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STUDIES OF THE CRYSTALLIZATION PROCESSES OF AMORPHOUS ZR-CO BASED ALLOYS BY DSC.

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SUMMARY

Kinetic parameters for the crystallization of amorphous $Zr_{0.67}Co_{0.33}$, $Zr_{0.67}Co_{0.28}P_{0.05}$ and $Zr_{0.67}Co_{0.27}Si_{0.06}$ have been determined with DSC-technique by three different methods: (i) isothermal data obtained from the Johnsson-Mehl-Avrami equation; (ii) isothermal data obtained from plots of ln $t_{max.}$ *versus* the annealing temperature; (iii) non-isothermal data derived from Kissinger plots. The derived parameters variation with the method applied and with the composition are discussed.

INTRODUCTION

It is well known that metallic glasses can be formed by rapid solidfication of melts and that they possess many properties beneficial for technical applications. Thus some amorphous alloys exhibit superior magnetic and/or mechanical properties, while others are less sensitive to oxidation than conventional alloys. One disadvantage is, however, the metastable character of the amorphous alloys, *i.e.* their tendency to transform to thermodynamically stable crystalline phases. It is also well known that many mechanical and physical properties of materials are set by their microstructures. Materials with favourable microstructures can thus also be obtained by controlled annealing of amorphous alloys.

In view of this, studies of factors affecting the thermal stability and the crystallization mode of metallic glasses are of great importance. In this article we will discuss the crystallization process of three different amorphous alloys: $Zr_{0.67}Co_{0.33}$, $Zr_{0.67}Co_{0.28}P_{0.05}$ and $Zr_{0.67}Co_{0.27}Si_{0.06}$. The kinetics of the transformation from the amorphous to the crystalline state are expected to be governed by polymorphic growth of pre-existing nuclei and/or of nuclei generated during the annealing, since solid solutions occur in the systems $Zr_{0.67}Co_{0.33-x}M_x$ with M = Si and P and for $x \lesssim 0.10$ in the crystalline state (1, 2, 3). Thus, studies of the crystallization of these alloys should yield information about how incorporation of glass-forming agents such as Si and P into an alloy which already forms glasses readily influences the thermal stability and the kinetics of crystallization. Kinetic parameters can be evaluated from determinations of the volume fraction transformed, α, as a function of time (t, isothermal annealing experiments) or temperature (T, non-isothermal experiments). The differential scanning calorimetry technique has been used to determine $\alpha = f\ (T, t)$, using both isothermal and non-isothermal conditions. The as-quenched materials and the phases formed upon crystallization have been characterized by means of X-ray diffraction techniques.

EXPERIMENTAL

Master alloys of compositions $Zr_{0.67}\ Co_{0.33}$-, $Zr_{0.67}\ Co_{0.28}\ P_{0.05}$ and $Zr_{0.67}\ Co_{0.27}\ Si_{0.33}$ were prepared from appropriate mixtures of Zr (3N5), Co (3N5), Si (5N) and $Co_2\ P$ (98%) by arcmelting in an argon atmosphere. Each alloy was remelted twice so as to yield homogeneous samples. Amorphous ribbons were prepared from the master alloys by the melt spinning technique in a helium atmosphere under reduced pressure. The preparative conditions otherwise resemble those used in Ref. (1). Structural information concerning as-quenched materials was derived from X-ray diffraction records obtained in the reflexion mode using monochromatized Mo $K\alpha$-radiation in a setup designed for studies of glasses. The crystalline phases were characterized by their X-ray powder patterns obtained in a Guinier-Hägg focusing camera using Cu $K\alpha_1$-radiation. The crystallization process of the amorphous ribbons was monitored by means of a differential scanning calorimeter (P-E, DSC-2C equipped with a TADS-system). The measurements were performed in argon on ~10 mg samples. The setup was calibrated as in Ref. (1). When the Kissinger method was applied (see below) the values for the peak maximum temperatures were corrected for thermal lags in the DSC setup as in Ref. (4).

