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CURIE TEMPERATURE STANDARDS FOR THERMOGRAVIMETRY: THE EFFECT OF MAGNETIC FIELD STRENGTH AND COMPARISON WITH MELTING POINT STANDARDS USING Ni AND Pb *

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Those of us fortunate enough to attend the 5th ICTA in Kyoto during August of 1977 will never forget the tremendously warm hospitality tendered by Professor Seki and his colleagues. It was only exceeded by the truly incredible warmth of the weather that August in Kyoto. Therefore, I take particular pleasure in participating in this special issue to provide a well-deserve honor and to commemorate the illustratious career of Professor Syûzô Seki.

ABSTRACT

Thermogravimetric (TG) runs were made with a Ni sample over a wide range of heating and cooling rates using an electromagnet at three different field strengths. The extrapolated onsets and endpoints of the weight change induced by the magnetic field gradient were obtained from both TG and the differential curves (DTG). The onset upon heating and endpoint on cooling are very clearly dependent upon magnetic field strength and hence unsuitable for temperature calibration using this method. The endpoint upon heating and onset upon cooling, however, showed only a slight dependence upon the cube root of the magnetic field strength. Observed values of T_c showed a linear dependence upon heating or cooling rates which extrapolated to a common point at zero rate. The value of T_c derived from extrapolation to zero rate and then zero field is 339.15°C, which is 16°C below the literature value.

Simultaneous measurements of the melting point (T_m) of Pb and the T_c of Ni using a different furnace/thermocouple/magnet combination indicated a value of $T_m = 311.8$°C and $T_c = 343.1$°C. The value of T_m is 15.7°C below the value from the International Temperature Scale. The value of T_c is uncorrected to zero magnetic field strength, which would probably lower it several degrees. It would appear that both methods of temperature calibration are suitable for TG and the choice is best determined by the convenience with the particular apparatus involved and the temperature range desired.

INTRODUCTION

A major problem in accurate thermogravimetry (TG), particularly kinetic studies, concerns the actual sample temperature. Generally the temperature

* Dedicated to Professor Syûzô Seki in honor of his contribution to Calorimetry and Thermal Analysis.

of a nearby thermocouple is equated to that of the sample. This is obviously an approximation which becomes more uncertain for small furnace, i.e., high temperature gradient systems. This situation is further complicated by reactions which involve high values of enthalpy, either positive or negative. It is difficult to compensate for the latter effect; however, reasonable calibration procedures can minimize the errors induced by the furnace/sample/sensor arrangement.

Several approaches to temperature calibration for TG are available. It is possible to use a material with well-resolved weight losses at several temperatures as a standard, e.g., $CaC_2O_4 \cdot H_2O$ with its loss of H_2O around 200°C, CO around 450°C, and CO_2 around 800°C [1]. The apparent temperature of these decompositions, however, will depend on several factors such as particle and sample size, total pressure, defect content, and partial pressure of the products from the reversible steps, i.e., H_2O or CO_2. Such an approach has therefore been shunned, although a particular batch of such a material may be useful for an interlaboratory study to reveal the great variations possible from one apparatus and set of operating conditions to another.

Other suggested methods of temperature calibration for TG have been to use fusible links of pure metals which will provide a weight change or disturbance associated with the well-defined first-order phase transition at the melting points (T_m) of these links [2,3], or to use the change in apparent weight of a magnetic sample in the presence of a magnetic field gradient as it undergoes the generally second-order transition to the paramagnetic state at the Curie or Neel temperature, T_c [4–9]. This latter transition point is associated with the essential disappearance of the magnetic attraction or repulsion (based upon the direction of the field) and, hence, corresponds to the last stage of reduction in the apparent weight gain or loss induced by the magnetic field gradient.

It has been suggested that during the heating cycle, the onset of this apparent weight gain or loss induced by the magnetic field gradient is a more easily and reproducibly determined point than the end, and hence should be used for such calibration purposes [9]. There are two drawbacks involved with such an approach. The first is concerned with the fact that by definition, T_c corresponds to the final transition to the nonmagnetic state and hence the standard values of T_c obtained by other techniques refer to the end. If, however, it could be demonstrated that the onset during heating was more precisely measurable and that there was a constant offset between the onset and endpoint, then a case could still be made for the measurement of the onset and subsequent application of the correction factor.

