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SOME APPLICATIONS OF THERMOMAGNETOMETRY TO THE STUDY OF CHROMINDUR ALLOYS *

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ABSTRACT

Thermomagnetic experiments are shown to be a useful and rapid technique for studying phase changes involving magnetic materials. Particular examples are chosen from Chromindur II (Fe—28Cr—10.5Co) alloys having different thermal histories. The Curie temperature of the single phase alloy is found to be ~650°C and the metastable spinodal decomposition boundary is at essentially the same temperature. The Cr-rich near equilibrium decomposition product is less magnetic and has a lower T_c, while the Cr-deficient product is more magnetic, with a $T_c \leqslant 720°C$.

Comparisons are made at different heating and cooling rates between temperatures measured using magnetic standards and those measured by a thermocouple in close proximity to the sample.

INTRODUCTION

Recently, high energy magnet alloys have been developed within the Fe—Cr—Co system (Chromindurs). The magnetic properties of these alloys are highly dependent upon their thermal history, and achievement of the optimum properties requires close control of the spinodal decomposition of the alloy.

Thermomagnetometry has been used to determine the Curie temperature (T_c) of various materials [1—3] and conversely to define the temperature scale for thermogravimetric studies by using materials having well-defined values of T_c [4]. Thermomagnetometry is officially [5] defined as "a technique in which the magnetic susceptibility of a substance is measured as a function of temperature while the substance is subjected to a controlled temperature program", but is used herein to refer to conventional thermogravimetry where a relatively weak magnetic field is used to induce the necessary gradient. The observed changes in weight are proportional to changes in the magnetic susceptibility, but the specific relationship is not determined. Under these conditions, the T_c of the phase is evidenced by either a diminution or an enhancement of the weight change, induced by the

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magnetic field, as the temperature is raised or lowered. If there are several magnetic phases present, there will be several such changes in the thermogravimetric curve provided that the phases are not exchange coupled. However, the relative amounts of the individual phases cannot be readily determined without further work [2] since that depends upon the magnetic susceptibility and field strength as well as the amounts of each phase.

Because the useful magnetic properties of these spinodal alloy materials depend upon the nature and degree of the separation of metallurgical phases present, it was felt that thermomagnetometry should provide a rapid sensitive technique to study the alloy system. The method would provide complimentary information to X-ray diffraction studies of changes in the crystal structure and differential scanning calorimetry (DSC) studies [6] which depend upon changes in enthalpy and heat capacity. The sensitivity of each of these techniques for various transitions is markedly different. In order to establish this usefulness, several samples of Chromindur II (Fe—28Cr—10.5Co) [7] having different thermal histories were studied under varying conditions.

EXPERIMENTAL PROCEDURES

Samples

A 300 kg ingot of Chromindur II alloy with a nominal composition of Fe—28Cr—10.5Co was prepared by vacuum induction melting. The ingot was soaked at ~1200°C for 4 h and hot rolled to ~1.2 mm thick sheets. Type I sample was solution annealed at ~930°C/30 min under argon atmosphere and water quenched. Type II sample was given an aging heat treatment after solution annealing and quenching. The aging heat treatment which yields optimum isotropic permanent magnet properties in Chromindur II was employed [7].

Thermomagnetometry

A Perkin—Elmer TGS-1 thermobalance which had been modified [8] to take data in a digital format was used. The temperature was monitored by a Chromel/Alumel thermocouple about 1 mm below the sample pan, and magnetic calibration was performed using standards provided by the manufacturer, i.e. Alumel, nickel, Perkalloy and iron. Argon was passed through a deoxygenating cartridge (Diamond Tool and Die Co.), a column of molecular sieve and finally a submicron membrane filter prior to flowing through the balance and sample compartment at about 40 $\mathrm{cm}^3\ \mathrm{min}^{-1}$.

Chunks of the alloy, 2—7 mg each were used. These underwent an apparent weight gain of about 50% when the small magnet, supplied by Perkin—Elmer for calibration purposes, was in position. Earlier measurements [3] indicated that the field at the sample position was approximately 150 gauss. A wide variety of temperature programs was used. Checks were made using a stronger magnet (850 gauss) while cooling (0.62° C min^{-1}) Type I material and while heating (0.40° C min^{-1}) Type II material. The results for Type II were virtually identical, indicating that factors based upon coercive forces were not complicating the interpretation of that curve. The curve for the slow cooling of Type I material, however, was noticeably sharper, tending towards that observed at faster cooling rates.

