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A STUDY OF THE EFFECT OF PURITY ON THE USE OF NICKEL AS A TEMPERATURE STANDARD FOR THERMOMAGNETOMETRY

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Samples of nickel, varying by four orders of magnitude in their purity, were studied by thermomagnetometry (TM), to determine if the extrapolated end point (T_C) changes. T_C is virtually identical for the 99.99 and 99.999% samples. Samples of less purity did show changes.

Simultaneous DTA/TM can accurately define T_C by comparing with the melting points of pure metals determined simultaneously. The melting points of lead and zinc bracket the T_C for nickel. They were added to the sample pan prior to TM of nickel. Experiments were performed at heating rates in the range from 1 to 20 deg·min^{-1}. It serves as a pilot study for the ICTAC Committee for Standardization to more accurately define the recommended values of T_C.

Keywords: Ni as a temperature standard, thermomagnetometry

Introduction

Faster experimental turn-around times can be achieved in TG by using smaller furnaces that will heat and cool more rapidly. This requires a smaller sample to assure a homogeneous temperature throughout the sample zone. It also places greater demands on the precise placement of the temprature sensor in order to correspond with the sample temperature. This concern led to the proposal by Noren *et al.* [1], to use magnetic materials in the exact position of the sample and utilize the transformation temperature, T_C, from the ferri or ferromagnetic form to the paramagnetic one to calibrate the true sample temperature more accurately.

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They indicated that several magnetic materials could be run simultaneously and proposed a series of pure metals and alloys to cover the temperature range 100°–1000°C. This suggestion was adopted immediately by others [2] using this type of instrumentation. The strength of the magnetic field gradient necessary to achieve a measurable effect is low and can be provided by an inexpensive, small, permanent magnet. In fact a high magnetic field is undesirable for this purpose [3]. Comparisons of such standards with others have been made over the intervening years [4–6].

The Standardization Committee of ICTAC conducted a detailed program and round-robin, under the direction of Garn, Menis, and Wiedemann, to establish nickel and four magnetic alloys as standards for the comparison of temperature in TG [7]. This effort culminated in the availability of these materials through N.I.S.T. [8].

Although individual participants in the program had relatively good precision, there was a wide range of results reported from one laboratory and/or type of instrument to another. These are described in detail in Refs [7] and [8]. As an example, the range of reported values for nickel was 345°–363°C with an average of 354.4°C.

Recommended values ranged from 354° [1] to 361°C [9].

The advent of modern simultaneous TG/DTA instrumentation provides an opportunity to re-evaluate these magnetic transitions using the melting points of pure metals for direct comparison [6]. Metals can be selected whose melting points bracket the magnetic transition and whose temperatures of melting form the basis for the practical realization of the current international temperature scale [10]. Both melting and the magnetic transitions can be measured simultaneously on the same instrument using the identical temperature sensor.

This paper presents the results of a brief pilot study by the Task Group on Magnetic Standards of the Committee for Standardization of ICTAC. It represents the combined efforts of five laboratories in North America, Europe, and Asia using instruments from four different manufacturers. One laboratory was chosen to utilize high-sensitivity DTA in place of TM to determine the values of T_C.

The study has three basic goals: 1) to determine the feasibility of obtaining accurate results with a high degree of interlaboratory agreement, 2) to evaluate the effect of heating rate on the results in order to set the proper protocol for a much larger and broader study, 3) to establish the degree of purity that is required for the standard materials, and 4) to compare the values of T_C obtained by TM and DTA. Nickel was selected for this initial study.

Experimental procedures and results

Wires of lead and zinc having a purity of 99.99 wt% or better were obtained along with foils of nickel having purities of 99, 99.9, 99.99, and 99.999 wt% from Goodfellows, Inc. Approximately 5 mm×5 mm samples of nickel were cut from a

single piece of foil. Several foil samples of each purity and a length of each wire were distributed to the participants.

Experimental protocol called for a flow of inert gas (argon or nitrogen) at the flow rate normally used by the investigator for that apparatus. Each sample was to be heated briefly above T_C and cooled once prior to taking any data for record [1]. This anneal made no significant difference, based on a few checks that were made. The sample was to be placed in good thermal contact with the sample pan. A magnetic field gradient adequate to note the effect without being excessive was to be used. Samples of lead and zinc were to be placed alongside the nickel. Sample sizes were left to each investigator depending upon the particular instrument used. Prior temperature calibration of the instrument was deliberately not specified. One laboratory (C) purposely did not calibrate the instrument in advance in order to test the calibration algorithm more extensively.

