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THERMAL STABILITY OF AMORPHOUS ALLOYS

K.H.J. Buschow


Abstract. - The crystallization of the amorphous alloys Zr-Rh, Zr-Fe, Dy-Co and Gd-Co was studied by means of differential scanning calorimetry and X-ray diffraction. In several of these alloys we determined the apparent activation energy for diffusion by means of the Kissinger method. There appears to be no simple relationship between the crystallization temperatures and these apparent activation energies. The present results together with data available on many other amorphous alloys between two metals (including alloys between Eu, La, Gd or Zr with 3d metals or Cu) were analysed in terms of the kinetic approach to the thermal stability. It is shown that the proportionality between the crystallization temperature and the hole formation enthalpy (pertaining to the size of the smaller type of atoms) is quite generally valid.

Various models have been proposed for discussing the stability of amorphous alloys. Nagel and Tauc \cite{1} considered the influence of the conduction electrons. In their approach good stability is expected when the number of conduction electrons leads to a Fermi momentum $k_F$ such that $2k_F^2\hbar^2=\frac{8}{3}\pi^2\hbar^2$. Here $Q_{\text{max}}$ corresponds to the wave vector at which the X-ray interference function has its main peak. Later on Beck and Oberle \cite{2} also considered the effect of the conduction electrons on stability. In their model stable amorphous alloys can be obtained in cases where the consecutive maxima of the pair correlation function match the consecutive minima in the corresponding pair potential function. Models considering geometrical factors such as the relative size of the parent metal atoms have also been proposed \cite{3}.

All these models can only give an indication of the relative stability of an amorphous alloy with respect to the corresponding crystalline phases in the binary phase diagram. This relative stability is closely related to the heat released upon crystallization of the amorphous alloys. Unfortunately the heat of crystallization is less suited to characterize the thermal stability of amorphous alloys. This latter quantity determines the resistance of the amorphous alloys to spontaneous crystallization at a given temperature. This resistance towards crystallization is obviously of prime importance in cases where amorphous alloys find technical applications.

In this paper it is shown that a reasonable description of the thermal stability can be obtained by means of the kinetic approach if reasonable assumptions are made regarding the activation energy which controls the diffusion of the atoms. First some new results are presented regarding the thermal stability in some amorphous Gd-Co, Dy-Co, Zr-Rh and Zr-Fe alloys. The results obtained are then discussed together with results reported in previous investigations.

The amorphous alloys were prepared by arc melting followed by melt spinning in a purified argon gas atmosphere. Small parts of each ribbon were investigated by means of X-ray diffraction. The thermal stability of the alloys was studied by means of a Du Pont 910 differential scanning calorimeter (DSC), using an atmosphere of purified argon gas. In most cases practical heating rates of 50 K/min were applied. The origin of the observed heat effects was studied by heating the ribbons to the distinct stages in the crystallization process, followed by cooling and X-ray diffraction. In several alloys the crystallization behaviour was studied in more detail by applying different heating rates, varying from 0.5 K/min to 100 K/min.

Fig. 1 gives some experimental results obtained on the amorphous alloys Zr$_{1-x}$Rh$_x$. X-ray diffraction showed that the first exothermic heat effect ($\approx 440^\circ$C), in Zr$_{80}$Rh$_{20}$ corresponds to the crystallization into a metastable simple cubic phase (a = 2.52 Å). At higher temperatures ($\approx 525^\circ$C) this phase transforms into α-Zr and Zr$_2$Rh (CuAl$_2$ type a = 6.486 Å, c = 5.583 Å). In the two other amorphous alloys shown in the figure, crystallization is much more simple and does not involve a metastable phase. In the following we will define the crystallization temperature ($T_x$) as corresponding to the maximum of
Table 1. Crystallization temperatures ($T_x$) determined by means of DSC and a heating rate of 50 K/min in various amorphous alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$T_x$ (K)</th>
<th>Alloy</th>
<th>$T_x$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr$_{1-x}$Rh$_x$</td>
<td></td>
<td>Dy$_{1-x}$Co$_x$</td>
<td></td>
</tr>
<tr>
<td>$x = 0.30$</td>
<td>712</td>
<td>$x = 0.25$</td>
<td>555</td>
</tr>
<tr>
<td>$x = 0.25$</td>
<td>741</td>
<td>0.40</td>
<td>591</td>
</tr>
<tr>
<td>$x = 0.30$</td>
<td>748</td>
<td>0.50</td>
<td>608</td>
</tr>
<tr>
<td>Zr$_{1-x}$Fe$_x$</td>
<td>Gd$_{1-x}$Co$_x$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x = 0.24$</td>
<td>663</td>
<td>$x = 0.26$</td>
<td>583</td>
</tr>
<tr>
<td>0.30</td>
<td>679</td>
<td>0.45</td>
<td>593</td>
</tr>
<tr>
<td>0.33</td>
<td>700</td>
<td>0.50</td>
<td>597</td>
</tr>
</tbody>
</table>

plotted versus $T_x^{-1}$. If the crystallization process is governed by a single activation law these plots are straight lines. The slope of these lines is proportional to $\Delta \dot{E}$. Examples of such plots are shown in Fig. 3. For the Zr$_{1-x}$Rh$_x$ alloys with $x = 0.20$, 0.25 and 0.30 the values of $\Delta \dot{E}$ are 3.64, 4.21 and 4.73 eV, respectively. The values of Gd$_{50}$Co$_{50}$ and Gd$_{65}$Co$_{35}$ are 3.67 eV and 2.51 eV.