RESULTS AND DISCUSSION

Considerable differences are observed between the methods of temperature measurement. Values based upon the thermocouple were consistently higher than those based upon the magnetic calibration. Because the magnetic calibration is related to the actual temperature of the sample and, in fact, is measuring the same experimental process of interest, it has been selected as the basis for the data reported herein. The magnitude of the disagreement is dependent upon the heating rate and direction as shown in Fig. 1. Values presented in Fig. 1 are based upon observations of T_c for Perkalloy during the various calibration experiments. At 596^c C, the value of T_c for Perkalloy falls within the temperature region of interest and thus represents a convenient basis for comparison.

It is presumed that any differences between heating and cooling would disappear at zero rate and therefore the lines for the two modes in Fig. 1 converge at 0° C min^{-1}. The physical arrangement of the sample, thermocouple and furnace in the TGS-1 system as modified herein is such that there is a smaller and more rate independent difference in the two methods of measuring the temperature during the cooling portion of the cycle than during heating. The permanent offset, i.e. even at zero heating rate, is about 20° C. This arises from the diminutive furnace—sample—gas flow arrangement which emphasizes exact thermocouple placement.

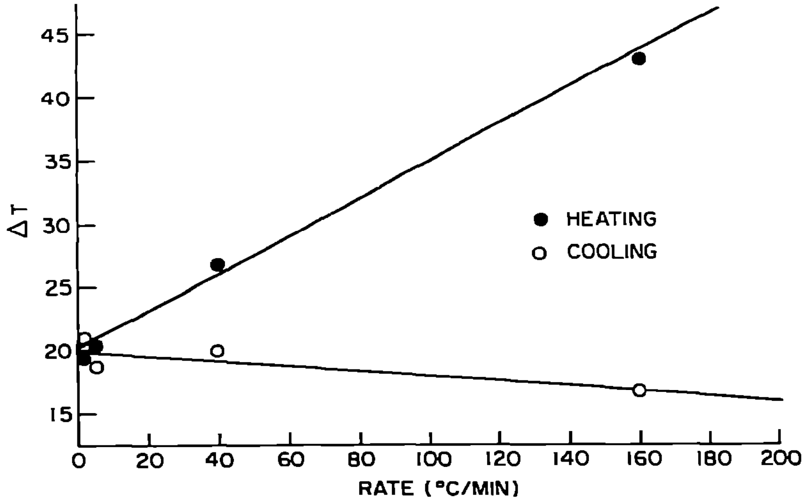

Fig. 1. Temperature differences between thermocouple and magnetic calibration at 596°C as a function of heating and cooling rates.

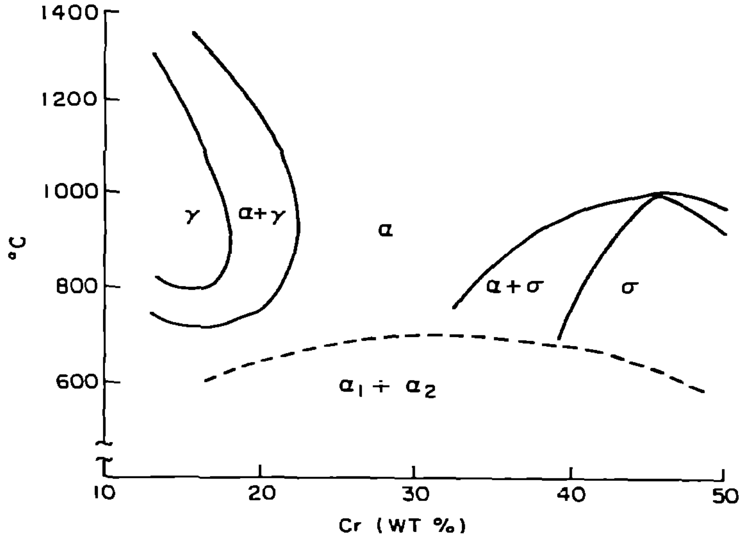

Fig. 2. Approximate equilibrium phase diagram in the Chromindur system (0% Cr = 89.5% Fe + 10.5% Co).