Each purity was to be run at 10 deg·min^{-1}. A second series was to be run at nominally 1.0, 2.5, 5.0, 10, and 20 deg·min^{-1} using a sample of the highest purity. Each investigator was asked to make several runs using the same set of conditions in order to evaluate their reproducibility. The types of apparatus used in this study were two Seiko model TG/DTA 320, Stanton Redcroft model STA 1500, TA Instruments model SD2960, and MAC Science HT-TG/DTA.

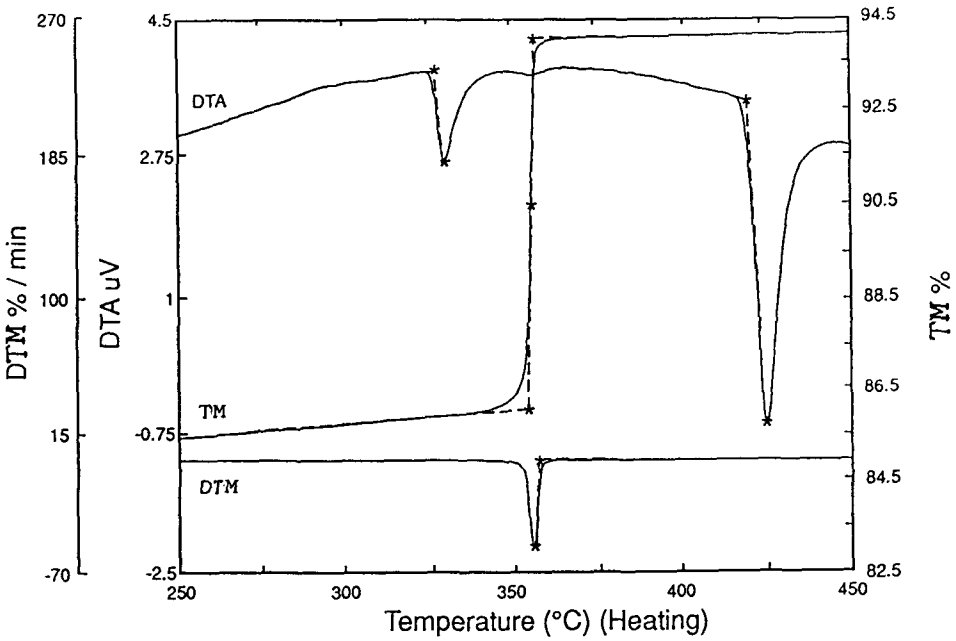

Fig. 1 Simultaneous TM/DTM/DTA curves for Ni, Pb, and Zn at 20 deg·min^{-1} in Ar (Lab A)

Table 1 Measured values of melting temperatures of Pb and Zn, and measured and corrected values for magnetic transition temperature, T_C, of Ni, having different purities, from simultaneous TM/DTA in an inert gas at 10 deg·min^{-1}. T^m = measured, T^c = corrected, Lab. = code Data from Lab. E are based entirely on DTA (see text)

Purity / wt%	Lab. °C	T^m_{Pb}/ °C	T^m_{Zn} / °C	T^m_{CNi}/ °C	T^c_{CNi}/ °C	σ / °C
99.999	A	326.6	419.6	357.4	358.4	0.2
	B	327.8	420.1	358.4	358.0	0.2
	C	323.8	417.0	355.0	358.4	0.2
	D	329.5	421.1	360.2	358.4	0.1
	E	327.7	419.9	357.9	357.8	0.2
99.99	A	326.4	419.8	357.2	357.8	
	B	327.8	419.8	358.3	358.0	
	C	323.9	416.9	355.2	358.4	
	D	329.5	421.1	360.2	358.3	
	E	327.8	419.9	358.0	357.5	
99.9	A	326.0	419.6	357.5	358.5	
	B	327.6	420.1	358.8	358.6	
	C	323.8	417.0	356.2	359.5	
	D	329.5	421.1	361.1	359.2	
	E	327.8	419.9	358.4	358.1	
99	A	325.7	423.4	349.3	350.7	
	B	327.8	420..0	350.5	350.1	
	C	323.5	416.8	347.2	350.9	
	D	329.5	421.1	351.8	349.9	
	E	327.9	420..0	347.8	347.3	

A typical set of simultaneous TM/DTM/DTA curves is presented in Fig. 1. Extrapolated onsets are used to determine the observed melting temperatures for lead and zinc. T_C was measured as the extrapolated end point based on both the TM and DTM curves. The end point is used for T_C as the loss of magnetism defines the transition temperature [3]. The DTM results proved more sensitive to the extrapolated end point (about 0.2° to 0.4°C) than TM. Hence, the values reported for T_C are derived from DTM.