PHASE ANALYSIS

The amorphous character of the as-quenched materials was verified by their X-ray diffractograms. The diffractograms thus contained two broad peaks with $d_1 \approx 2.44$ Å and $d_2 \approx 1.48$ Å for $Zr_{0.67}\ Co_{0.33}$, $Zr_{0.67}\ Co_{0.28}\ P_{0.05}$ as well as for $Zr_{0.67}\ Co_{0.27}\ Si_{0.06}$. All three diffractograms thus resemble each other and that given in Ref. (2).

The DSC thermograms of amorthous $Zr_{0.67}\ Co_{0.33}$, $Zr_{0.67}\ Co_{0.28}\ P_{0.05}$ and $Zr_{0.67}\ Co_{0.27}\ Si_{0.06}$ given in Fig. 1 were obtained with a heating rate of 10 K per minute. The main crystallization peak of $Zr_{0.67}\ Co_{0.33}$ occurs at 714 K (the peak maximum temperature is used to define the transition temperature). Previous X-ray and electron microscope studies of $Zr_{0.67}\ Co_{0.33}$ (1) have shown that upon crystallization a microcrystalline (X-ray amorphous) material is formed, which upon prolonged heat treatment becomes more coarse-grained. This phase was identified as the metastable cubic modification of $Zr_2\ Co$. The second peak, at 835 K, in the DSC thermogram of $Zr_2\ Co$ was found to be asso-

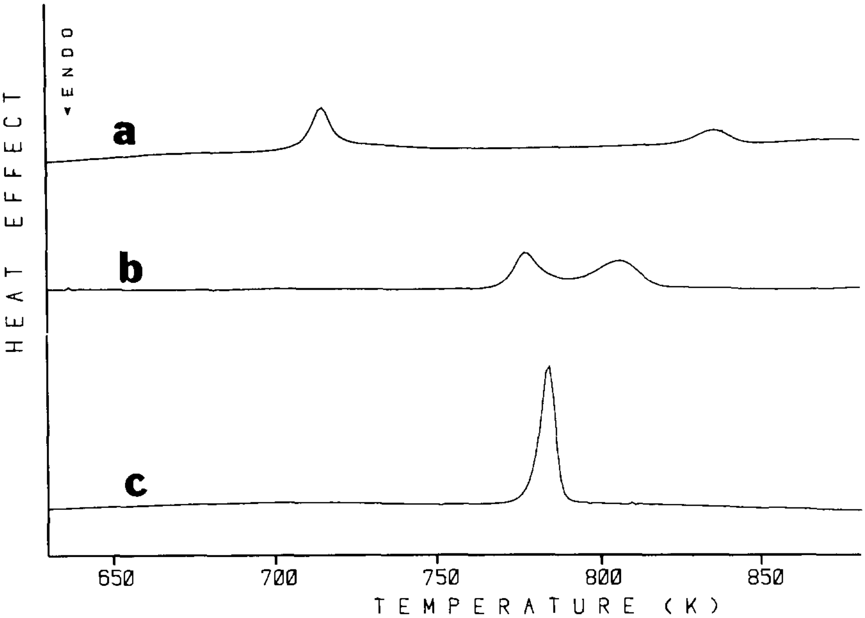

Fig. 1. DSC-thermograms of amorphous $Zr_{0.67}$ $Co_{0.33}$ (a), $Zr_{0.67}Co_{0.28}$ $P_{0.05}$ (b) and $Zr_{0.67}$ $Co_{0.27}$ $Si_{0.06}$ (c), obtained at a heating rate of 10 K/min.

ciated with the transformation from the cubic to the stable tetragonal modification of Zr_2 Co. The lattice parameters of the latter were found to be $\underline{a}$ = 6.390 (1) Å and $\underline{c}$ = 5.481 (1) Å.

