A major purpose of the Technical Information Center is to provide the broadest dissemination possible of information contained in DOE's Research and Development Reports to business, industry, the academic community, and federal, state and local governments.

Although a small portion of this report is not reproducible, it is being made available to expedite the availability of information on the research discussed herein.

1

$C_{ONF}-831174--78$

LA-UR--84-136

DE84 006013

TITLE: ISOTHERMAL CALORIMETRIC INVESTIGATION OF A REVERSIBLE REACTION
IN RAPIDLY SOLIDIFIED $Fe_{40}Ni_{40}B_{20}$

AUTHOR(S): J. R. Cost
R. O. Elliott
J. T. Stanley

SUBMITTED TO: Proceedings of Symposium
Rapidly Solidified Metastable Materials
Boston, Mass., Nov. 15-17, 1983

Los Alamos
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

ISOTHERMAL CALORIMETRIC INVESTIGATION
OF A REVERSIBLE REACTION IN RAPIDLY SOLIDIFIED $Fe_{40} Ni_{40} B_{20}$

J.R. Cost. R.O. Elliott[a]. and J. T. Stanley[b]
Los Alamos National Laboratory. Los Alamos. N M. 87545. USA
[a]Consultant. [b]On sabbatical leave from Arizona State University Tempe. AZ

ABSTRACT

A new method is described for isothermal calorimetric measurement of time-dependent reversible reactions in which the rate of heat flow is small compared to the noise and zero drift of the measurement. Results using this method are presented which measure enthalpy changes associated with reversible phase changes in a rapidly solidified $Fe_{40} Ni_{40} B_{20}$ alloy.

INTRODUCTION

Studies of reversible phase changes induced by relatively small changes in temperature provide an important method for furthering our understanding of kinetic phenomena in rapidly solidified alloys. Typically. time-dependent phase changes are monitored isothermally by measurement of some physical property such as electrical resistance. elastic modulus. or density Isothermal measurements of the enthalpy changes concomitant with the transformations have not been widely used to study the kinetics because calorimetric techniques measure the rate (as opposed to the amount) of heat flow so that accurate determination of enthalpy changes is not possible unless the reaction occurs relatively rapidly. For example. Scott et al [1]. in a study of reversible relaxation to a new state of short-range order in amorphous $Fe_{40} Ni_{40} B_{20}$. report isothermal calorimetric measurements at 380°C and 330°C which show heat flow but. because the effect is so small. do not allow either the magnitude of the enthalpy change or the kinetics of the reaction to be determined.

The problem of making calorimetric measurements to monitor phase changes which occur with relatively long time constants can best be understood by assuming an example of simple exponential decay toward a new enthalpy state following a change in temperature at $t=0$.

$$\Delta H(t) = \Delta H_{tot} \left[1-\exp(-t/\tau)\right] \tag{1}$$

where ΔH_{tot} is the total enthalpy change and τ is the time constant for the reaction. The rate of this reaction. which is what is measured by the calorimeter. is

$$d\Delta H(t)/dt = \Delta H_{tot} \exp(-t/\tau)/\tau . \tag{2}$$

Because the rate of heat release is inversely proportional to the time constant τ. then when the latter becomes large. as it does at low temperature. the calorimeter signal becomes increasingly small until it becomes lost in the experimental noise of the measurement. This inability to follow reactions with long time constants is unique for calorimetric measurments compared to other physical properties. Because of this difficulty. special techniques must be used if reaction kinetics are to be studied calorimetrically. The primary purpose of this paper is to describe and demonstrate such a special technique for the reversible reaction which we have observed in as-crystallized $Fe_{40} Ni_{40} B_{20}$.

