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USE OF TEMPERATURE CHANGE EXPERIMENTS IN CALORIMETRY

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ABSTRACT

This paper discusses the applications of temperature change experiments in calorimetry. The activation energy of crystallization which is an important parameter for metallic glasses can be determined for small temperature intervals. In addition the activation energy can be determined as a function of the transformed volume. Since no additional apparatus is required, temperature change experiments are a simple and effective extension to other techniques of studying crystallization.

INTRODUCTION

Several techniques are available to study crystallization; thermal analysis shows the development of the process macroscopically but cannot study or provide microscopic detail. The metallographic and electron optical analysis reveal local details but are not suitable for observing changes with time; hot stage experiments cannot be considered representative as only surface effects are observed. Hot stage X-ray methods indicate which phases occur but give no information on the morphology. Simulating can take time into account, produce statistically reliable information on phases and morphology but make statements on the local distribution.

The present work considers the various methods of thermal analysis.

EXPERIMENTAL

Transformations can be studied differentially (DSC) or integrally (TMS, TGS). The results are the same within experimental limits (see Fig. 1) and agree with metallographic work, Fig. 2. The experiments can be conducted isothermally, continuously or involve temperature changes. Hitherto two techniques have been used (ref.1,2).

From isothermal measurements it is possible using the equation by Johnson, Avrami and Mehl (ref.3,4)

$$- \ln (1 - Z(t)) = (t/\tau)^n \qquad (1)$$

to determine the time constant n. Combining several measurements the activation energy ΔH, and time constant τ can be determined.

$$\tau = \tau_o \exp \frac{\Delta G}{RT} = \tau_o^* \exp \frac{\Delta H}{RT} \qquad (2)$$

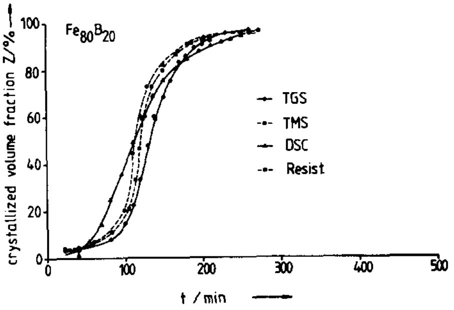

Fig. 1. Crystallized volume fraction as function of time for different measuring methods, $Fe_{80}B_{20}$, T = 665 K.

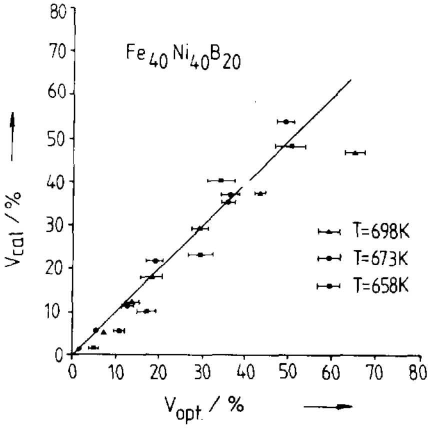

Fig. 2. Correlation between optical and calorimetrical determined volume fractions for different isothermal crystallization temperatures, $Fe_{40}Ni_{40}B_{20}$.

The second method is based on curves obtained by continuously heating and evaluated by Kissinger (ref.5). The activation energy is calculated from the equation

$$\ln(\frac{T_p^2}{T}) = \frac{\Delta H}{RT_p} \qquad (3)$$

The method was further developed for example by Ozawa (ref.6). Recently two other methods have been developed: a) Cao et al. (ref.7) which is based on a segmentation of the Johnson-Avrami-Mehl curve and b) temperature change technique which will be developed below. The method is similar to the isothermal method. After a certain isothermal anneal the temperature is suddenly changed by 5 - 10 °C (Fig. 3). The crystallization rate $\dot{z}$ changes correspondingly as

$$\dot{z} = F \cdot \exp - \frac{\Delta H}{RT} \qquad (4)$$

where F is assumed to be a temperature independent parameter.

At the point of the temperature change

$$\ln\left(\frac{\dot{z}}{\dot{z}_2}\right) = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{5}$$

The relationship of the two crystallization rates $\dot{z}_1/\dot{z}_2$ corresponds to the rate of the distances v_1 and v_2. These can be taken from the curves, Fig. 4. If several temperature changes are made the activation energy can be determined as function of the volume fraction transformed.

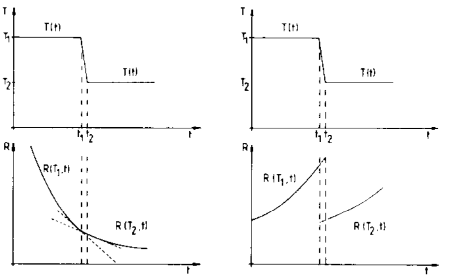

Fig. 3. Schematic drawing of the temperature change experiment.