The DSC thermogram of $Zr_{0.67}$ $Co_{0.28}$ $P_{0.05}$ also contains two peaks which, however, partly overlap. The first peak at 768 K is associated with the main crystallization process, while the second at 796 K can be ascribed to the cubic-to-tetragonal phase transition of Zr_2 Co (2). The lattice parameters of the tetragonal modification were found to be $\underline{a}$ = 6.419 (2) and $\underline{c}$ = 5.388 (2).

The DSC thermogram of $Zr_{0.67}$ $Co_{0.27}$ $Si_{0.06}$ exhibits only one peak, at 777 K, implying that the amorphous material transforms directly to the tetragonal modification of Zr_2 Co. The observed lattice parameters for this material are $\underline{a}$ = 6.408 (2) Å and $\underline{c}$ = 5.452 (2) Å.

CRYSTALLIZATION KINETICS

Studies of $Zr_{0.67}$ $Co_{0.27}$ $Si_{0.06}$

Samples of $Zr_{0.67}$ $Co_{0.27}$ $Si_{0.06}$ were isothermally crystallized in the DSC setup at 26 temperatures between 720 K and 795 K. The upper temperature limit

(795 K) is set by the time required for the equipment to equilibrate, while the lower limit is essentially set by its resolution. The DSC thermograms from three different isothermal heat treatments are given in Fig. 2. The volume fraction transformed, $\alpha(t)$, at any time t is taken to be proportional to the fractional area under the peak at this time. For the kinetic calculations it is of importance to fix the starting point (t = 0) and the end point ($t = \infty$) of the reaction correctly.

Greer (5) has shown that for a partially transformed material the volume fraction transformed (α) is related to the extended volume fraction $\alpha_{ex.}$ by:

$$\alpha = 1 - \exp(-\alpha_{ex.}) \qquad (1)$$

If there is N nuclei per unit volume which grow radially at a constant velocity G then $\alpha_{ex.}$ is

$$\alpha_{ex.} = N \frac{4}{3}\pi G^3 t^3 \qquad (2)$$

where t is time of annealing. If, however, nucleation occurs at a constant rate I per unit volume

$$\alpha_{ex.} = \frac{\pi}{3} I G^3 t^4 \qquad (3)$$

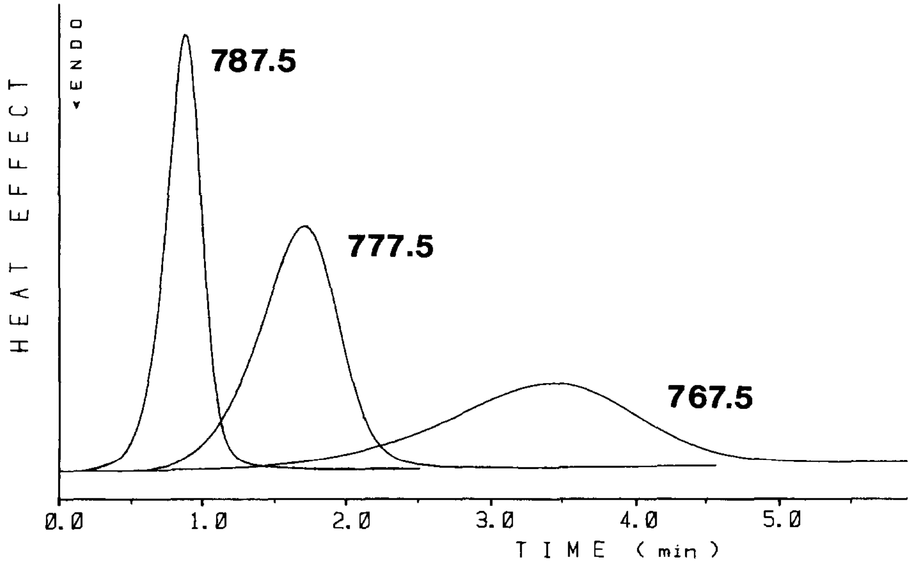

Fig. 2. DSC records from isothermal heat treatments of $Zr_{0.67}Co_{0.27}Si_{0.06}$ at 767.5 K, 777.5 K and 787.5 K.