METHOD

Melt-spun metallic glass alloy with nominal composition $Fe_{40} Ni_{40} B_{20}$ was supplied as 6 mm-wide ribbon of roughly 25 μm thickness compliments of Allied Chemical. Calorimetric measurements were made on a single disc-shaped sample roughly 3 mm in diameter. Before measurement the sample was given a pre-anneal for 60 minutes at 360°C which caused crystallization as indicated by x-ray measurements. Diffraction lines were observed which which were consistent both with the phases $(Fe/Ni)_{23} B_6$ and γ-Fe/Ni reported for this alloy by Gerling and Wagner [2] and with $(Fe/Ni)_3 B$ reported for the crystallized glass $Fe_{50} Ni_{30} B_{20}$ by Walter et al [3].

Calorimetric measurements were made with a Perkin-Elmer DSC-2 differential scanning calorimeter equipped with an intercooler attachment to give optimal baseline stability for isothermal operation. The analog signal of heat flow rate versus time was monitored with a chart recorder. Measurements were made according to the following temperature schedule: After the pre-anneal the sample was cycled between two temperatures. a holding or annealing temperature of either 250°C or 300°C. and a measuring temperature of 360°C. At the former temperature the sample was held for a variable hold time. t_{hold}, ranging from less than one minute to more than 12 hours. During annealing at this holding temperature. the reaction approaches its equilibrium value to an extent depending upon t_{hold}: however. the heat release rate at this temperature was only just measurable and then only during the initial time of the reaction. Thus no attempt was made to study the heat release during t_{hold}. After each anneal at the holding temperature the sample was rapidly heated to the measuring temperature. (All temperature changes were made at the maximum heating rate of the calorimeter, 320°C/minute.) At the measuring temperature of 360°C it was determined that the new equilibrium was established relatively rapidly (≤ 60 minutes) and importantly. the rate of heat absorption was of sufficient magnitude so that it could be measured during this period and subsequently integrated to obtain the magnitude of the heat. ΔH. Thus the net result of this measurement procedure was that after each measurement at 360°C the sample was returned to the same initial state so that a later anneal at T_{hold} and measurement at 360°C gave a point on the plot of $\Delta H(t)$ vs time. This allowed the enthalpy changes associated with the reaction to be followed.

RESULTS

Fig. 1 shows a plot of the rate of heat absorption. dH/dt versus time at the measuring temperature of 360°C for the sample held at $T_{hold} = 300°$ for four different hold times. To correct for instrumental transients. each of these curves has had a zero hold-time curve (obtained by cooling to 300°C followed by immediately heating to 360°C) subtracted from it. This relatively small correction was particularly important for the heat absorption measurements after short hold-times. e.g.. the curve for $t_{hold} = 10$ minutes. It is clear that this heat absorbed at the measuring temperature is due to heat being released at the holding temperature as the specimen approaches the equilibrium state associated with lower temperature. It may be observed in Fig. 1 that the rate of heat absorption at 360°C decays roughly exponentially with time in agreement with Eq. 1. Also. there is measurable heat absorption for hold times as low as 10 minutes. indicating that at the 300°C hold temperature some of the reaction toward the new equilibrium was taking place even for relatively short times. The maximum value for the heat absorption rate in Fig. 1 of roughly 0.02 mcal/s represents roughly 20% of full scale on the chart recorder with the calorimeter at its optimal sensitivity. Since this signal had noise which was roughly 2% of full scale. there is appreciable uncertainty in the results shown in Fig. 1.
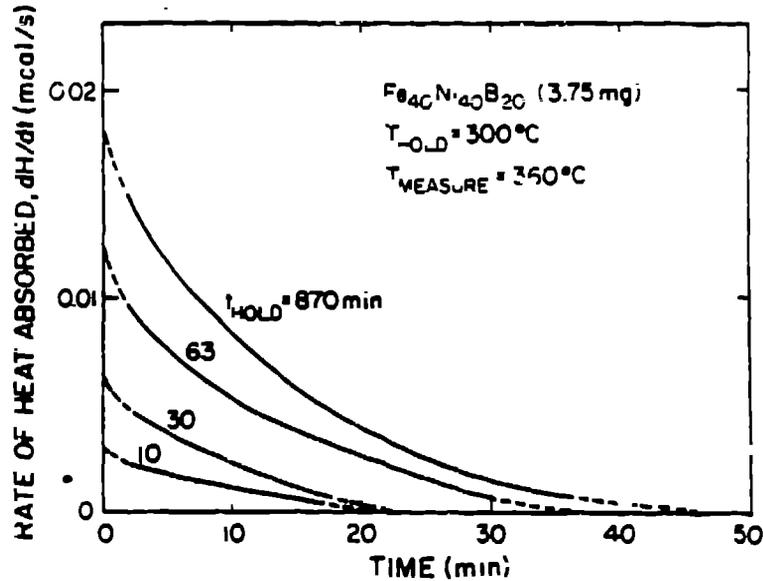
FIG. 1. Curves of rate of heat absorption. dH dt. versus time of measurement at 360° for four different holding times at 3C0°C.