The difference between the observed melting point and the defined values [10] (419.527°C zinc, 327.5°C lead) was used for calibration. A linear interpola-

tion between these correction factors was used to determine the correction factor applied to the observed magnetic transition temperature for each experiment. The results are summarized in Tables 1 and 2 for the DTM and DTA measurements.

Table 2 Measured values of melting temperatures of Pb and Zn, and measured and corrected values for megnatic transition temperature, T_C, of Ni, 99.999 wt%, from simultaneous TM/DTA in an inert gas at the indicated heating rates. T^m = measured, T^c = corrected, Lab. = code Data from Lab. E are based entirely on DTA (see text)

H.R.deg·min^{-1}	Lab.	T^m_{Pb} / °C	T^m_{Zi} / °C	T^m_{CNi} / °C	T^c_{CNi} / °C
20.0	A	326.0	419.5	358.0	359.0
	B				
	C	323.5	417.2	355.0	358.5
	D				
	E	328.2	420.2	358.6	357.9
10.0	A	326.2	419.6	357.4	358.4
	B	327.8	420.1	358.4	358.0
	C	323.8	417.0	355.0	358.4
	D	329.5	421.1	360.2	358.4
	E	327.7	419.9	358.0	357.5
5.0	A	325.4	418.6	356.4	358.2
	B				
	C	324.1	417.1	355.4	358.5
	D				
	E	327.8	420.0	357.9	357.6
2.5	A	325.4	419.0	356.8	358.0
	B				
	C	324.6	417.3	355.9	358.6
	D				
	E	327.5	419.8	357.7	357.6
1.0	A	325.2	418.0	356.0	358.1
	B				
	C	324.3	416.6	355.7	358.8
	D				
	E	327.3	419.5	357.3	357.5

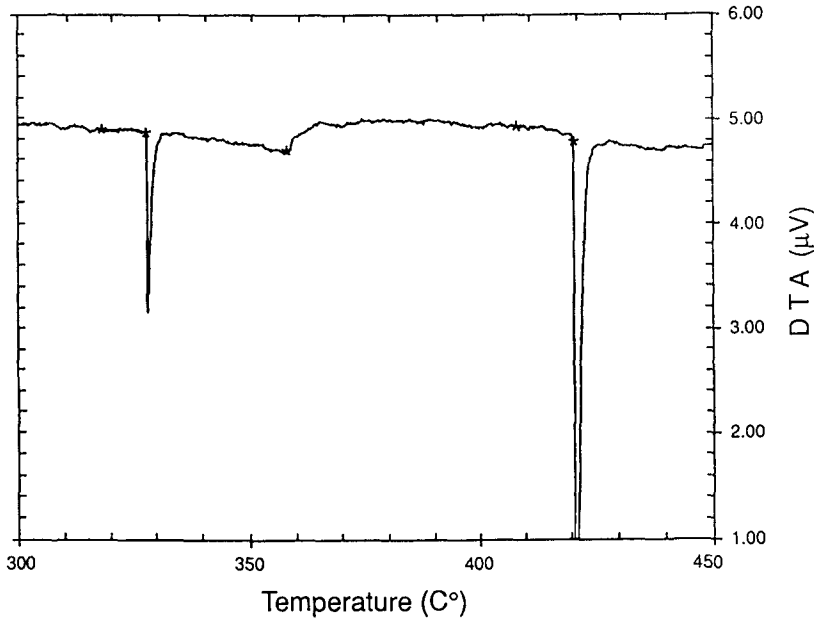

Fig. 2 Simultaneous DTA curves for Ni, Pb, and Zn at 10 deg·min^{-1} in N_2 (Lab E)

The same correction procedure was used for the values of T_C obtained by DTA. A typical DTA experiment is shown in Fig. 2. The peak temperature of the DTA excursion was used to establish T_C on the basis that the process was over at that point and the return to baseline was controlled by instrumental factors.

The trends in corrected T_C with heating rate for both the DTM and DTA methods are presented in Fig. 3.

Discussion

Limitations of space preclude an extensive discussion of the results and only the major issues and conclusions are described here.

Comparison of the DTA with the DTM results indicates that the T_C based on the peak temperature of the DTA excursion is consistently lower (about 0.7°C) in temperature at all heating rates and sample purities. The implication is that the selection of the peak temperature for T_C is probably incorrect. The selection of the return to baseline will obviously lead to an increase in the reported DTA temperatures and better agreement with the DTM results.

