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THE USE OF INDEXED SENSITIVITY FACTORS IN THE ANALYSIS OF NICKEL AND IRON BASED ALLOYS: A STUDY OF THE DECALIBRATION OF SHEATHED CHROMEL/ALUMEL THERMOCOUPLES*

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Abstract

Sheathed Chromel versus Alumel thermocouples decalibrate when exposed to temperatures in excess of 1100°C. Thermocouples sheathed in Inconel-600 and type 304 stainless steel were studied in this work. Quantified SIMS data showed that the observed decalibrations were due to significant alterations that took place in the Chromel and Alumel thermoelements. The amount of alteration was different for each thermocouple and was influenced by the particular sheath material used in the thermocouple construction. Relative sensitivity factors, indexed by a matrix ion species ratio, were used to quantify SIMS data for three nickel-based alloys, Chromel, Alumel, and Inconel-600, and an iron-based alloy, type 304 stainless steel. Oxygen pressure $>2 \times 10^{-6}$ torr in the sputtering region gave enhanced sensitivity and superior quantitative results as compared to data obtained at instrumental residual pressure.

Introduction

In this study we have used secondary ion mass spectrometry (SIMS) to determine the failure mode responsible for the large decalibrations observed in sheathed, MgO-insulated Chromel versus Alumel, compacted thermocouple assemblies, exposed to temperatures above 1100°C.

These thermocouples presented a challenge for SIMS analysis. Segregation and precipitation of Al and Si were frequently observed in these specimens. The small size (100 μm dia.) of the thermoelements and the relatively large grain size induced by high temperature exposure were problems that had to be contended with. Tamura, Ishitami, and Kanomata[1] have shown that an analytical curve using relative sensitivity factors (S.F.) indexed by a matrix species (for example, M^{++}/M^{+}) can be generated from a single standard. The curve is prepared by recording ion yields from the standard as a function of O_2 pressure in the sputtering region. They also report that increased oxygen surface coverage of the specimens gave improved analytical reproducibility. Konishi et al.[2] studied the variation of secondary ion yields from metals as a function of increasing O_2 partial pressure in the sputtering region. These investigators found that the intensity of secondary matrix ions M^+ and MO^+ increased, whereas the intensities of the matrix ions, M_2^+, M_3^+, M^{++}, and M^{+++} decreased with increasing O_2 partial pressure. Gangei, Leta, and Morrison[3] in a modification of the method of Tamura et al.[1] used the above reported variation in M^+, MO^+, and M_2^+ as an indexing technique in investigating the quantitative analysis of various standard materials. They showed that significantly more accurate analytical results could be obtained as opposed to the single S.F. method. In this study we have used oxygen flooding of the sputtering region to enhance sensitivity, reproducibility, and analytical accuracy. Sensitivity factors, indexed by matrix ion species ratios, were used for calculating the analytical results.

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DISCLAIMER

Experimental

The ion microprobe mass analyzer (IMMA) used in this work was manufactured by Applied Research Laboratories, Sunland, California, and is based on the design of Liebl.[4] The capabilities of the instrument have been described by Andersen and Hinthorne[5] and by McHugh.[6]

Two Chromel-Alumel thermocouples were investigated. The first thermocouple, designated I, was sheathed in 304 stainless steel, and the second thermocouple, designated II, was sheathed in Inconel-600. After exposure to high temperature in air in a calibrated temperature gradient tube furnace, a number of transverse cross sections were cut from the thermocouples for analysis. The specimens and the required standards were imbedded in epoxy and polished until a smooth metallographic finish was obtained prior to IMMA analysis. Table 1 lists the compositions of the various materials analyzed in this work.

Table 1. Nominal Compositions (Atom %) of Materials Investigated in this Study

	Chromel	Alumel	304* S.S.	Inconel 600	NBS NX** -980	NBS NX** -1285
Al	0.02	4.19	0.0014	0.40	0.55	0.38
Si	0.92	3.53	1.95	0.41	0.22	0.49
Cr	10.37	0.0008	19.96	17.42	16.73	17.85
Mn	0.01	3.01	1.99	0.21	0.40	0.32
Fe	0.35	0.031	66.42	7.39	8.93	6.92
Ni	88.33	88.76	9.32	74.28	72.31	73.16
Co	0.04	0.48	0.014	-	-	-

*Minor elements C, P, and S omitted.
**C, S, Ti and Cu omitted.