It is possible to obtain the integral under the curves in Fig. 1 as a function of the time of measurement and thus obtain a plot of the enthalpy change with time Such a plot is shown in Fig. 2. Here it may be seen that the heat absorption reaction at 360°C is complete after roughly 30 minutes for all four different nold times. It snould be noted that the curves shown in Fig. 2 are not known with particularly good accuracy. This is because of uncertainty in the differential curves, especially during the early part of the measurement. A rough indication of the kinetics of the heat absorption is obtained by measurement of $t_{1,2}$, the time required for the heat absorption to decrease to 1/2 of the initial value. In Fig. 2 these times have oeen marked on the curve for each hold time; they vary between roughly 6 and 8 minutes. Interestingly, this time increases with increasing hold time. This can be understood in terms of the reaction kinetics being governed by a spectrum of time constants so that as t_{hold} at 300°C is increased. the approach to the new equilibrium at that temperature includes the contributions to the reaction which have longer time constants.
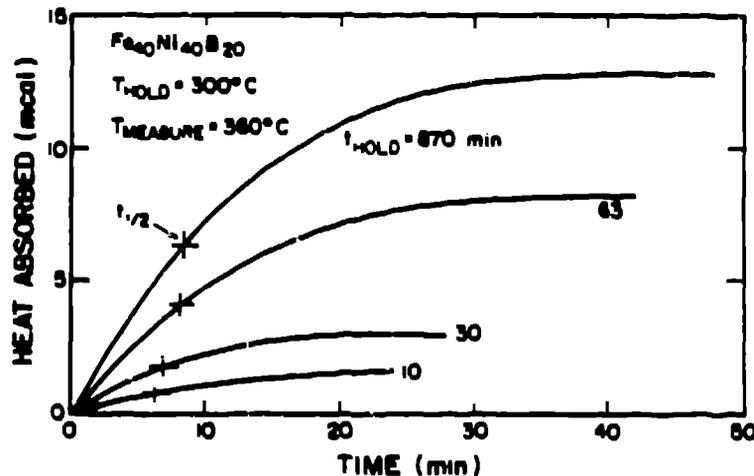

FIG. 2. Curves of heat absorbed versus time of measurement at 360°C for four different holding times at 300°C. Each curve was obtained by integrating the app·opriate