As the extended volumes are additive the following equation holds for a material with both preexisting and new nuclei

$$\alpha = 1 - \exp\left(- \left(\frac{\pi}{3}\right) G^3 \left(4\, N\, t^3 + I\, t^4 \right)\right) \qquad (4)$$

This equation is equivalent to the Johnsson-Mehl-Avrami (JMA)-equation.

$$\alpha = 1 - \exp\left(- K\, t^n\right) \qquad (5)$$

where the Avrami exponent n will be 3 for growth of a constant number of preexisting nuclei or 4 for a constant nucleation rate, and where K is a temperature dependent kinetic parameter.

$$K = K_0 \exp\left(- E/_{RT} \right) \qquad (6)$$

where E is the activation energy for growth on preexisting nuclei (E_G) or for nucleation (E_N) depending on the n-value.

Calculations have shown that equation (5) is applicable for $\alpha(t)$ values in the interval $0.05 \leq \alpha(t) \leq 0.95$ for all annealing temperatures applied. Plots of $\ln(-\ln(1-\alpha))$ <u>versus</u> ln t thus yielded straight lines, as illustrated in Fig. 3. The n-values derived from those calculations are plotted <u>versus</u> the annealing temperature in Fig. 4. At lower annealing temperatures ($T \leq 745$ K) an n-value of 2.7 ± 0.1 is found while at higher temperatures ($T > 765$ K) the n-value is 4.1 ± 0.2. These observations can be interpreted by the assumption that at lower annealing temperatures growth of preexisting nuclei occurs, while at higher temperatures the nucleation process dominates the reaction.

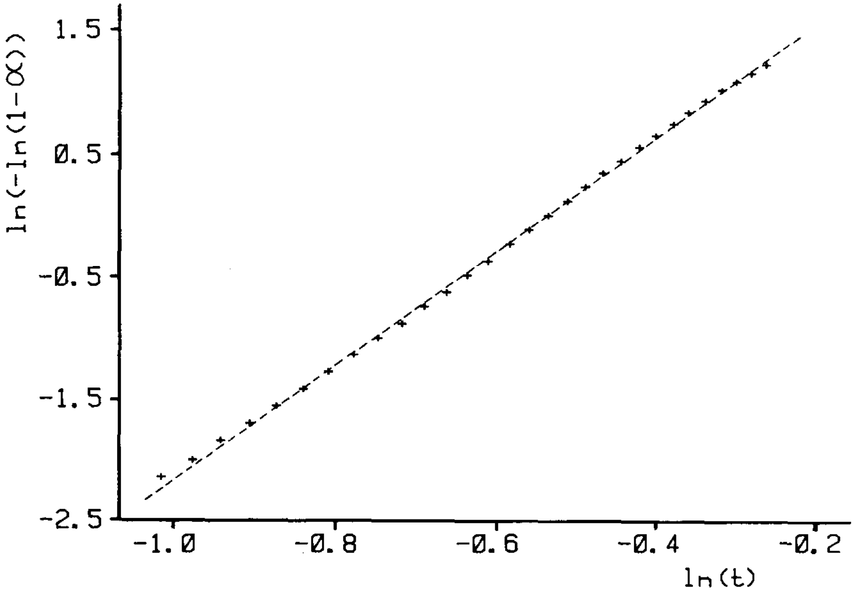

Fig. 3. JMA plot of $Zr_{0.67}\,Co_{0.27}\,Si_{0.06}$ obtained at 787.5 K.

