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MAGNETIC TEMPERATURE STANDARDS FOR TG

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Abstract

Magnetic transition temperatures, T_C, are measured by simultaneous TM/DTA for Alumel, cobalt, nickel, and three alloys of Ni and Co. The observed values of T_C are corrected using the values for the melting temperatures of pure metals used to define the International Temperature Scale. These corrections are based on the simultaneous melting of these pure metals alongside, but separate from, the magnetic sample. Nine investigators, using a wide variety of instrumentation, have made these measurements utilizing a standard protocol. The results are compared for several heating rates. It is planned to make these same magnetic materials ultimately available to the public for calibration of temperature of their TG instruments.

Keywords: calibration of temperature, magnetic temperature standards, TG

Introduction

The use of magnetic transition temperatures, T_C, to calibrate the temperature axis in TG was first proposed by the Perkin–Elmer Co. [1]. They packaged recommended materials with their instruments and the technique was widely accepted and readily adapted for automated use [2]. The Committee for Standardization of ICTA (now ICTAC) conducted a certification program and developed a different series of metals for distribution through N.I.S.T. [3, 4]. The original supply of several of those materials has become exhausted and N.I.S.T. no longer participates in the program.

A Task Group of ICTAC's Committee for Standardization was formed to produce a new and better series of materials for this purpose. With the advent of simultaneous TG/DTA or DSC and the widespread availability of commercial instrumenta-

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tion, it is now possible to use the pure metals, whose melting points define the International Temperature Scale [5], to serve as internal primary standards during the measurement process. Not only will this markedly improve the accuracy of the corrected values, but it should also greatly enhance the precision of each investigator and largely remove the dependency upon heating rate since the primary standard is being measured simultaneously under virtually identical conditions.

Several preliminary studies or reports have been presented [6–8]. The outcome of these preliminary studies was greatly encouraging and lead to the selection of a series of materials based primarily on nickel, cobalt, and their alloys.These were selected to have nominally equally spaced values of T_C in the range from room temperature to 1200ºC. The ultimate selection consists of Alumel, nickel, cobalt and three alloys of nickel and cobalt. Large (approximately 4 kg) homogeneous batches of these materials were obtained along with quantities of pure metals having melting points in that same temperature range. This report presents the results of the ICTAC Task Group using a wide range of commercial instruments and a common protocol to determine the recommended values of T_C for these materials. These materials along with their recommended values can then be used for the temperature calibration of simple TG instruments.

A protocol for the round robin was determined through the preliminary studies [5]. Several earlier reports had conflicting conclusions concerning the dependence of T_C upon the strength of the magnetic field gradient [9, 10]. Regardless of that specific dependence, it was felt that simply using the minimum magnetic field needed to achieve a clearly detectable magnetic transition was more advisable than an expanded protocol that would require extrapolation to zero magnetic field gradient.

Experimental procedures and results

Approximately 4 kg batches of Ni, Co, $Ni_{.83}Co_{.17}$, $Ni_{.63}Co_{.37}$, and $Ni_{.37}Co_{.63}$ were purchased from the US National Metallurgical Laboratories in Ames, Iowa. The material was to be of the best attainable purity, highly homogeneous, and in sheet form where possible. The Co and the highest Co alloy were too brittle to obtain in sheet form and powder was accepted instead. For the lowest value of T_C, a large quantity of Alumel from the same production batch was purchased from the Hoskins Co. Much smaller quantities of In, Sn, Pb, Zn, Al, Ag and Au having a purity of 99.999% were purchased from Alpha Co. in foil form.

Approximately 1 g quantities of each magnetic material and pure metal were sent to the Task Group members (authors) along with the recommended protocol for the measurements. The protocol calls for the simultaneous measurement of 1) the T_C for each magnetic material using a near minimum magnetic field gradient and 2) the melting point of two pure metals whose melting points bracket T_C or a single melting point if very near T_C.

The value of T_C would be based upon the extrapolated end point of the thermomagnetometric curve, TM. Investigators were also asked to report their values based on the extrapolated end point of the differential curve, DTM. The values based on the

DTM are naturally higher because of its greater sensitivity, however, they were deemed less reproducible and are not reported.