A phase diagram for the metastable system is shown in Fig. 2. Type I sample has been quenched and consists essentially of unstable single phase α material. Upon initial reheating of this material, it will pass through the region of immiscibility and as such will tend to disproportionate into a variety of α_1 and α_2 metastable spinodal phases depending upon the kinetics of the system and the heating rate. At longer times they will convert to more

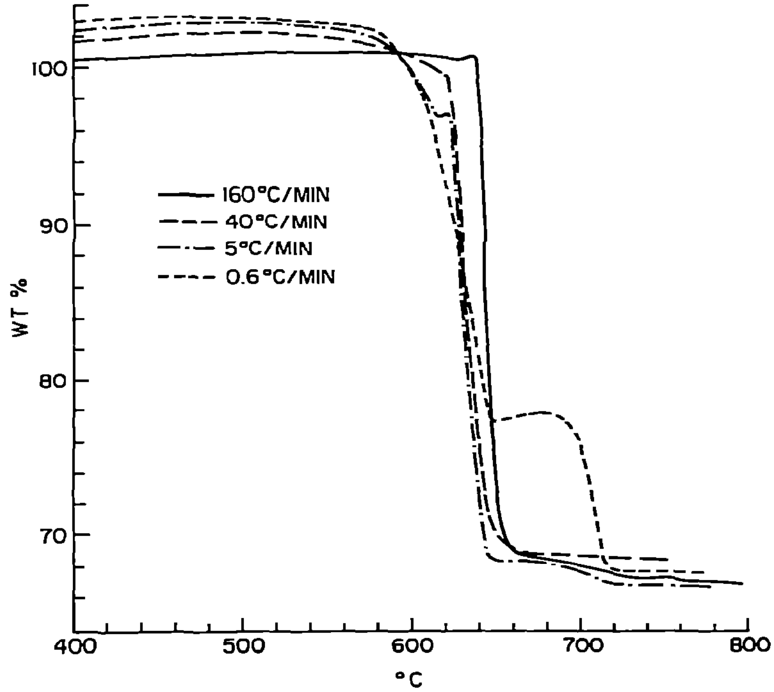

Fig. 3. Thermomagnetometric curves for Chromindur II (Type I) at various heating rates.

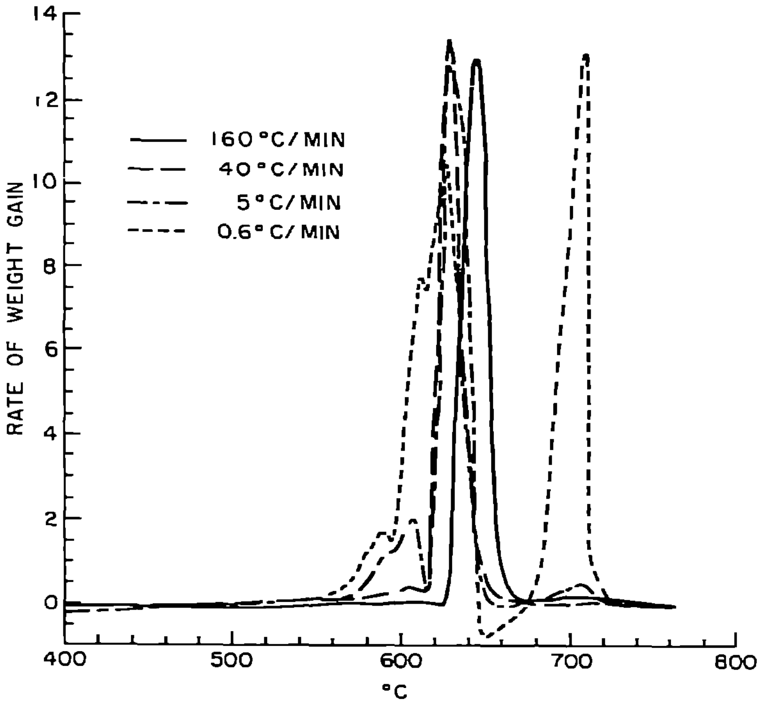

Fig. 4. Differential thermomagnetometric curves for Chromindur II (Type I) at various heating rates.

stable phases with greater compositional differences. As the temperature increases, the α_1 and α_2 phases will eventually redissolve. Of course, the rate of solution of the metastable spinodal phases should be much greater than that of the phases closer to equilibrium. The actual extent of the σ phase field is not well established. The σ phase is presumed to be weakly magnetic above room temperature.