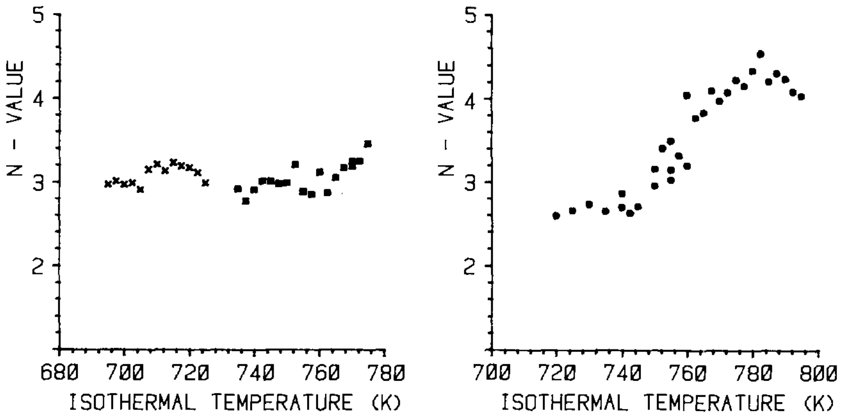

Fig. 4. The Avrami factor, n, plotted versus the isothermal annealing temperature for $Zr_{0.67}Co_{0.33}$ (x), $Zr_{0.67}Co_{0.28}P_{0.05}$ (■) and $Zr_{0.67}Co_{0.27}Si_{0.06}$ (●).

The linear relation between ln K and T^{-1} (equ. 6) for $Zr_{0.67}Co_{0.27}Si_{0.06}$ is shown in Fig. 5. Two straight lines with different slopes are observed. From these slopes an E_G value of 756 kJ/mol is derived at lower temperatures, while at higher temperatures an E_N value of 1405 kJ/mol is found.

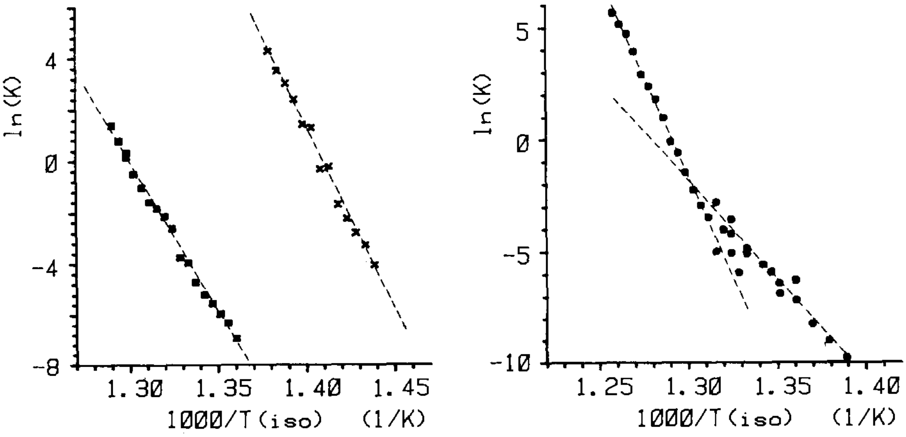

Fig. 5. ln K from equation (5) plotted versus the inverse of the isothermal annealing temperature for $Zr_{0.67}Co_{0.33}$ (x), $Zr_{0.67}Co_{0.28}P_{0.05}$ (■) and $Zr_{0.67}Co_{0.27}Si_{0.06}$ (●).

The second derivative of the JMA-equation (5) yields

$$\frac{d^2\alpha}{dt^2} = K\ n \exp\ (\ -\ K\ t^n\ )\ ((n-1)\ t^{n-2}\ -\ K\ n\ t^{2n-2}\ ) \qquad (7)$$

At the DSC peak maximum in the annealing thermograms $d^2\alpha\ /\ d\ t^2 = 0$ ($t = t_{max.}$ at this point). Thus for $n \neq 0$

$$(\ n\ -\ 1\ )\ .\ t_{max.}^{n-2}\ -\ K\ n\ t_{max.}^{2n-2} = 0 \qquad (8)$$

Combining equation (6) and (8) yields

$$\ln t_{max.} = K^1 + \frac{E}{nRT} \qquad (9)$$

A plot of $\ln t_{max.}$ versus T^{-1} would thus yield a straight line with the slope E/nR. In this case one needs to determine the starting point ($t = 0$) and $t_{max.}$ As it is usually easier to find a correct value of $t_{max.}$ than of $t = \infty$ (see above), this method would yield more reliable data than the above one. However this method does not yield any information about the n-values.