It is important to know the extent of the approach to equilibrium while holding at 300°C. A measure of this is obtained from the saturation values of the curves in Fig. 2. This total heat absorbed for each of the various hold times is also the heat that was released during the anneal at 300°C as the specimen approached equilibrium at that temperature. Fig. 3 shows a plot of this heat absorbed at the measuring temperature for the various hold times at 300°C. Also shown is a similar curve for a holding temperature of 250°C which was obtained using the same method with the same sample. The two curves in Fig. 3 both show the same general form for the heat absorption. a fairly rapid increase with the sample held for short hold times and then a decrease in the rate at longer times. For the rapid enthalpy increase at short hold times. there are insufficient data to be able to characterize rate constants for the enthalpy change. For the longer hold times. the fact, that both curves appear to be approaching saturation values suggests that the sample was close to the equilibrium at both holding temperatures.
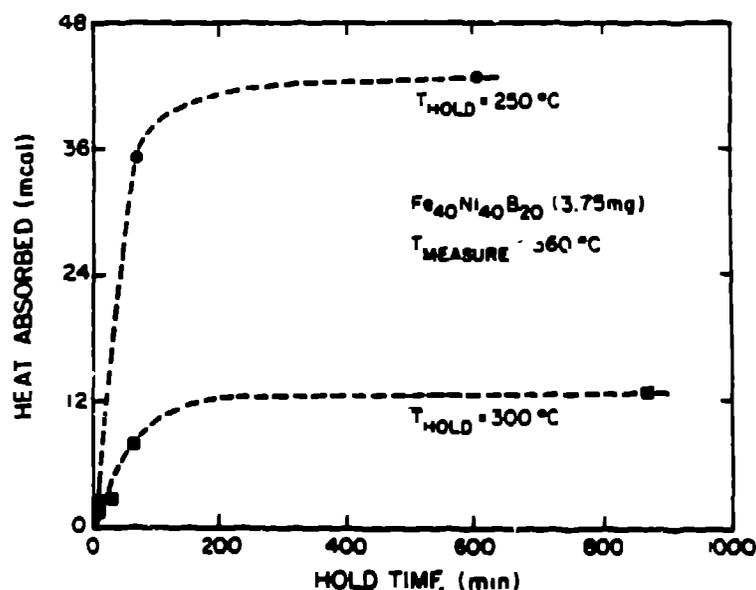

FIG. 3. Total heat absorbed (as given by final value in Fig 2) versus holding time for holding temperat. es of 250°C and 300°C.

DISCUSSION

Assuming that equilibrium is established for the long hold times in Fig. 3, we can then obtain the enthalpy changes between the holding and the measuring temperatures. For the holding temperatures of 300°C and 250°C the enthalpy changes are 165 cal/mole and 550 cal/mole. respectively. These values certainly include appreciable experimental error reflecting the above-mentioned experimental uncertainty.

We believe that the most probable mechanism for the reversible reaction that we see in the crystallized alloy is long-range ordering in the γ-Ni$_{50}$ Fe$_{50}$ [2] crystallites that form in this alloy. Brosson [3] determined the critical temperature for long-range order in Ni$_{50}$ Fe$_{50}$ to be 321°C. The relative amounts of heat release for equilibration at 250°C and 300°C fit reasonably well with a Bragg-Williams treatment of long-range order based on a critical temperature of 321°C. The only thing that doesn't fit well with the assumption of long-range order is the reaction rate. In order to establish long-range order in the bulk crystalline alloy it was necessary to introduce excess vacancies by neutron irradiation [3]. A possible explanation of the rapid reaction rate in the crystallized alloy is that excess vacancies are introduced by movement of dislocations during heating or cooling to relieve stresses generated by differential thermal expansion.

It's interesting to note that this reversible reaction in the crystallized melt-spun alloy follows kinetics which are similar to those reported for reversible changes of short-range order in amorphous melt-spun alloys. Because of this it is particularly important that the condition of the sample after completion of the various heat treatments be determined as either crystalline or amorphous by some definitive technique.

CONCLUSION

An isothermal calorimetric technique for determining enthalpy changes associated with reversible reactions with long time constants has been described and demonstrated. This method has been applied in an investigation of crystallized melt-spun $Fe_{40} Ni_{40} B_{20}$ to obtain time-dependent enthalpy changes believed to be due to long-range ordering of the γ-Fe/Ni phase.

ACKNOWLEDGMENTS

REFERENCES

1. M.G. Scott and A. Korsumovic. Acta Metall. 30. 853 (1982).
2. R. Gerling and R. Wagner. Scripta Metall. 17. 1129 (1983).
3. P. Brosson. Thesis. Faculty of Sciences, University of Grenoble. Oct. 1966.