The second drawback, however, is that the onset is field-dependent and hence precludes this approach. Figure 1 [10,11] shows the typical behavior of the magnetization, neglecting any demagnetizing effects, for a ferromagnetic material as a function of temperature. However, for most sample shapes

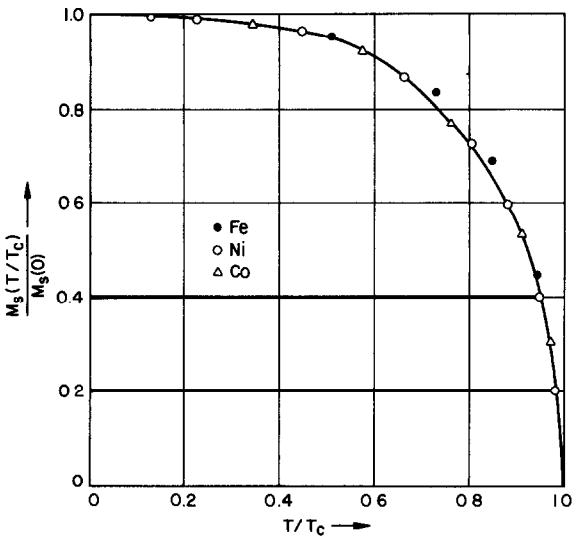

Fig. 1. Relative magnetization versus T for Fe, Ni, and Co (after refs. 10 and 11).

demagnetizing effects play a large role and the maximum magnetization, M, that can be reached with an applied field, H_a, is given by $M = H_a/N$ [11]. For example, for a thin disc with H_a along the normal to the surface $N = 4\pi$ and for a cylinder with a diameter-to-length ratio of 100 and H_a parallel to the long axis $N = 1.2\ \pi \times 10^{-2}$. Consequently, for a given H_a and N as the ferromagnetic material is cooled from T_c, the magnetization will saturate when $M(T)$ reaches H_a/N and be temperature-independent for all lower temperatures. This is illustrated in Fig. 1 where two values of H_a/N are chosen so that saturation occurs at $M_s(T/T_c)/M_s(0) = 0.4$ and 0.2. Then the extrapolated onset would occur at $0.95T_c$ and $0.98T_c$, which for iron (T_c = 1043 K) would be a difference of about 30°C. From this standpoint it would seem best to use the weakest magnetic field consistent with observing the effect. In principle the end of the magnetization, which corresponds to the definition of T_c, should have no dependence upon the magnetic field strength.

One purpose of this work is to verify the unsuitability of the extrapolated onset during heating as a valid point for temperature calibration. A second purpose is to determine the effect of magnetic field strength upon the endpoint of the apparent weight change during heating and to see if there is any influence upon the trends in this temperature with heating rate. Finally, it is intended to simultaneously check the calibration temperature and its trends with heating rate as determined using both the T_c and fusible link or T_m techniques.

The extensive interlaboratory study [6] of the T_c for several metals and alloys indicated that Ni exhibited the most well-defined effect in that the

apparent change of weight occurred in the narrowest temperature interval and with the highest reproducibility both intra- and interlaboratory. This metal had the added advantage that it was also one of the other commonly used set of standards for this purpose supplied by the Perkin-Elmer Corporation in conjunction with its instrumentation [4,5,7,8]. The reported recommended value of T_c for Ni is around 354°C [4,6]. The melting point of Pb at 327.5 [12] makes it a convenient choice for the comparison between the two methods of calibration.