In Fig. 6 $\ln t_{max.}$ is plotted versus T^{-1}, and two straight lines are observed. From the slope of the line associated with higher annealing temperatures an E/n value of 366 kJ/mol could be deduced, to be compared with $E_N/4.1$ = 343 kJ/mol. Corresponding data for lower annealing temperatures were E/n = 285 kJ/mol and $E_G/2.7$ = 280 kJ/mol. The agreement is good, especially in the low temperature region.

An effective activation energi, Q, for the crystallization process can be determined with the Kissinger method (6). In this method DSC curves are

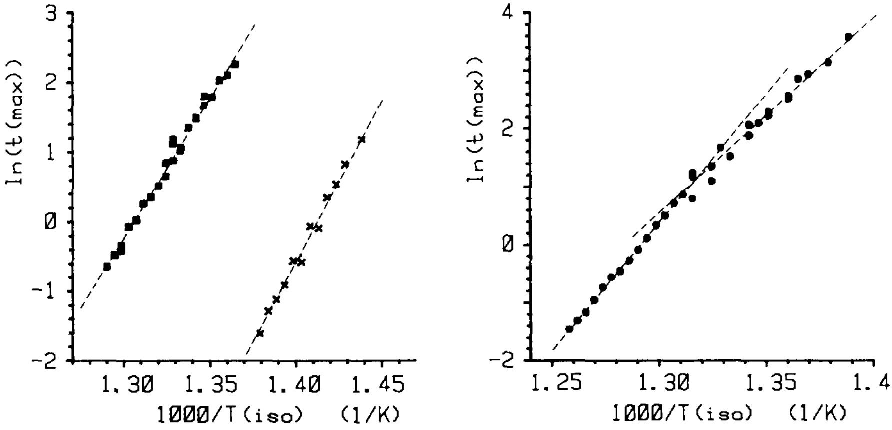

Fig. 6. Plots of $\ln t_{max.}$ versus the inverse of the isothermal annealing temperature for $Zr_{0.67}\ Co_{0.33}$ (x), $Zr_{0.67}\ Co_{0.28}\ P_{0.05}$ (■) and $Zr_{0.67}\ Co_{0.27}\ Si_{0.06}$ (●).

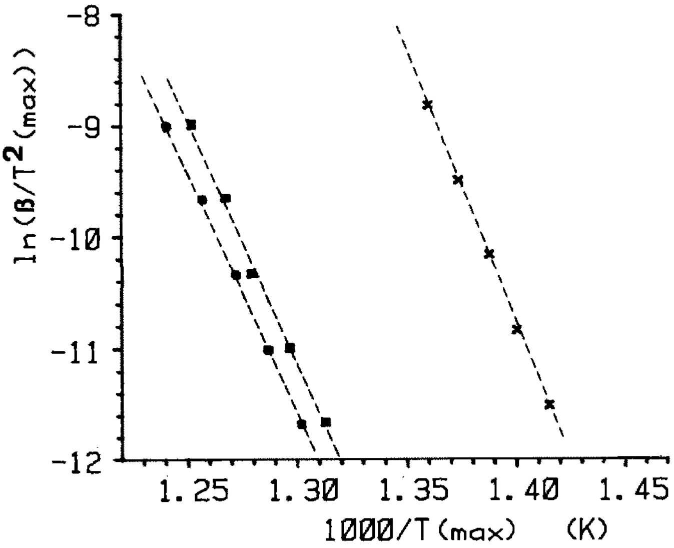

Fig. 7. Kissinger plots for $Zr_{0.67}$ $Co_{0.33}$ (x), $Zr_{0.67}$ $Co_{0.28}$ $P_{0.05}$ (■) and $Zr_{0.67}$ $Co_{0.27}$ $Si_{0.06}$ (●).

recorded at various linear heating rates, β; in our case 5, 10, 20, 40 and 80 degrees per minute. The peak maximum temperature, $T_{max.}$ is determined, and a plot of ln (β / $T^2_{max.}$) versus $T^{-1}_{max.}$ will yield a straight line with a slope equal to - Q/R.

