KRISS used XPS with a VSW5000 using Mg K α X-ray source with the pass energy of 10 eV. The surface contaminants were removed by sputtering with a 5 keV Ar⁺ ion beam at 60° incidence angle for 120 minutes using a raster size of 5 mm x 10 mm. The compositions were measured from the peak areas of the Fe 2p and Ni 2p core level spectra.

The relative intensities of the two elements were measured from peak areas by integration of the two peak intensities after peak smoothing with 5 data points and background subtraction by the Shirley method. The peak areas were determined about the binding energies of Fe 2p3/2 (E_b^{Fe}) and Ni 2p3/2 (E_b^{Ni}). The integration ranges for the area measurement were from $E_b^{Fe} + 9 \text{ eV}$ to $E_b^{Fe} - 5 \text{ eV}$ and from $E_b^{Ni} + 11 \text{ eV}$ to $E_b^{Ni} - 5 \text{ eV}$ for the Fe 2p and Ni 2p peaks, respectively. The RSFs and atomic fraction of Fe were determined using equations (1) and (2), respectively. The XPS spectra for the determination of RSFs and, later on the fraction of Fe were measured each six times.

4) NIM used XPS for the analysis of composition of Fe-Ni alloy films. The experiments were carried out on a Thermo VG Scientific ESCALAB 250 spectrometer using a monochromatic Al K α radiation source with the pass energy of 30 eV. The composition of Fe-Ni alloy films was determined from the peak area of the Fe 2p and Ni 2p core level spectra. The binding energy of Fe 2p3/2 (E_b^{Fe}) and Ni 2p3/2 (E_b^{Ni}) are 706.8 eV and 852.8 eV, respectively. The peak areas of the two elements were measured by integrating their respective peak intensities after Shirley background subtraction. For the test and reference specimens, the integration range was selected on a consistent basis, viz. from $E_b^{Fe} + 10$ eV to $E_b^{Fe} - 4$ eV and from $E_b^{Ni} + 11$ eV to $E_b^{Ni} - 5$ eV for the Fe 2p and Ni 2p peaks, respectively. The composition of the alloy film was be calculated by the equations (1) and (2).

Before each XPS measurement, the surface of two Fe-Ni alloy films as received was sputtered for 30 seconds over a raster area of 2.4 mm × 2.4 mm with 3 keV Argon ions at 50° incident angle to remove surface contaminants. After the surface treatment, the relative ratios for $I_{C1s}/I_{Fe2p_{3/2}}$ and $I_{C1s}/I_{Ni2p_{3/2}}$ were both less than 0.025. A similar result was obtained for the O1s peak intensity.

The reference specimen, the Fe51-Ni49 alloy film, was used to derive the RSFs of the constituent elements in the test alloy film. The XPS spectra of the reference specimen were measured six times.

- 5) NMIJ used XPS for the quantification. The XPS measurements were carried out with the XPS system VG ESCALAB 220i-XL. The Mg K α line at 1253.6 eV was used as the X-ray source and the pass energy of the concentric hemispherical energy analyzer was 10 eV. The surface contaminants were removed by sputtering with a 3-keV Ar⁺ ion beam at 60° incidence angle until the relative ratio for I(C 1s)/I(Fe 2p3/2) less than 0.025. The RSFs of Fe and Ni were determined by dividing the average intensities of five measurements by the certified compositions for the supplementary Fe51-Ni49 alloy film. The intensities of the two elements were measured from peak areas by integration of the two peak intensities after peak smoothing and background subtraction by the Shirley method.
- 6) BAM also participated in CCQM P108 pilot study using X-ray spectrometry with electron excitation (EPMA electron probe microanalysis) and XPS.

In the EPMA (Energy Dispersive X-ray Analysis mode) approach, composition and film thickness (mass thickness in μ g/cm²) of the test sample were determined. A special commercially available program (STRATAgem from SAMx, Guyancourt, France) was applied to evaluate the raw data. The principle of this kind of thin film analysis consists in measurement of electron excited X-ray spectra at different beam energies for the specimen

and the standards. Intensities from both the film and substrate must be taken into account. The program fits the calculated intensity ratios ($I_{specimen}/I_{standard}$) versus beam energy in order to determine composition and mass thickness in $\mu g/cm^2$. By measuring pure standards (Fe, Ni and Si) a mass thickness of 152 $\mu g/cm^2$ has been calculated for the test specimen. Because the Fe51-Ni49 reference specimen is used for calibration the mass thickness of the layer on the test specimen was "tuned" until its mass thickness reached the same value. This would correspond to a 212 nm thickness and a density of 6.90 g/cm³. A thickness estimate of "about 200 nm" was noted by KRISS in the "Protocol for the Measurements". Spectra were measured for beam energies of 12.5, 15, 20, 25 and 30 keV. The determined composition is the result of a least squares fit to 5 measured intensity ratios (each of them being in turn the average of 6 measurements). Statistical errors were in this way reduced. The method described above does not need relative sensitivity factors. There is no normalisation to 100% of concentration. Instead, any deviation from 100% means a check for the correctness of the result. The reference specimen of Fe51-Ni49 (50.58 at. % Fe), specimens of pure nickel and iron and bulk pure silicon were used as reference materials.