EXPERIMENTAL PROCEDURES

The nickel wire (0.44 mm diameter, 3.439 mg) was that supplied by the Perkin-Elmer Co. Lead was Johnson Matthey Puratronic grade (99.9985%) wire of 0.25 mm diameter. In order to assure that the Ni was not free to shift about in the magnetic field, it was cemented into one hole of a short section (3 mm) of two-hole ceramic rod normally used for thermocouple construction. This ceramic section was then cemented onto the Pt pan normally used in conjunction with the Perkin-Elmer TGS-2 thermogravimetric system. A hole was made in the sample pan which aligned with the free hole in the ceramic. This was used for the PT wire weight suspended from the fusible link (Pb wire). Figure 2 shows a sketch of this sample holder arrangement.

A Perkin-Elmer System 2 thermobalance was used in conjunction with their System 4 furnace controller and a digital data acquisition system [13] based upon the Fluke 2500 measurement and control system. Two magnets

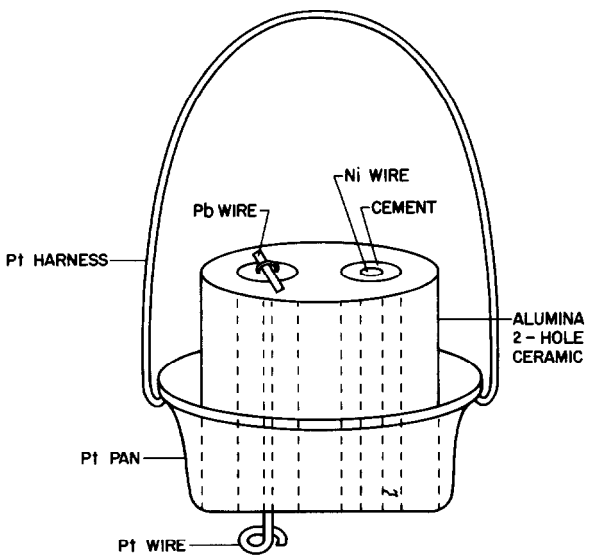

Fig. 2. Sketch of sample holder.

were used for different aspects of this study. In order to maintain the other factors constant during the investigation of the effect of field strength, an electromagnet was wound on an Al frame, about 2 in. inside diameter. This tube was slipped over the pyrex protective sheath surrounding the furnace and then clamped. Since the sample was not destroyed in the inert N_2 flow (40 ml min^{-1}), there was no need to vary any of the experimental parameters other than current to the coil of the electromagnet. A flow of 1 A generated a magnetic field of 105 Oe. Currents of 4, 1, and 0.25 A were used. Heating rates of 40, 20, 10, 5, 2.5, and 1.2°C min^{-1} were employed at each field setting. Since simultaneous measurement using the fusible link would have necessitated opening the system each time to replace the lead wire, this would have required precise repositioning each time. Consequently, the simultaneous comparison of the two techniques was done in a separate series of experiments using the small permanent magnet (125 Oe) supplied by Perkin-Elmer with their equipment. Reasonable care was made to replace the magnet in the same position each time. It should be pointed out that the direction of the field for this permanent magnet was essentially orthogonal to that of the electromagnet. The same heating rates and sample of Ni were used. Unfortunately, the furnace burned out in work between the two series of experiments and had to be replaced. This invalidates a direct comparison between these two series of experiments.

RESULTS AND DISCUSSION

Use of onset versus endpoint

As described in the introductory section, one of the purposes of this work was to establish the inadvisability of using the extrapolated onset of the

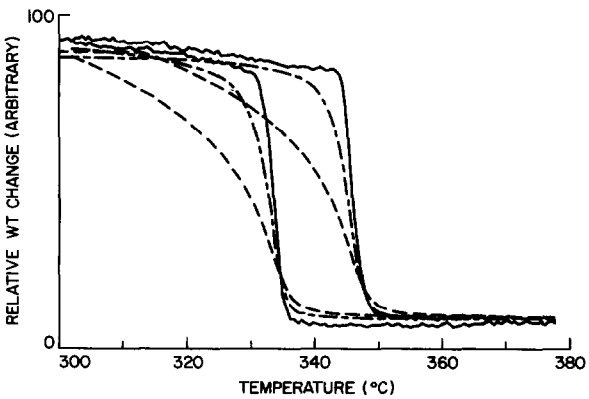

Fig. 3. TG curves during heating and cooling 3.439 mg of Ni at 20°C min^{-1} in N_2 as a function of magnetic field strength. (———) 26.2 Oe, (— - —) 105 Oe, (- - - - -) 420 Oe.