Mass spectra were taken from each wire and sheath section to determine which elements were present and would require further study. Raster mode ion imaging and X-line scanning were performed on each section to ascertain how the elements of interest were distributed in the wires. Fast raster mode was then used to take quantitative data for all elements of interest from wire regions that demonstrated suitable homogeneity in line scan and ion imaging mode. Data were taken both at residual instrument pressure and with oxygen flooding up to a specimen chamber pressure of approximately 1×10^{-5} torr.

Results and Discussion

Line scans were made to determine the radial distributions of Mg, Al, Si, Cr, Mn, Fe, Ni, and Co in all of the wire sections. The thermocouple I, E section, and the thermocouple II, D section, were used as "standards" for the IMMA studies because these sections were typical of the as-received thermocouple materials and were never exposed to elevated temperatures during the decalibration studies. Magnesium was observed to exhibit diffusion-like profiles in all of the wires (i.e., high signals at the wire edges which decrease in an inward direction). No significant differences in Mg profiles were seen in any of the wire sections exposed to temperatures of over 1100°C when compared to the as-received sections that remained at 20°C.

In the nickel-based alloys, Alumel, Chromel, Inconel-600 and two NBS standards, we found that the ratio NiO^+/Ni_3 was very sensitive to oxygen surface coverage. Sensitivity factors for Cr and Fe, determined from Chromel and the two NBS standards were plotted as a function of the NiO^+/Ni_3^+ indexing ratio and are shown in Fig. 1. Although these three standard materials are different in composition (see Table 1), the S.F.'s for Cr when indexed by the NiO^+/Ni_3^+ ratios fall on the same line. The S.F. plots that we used in analyzing the Chromel and Alumel wires of thermocouples I and II are presented in Figs. 1 and 2. Aluminum, Mn, Co, and Si values were determined from the Alumel standard as these elements were present at higher abundances than in the Chromel standard. The S.F.'s for Cr and Fe were determined from Chromel for similar reasons.

The shape of these S.F. curves verifies the observation that higher accuracy and more reproducible results are obtained with O_2 flooding in the sample region when oxidizable metallic samples are being analyzed. In this system of Ni based alloys, we found that oxygen pressures of 4-8 x 10^{-6} torr and current densities of -mA cm^{-1} tended to keep the NiO^+/Ni_3^+ ratio above 20 and thereby allowed S.F.'s from that flat region of the S.F. response curve to be used. In this system, the S.F. indexing technique approaches a single S.F. method if sufficient O_2 surface coverage is maintained.

The stainless steel sheath of thermocouple I, being an iron alloy, was analyzed using a different set of S.F.'s based on Fe as the reference element. The indexing ratio used was FeO^+/Fe^+. The S.F.'s derived from this alloy are shown in Fig. 3. A different type response was observed in this system. As O_2 surface coverage increased the observed S.F. range decreased and at high coverage tended to converge on the reference element value (Fe ≡ 1). This effect was also observed by Konishi et al.[4] for impurity elements in low alloy iron standards. The quantified results for thermocouple I Chromel and Alumel wires and type 304 stainless steel sheath are presented in Table 2. The Alumel and Chromel standards, reported in this table, were run as unknowns.

Thermocouple II was sheathed in Inconel-600, a nickel-based alloy (see Table 1). The nominal compositions, supplied by the manufacturer, were used as standard values in determining a set of indexed (NiO^+/Ni_3^+) S.F.'s for this alloy. Some inconsistencies were observed for these S.F.'s when compared to the S.F.'s from Chromel and Alumel standards. This difference is probably due to inaccuracies in the nominal values used for some of the minor elements in these alloys. Although undesirable, this shortcoming was of little consequence in detecting compositional changes in the sheath sections for this thermocouple. The S.F.'s presented in Figs. 1 and 2 were used to quantify data taken from the Chromel and Alumel wires in this thermocouple. The quantified results are given in Table 3.