Interaction of the metals with the crucible and atmosphere were to be minimized as best possible. Consequently, alumina crucibles were generally used in flowing pure nitrogen or argon. The flow rate used was optimized by the investigators based on their particular instrument. If Pt crucibles were used, the samples were surrounded by powdered alumina to prevent interaction with the metals. Several heating rates in the range from 1 to

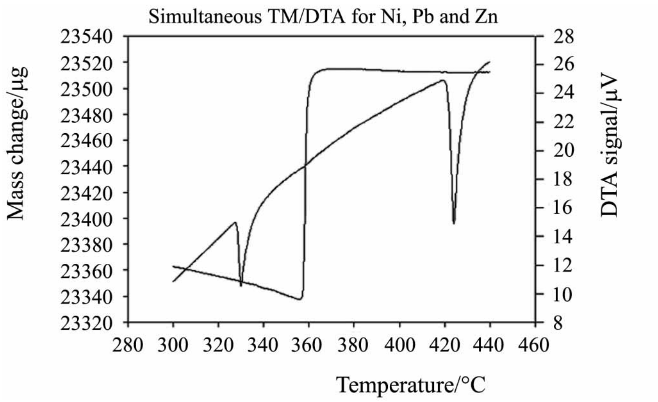

Fig. 1 Curves for the simultaneous TM/DTA of a sample of Ni, Pb, and Zn heated at 10°C min^{-1} from row 4 in Table 2

20ºC min^{-1} were to be used. Figure 1 is an example of such an experiment based on the TM of Ni and the DTA or DSC curves for Pb and Zn.

The pertinent results for each magnetic material are summarized in Tables 1 through 6. In the cases of Alumel and $Ni_{.37}Co_{.63}$, a single melting point was used for correction since its melting point was so close to T_C. Only the melting of Au was used to correct the observed T_C of Co, because the next highest pure metal in the International Temperature Scale was beyond the range of this study.

Discussion

A general observation for all of the materials is that there does not appear to be any consistent trend in the corrected value of T_C as a function of heating rate. As was expected, the shift in the observed melting temperature of the primary standards with heating rate is apparently adequate to remove that factor.

The values reported in the 'average' row are those for the average of their respective columns, while those in the 'average' column are the average for the respective rows. It is recognized that they are not exactly comparable among each other because of the differences in the number of values being averaged is not consistent, i.e., the number of investigators at each heating rate or the number of heating rates for each investigator varies. It is satisfying, however, that the average of the 'averages' for each heating rate is always within a 0.3°C of the value of the average other 'averages' for each investigator.

The results for Alumel are summarized in Table 1. Even though this is a commercial alloy where one might anticipate the greatest inhomogeneity, the results show the least spread in corrected values. The corrected values of T_C range from 151.6 to 153.8ºC, a spread of only 2.2ºC. This is attributed to two factors. The first and foremost is that the primary standard, In, melts so near the value of T_C. Secondly this is the lowest temperature for the series and oxidation or relaxation phenomena are least likely to occur for this material. Both the average based on the heating rates and that based on the investigators is 152.6ºC.

Table 1 Results for Alumel in °C, corrected using the melting of In

Instrument	Heating rate/°C min^{-1}					Average
	1	2 or 3	5	10	20	
Ulvac		152.6	152.9	152.5		152.6
MacSci		152.0	153.0	152.8		152.6
SETARAM	152.3	152.2	152.1	151.9	152.3	152.2
Seiko		153.1	152.6	152.5		152.7
Rigaku			151.6	152.0		151.8
Netzsch		152.4	152.6	152.4		152.5
TAI		152.4	152.3	152.2	152.4	152.3
Mettler			152.2	154.3	154.9	153.8
Averages	152.3	152.4	152.4	152.6	153.6	152.6