magnetic transition during heating regardless of its apparent reproducibility under a particular set of circumstances. Figure 3 shows a set of thermomagnetic curves taken during heating at 20°C min^{-1} for the three different magnetic field strengths. Similar curves were obtained at all heating and cooling rates. Even at this relatively rapid heating rate it is immediately obvious that the sharpness of the onset of weight loss deteriorates dramatically with increasing magnetic field gradient. Clearly the extrapolated onset temperature shifts many degrees towards lower temperature while the extrapolated endpoint shows very little variation. This point, in conjunction with the definition of T_c, dictates the use of the extrapolated endpoint on heating or onset on cooling as the clearly preferred reference points. The point of inflection or peak in the DTG curve may be an easily defined point but it suffers, albeit to a much lesser extent than the onset on heating, from the same general problems.

Use of DTG or TG curves and heating versus cooling curves

The TG and DTG curves are shown in Fig. 4 for the full cycle of a typical experiment. The extrapolated endpoints are indicated for the heating por-

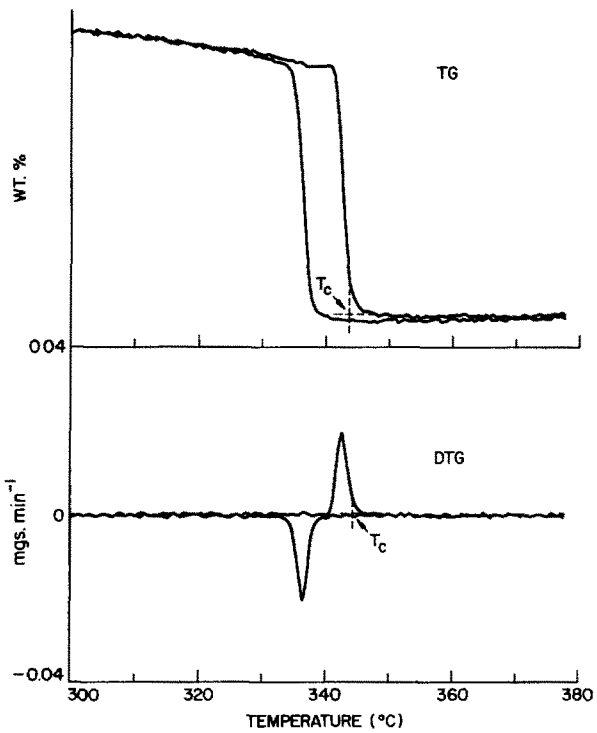

Fig. 4. Typical TG and DTG curves showing the method of evaluating T_c. Heating and cooling of 3.439 mg of Ni at 10°C min^{-1} in N_2 and a magnetic field strength of 26.2 Oe.

tion of both curves. As pointed out by Garn et al. [6], the usefulness of the DTG curve depends upon whether it is a calculated version, such as herein, or whether it is generated by an RC analog computer in which case there may be too much time lag to be of value. As observed by others [6] the extrapolated value based upon the DTG curve is slightly higher upon heating and cooling than the value based upon the TG curve. This difference increases slowly with increasing heating rate.

The extrapolated endpoints upon heating and onsets upon cooling from both the TG and DTG curves are plotted in Figs. 5–7 as a function of heating rate for all three field strengths. It should be kept in mind that the cooling at the higher rates may be inadequate to keep up with the preset rate. There appears to be a nearly linear dependence of measured T_c upon heating or cooling rate and the least-squares fits are indicated by the solid lines. Table 1 lists the values of the slopes and intercepts for these lines. It would seem advisable that if the situation were reversed, i.e., one was using a calibrated TG system to determine an unknown T_c (thermomagnetometry),