In the kinetic approach to thermal stability of amorphous alloys [5-8] crystallization is expected to set in at a temperature $T_x$ where the viscosity $\eta$ reaches a critical value (about $10^{13}$ Poise). In terms of the entropy theory of viscous flow this latter quantity can be given by

$$\eta = \eta_0 \exp(\Delta \dot{E} / ST)$$  \hspace{1cm} (1)

where $\eta_0$ is a constant and $\Delta \dot{E}$ is a measure of the potential energy barrier for cooperative atomic transitions. The configurational entropy $S$, which decreases exponentially with $T$ below the melting temperature, can be regarded as being frozen in and approximately constant in amorphous alloys near the crystallization temperature. The crystallization temperature scales therefore as the energy $\Delta \dot{E}$ in eq. (1). It was proposed earlier [9] that a substantial portion of $\Delta \dot{E}$ consists of the enthalpy $\Delta \dot{H}$ needed to create a hole the size of the smaller type of atom of the amorphous alloys. The crystallization temperature is then expected to scale roughly as the hole formation enthalpy. In order to test the general applicability of this model we have plotted in Fig. 4 the crystallization temperature of several different alloy systems versus their corresponding hole enthalpies.
where \( c \) is an effective surface concentration

\[
c = xV_B^{2/3} \left[ xV_B^{2/3} + (1-x)V_A^{2/3} \right]^{-1}
\]

Values of the quantities \( \Delta H_{1V}^A(B) \) are given by Miedema [12] excepting those of Eu. This latter value was obtained by using the relation

\[
\Delta H_{1V}^A = \Delta H_{1V,0}^A/3.4
\]

and the enthalpy of sublimation \( \Delta H_{v,0}^A \) listed by Hultgren et al. [13].

A glance at Fig. 4 shows that there is rather good agreement between the experimental data and the predictions of the model. Although it is not immediately apparent from the results shown in Fig. 4, we would like to stress that in binary systems \( A_{1-x}B_x \), the present model predicts the correct concentration dependence [14]. In general one observes an increase of \( T_x \) with increasing B concentration (see for instance Fig. 1 and Table 1). The reason for this is the fact that the A metal in the amorphous \( A_{1-x}B_x \) alloys of Fig. 4 has a considerably higher \( \Delta H_{1V}^A \) value than the B component. If one were to approximate \( \Delta H_h \) by a weighted mean value of the corresponding \( \Delta H_{1V}^A \) (or \( \Delta H_{v,0}^A \) values since \( \Delta H_{1V}^A \approx \Delta H_{v,0}^A \)) one would expect \( T_x \) to decrease with \( x \), whereas experimentally one observes the opposite behaviour, i.e. \( T_x \) increases with \( x \). In the present approach it is assumed, however, that (for all concentrations) the hole size pertains to the smaller type of atoms (B). Since the A atom has the smaller surface energy it is relatively easy to make a hole the size of the smaller type of atom in the A metals or in alloys of high A concentration. In eq. (2) this fact is accounted for by the factor \( (V_B/V_A)^{5/6} \).

A point that needs further discussion is the discrepancy between the magnitude of the \( \Delta H_h \) values used in Fig. 4 and the experimental values derived from Kissinger plots. In the first place it should be remembered that \( \Delta H_h \) is only a part of the activation energy for diffusion. A large contribution might come from the so-called saddle-point energy. One expects therefore that the real activation energy will be larger than \( \Delta H_h \). More important, however, is the fact that the experimental \( \Delta \bar{E} \) values have to be considered as apparent activation energies [7]. Due to a slight temperature dependence of \( S \) in eq. (1), the values of the apparent activation energies may become a few times higher than they would be.
if $S$ were really temperature-independent. High values of $\Delta E$ occur in those alloys in particular that can give rise to structural relaxation at temperatures preceding $T_x$ [17].

In the above approach we have not considered amorphous alloys such as Fe-B and Pd-Si in which one of the components is a non-metal. In these alloys the metalloid atoms often show a tendency to form a network, so that other effects than those considered here may control the rate of crystallization. Of the binary alloys between metal atoms $A_{1-x}B_x$ one expects deviations from the linear relationship between $T_x$ and $\Delta H_B$ if the concentration in the B component becomes very high. In that case pure B metal will precipitate out of B-rich regions. Only a local spatial re-orientation of the B atoms may be required and the activation energy may be smaller than that corresponding to a hole the size of a whole B atom. Exceptions are furthermore amorphous alloys such as those of Ag and Au with 3d metals. In contrast to the alloys considered in connection with Fig. 4, these latter alloys have a positive heat of mixing [15] so that $\Delta H_B$ is expected to be lower than in cases where the heat of mixing is negative [14, 16].

In the liquid as well as in the glassy state there will be clustering between like atoms. In the phase diagrams no intermetallics occur, so that crystallization involves the pure components. For all these reasons $T_x$ will occur at lower temperatures than expected from Fig. 4, which is indeed the case [8].

A similar relationship between $T_x$ and $\Delta H_B$ has been reported elsewhere between amorphous alloys of Cu and either La, Gd, Er, Y, Ca or Zr [17]. The same analysis was also given of the crystallization in amorphous alloys occurring in the systems Y-Fe, Y-Co, Pr-Ni, Hf-Fe, Hf-Cu, Th-Cu, No-Wi and in several alloys based on the alkaline earth metals [16]. It can be concluded therefore that the hole model presented above is rather uniformly valid and may serve for obtaining an estimate of the thermal stability of amorphous alloys not yet investigated.

An advantage of the present model is the easy accessibility of the hole formation enthalpy for almost all binary alloy system.

A more detailed discussion of the relationship between $\Delta H_B$ and the experimental $\Delta E$ values will be presented elsewhere [18].

References

/18/ Buschow, K.H.J. and Verbeek, B.H. (to be published).