In the XPS approach an AXIS Ultra DLD XPS spectrometer manufactured by Kratos Analytical, UK, was used for analysis. The binding energy scale of the instrument was calibrated following a Kratos Analytical procedure which uses ISO 15472 binding energy data. XPS was done employing non-monochromatized Mg x-rays at a pass energy of 20 eV. Spectra were measured from BE = 690 eV to BE = 900 eV with 0.2 eV steps. Spectra were taken by setting the instrument to the hybrid lens and slot modes providing a 300 x 700 μ m² analysis area, approximately. Seven measurements have been made for each the test and reference samples. The XPS measurements were performed after sputtering the surface with argon ions (5 keV) until the intensity ratio I(C 1s) / I(Fe 2p3/2) is less than 0.025. RSFs were determined using the Fe51-Ni49 reference specimen. Data quantification was performed by using the CasaXPS software, Version 2.3.10. First the Mg x-ray satellites were removed. Subsequently a segmented Shirley background was removed in the Fe2p3/2 spectra between data point A at BE = 701.8 eV and data point B at BE = 715.8 eV using a average width of 5 channels for both A and B; and for Ni2p3/2 between data point C at BE = 847.8 eV and data point D at BE = 863.8 eV using a average width of 5 channels for both C and D. The Fe2p3/2 and Ni2p3/2 intensities were determined by integrating the peak area above the background from 701.8 eV to 715.8 eV and from 847.8 eV to 863.8 eV, respectively.

5. Results

The submitted values (x_i) of the CCQM-K67 were measured as the atomic fraction of Fe as shown in Table 3. The expanded uncertainties (U_i) were evaluated at 95% confidence level. The submitted data of the P-108 are shown in Table 4.

Participant	Method	x_i (atomic %)	U_i (atomic %)
BAM	AES	50.28	3.22
NIM	XPS	51.48	2.88
NMIJ	XPS	47.74	2.95
NMISA	XPS	50.25	3.40
KRISS	XPS	50.34	2.88

Table 2	Submitted y	values of CC	OM V67 with	h un cortainty of	at 05% aanfidan	an laval
	Submitted	values of CC	QIVI-KU/ WIL	i uncertainty a	at 9570 connuen	

Participant	Method	x_i (atomic %)	U_i (atomic %)
BAM	EPMA	50.6	2.1
BAM	XPS	46.8	3.3

Table 4. CCQM-P108 result for the atomic fraction of Fe with uncertainty at 95% confidence level.

6. Estimation of Key Comparison Reference Value

Key Comparison Reference Value (KCRV) of K67 was calculated by the arithmetic mean method as agreed at the SAWG meeting in April 2009. The uncertainty (U_{ref}) of KCRV (x_{ref}) was calculated from the standard deviation of the individual laboratory values (s) and a coverage factor (k) of 2.

$$KCRV = x_{ref} = \sum_{i=1,m} x_i / m$$

$$u_{ref} = s(x_i) / \sqrt{m}$$

$$U_{ref} = ku_{ref}$$
(4)
(5)
(5)

$$U_{ref} = k u_{ref} \quad \dots \qquad (6)$$

Table 5. KCRV and it's uncertainty of K67.

KCRV, <i>x_{ref}</i> [atomic %]	50.02
Expanded uncertainty of KCRV, Uref [atomic %]	1.23



Figure 1. Key comparison reference value and uncertainties in CCQM K67/P108.

7. Equivalence Statements

The equivalence statements were calculated for each of the five laboratories following BIPM guidelines. The degrees of equivalence (d_i) of the submitted results, x_i , and the KCRV, x_{ref} , were calculated using the following expression:

$$d_i = x_i - x_{ref} \tag{7}$$

The standard uncertainty for the degree of equivalence $[u(d_i)]$ was calculated from the combination of the standard uncertainties of the individual data (u_i) and the standard uncertainty of the KCRV (u_{ref}) . Coverage factor of 2 was applied in the calculation of the expanded uncertainty $[U(d_i)]$ by the following equation:

$$u(d_{i}) = \sqrt{u_{ref}^{2} + u_{i}^{2}}$$
(8)

$$U(d_{i}) = ku(d_{i})$$
(9)

Table 6. Degrees of equivalence (DoE) and their uncertainties for K67.

Participant	d_i (atomic %)	$U(d_i)$ (atomic %)
BAM	0.26	3.44
NIM	1.46	3.13
NMIJ	-2.28	3.19
NMISA	0.23	3.61
KRISS	0.32	3.13



Figure 2. Degree of equivalence for the atomic fraction of Fe in CCQM K67.