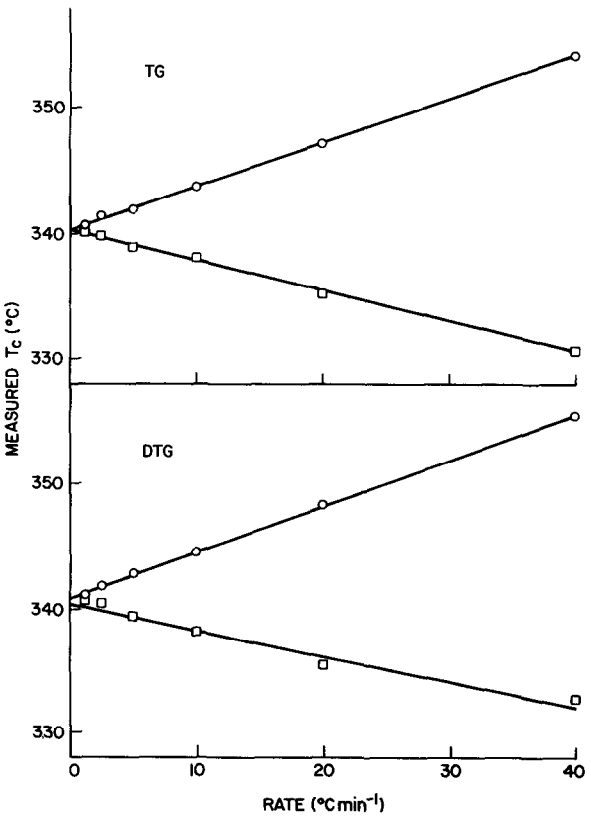

Fig. 5. Observed values of T_c as a function of heating and cooling rates for 3.439 mg of Ni in N_2 at a magnetic field strength of 26.2 Oe. (○) Heating, (□) cooling.

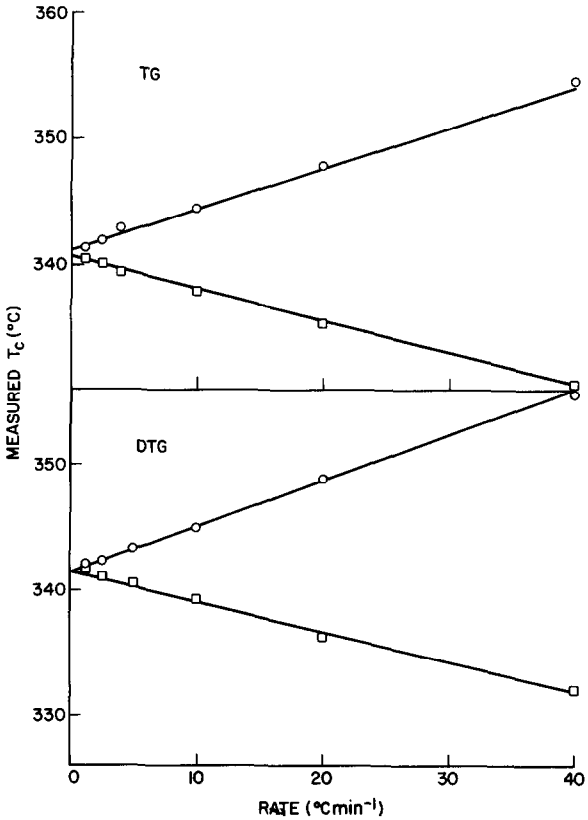

Fig. 6. Observed values of T_c as a function of heating and cooling rates for 3.439 mg of Ni in N_2 at a magnetic field strength of 105 Oe. (○) Heating, (□) cooling.

one should run the experiment at several heating rates and extrapolate to zero heating rate. Undoubtedly each system would have its own characteristics function for this extrapolation.

Examination of the parameters in Table 1 indicates that the values of T_c at zero heating or cooling rate are invariably higher for DTG derived values. The dependence upon heating rate for both the TG and DTG derived values is greater in heating than during cooling. The dependence of DTG compared to TG is greater in heating but less during cooling.