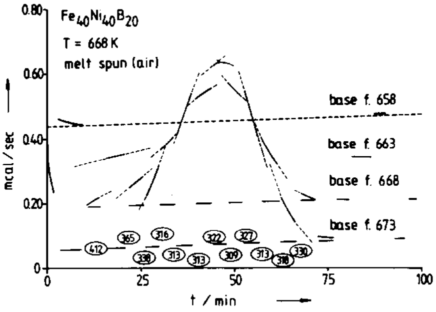

Fig. 4. Temperature change experiment for $Fe_{40}Ni_{40}B_{20}$. 330 means the activation energy at this time is 330kJ/mol.

RESULTS AND DISCUSSION

The results for binary Fe-B alloys are presented in Figs. 5 and 6. For single stage crystallization ($Fe_{75}B_{25}$) the activation energy becomes constant after about 15 %. The initially high value indicates that a nucleation term is included. In the case of $Fe_{85}B_{15}$ the crystalliation is two stage. After primary crystallization is complete the activation energy increases strongly as the second phase also requires nuclei. Thereafter the activation energy falls to a constant value. The transition from one to multistage transformation is clearly recognisable in temperature change experiments. This is not the case in other methods.

A further advantage is the possibility of determining the activation energy as function of temperature. Figs. 7 and 8 show that this is very important for some alloys. Whereas the activation energy for $Ni_{81}P_{19}$ increases only slightly with the temperature, large steps are observed for $Fe_{40}Ni_{40}B_{20}$. It has been shown by TEM (Fig. 9) and Mößbauer experiments that on increasing the temperature the phases form in a different sequence. Above 685 K an ordered γ-Fe-Ni was observed by both methods. On the other hand between 670 and 675 K essentially a change in the crystallizing phase was observed. Methods, used hitherto, do not reveal this effect as only an average activation energy of the total process can be determined.

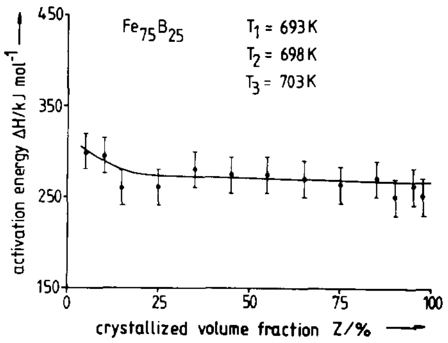

Fig. 5. Activation energy as function of time for $Fe_{75}B_{25}$. The temperature was changed between T_1, T_2 and T_3.

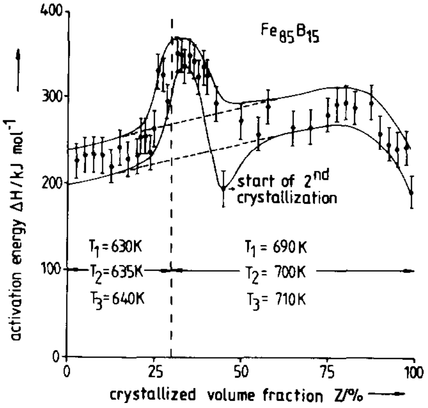

Fig. 6. As Fig. 5 for $Fe_{85}B_{15}$.

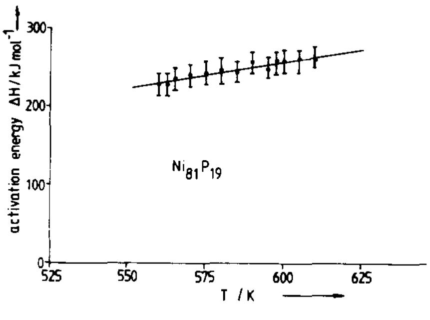

Fig. 7. Activation energy as function of temperature for $Ni_{81}P_{19}$.

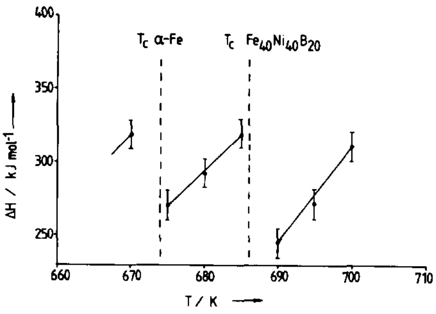

Fig. 8. Activation energy as function of temperature for $Fe_{40}Ni_{40}B_{20}$.

CONCLUSIONS

The temperature change technique has the advantage that the activation energy of crystallization can be determined as function of volume fraction of the crystallized material. This can be very important in some systems to characterise the crystallization behaviour, eg $Fe_{40}Ni_{40}B_{20}$. Without the results of temperature change measurements the results of other techniques would have probably been incorrectly interpreted, although the results usually agree. (cf Table 1). In principle temperature change experiments can be applied to other materials eg polymers.

