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Further studies on the use of simultaneous TM/DTA to establish magnetic transition temperatures

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Abstract: Earlier work reported on the use of simultaneous thermomagnetometry/ differential thermal analysis (TM/DTA) to obtain the Curie temperature (T_C) of nickel. The precision of the measurement was substantially improved through the simultaneous use of appropriate DTA standards involving the melting of pure metals which define the International Temperature Scale. That work was confirmed using two additional operators. It also was extended to include other alloys and metals, some of which are also in the ICTAC/NIST series of standards. It is suggested that an appropriate set of standards would involve homogeneous alloys in the nickel-cobalt system that could cover the wide range of temperature from approximately 358 to 1130 °C. The feasibility of preparing such alloys through the controlled decomposition of solid solutions in the (nickel-cobalt) oxalate system is also described.

INTRODUCTION

It has been difficult to accurately calibrate the temperature of thermogravimetric (TG) instruments because of the necessity to avoid direct contact with the sample. Norem *et al.* (1) proposed placing magnetic materials directly in the sample pan during analysis in order to more accurately and easily calibrate the exact temperature of the sample. This approach gained wide acceptance and eventually led to the publication of NIST* Certificate GM-761 ICTA** Certified Reference Materials for Thermogravimetry (2). The publication details the protocol used and the results of an international round-robin (ICTA) with five metals suitable for use as temperature references.

An alternative method of temperature calibration was developed by McGhie *et al.* (3,4) involving abrupt changes in weight associated with a melting link. Comparison with the magnetic approach indicated that either approach could be successful (5). The latter work also established that it was inadvisable to use a stronger magnetic field gradient than necessary to obtain a conveniently detectable change in weight.

The data in the NIST certificate indicated unusually broad ranges and thus high standard deviations in the reported mean values of the magnetic transition temperatures, T_C, of the metals studied. In the NIST study, all of the instruments were to be calibrated to the best of the participant's ability before the determination of the magnetic transition temperature. Gallagher *et al.* (6) demonstrated, however, that these large ranges were due, at least in part, to the calibration of the instrument. Much better calibration was obtained for nickel by using the technique of simultaneous TM/DTA and the well established melting temperatures that define the International Temperature Scale of 1990 (7). This work extends that initial study to include the remaining ICTA/NIST materials and two others from the series supplied by the Perkin-Elmer Company.

* The National Institute of Standards and Technology (formerly NBS, the National Bureau of Standards)
** The International Confederation for Thermal Analysis (now ICTAC, the International Confederation for Thermal Analysis and Calorimetry)

Because of difficulties associated with several of these alloys, it may be advisable to consider other choices. Since cobalt has a very high T_C, alloys of nickel and cobalt may be ideal candidates to cover the entire range from 358 to 1130 °C. A possible source of homogeneous alloys may be via coprecipitated nickel and cobalt oxalate dihydrates (8). They decompose to directly form nickel-cobalt alloys. The current work on this project involves the evaluation of the magnetic transitions of these alloys with respect to their reproducibility and suitability for use as temperature references.

EXPERIMENTAL PROCEDURES

A Seiko Instruments, Model 320 simultaneous TG/DTA was used for these measurements. The furnace was wound in a bifilar fashion to minimize the resulting magnetic fields induced during heating. The balance has a horizontal configuration and the permanent magnet was placed above the sample. This gave an apparent weight loss for a magnetic material due to the magnetic field gradient at the sample position. Alumina sample pans were used with 2-5 mg of the magnetic sample and a similar weight of each of the temperature standards. Care was taken that the samples were not in direct contact with each other.

A flow of argon at 100 mL min^{-1} was begun one hour prior to the start of heating in order to purge the sample and balance chambers. The temperature program consisted of four heating and cooling cycles starting well below the transition and continuing to clearly above the transition. The initial cycle was disregarded as recommended by others (1). Two different samples were run for each material at each heating rate, 2.5, 5.0, and 10 °C min^{-1}. That gave six data points on heating for each combination of material and heating rate. These six data points were used for the calculation of the standard deviations presented in Tables 2 and 3. Alumel was not investigated at 10 °C min^{-1} since the heating rate was not under control before the first transition temperature.

The magnetic transitions of nickel, Mumetal, Permanorm 3, Permanorm 5, Alumel, and Perkalloy were studied. The nickel was obtained from Goodfellows, Inc. and had a purity of 99.999 wt%. The Mumetal and Permanorms were from the ICTA/NIST stock. The Alumel and Perkalloy were from the Perkin-Elmer series of standards. The melting point standards used to bracket were 99.99 wt% or better from either Goodfellows or Johnson Matthey. The potassium nitrate solid-solid transition (ICTA/NIST potassium nitrate after the appropriate anneal) was used as the lower temperature standard for alumel, because the melting point of indium was too close to the magnetic transition temperature. A value of 130.1 °C, obtained consistently after calibration of the instrument with indium, was used for the calibration. Table 1 lists the magnetic materials and indicates the bracketing temperature standards that were used.