Figures 3 and 4 show results obtained for the initial reheating of Type I materials at various rates. In Fig. 3 the various sample weights have been normalized by plotting weight %. The differential curves herein have an arbitrary ordinate scale in order to make the peak heights of comparable size and thus facilitate comparison. The fastest heating rate, 160°C min^{-1}, should minimize the extent of the spinodal decomposition and hence give a curve most representative of the pure α phase. Indeed, this is obvious in Figs. 3 and 4 where the apparent weight loss at 640—650°C is overwhelmingly predominant. The sharpness of the transition is also evident. A T_c of 650°C is therefore assigned to the single phase α alloy.

As the heating rate is decreased, the extent of α_1 and α_2 formation should increase, resulting in the maximum variation in composition between the two phases. Since the spinodal decomposition results in phases of higher and lower Cr content than the parent, α, alloy, there should be apparent weight losses at higher temperatures depending upon the magnetic properties of the various α_1 and α_2 phases. If the time/temperature relationships are favorable, then the phases closer to equilibrium may nucleate and grow and the separation of properties should be even greater. This is particularly evident for the alloy heated at the slowest rate, 0.62°C min^{-1}. As anticipated, intermediate heating rates show less of this resolved behavior; therefore, a rapid (e.g. 160°C min^{-1}) thermomagnetometric experiment will quickly reveal whether the alloy had previously undergone significant spinodal decomposition during its prior thermal history.

For the spinodal region, where the separation of phases is <1000 Å and the phases form a continuous network, only the higher T_c should be observed. The strong exchange coupling with the phase having the higher T_c will prevent the demagnetization of the other phase. This should also be reflected in other measurements, e.g. DSC or Mossbauer spectroscopy. When the nucleation and growth beyond ~1000 Å of the phases approaching equilibrium have had time to occur, then separate T_c's associated with each phase should be discernible.

If the experiments in Figs. 3 and 4 are continued by holding briefly (5—50 min) above 750°C and then cooling at the same rates as they were heated, the curves shown in Figs. 5 and 6 are obtained. The brief hold at high temperature is sufficient to bring all of the spinodal decomposition products back into solution. Cooling at the faster rates (40 and 160°C min^{-1}) does not allow for significant phase separation, and cooling curves similar to pure calibration materials are obtained. The T_c of ~650°C is again verified for the α phase. However, cooling at 5 and 0.62°C min^{-1} is sufficiently slow that the spinodal decomposition and perhaps some further intermediate or equilibrium phase formation has an opportunity to occur and the curves show considerable distortion, particularly at 0.62°C min^{-1}. The higher temperature peak in Fig. 6 at the slowest cooling is indicative of some high temperature intermediate or equilibrium phase (weakly magnetic) formation which gradually converts to lower temperature phases at longer times and lower temperatures. If the products were simply α or α_1 and α_2, then one would expect a rapid gain in weight at either the T_c of α or at the spinodal decomposition. However, it might be possible that the spinodal products initially formed at this slow heating rate have a microstructure which is difficult to align at low magnetic fields. This is consistent with the more pronounced change noted earlier at higher fields. The progressive increase in weight at low temperatures could be due to the conversion of this unfavorable microstructure into a more favorable spinodal microstructure or to phases closer to equilibrium.

There may be preferential alignment upon cooling in the presence of a magnetic field; however, the exaggerated apparent peak in the weight gain near 600°C for the sample cooled at 5°C min^{-1} in Fig. 5 is puzzling. It is reproducible, as are all the curves shown herein. It suggests a temporary period where a more magnetic intermediate phase exists, perhaps the initial nonequilibrium spinodal products, or the peak may be the artifact resulting from a temporary microstructure.