Conclusions

Chromel and Alumel thermocouples, sheathed in reactive metals (Inconel-600 and type 304 stainless steel) decalibrate significantly when exposed to temperatures above 1100°C. The decalibration is caused by the alteration in composition of the Chromel and Alumel thermoelements. Significant migrations of Al, Si, Cr, Mn, and Fe were seen to occur in the Chromel and Alumel thermoelements and in the sheath materials. For example, Cr which was present in virgin Alumel at the 0.0008 atomic % level was observed to increase a factor of 1500 in regions of the thermocouple exposed to temperatures above 1100°C. The source of this Cr was the Chromel thermoelement and the sheath. The specific nature of the compositional alteration was influenced by the chemical environment present in the hot thermocouples. Thermocouple I was sheathed in a nickel-based alloy, whereas thermocouple II was sheathed in an iron-based alloy. Alterations related to these particular environments are discernible in Tables 2 and 3.

The use of single, unindexed S.F.'s for calculating these data was found unacceptable. Oxygen pressure >2 x 10^{-6} torr in the sputtering region gave a more reproducible set of sensitivity factors and indexing with a matrix ion species ratio allowed the correct set of S.F.'s to be chosen for any given set of analytical conditions (oxygen pressure, current density, sample composition, etc.). Our findings were in agreement with other workers in that the matrix ion species indexing method did achieve substantial improvement in analytical accuracy as compared to the residual pressure single S.F. method.

List of References

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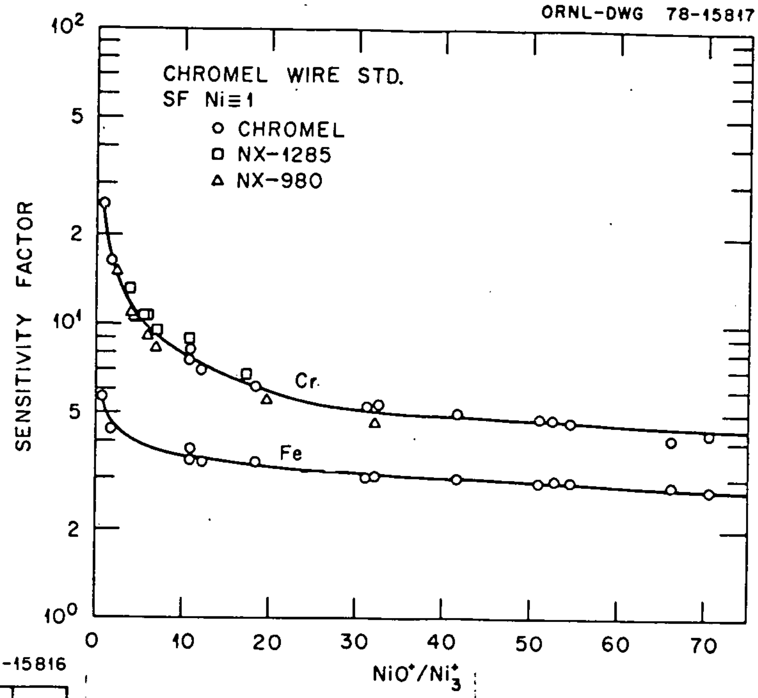
FIGURE 1.
Cr and Fe Sensitivity Factors determined from Chromel, NBS standards NX-1285 and NX-980