Values of T_C based on DTM show a very high degree of reproducibility among the different laboratories. In Table 1, for the highest purity, the spread of values is

only ±0.2°C, consistent with the reported values of σ. Values throughout Tables 1 and 2 are generally within 2σ. This degree of agreement between several laboratories is vastly superior to the results of the earlier round-robin [7]. Clearly the use of simultaneous TM/DTM/DTA is an excellent way to define the value of T_C and has direct correspondence with the International Temperature Scale.

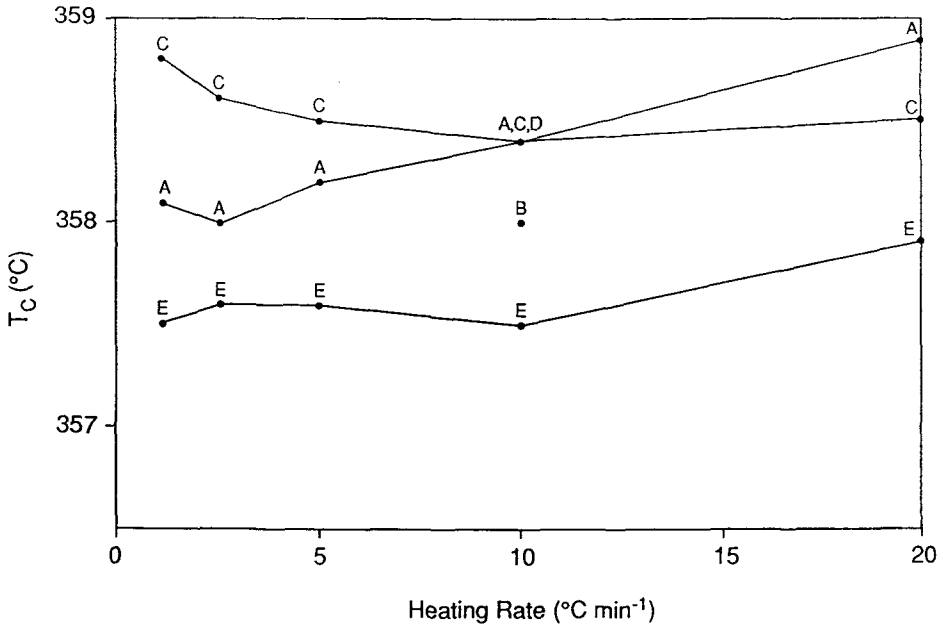

Fig. 3 T_C for Ni as a function of heating rate in an inert gas. The letters represent the laboratory code

The method has the added advantage of largely removing the dependency of T_C on the heating rate. Unfortunately, only three laboratories reported their results as a function of heating rate and one of these is based on DTA results. The results, however, reveal very little change with heating rate over the range reported. The trends are inconsistent as seen in Fig. 3. Apparently the shift in melting points, used as calibration, provides an adequate correction for the lag induced by increased heating rates.

A minimum purity of 99.99 wt% seems to be required for this source of nickel. Naturally, the absolute purity required depends on the specific impurities present. Iron or cobalt will raise the value of T_C but other impurities lower it. Apparently there is significant iron or cobalt in the 99.9 wt% sample and much greater quantities of other impurities in the 99 wt% specimen.

A greatly expanded program will redetermine the magnetic transition temperatures for the metals and alloys currently used to calibrate the temperature axis in TG and TM. These preliminary results clearly demonstrate that a substantial improvement, perhaps an order of magnitude reduction in the uncertainty, can be expected and also provide some basis for selecting the purity of the materials.

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Zusammenfassung — Zur Bestimmung der Änderung von T_C wurden mittels Thermomagnetometrie (TM) Nickelproben untersucht, die sich ihrer Reinheit nach über vier Größenordnungen unterscheiden. Für 99.99% und 99.999% Proben sind die Werte für T_C scheinbar identisch. Proben mit geringerem Reinheitsgrad zeigen Abweichungen.
Mittels simultaner DTA/TM kann T_C durch Vergleich mit den simultan ermittelten Schmelzpunkten reiner Metalle präzise bestimmt werden. T_C für Nickel liegt zwischen den Schmelzpunkten von Blei und Zink. Sie werden der Probenschale mit dem Nickel vor der TM zugesetzt. Die Versuche wurden mit Aufheizgeschwindigkeiten zwischen 1 und 20 deg/min durchgeführt. Diese Arbeit dient dem ICTAC Committee for Standardisation als eine Pilotstudie zur präziseren Definition empfohlener T_C-Werte.