If these samples which have been through an initial heating/cooling cycle are cycled a second time at the same rates, the heating curves are markedly different since they are no longer the nearly pure α phase present originally. They are now the products of their cooling rates. The rapidly cooled samples are again very predominantly α material but those cooled slowly have undergone extensive decomposition. Consequently, upon reheating,

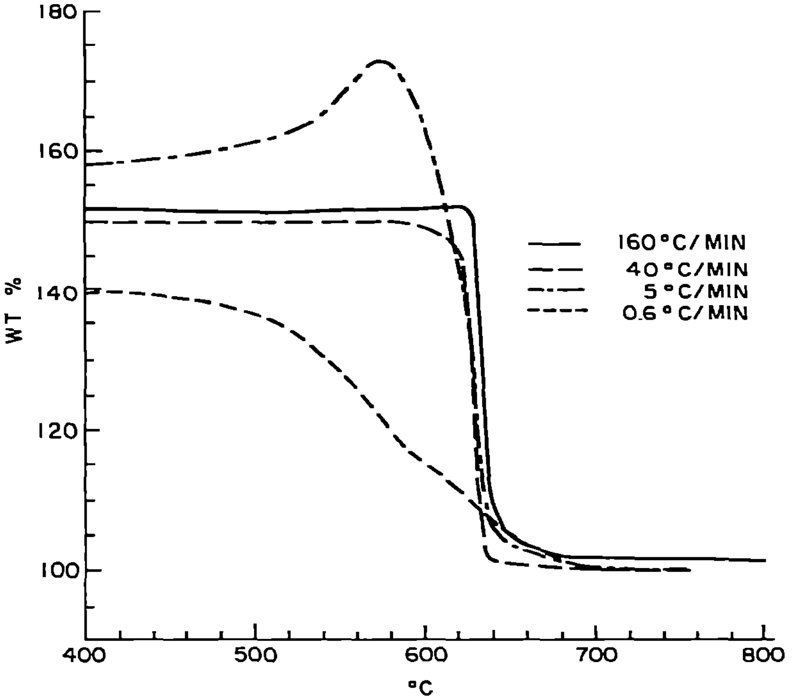

Fig. 5. Thermomagnetometric curves for Chromindur II (Type I) at various cooling rates.

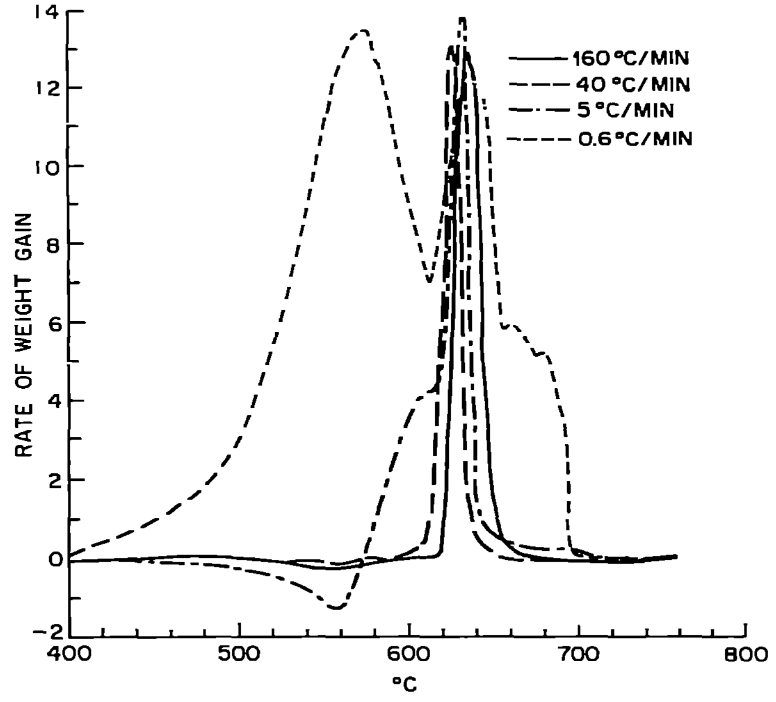

Fig. 6. Differential thermomagnetometric curves for Chromindur II (Type I) at various cooling rates.