Dependence of measured T_c *upon field strength*

The values of T_c at zero rates for heating and cooling are averaged for each field and plotted in Fig. 8 as a function of field strength. The cube root dependence upon field strength was chosen based upon the model described in ref. 14. The least-squares fit is indicated by the solid line in Fig. 8 and the values of the slopes and intercepts are given. Both the DTG and the TG

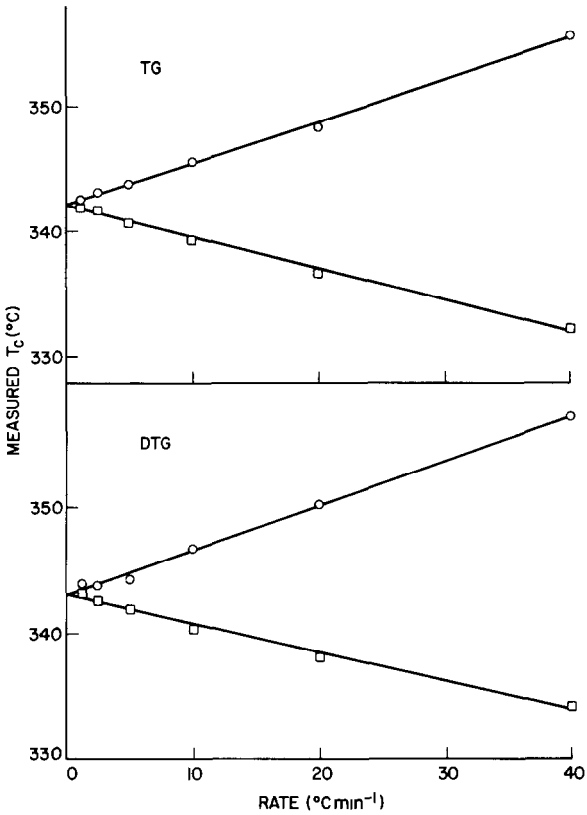

Fig. 7. Observed values of T_c as a function of heating and cooling rates for 3.439 mg of Ni in N_2 at a magnetic field strength of 420 Oe. (○) Heating, (□) cooling.

data extrapolate to 339.15°C (for the value of T_c at 0 rate) at zero field strength. This value of 339.15°C would, therefore, seem to be the T_c as best determined using this particular experimental configuration. The reported

TABLE 1

Linear least-squares parameters for the observed value of T_c (°C) as a function of heating rate (°C min^{-1})

Field strength (Oe)	Source	Heating		Cooling	
		Intercept (°C)	Slope (min)	Intercept (°C)	Slope (min)
26.2	TG	340.3	0.350	340.4	−0.243
	DTG	340.8	0.368	340.6	−0.208
105	TG	341.1	0.323	340.6	−0.255
	DTG	341.5	0.366	341.7	−0.245
420	TG	342.1	0.331	342.0	−0.280
	DTG	343.0	0.357	343.1	−0.229

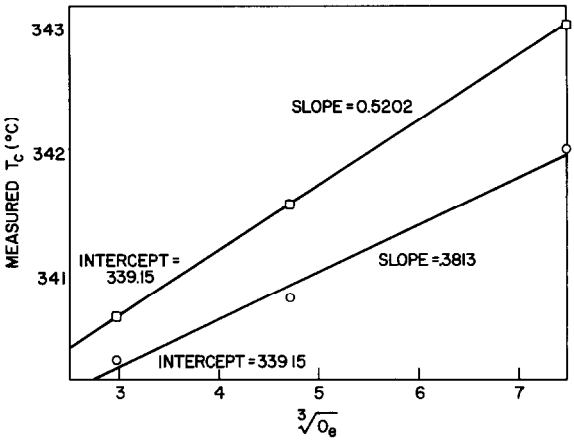

Fig. 8. Values of T_c at zero heating or cooling rate as a function of the cube root of the magnetic field strength. (O) TG, (□) DTG.

values for the T_c of Ni show considerable spread; however, one of the more recent careful studies [15] gives a value of 355.2 ± 1°C. Based upon such a value, 16°C should be added to the TG temperatures measured in this general temperature range with that specific thermocouple/furnace/hang-down combination. In the next section a comparison is actually made with an independent calibration technique. Unfortunately, it is with a different thermocouple/furnace combination. While this will probably change the specific 16°C correction it should not affect the validity of the intercomparison of techniques.