Table 2 Results for nickel in °C, corrected using the melting of Pb and Zn

Instrument	Heating rate/°C min^{-1}					Average
	1	2 or 3	5	10	20	
Ulvac		359.5	359.7	359.6		359.6
MacSci						
SETARAM	358.3	358.2	358.6	359.1	360.3	358.9
Seiko		357.5	357.9	357.5		357.6
Rigaku			356.8	357.6		356.2
Netzsch		358.0	357.5	357.2	357.0	357.4
TAI		357.7	357.5	357.5	357.7	357.6
Stan-Red		359.4				359.4
Mettler			356.1	357.3	358.5	357.3
Averages	358.3	358.4	357.7	358.0	358.4	358.0

The results for pure nickel are summarized in Table 2. They are not quite as good as those observed in the earlier abbreviated study Magnetic Task Group, ICTAC Committee for Standardization [6]. This is attributed to the expanded number of investigators and particularly the wider range of instrumentation. The corrected values of T_C range from 356.1 to 360.3ºC, a spread of 4.2ºC. The average based on heating rates is 358.2ºC and is in excellent agreement with that based on the investigators. The recommended value is 358.2ºC.

Table 3 presents the summary of results for the alloy $Ni_{.83}Co_{.17}$. These results show a wider spread of 7.0ºC over the range from 550.2 to 557.2ºC. Since the spread of results for each investigator is on the order of only two degrees, it is concluded that there is less homogeneity in this alloy and hence a greater sampling error. The average of the 'averages' based on heating rates 554.3ºC, in good agreement with that based on the investigators. A T_C of 554.4ºC is recommended.

Table 3 Results for $Ni_{.83}Co_{.17}$ in °C. corrected using the melting of Zn and Al

Instrument	Heating rate/°C min^{-1}					Average
	1	2 or 3	5	10	20	
Ulvac		555.1	554.2	553.7		554.3
MacSci		557.0		555.9		556.4
SETARAM	554.2	554.2	554.1	554.2	553.9	554.1
Seiko		556.8	557.2	556.3		556.7
Rigaku			550.2	552.2		551.2
Netzsch		552.6	553.6	554.6	554.5	553.8
TAI		553.6	553.2	552.7	552.3	553.2
Stan-Red		555.0				555.0
Mettler			555.6	555.6	555.9	555.7
Averages	554.2	554.9	554.0	554.4	554.2	554.5

Table 4 Results for $Ni_{.63}Co_{.37}$ in °C, corrected using the melting of Al and Ag

Instrument	Heating rate/°C min^{-1}					Average
	1	2 or 3	5	10	20	
Ulvac		748.9	748.4	747.4		748.2
MacSci		745.4	745.8	746.8	749.6	746.9
SETARAM	746.4	746.3	746.2	745.8	745.6	745.6
Seiko		747.3	746.6	745.0		746.3
Rigaku			743.4	744.4		743.9
Netzsch		746.6	746.2	746.2	748.9	747.0
TAI		745.7	745.3	744.7	743.8	744.9
Stan-Red		747.8				747.8
Averages	746.4	746.9	745.8	745.8	747.0	746.3

Results for the alloy $Ni_{.63}Co_{.37}$ are summarized in Table 4. The range of corrected values is 5.8ºC, somewhat less than for the previous alloy. It ranges from 743.8 to 749.6ºC. The variation is again felt to be an indication of the homogeneity of the alloy, although relaxation of stresses induced during fabrication of the sheet form may also be partially responsible. The average based on heating rate is 746.4ºC, in excellent agreement with that based on the investigators. A T_C of 746.4ºC is recommended.

Table 5 is a summary of the results for the alloy, $Ni_{.37}Co_{.63}$. The spread in T_C is again 5.8ºC. It covers the range from 928.1 to 933.8ºC. This alloy is in powder form and should be more vulnerable to oxidation than the previous two. It has not been subjected to rolling stresses, however. The relatively good precision for each investigator suggests that the variation is predominantly an indication of the degree of homogeneity. The average based on heating rates is 930.7ºC, in fine agreement with the average based on the investigators. The recommended value for T_C is 930.8ºC.