The Kissinger method was not originally derived for solid state transformations, but Hendersson (7) and Marseglia (8) have shown that it is also applicable for devitrification reactions. A Kissinger plot for $Zr_{0.67}$ $Co_{0.27}$ $Si_{0.06}$ is given in Fig. 7. A Q-value of 366 kJ/mol was obtained, which compares favourably with the E/n-value obtained in the high temperature region above.

Studies of $Zr_{0.67}$ $Co_{0.28}$ $P_{0.05}$

As described above, the transformation of amorphous $Zr_{0.67}$ $Co_{0.28}$ $P_{0.05}$ to the cubic modification of Zr_2 Co is partly overlapped by the transformation of the latter to tetragonal Zr_2 Co. The unsymmetrical shape of the DSC thermogram of isothermally annealed $Zr_{0.67}$ $Co_{0.28}$ $P_{0.05}$ (see Fig. 8) also reflects this overlap. The X-ray powder pattern of annealed material could accordingly be indexed on the basis of the tetragonal unit cell of Zr_2 Co. The overlap also implied that the JMA-equation could only be applied for α(t)-values in the interval $0.05 \leq \alpha(t) \leq 0.40$. 18 heat treatments were carried out between 735 and 775 K.

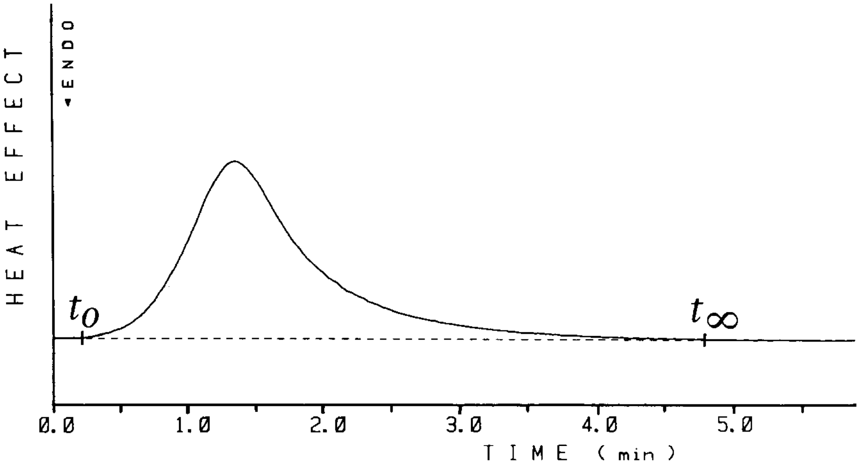

Fig. 8. DSC record for isothermal heat treatment of $Zr_{0.67}$ $Co_{0.28}$ $P_{0.05}$ at 767.5 K.

The derived n-values are given in Fig. 4. As seen in this figure, the n-values do not vary with the annealing temperature, and they yield an average of 3.0 ± 0.1. From the plot of ln K versus T^{-1} (Fig. 5) an E_G value of 981 kJ/mol was found.

In the Fig. 6 the ln t_{max}. is plotted versus T^{-1}, and from the slope of the straight line an E/n-value of 333 kJ/mol could be derived, which compares well with $E_G/3.0 = 327$ kJ/mol.

The Kissinger method finally yielded an effective activation energi, Q, of 370 kJ/mol for the main crystallization peak (see Fig. 7) and 242 kJ/ mol for the phase transformation from cubic to tetragonal Zr_2 Co.

