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A QUANTITATIVE SIMS ANALYSIS OF DECALIBRATED CHROMEL VERSUS ALUMEL THERMOCOUPLES USING INDEXED SENSITIVITY FACTORS*

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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. 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.

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 SIMS analysis. Table 1 lists the compositions of the various materials analyzed in this work.

Table 1. Nominal Compositions (Atom %) of Standard 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	3.0[illegible]	1.99	0.21	0.40	0.32
Fe	0.35	0.[illegible]	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	-	-	-

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 from the decalibrated thermocouples 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 $4\text{-}8 \times 10^{-6}$ torr and current densities of .2 mA cm^{-2} tended to keep the NiO^+/Ni_3^+ ratio above 20 and thereby allowed S.F.'s from the flat region of the S.F. response curve to be used.

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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, with the exception of silicon, decreased and at high coverage tended to converge on the reference element value (Fe ≡ 1).

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.

The use of single, unindexed S.F.'s for calculating these data was found unacceptable. Oxygen pressure $>2 \times 10^{-6}$ 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.). A detailed account of this work has been accepted for publication in *Applications of Surface Science*.

FIG. 1. Cr AND Fe SENSITIVITY FACTORS DETERMINED FROM CHROMEL, NBS STANDARDS NX-1285 AND NX-980

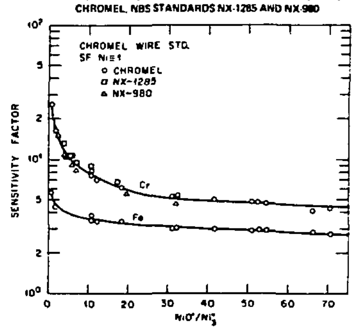

FIG. 2. Al, Mn, Co AND Si SENSITIVITY FACTORS DETERMINED FROM ALUMEL

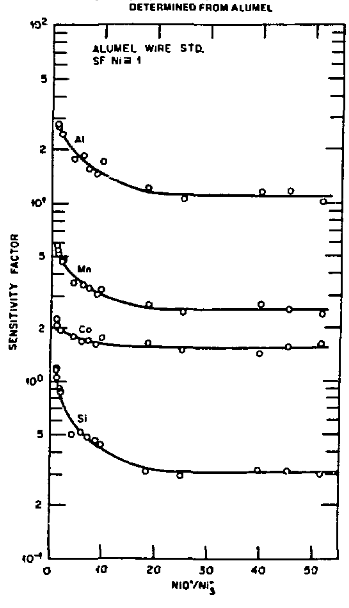

FIG. 3. Cr, Mn, Si, AND Ni SENSITIVITY FACTORS DETERMINED FROM TYPE 304 STAINLESS STEEL