References

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- (2) ISO 18118:2004 Surface chemical analysis Auger electron spectroscopy and X-ray photoelectron spectroscopy Guide to the use of experimentally determined relative sensitivity factors for the quantitative analysis of homogeneous materials.
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APPENDIX

CCQM-K67 SURFACE ANALYSIS MEASUREMENT OF The COMPOSITION OF Fe-Ni ALLOY FILMS A key comparison for the Consultative Committee on Amount of Substance

Protocol for the Measurements

K J Kim

Division of Advanced Technology Korea Research Institute of Standards and Science, 1 Doryong, Yuseong, Daejeon 305-600, Korea [Tel: +82 42 868 5391; Fax +82 42 868 5032; email : kjkim@kriss.re.kr] 30 May 2008

1. OBJECTIVE

The objective of this key comparison is to compare the relative composition of Fe and Ni in a thin Fe-Ni alloy film. The measurand in this key comparison is the relative composition of a Fe-Ni alloy film in a unit of atomic percent (at. %). The uncertainties in the measurements should be described at a confidence level of 95 %.

2. TIMETABLE

The analysis results should be reported within three calendar months from the receipt of this package.

3. THIS PACKAGE

This package comprises this protocol and a box of a test specimen (Fe-Ni alloy film) for the key comparison. A box of a Fe51-Ni49 alloy film with a certified composition is supported as a reference specimen to determine the relative sensitivity factors of Fe and Ni. The geometric dimensions of all specimens are10 mm x 10 mm x $\sim 600 \mu m$.

4. THE MATERIAL

The reference specimen is one of the three Fe-Ni alloy films used in the pilot study P-98. The relative sensitivity factors (RSF) of Fe and Ni for XPS and AES analyses can be determined from a pure Fe and a pure Ni film. The RSF values can be also determined using the reference Fe51-Ni49 alloy film. The films were grown by ion beam sputter deposition. Fe and Ni targets were sputtered by an argon ion beam of 1.0 keV enabling co-deposition on rotating 6" Si (100) substrates. The thicknesses of the test and reference films are about 200 nm. The composition of the Fe51-Ni49 alloy film was certified by ICP-MS with isotope dilution method as shown in Table 1. The homogeneity of alloy composition in the direction of depth

was confirmed by SIMS depth profiling using C_{60} ions. The compositions in the growth positions on the whole wafer were found to be homogeneous within 1.0 %. (K. J. Kim et al., Surf. Interface Anal.39, 665-673. (2007))

Table 1. Certified composition of the reference specimen with the uncertainty at 95 % confidence.

	Fe at. %	Uncertainty at 95 % confidence (%)
Fe51-Ni49	50.58	2.84

5. ELIMINATION OF SURFACE OXIDES

When applying surface analysis methods, dust and particles on the sample surface may need to be removed before introducing the samples into the analysis chamber. Surface contaminants may easily be removed by ion beam sputtering in the analytical instrument. In particular, the oxidized surface layer may also need to be removed by sputtering (e.g. with an Ar^+ ion beam) so that the peak intensities, O 1s and C 1s, are minimized. Sputtering to reduce the relative ratio for *I*(C 1s)/*I*(Fe 2p3/2) to less than 0.025 is recommended (Th. Gross et al., Surf. Interface Anal. 29, 891 (2000)). A similar reduction is required for the O 1s peak intensity. However, O 1s peak is difficult to confirm the complete elimination of oxide layer because it is overlapped with a Ni Auger (L₂M₂₃M₂₃) peak in XPS with Mg K α line (1253.6 eV). Any changes of the surface compositions, arising from preferential sputtering, were found to be negligible when sputtering these samples by 5 keV Ar⁺ ions at 60° from the surface normal. (K. J. Kim et al., Surf. Interface Anal.39, 665-673. (2007))

6. REPORTING THE RESULTS

Please provide a report for the following data regarding the description of the methods, and the evaluation of the uncertainty.

A. Analytical method;

Describe the principle and the calibration method in the analysis of composition by the applied analytical method and report the details of the instrument (maker, model, specifications etc.)

B. Surface treatment (if necessary);

Describe the method to eliminate the surface contaminants (ion species, ion energy, incidence angle etc.)

C. Calibration method;

- How to determine the relative sensitivity factors
- Reference materials

D. Uncertainty;

Please describe the procedure to determine the uncertainty and the uncertainty budget according to the ISO Guide to the Expression of Uncertainty in Measurement (GUM).

- (1) The measurements must be repeated more than 5 times to estimate the statistical errors.
- (2) All sources of uncertainty depending on the applied analytical method and the equipment must be taken into account. Type A (statistical) and type B (expert based estimation of systematic errors or biases) contributions according to GUM should be included.
- (3) Participating laboratories should report the standard uncertainties and the expanded uncertainties at 95% confidence in the uncertainty budget.

E. Table of the measured composition of the test Fe-Ni alloy film;

Report the relative composition of the test alloy film and tabulate them with the estimated uncertainties. Four digits of the compositions are recommended.

	Fe at. %	Ni at. %	Expanded uncertainty at 95% confidence
Test Fe-Ni alloy			

7. SENDING THE REPORT

Dr. Kyung Joong Kim Division of Advanced Technology Korea Research Institute of Standards and Science 1 Doryong, Yuseong, Daejeon 305-600, Rep. of Korea Tel : +82 42 868 5391 Fax : +82 42 868 5032 email : kjkim@kriss.re.kr