Studies of $Zr_{0.67}$ $Co_{0.33}$

X-ray diffraction and DSC studies have shown that the metastable cubic modification of Zr_2 Co is formed during isothermal heat treatment in the vicinity of the main crystallization peak at 714 K (see Fig. 1). 13 isothermal DSC thermograms were recorded between 695 K and 725 K. The JMA-equation was found to be applicable for $\alpha(t)$ values in the interval $0.05 \leq \alpha(t) \leq 0.80$. The somewhat more restricted upper limit might, in this case, be associated with the observation that the microcrystalline material formed becomes more coarse-grained upon prolonged heat treatment.

As seen in Fig. 4, an n-value of 3.0 ± 0.1 is found from the JMA-plots. From

TABLE 1

A summary of the kinetic parameters derived from the methods applied (A, B, C see text) for $Zr_{0.67}$ $Co_{0.33}$ (1), $Zr_{0.67}$ $Co_{0.28}$ $P_{0.05}$ (2), $Zr_{0.67}$ $Co_{0.27}$ $Si_{0.06}$ at low annealing temperatures (3) and $Zr_{0.67}$ $Co_{0.27}$ $Si_{0.06}$ at high annealing temperatures (4).

Sample	n	Method A E (kJ/mol)	E/n	B E/n (kJ/mol)	C Q=E/n (kJ/mol)
1	3.0	1188	396	392	411
2	3.0	981	327	333	370
3	2.7	756	280	286	366
4	4.1	1406	343	366	

the plots of ln K and ln t_{max}. versus T^{-1} (Fig. 5 and Fig. 6) an $E_G/3.0$ = 396 kJ/mol and an E/n-value of 392 kJ/mol, respectively, could be derived.

The Kissinger method, finally, gave an effective activation energy of 411 kJ/mol for the main crystallization peak and 342 kJ/mol for the cubic-to-tetragonal phase transformation.

CONCLUDING REMARKS

Kinetic parameters have been determined by three different methods: (i) isothermal data obtained from plots of ln (- ln (1 - α)) versus ln t (providing both E and n, method A); (ii) isothermal data obtained from plots of ln t_{max}. versus the annealing temperature (method B, yielding E/n-values); (iii) non-isothermal data extracted from Kissinger plots (Q = E/n-values, method C). The various E/n-values obtained are summarized in Table 1.

The crystallization process differs among the alloys studied. Thus $Zr_{0.67}$ $Co_{0.27}$ $Si_{0.06}$ crystallizes directly to the tetragonal modification of Zr_2 Co. Method A and B give comparable E/n-values, and the E/n-value derived from method C is in agreement with those obtained by method A and B applying high annealing temperatures.

In the case of $Zr_{0.67}$ $Co_{0.28}$ $P_{0.05}$ only one n-value is observed, and method A and B give quite comparable data, while method C gives somewhat higher E/n-values. This might be due to the occurrence of overlapping reactions when isothermal conditions are applied (see above).

As shown above, the cubic-to-tetragonal phase transformation does not overlap with the crystallization process for $Zr_{0.67}$ $Co_{0.33}$. The E/n-values obtained from all three methods are in good agreement with each other.

It can also be seen that method C yields a higher E/n-value for $Zr_{0.67}Co_{0.33}$ than for the P and Si containing materials. The E/n-values derived from method

A and B also vary with the composition; they are highest for $Zr_{0.67}$ $Co_{0.33}$ and lowest for the Si containing material.

Finally, it is tempting to interpret the variation of n with the isothermal annealing temperature for $Zr_{0.67}$ $Co_{0.27}$ $Si_{0.06}$ by the assumption that at lower annealing temperatures growth of preexisting nuclei of the cubic modification dominates the process, while at higher temperatures the process is governed by nucleation and growth of the tetragonal modification of Zr_2 Co. This hypotesis will be further evaluated in a forthcoming article.

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