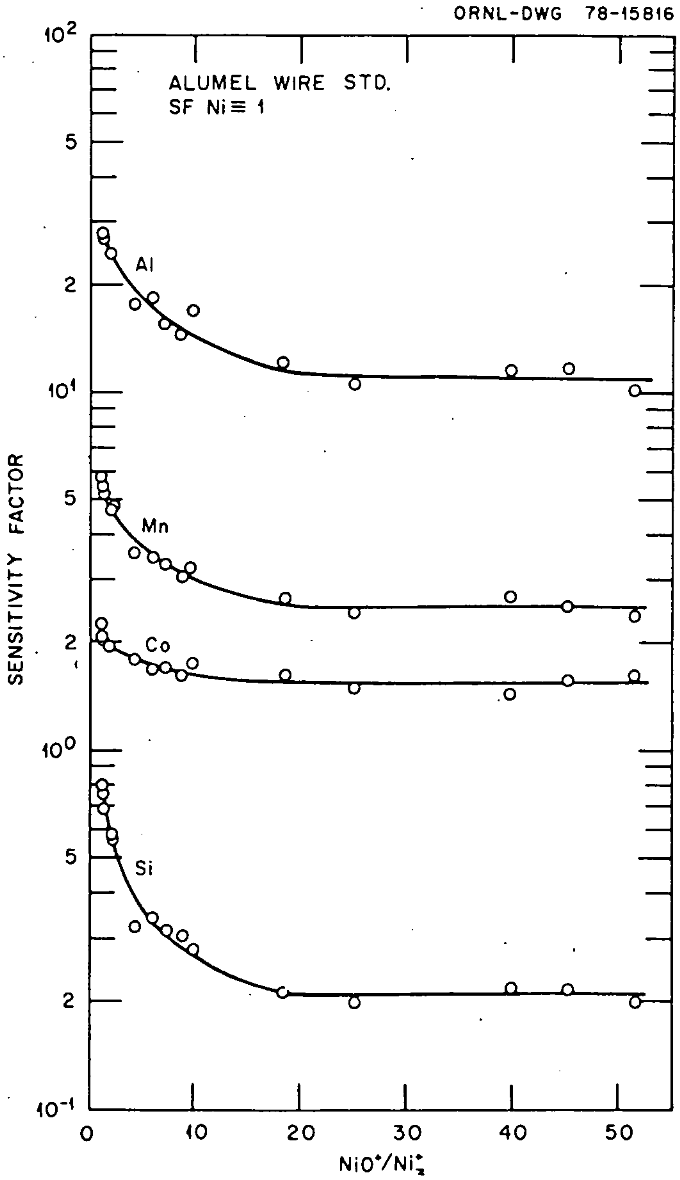


FIGURE 2
Al, Mn, Co and Si Sensitivity Factors determined from Alumel

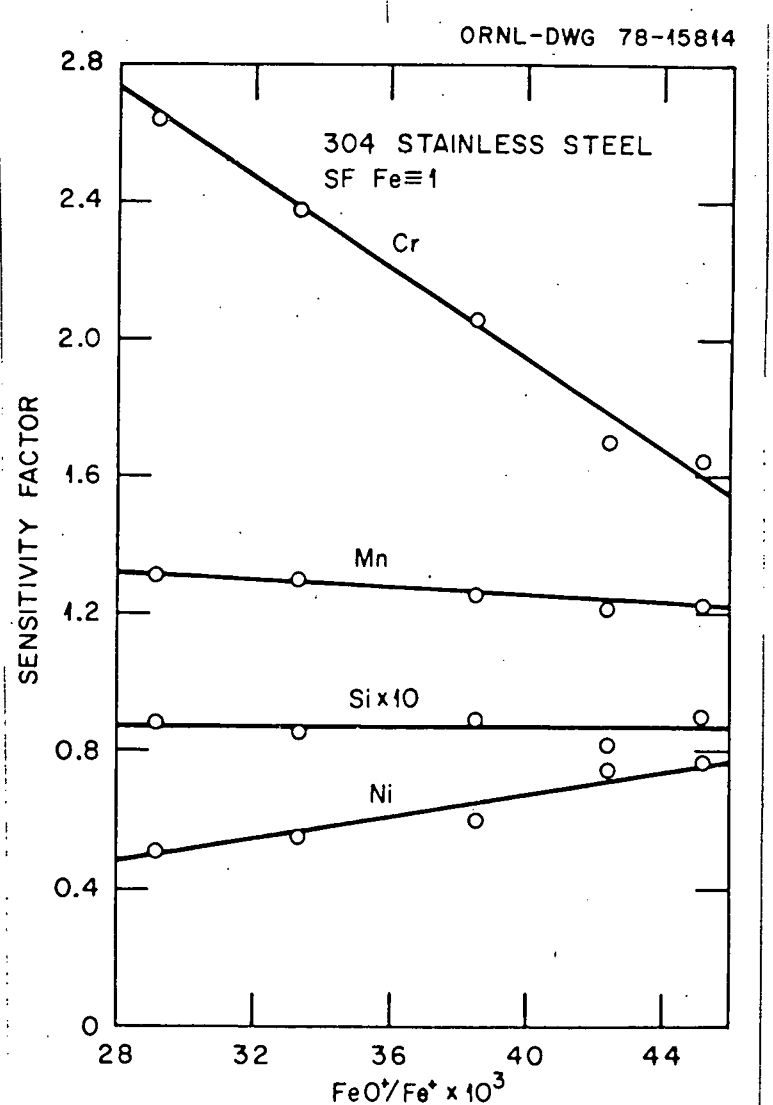


FIGURE 3
Cr, Mn, Si and Ni sensitivity factors determined from type-304 stainless steel