Table 5 Results for $Ni_{.37}Co_{.63}$ in °C, corrected using the melting of Ag

Instrument	Heating rate/°C min^{-1}					Average
	1	2 or 3	5	10	20	
Ulvac		932.6	931.7	932.1		932.1
MacSci						
SETARAM	930.1	930.3	930.3	930.4	930.6	930.3
Seiko		930.8	931.4	929.7		930.6
Rigaku			928.1	928.2		928.2
Netzsch		928.0	928.6	928.1	928.5	928.4
TAI		932.4	932.5	932.2	931.7	932.2
Stan-Red		931.4				931.4
Mettler			933.7	933.8	933.6	933.7
Averages	930.1	931.0	930.9	930.6	931.1	930.9

Finally Table 6 presents a summary of the results for the pure Co powder. These results show a wide variation from 111.4 to 1124.0ºC. This greatly exceeds the precision of each investigator. Because it is a pure material, explanation predicated on inhomogeneities seems less plausible and the variations are attributed to oxidation at this high temperature of the powdered material. The partial pressure of oxygen necessary to preclude oxidation is very low. The atmosphere for each investigator would undoubtedly vary based on the source of the gas, its flow rate, and the specific nature of each instrument and experimental arrangement. The formation of a simple oxide second phase should only diminish the level of the TM signal. If oxygen or an oxide dissolves in the metal, then the value of T_C would be lowered. The average based on the heating rates is 1115.8ºC, in fair agreement with that based on the investigators. A value of 1116ºC is recommended for T_C.

Table 6 Results for cobalt in °C, corrected using the melting of Au

Instrument	Heating rate/°C min^{-1}					Average
	1	2 or 3	5	10	20	
Ulvac		1120.8	1120.8	1120.2		1120.6
SETARAM	1114.6	1114.9	1115.2	1115.5	1116.3	1115.1
Seiko		1122.4	1123.4	1124.0		1123.3
Rigaku			1111.4	1111.6		1111.5
Netzsch		1113.0	1112.1	1112.1	1114.5	1112.9
TAI		1114.5	1114.3	1114.0	1113.3	1114.0
Stan-Red		1114.5				1114.5
Mettler			1116.0	1115.9	1117.8	1116.6
Averages	1114.6	1116.7	1116.2	1116.2	1115.5	1116.1

Figure 2 is a plot of the recommended values of T_C *vs.* composition for the Ni–Co system. The smooth line is a spline fit to the five points.

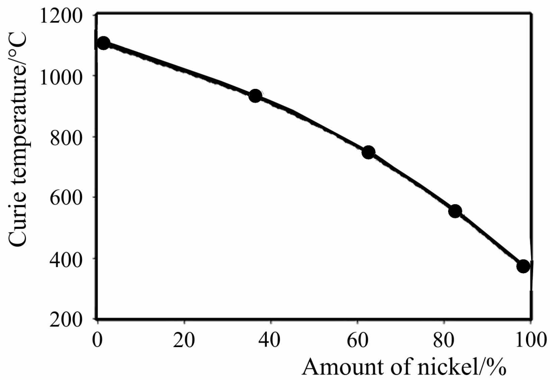

Fig. 2 Curie temperature as a function of composition in the Ni–Co system

In general, the variations in the results among investigators are attributed to several factors:

- Instrumental differences, e.g., furnace to sample relationship; thermal radiation; atmospheric flow patterns; sample holder size, thickness, and emissivity; etc.
- Non-uniformity in arranging the samples and standards within the holder.
- Oxidation of the metals. This varies substantially among investigators, some reporting none others reporting over 1 mass% for the higher temperatures.
- Inhomogeneities and strains in the magnetic samples.
- Potential interactions between the metals.

Table 7 Summary of results

Material	Recommended T_C/°C	Accuracy/±°C
Alumel	152.6	2.0
Nickel	358.2	2.1
$Ni_{.83}Co_{.17}$	554.4	4.3
$Ni_{.63}Co_{.37}$	746.4	3.1
$Ni_{.37}Co_{.63}$	930.8	3.7
Cobalt	1116	7.4

Hence, the precision attainable by each investigator is markedly better than that of the collected group. Accuracy, however, must reflect the full range of diversity in all the data. Table 7 summarizes the results of the round robin. The limits given for accuracy are twice the standard deviation of all the individual values listed in the appropriate table. These limits would be improved if a specific heating rate had been selected.

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