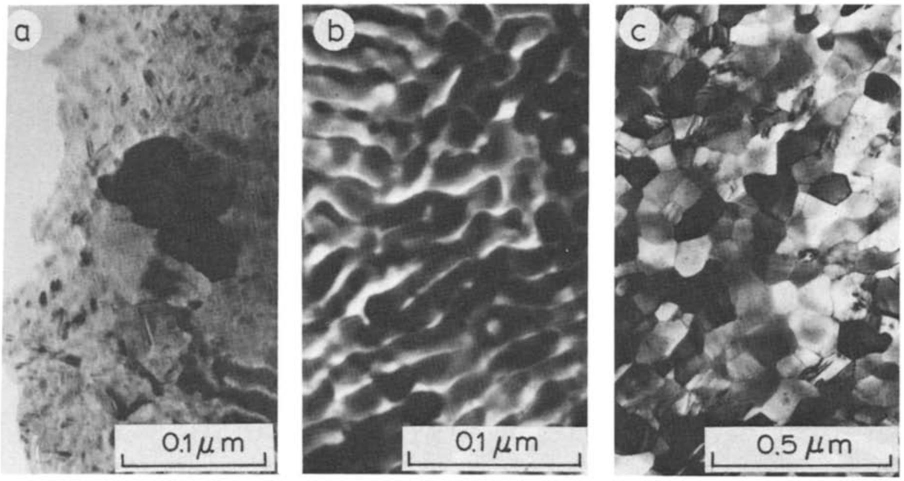

Fig. 9. Microstructure of crystallized $Fe_{40}Ni_{40}B_{20}$
a) eutectic with primary crystals of γ-(Fe, Ni) b) eutectic c) $(Fe, Ni)_{23}B_6$

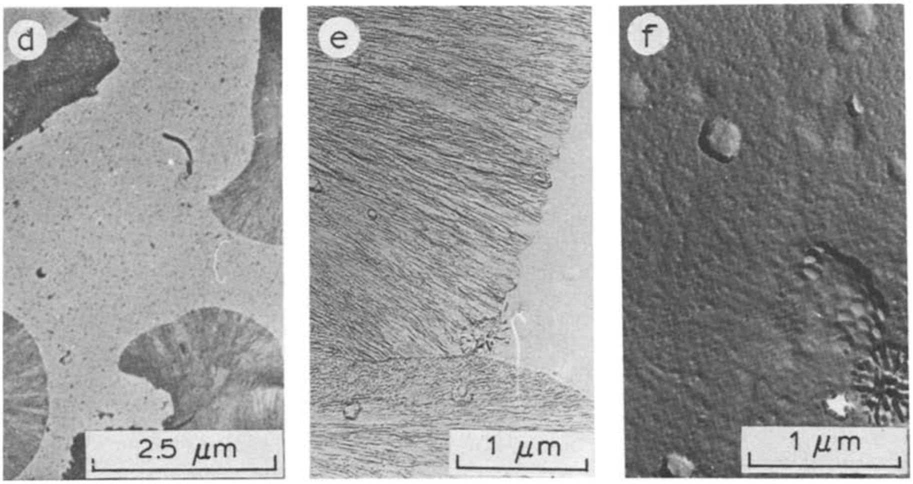

Fig. 9. d) replica e) enlargement of d) eutectic cell
f) as e) between the eutectic cells.

TABLE 1

Comparison of crystallization temperature, reaction constant, time exponent, hardness and activation energies of crystallization determined by different methods.

Alloy	T_x K	τ_o s	m	$\Delta H_{T.C.}$ kJ/mol	$\Delta H_{P.S.I.}$ kJ/mol	ΔH_{ISO} kJ/mol	$HV_{0,05}$ N/mm²
60A($Ni_{81}P_{19}$)	601	10^{-18}	4	245	241	240	672
$80A_I$ ($Ni_{68}Cr_{14}B_{18}$)	680	10^{-22}	2	323	328	312	935
$80A_{II}$ ($Ni_{68}Cr_{14}B_{18}$)	713	10^{-26}	3	364	368	370	---
$Fe_{40}Ni_{40}B_{20}$(air)	694	10^{-24}	3-4	350	374	350	985
$Fe_{40}Ni_{40}B_{20}$(vac)	690	10^{-22}	3	330	344	318	1000
$Fe_{41}Cr_{40}C_{19}$	830	---	-	---	451	---	1503
$(Fe_{75}Cr_{25})_{83}B_{17}$	795	10^{-22}	6	293	397	356	1120
$(Fe_{95}Cr_{5})_{83}B_{17}$	736	10^{-20}	4	280	288	304	920
$(Fe_{95}Mo_{5})_{83}B_{17}$I	743	10^{-20}	2	339	320	322	1050
$(Fe_{95}Mo_{5})_{83}B_{17}$II	802	10^{-25}	3	413*	564	414	---
$(Fe_{95}W_{5})_{83}B_{17}$I	764	10^{-25}	2	330	320	394	1155
$(Fe_{95}W_{5})_{83}B_{17}$II	821	10^{-34}	3	576	582	554	---

* 590 kJ/mol was found for the start of the 2. crystallization

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