TABLE 1. The magnetic materials studied and the temperature reference materials (RM's) used for each.

Magnetic Material	Lower Temp. RM	Higher Temp. RM
Alumel	KNO_3	Tin
Mumetal	Lead	Zinc
Nickel	Lead	Zinc
Perkalloy	Zinc	Aluminum
Permanorm 3	Tin	Lead
Permanorm 5	Zinc	Aluminum

Fig. 1 shows a typical heating curve for nickel. The indicated temperatures represent the extrapolated values. The magnetic transition appears as an apparent weight gain as the sample becomes paramagnetic and the upward magnetic attraction is lost. The corrected value of T_C was obtained using the extrapolated onsets for melting and the extrapolated end point for the magnetic transition. The temperature of the observed magnetic transition was corrected by using a linear interpolation between the correction factors for the bracketing melting transitions.

In a quest for other suitable candidates for standards, nickel-cobalt alloys are particularly attractive because of their complete solid solubility and the resulting wide range of transition temperatures available.

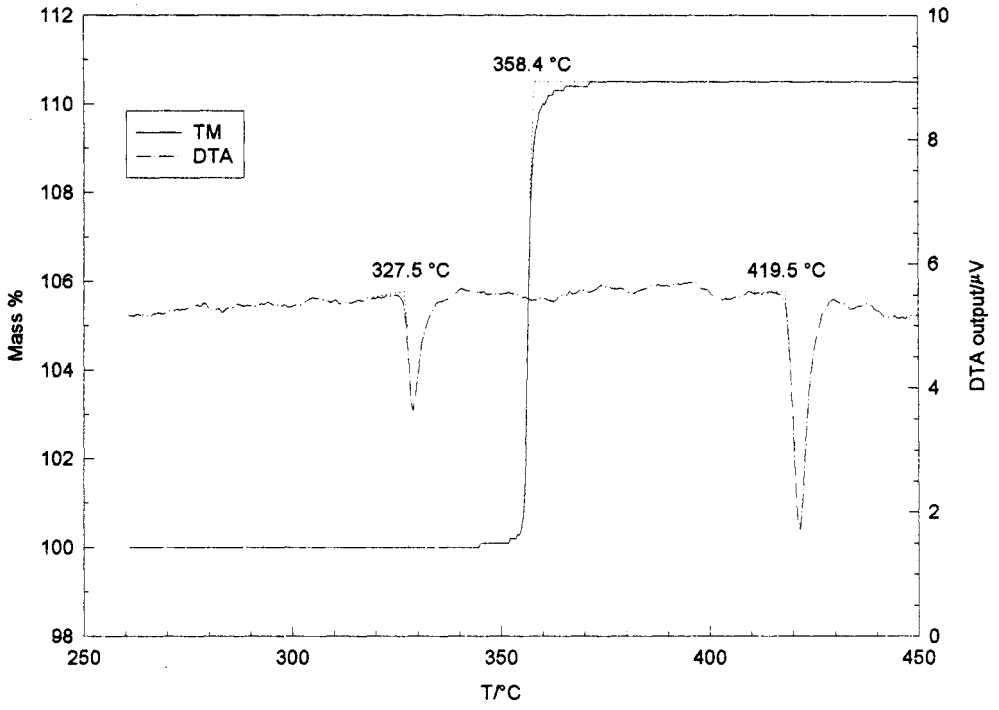

Fig. 1. A sample TM/DTA curve for nickel, lead, and zinc heated at 10 °C min^{-1} in argon.

Three compositions were prepared by the thermal decomposition of coprecipitated oxalates in an inert atmosphere (8). Three coprecipitated oxalates having the nominal compositions 75, 50, and 25 at% of cobalt were heated at 1100 °C in argon for 10 hours. The partially sintered sponge that resulted was lightly ground in an agate mortar and pestle to form small irregularly shaped pieces. These pieces, 8-12 mg, were treated as the metal foils or wire in the preceding paragraph.

RESULTS AND DISCUSSION

The results are summarized in Table 2 for all of the magnetic materials. The mean transition temperatures observed for nickel are in reasonably good agreement with the earlier work (6). Results for the other five materials are new.

The range of transition temperatures observed is smallest and the precision is greatest for the only pure metal in the series, nickel. These values are only slightly worse for the Alumel, Mumetal, and Perkalloy. The ranges expand considerably and the precision consequently degrades markedly for the Permanorm alloys. Even in these poorer cases, however, the range and precision are superior to those observed in the complete ICTA study. The values for the Permanorm alloys though are comparable to the values for individual investigators in that study.

Some consistent trends appeared with time for the Permanorm alloys. The values of T_C for both Permanorm 3 and 5 drifted to a higher temperature with each repeat. Since there was no significant weight gain, the drift can not be explained by the preferential oxidation in these alloys. There was some evidence of separation taking place, because the TM curves developed a reduction in the slope or tailing on the high temperature end. These drifts were 3-5 °C for Permanorm 3 and about half of that for the Permanorm 5. It would appear that these two alloys are the least desirable as potential temperature standards for TG.