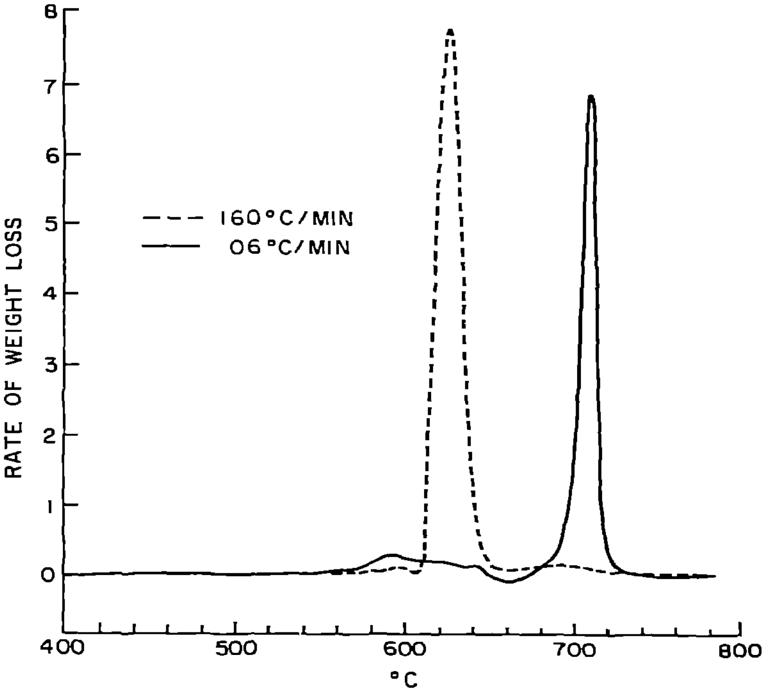

Fig. 7. Differential thermomagnetometric curves for Chromindur II (Type I) upon reheating at several rates.

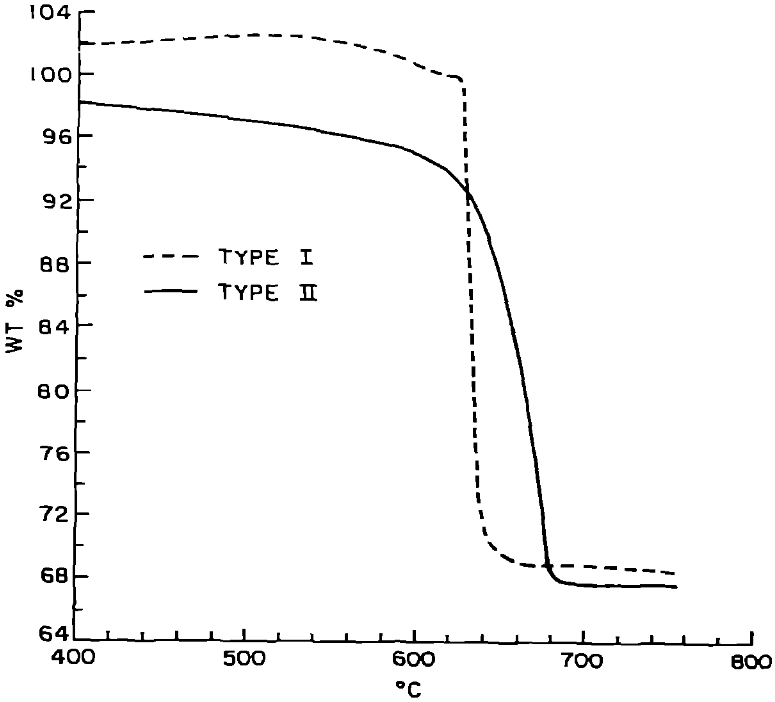

Fig. 8. Thermomagnetometric curves of Types I and II Chromindur II heated at 40°C min^{-1}.

the effects observed in the initial heating (Figs. 3 and 4) are exaggerated. The differential plots are shown in Fig. 7 for the extremes in the heating rates. Clearly the sample that has passed through the immiscibility region three times at the slow rate (solid curve) has completely converted to the low temperature intermediate or equilibrium products which are slow to redissolve. It is also clear from the small peak in the solid curve that the phase of $T_c \approx 590°C$ is probably less magnetic than the phase with $T_c \approx 715°C$. This is consistent with the diagram in Fig. 2 where one phase is low in Cr and the other rich in Cr. Not only is the low Cr phase expected to be more magnetic, but also, assuming the sample is to the left side of the peak in the immiscibility curve, there will be more of it. The T_c of the latter phase may actually be higher, and the observed weight loss associated with dissolution rather than a magnetic transition. Inferences regarding the relative magnetic strengths of the phases depend upon the relative amounts of each present. The sample heated at 160°C min^{-1} shows detectable but slight decomposition, as evidenced by the small peak near 700°C in Fig. 7.