Comparison of T_c *and* T_m *methods of calibration*

The simple configuration shown in Fig. 2 was utilized with both the Pb and Ni wires. The magnetic field gradient was orthogonal to that in the previous sections and was provided by the permanent magnet. Since it was necessary to reposition the magnet in each experiment it is assumed that the field gradient was not as constant as in the previous section. The bulk of the weight change was associated with the fall of the Pt wire weight. A typical run is shown in Fig. 9. The portions of the curve pertaining to the magnetic transition could be readily expanded to resemble Fig. 4.

Values of T_c determined as described earlier are plotted in Fig. 10. The intercepts and slopes for the least-squares fit lines are shown for both the DTG and TG data during heating and cooling. The average value of T_c at zero rate is 343.1°C for the TG and 343.55 for the DTG data. If one were to apply the correction to zero field that was applicable in the earlier section it would lower these values to 341.1°C, however, there is little validity for that precise correction since such important factors, i.e., furnace, thermocouple, and magnet have been changed.

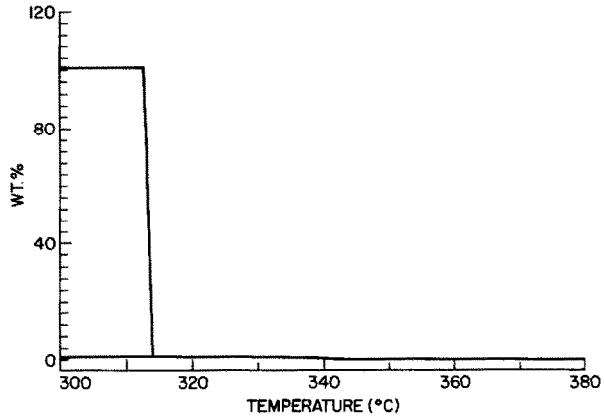

Fig. 9. Typical TG curve using simultaneous T_m and T_c techniques. The fusible link is Pb and the magnetic transition is for 3.439 mg Ni using the permanent magnet supplied by Perkin-Elmer Co. The heating and cooling rate is 1.2°C min^{-1} in N_2.

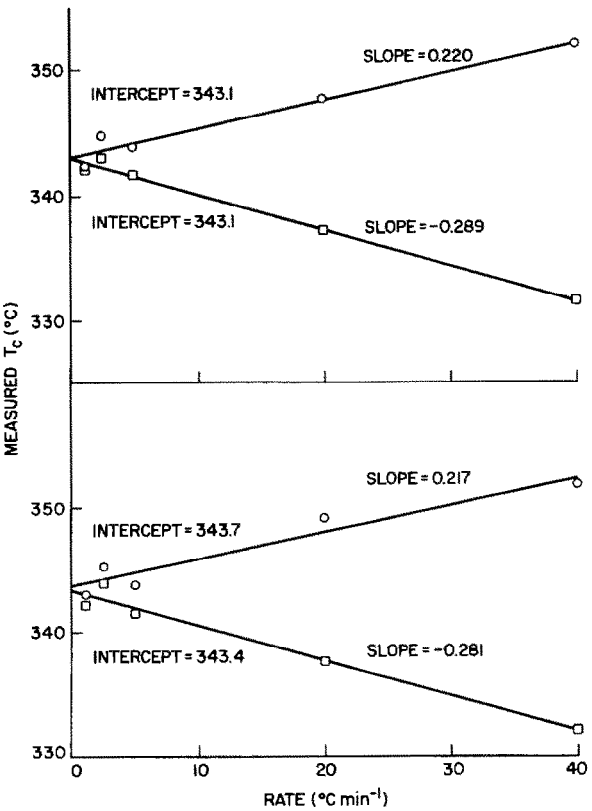

Fig. 10. Observed values at T_c as a function of heating and cooling rates for 3.439 mg of Ni in N_2 using the Perkin-Elmer permanent magnet. (○) Heating, (□) cooling.