Inspection of the phase equilibria for the iron, cobalt, or nickel based binary systems suggests that the most stable alloys should be in the nickel-cobalt system where there is nearly complete solid solution at all temperatures except below 400 °C at the very high cobalt side. The T_C for these alloys vary in a smooth fashion from the low end at pure nickel to above 1130 °C for pure cobalt.

The alloys prepared from the coprecipitated oxalates were partially sintered to a sponge in order to reduce their surface area. Preliminary results, obtained by direct decomposition of the oxalates in the simultaneous TM/DTA instrument at relatively low temperatures, indicated substantial oxidation (weight gain) during the subsequent TM experiment. This oxidation lead to a steady decrease in the T_C with each successive heating. It was speculated that this was the result of a preferential oxidation of the higher T_C component (cobalt). The oxidation, of course, is a greater factor for the higher cobalt alloys where the time and temperature required to detect the magnetic transition increases.

TABLE 2. Comparison of the present values of T_C at various heating rates and the values previously recommended.

Magnetic Material	Magnetic Transition Temperature/°C				
	Present work[a]	2.5 °C min^{-1}	5.0 °C min^{-1}	10 °C min^{-1}	Previous work
Alumel	Low	160.6	158.4		
	High	161.3	160.4	(unable to	
	Mean	160.9	159.5	measure)[b]	163[c]
	SD	±0.2	±0.9		
Mumetal	Low	395.0	395.5	395.1	370
	High	396.5	396.2	395.9	398
	Mean	395.7	395.9	395.6	385.9[d,e]
	SD	±0.6	±0.3	±0.2	±7.2
Nickel[g]	Low	358.3	357.8	357.9	345
	High	358.8	358.7	358.1	363
	Mean	358.6	358.4	358.0	354.4[d,f]
	SD	±0.2	±0.4	±0.1	±5.4
Nickel[g]	Low	358.9	358.2	358.2	345
	High	359.3	358.9	358.7	363
	Mean	359.1	358.6	358.6	354.4[d,f]
	SD	±0.1	±0.2	±0.2	±5.4
Perkalloy	Low	589.8	589.2	589.3	
	High	591.6	590.2	589.9	
	Mean	590.5	589.7	589.7	596[c]
	SD	±0.7	±0.4	±0.2	
Permanorm 3	Low	260.9	255.3	252.6	255
	High	266.7	264.7	262.7	278
	Mean	264.0	260.0	257.5	266.4[d]
	SD	±2.0	±3.6	±3.6	±6.2
Permanorm 5	Low	439.8	437.3	437.0	441
	High	443.1	442.3	438.3	470
	Mean	440.9	439.9	437.6	459.3[d]
	SD	±1.1	±1.8	±0.4	±7.3

[a]SD's for the present work represent the data from 3 heating cycles times 2 samples for each heating rate.

[b]For Alumel, the fastest heating rate was not used because it was not under control before the first transition temperature.

[c]Suggested value by Perkin-Elmer.

[d]Values from reference (2).

[e]393 °C is suggested by Perkin-Elmer.

[f]354 °C is suggested by Perkin-Elmer.

[g]Each row represents a different operator.

TABLE 3. Summary of T_C for nickel-cobalt alloys prepared from coprecipitated oxalates.

Composition/at%	Values[a]	Temperature/°C	Predicted T_C/°C[b]
72 Ni - 28 Co	Low	636.3	
	High	642.5	
	Mean	639.4	640
	SD	±2.8	
48 Ni - 52 Co	Low	754.9	
	High	766.1	
	Mean	760.3	848
	SD	±3.6	
26 Ni - 74 Co	Low	999.3	
	High	1002.4	
	Mean	1000.1	1010
	SD	±1.9	

[a]SD's represent the data from 3 heating cycles times 2 samples for each alloy.

[b]From the Co-Ni phase diagram in (9).

Some results are presented in Table 3 for the alloys prepared from the coprecipitated oxalates. The predicted T_C's in the fourth column of the table are derived from the Co-Ni phase diagram in (9). Much of the range in values arose from the differences between the two samples taken for each composition. It suggests that the alloys are not completely homogeneous. In addition the breadth of the transition was large and increased with the cobalt concentration, reaching a value of about 500 °C for 74 at% cobalt.

CONCLUSIONS

The simultaneous TM/DTA offers an excellent method for determination of T_C for materials. It is directly traceable to the International Temperature Scale. The accuracy and precision attainable with relatively pure nickel is outstanding, however, alloys present a greater problem. The drifts and variations though are probably indicative of the true situation and merely reflect the real problems associated with sampling difficulties, phase separation, oxidation, etc. Perhaps other magnetic materials such as oxides can be prepared in a more reproducible manner. Pure metals and alloys such as Alumel, Mumetal, and Perkalloy, however, show considerable promise for use as standards.

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