TABLE 2

THERMOCOUPLE I (STAINLESS STEEL SHEATH)

ALUMEL WIRES ATOMIC %

ECTION	Al	Si	Cr	Mn	Fe	Ni	Co
A	0.047	4.03	0.80	5.62	0.29	88.65	0.56
B	0.029	3.32	1.19	5.53	0.37	88.99	0.56
C	0.058	4.56	1.32	4.57	0.52	88.20	0.66
D	0.45	4.79	0.052	6.21	0.12	87.82	0.56
E*	4.38	3.99	0.0008	2.80	0.07	88.26	0.50
TD. WIRE	3.94	4.05	0.0010	2.89	0.07	88.59	0.47
OMINAL	4.19	3.53	0.0008	3.01	0.031	88.76	0.48

CHROMEL WIRES ATOMIC %

ECTION	Al	Si	Cr	Mn	Fe	Ni	Co
A	0.015	0.96	10.27	3.30	0.47	84.94	0.036
B	0.016	1.20	11.22	3.48	0.63	83.36	0.041
C	0.049	1.22	12.13	3.57	0.45	82.52	0.047
D	0.058	0.97	10.73	3.18	0.32	84.72	0.038
E*	0.023	1.06	10.80	0.012	0.29	87.78	0.035
TD. WIRE	0.012	1.08	11.47	0.009	0.38	87.00	0.046
OMINAL	0.021	0.92	10.37	0.010	0.35	88.33	0.040

TYPE 304 STAINLESS STEEL ATOMIC %

ECTION	Al	Si	Cr	Mn	Fe	Ni	Co
A	0.0036	0.55	16.34	0.24	73.23	9.61	0.016
B	0.0030	0.54	11.48	0.22	76.78	10.69	0.018
C	0.0033	0.78	16.75	0.20	72.18	9.67	0.017
D	0.0024	1.38	17.52	0.64	71.19	9.25	0.016
E*	0.0014	1.87	20.60	2.08	66.59	8.85	0.014
OMINAL	—	1.95	19.96	1.99	66.42	9.32	—

* AS RECEIVED REFERENCE SECTION

TABLE 3

THERMOCOUPLE II (INCONEL-600 SHEATH)

ALUMEL WIRES ATOMIC %

ECTION	Al	Si	Cr	Mn	Fe	Ni	Co
A	2.01	5.85	0.176	0.82	0.122	90.43	0.59
B	1.93	4.71	0.173	0.67	0.130	91.61	0.77
C	2.17	3.21	0.095	1.12	0.121	91.91	0.78
D*	4.09	3.39	0.0010	2.68	0.075	89.04	0.73
TD WIRE	4.04	4.81	0.0009	2.98	0.074	87.41	0.62
OMINAL	4.19	3.53	0.0008	3.01	0.031	88.76	0.48

CHROMEL WIRES ATOMIC %

ECTION	Al	Si	Cr	Mn	Fe	Ni	Co
A	0.202	1.03	11.87	0.410	0.38	86.03	0.07
B	0.249	1.09	10.89	0.385	0.40	86.91	0.07
C	0.177	1.02	10.93	0.138	0.38	87.28	0.07
D*	0.013	1.01	11.15	0.014	0.36	87.38	0.08
TD WIRE	0.011	0.99	10.90	0.008	0.36	87.69	0.05
OMINAL	0.021	0.92	10.37	0.010	0.35	88.33	0.04

INCONEL-600 ATOMIC %

ECTION	Al	Si	Cr	Mn	Fe	Ni
A	0.18	0.29	8.81	0.027	7.70	83.00
B	0.13	0.33	8.92	0.036	8.16	82.43
C	0.17	0.30	8.37	0.063	7.85	83.25
D*	0.40	0.40	16.48	0.211	7.72	74.79
OMINAL	—	0.41	17.42	0.210	7.39	74.28

* AS RECEIVED REFERENCE SECTION