Values for the T_m of Pb derived from the onset of the large weight loss associated with the fall of the Pt wire are plotted in Fig. 11 as a function of the square root of the heating rate. As in the case of the linear extrapolations used with T_c values, there is no obvious significance to this functional dependence but it does yield a convenient extrapolation to zero rate. At zero heating rate the least-squares fit indicates a value of 311.8°C for T_m. This is compared with 327.5°C from the International Temperature Scale. The difference of 15.7°C is remarkably similar to the 16°C correction obtained in the earlier sections and with the 12°C (+uncertain field correction) obtained from the simultaneous T_c work of this section.

Based on this comparison it would seem that either calibration method has validity and they are completely consistent with each other. Using T_m has the advantage of directly using primary standards in many cases. The T_c approach is somewhat easier experimentally in that several standards encompassing a wide temperature range can be run in a single experiment [4,5,8]. The convenience of the two methods depends upon the particular apparatus used. Some can easily accept a magnet and need no other modifications while others cannot. On the other hand there is generally no need to make even minor modifications to the sample holder such as are required for the T_m method.

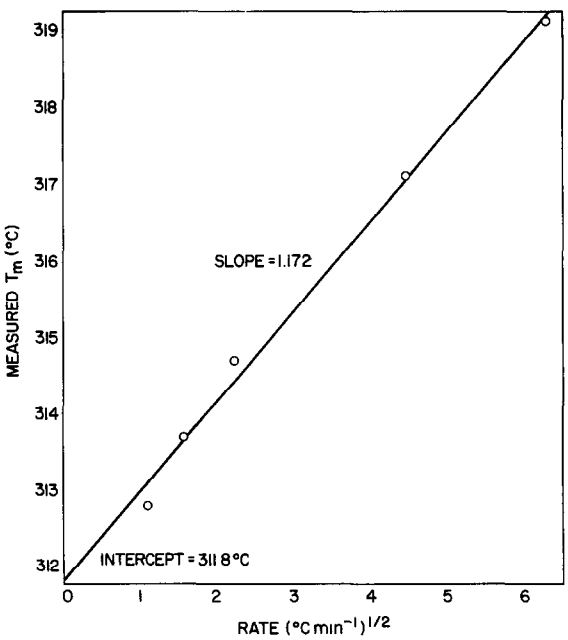

Fig. 11. Observed values of T_m for Pb wire as a function of the square root of the heating rate.

CONCLUSIONS

(1) The extrapolated onset upon heating or endpoint upon cooling is an unsatisfactory reference point for T_c calibration because of its dependence upon magnetic field strength.

(2) Both the TG or DTG curves are suitable for evaluating the value of T_c. The exact values will be slightly higher using DTG curves.

(3) Using the experimental apparatus described herein, the observed values of T_c showed a linear dependence upon heating or cooling rate and extrapolated to a common intercept at zero rate for each value of magnetic field strength. Because of conclusion (2), this value may be about 1°C higher for DTG-derived values.

(4) These values of T_c at zero rate follow the expected dependence upon the cube root of the field strength. The DTG-derived values have a greater slope and hence both sets of data extrapolate to 339.15°C at zero field. This value of T_c was 16°C below the literature value for the T_c of Ni.

(5) In simultaneous experiments using both the T_c of Ni and the melting point of Pb, but with a different furnace/thermocouple/magnet combination than previously, the values of T_c again exhibited a linear dependence upon heating rate. The T_m of Pb, however, followed a square-root dependence upon heating rate. The T_m of Pb extrapolated to zero heating rate was 311.8°C, 15.7°C below the accepted value. The extrapolated value for the T_c of Ni was 343.1°C based upon the TG and 343.55°C based upon the DTG data. Corrections to zero field would probably lower the value of T_c several degrees placing it in excellent agreement with the correction derived from T_m.

(6) Both techniques, T_m and T_c, work well and are in near perfect agreement with each other. The choice of method is best determined by the convenience associated with particular TG apparatus used and the number of calibration points desired.

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