Type II material has been previously heat treated to obtain optimum magnetic properties and therefore is not single phase α. This is evident from Figs. 8 and 9 which compare the initial heating curves, at a relatively rapid rate of 40°C min^{-1}, with the analogous curves in Figs. 3 and 4 for the single phase sample. Type II material has an apparent T_c value which is displaced towards higher temperature. This is evidence of the extensive spinodal decomposition which has been carefully controlled during the previous heat treatment. A more rapid heating at 160°C min^{-1} shifts the curve even more toward higher

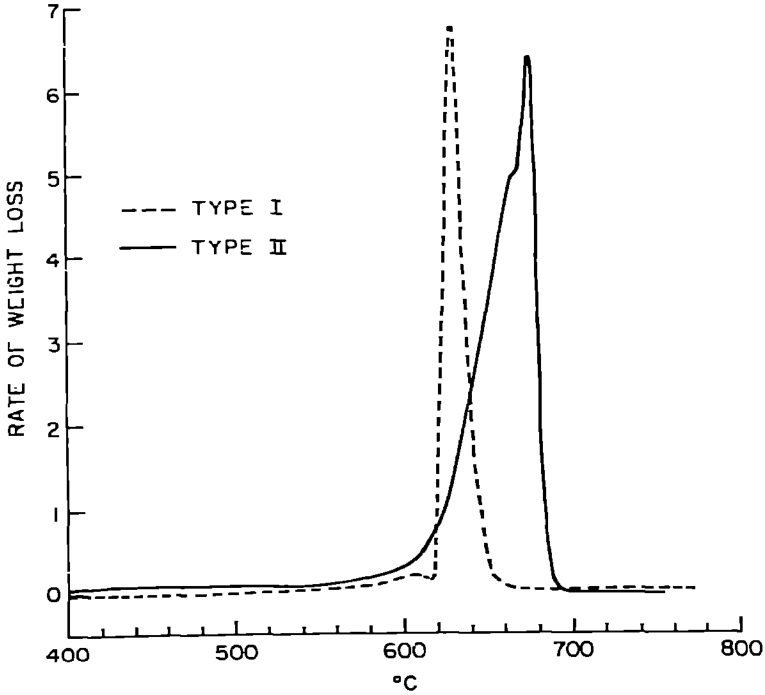

Fig. 9. Differential thermomagnetometric curves of Types I and II Chromindur II heated at 40°C min^{-1}.

temperatures. Obviously one of the spinodal products is low in Cr and has therefore a high T_c. What this magnetic curve measures is more related to the dissolution rate of the spinodal products than to the T_c of this phase. The earlier discussion pointed out that the T_c of the spinodal mixture is that of the phase with the highest T_c. When the heating was interrupted and the sample held around 650°C, the apparent weight decreased as the spinodal products dissolved. It did, however, increase again with time as equilibrium phases formed.

CONCLUSIONS

(1) Thermomagnetometry is a rapid simple technique for following phase equilibria in systems involving magnetic materials.

(2) In the Chromindur II system, the temperature for the onset of the spinodal decomposition is close to the T_c of the undecomposed α phase.

(3) The spinodal decomposition products rapidly redissolve at temperatures above ~650°C and little decomposition occurs during rapid cooling, i.e. $\geqslant 40°\text{C min}^{-1}$. When cooling slowly at $0.62°\text{C min}^{-1}$, there is formation of a microstructure which is more difficult to magnetize or a weakly magnetic intermediate or equilibrium phase by the time T_c of the parent, α, material is reached.

(4) T_c for the pure α material is ~650°C.

(5) The Cr-rich intermediate or equilibrium product of the low temperature decomposition is less magnetic and the T_c may be as low as 590°C. The Cr-deficient phase is more magnetic and the T_c value is $\leqslant 720°\text{C}$.

(6) Correlation was made between temperatures measured in the TGS-1 thermobalance based upon a thermocouple in close proximity with the sample pan or those based upon calibrations using magnetic standards. The difference between these temperatures increases with increasing heating rate but decreases with increasing cooling rate.

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