

2v, exhibit a linear dependence on K_I rather than the parabolic behaviour predicted by the Dugdale model (see Figs. 4a and b of [10]). From preliminary results discussed in our original paper, this seems to indicate that the craze formed by the pre-crack was not annealed out prior to loading.

In conclusion, we maintain our original position that the Dugdale model is not fully adequate for describing craze geometries in PMMA.

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Thermal stability of amorphous Co-Fe-B, Co-Si-B and Co-Fe-Si-B alloys

Cobalt containing amorphous alloys exhibit extremely soft magnetic properties and at the same time show favourable mechanical properties [1]. Proper selection of the composition affords materials with magnetostriction approaching zero, e.g. alloys $Co_{74}Fe_6B_{20}$, $Co_{75}Si_{15}B_{10}$, $Co_{70}Fe_5Si_{15}B_{10}$ [2-4]. Their magnetic properties suggest the possibility of applying these materials as improved substitutes for permalloys [1, 5]. They are also characterized by high resistance to oxidation, even at high temperatures and effective cooling of liquid metal can be achieved without any protective gas cover [6].

The present study concerned the crystallization behaviour of these 3 alloys plus 2 more of the Co-Fe-B, type with increased and reduced boron (Table I). It enabled us to characterize the effect of the amount and kind of metalloid on the behaviour of amorphous cobalt-based alloys.

Alloys were prepared from elements of the following purity: Co, Si 99.9%, Fe, B 99%. Samples of 5 to 7g in weight were remelted several times by argon arc melting. Metallographic observations confirmed that the resulting samples exhibited no

segregation, so were suitable for production of ribbons. The resulting ribbons were completely amorphous according to X-ray studies; they were 20 to 30 μm in thickness and several metres in length.

Calorimetric studies were performed using a Perkin Elmer DSC-2 calorimeter in which the course of crystallization during continuous heating at a heating rate of 10 to 80 $K min^{-1}$ was determined. The values of activation energy were obtained from Kissinger's method [7]. The structure of samples both in the initial state and after different crystallization stages was determined with a Philips X-ray diffractometer, using $CuK\alpha$ radiation.

The exothermic effects associated with the

TABLE I Calculated value of the activation energy of crystallization and temperature of peak I (heating rate = 10 $K min^{-1}$), for investigated alloys

Alloy	ΔE (kJ mol ⁻¹)	T _x (K)
1. $Co_{76.8}Fe_{6.2}B_{17}$	274 ± 6	718
2. $Co_{74}Fe_6B_{20}$	257 ± 2	720
3. $Co_{71.2}Fe_{5.8}B_{23}$	235 ± 1	747
4. $Co_{70}Fe_5Si_{15}B_{10}$	324 ± 3	786
5. $Co_{75}Si_{15}B_{10}$	328 ± 9	792

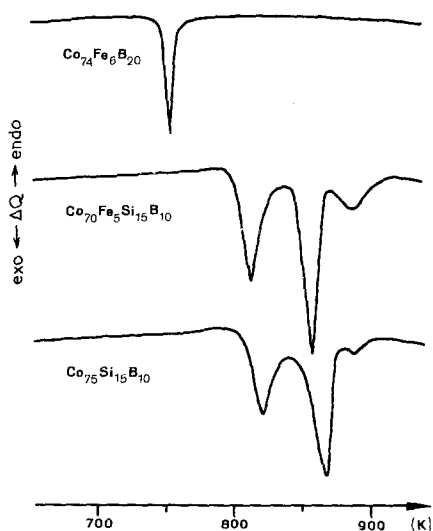


Figure 1 Calorimetric curves of the investigated alloys at a heating rate of 80 K min^{-1} .

crystallization of the investigated amorphous alloys are presented in Fig. 1. There were essential differences in the nature of the calorimetric records between alloys containing one and two metalloids.

All three Co–Fe–B compositions (alloys 1 to 3) exhibited only one exothermic effect during crystallization which was shown by X-ray diffraction to result from the formation of αCo solid solution and the formation of compound Co_2B . Alloys 1 to 3 with a constant ratio of Co:Fe but with different contents of boron (17, 20 and 23 at%) showed that they were amorphous and that an increase in boron content enhanced their thermal stability (Table I). The increase in crystallization temperature T_x between alloys with 17 and 23 at% B was about 30 K. It is of interest that simultaneously the activation energy decreased; this was possibly due to easier nucleation of the phase Co_2B resulting from the higher boron content.

Furthermore, comparison of T_x for alloys 3 and 4 pointed to a stabilizing effect on the metallic glass of silicon partially replacing boron. This introduction of silicon in alloy Co–Fe–B also very greatly increased the value of ΔE for alloy 4 compared with alloy 3. Moreover, comparison of alloys 4 and 5 indicated that introduction of a small amount of iron substituting partially for cobalt reduced T_x only slightly.

Results for the Co–Si–B composition (alloys 4, 5) were consistent with the literature data [8] in pointing to the possibility of obtaining amorphous materials within the composition range 20 to 30 at% metalloid. These calorimetric records for alloys 4 and 5 showed three distinct stages of the process, greatly differing in the intensity and position. For detailed studies we selected alloy 5 ($\text{Co}_{75}\text{Si}_{15}\text{B}_{10}$) whose crystallization proceeds as follows, according to other authors [7] $\text{Am} \rightarrow \text{Am} + \text{Ms I} \rightarrow \text{Ms I} + \text{Ms II} \rightarrow \text{stable phases}$, although the published calorimetric records show two crystallization stages. In our case a third peak, though small and somewhat diffuse, appeared.

X-ray phase analysis of samples annealed to temperatures exceeding each successive peak permitted identification of the phases formed. X-ray measurements of samples heated above peak I pointed to the presence of phase hcp- αCo . This indicated that the first exothermic effect resulted from nucleation and growth within amorphous matrix of crystals of a supersaturated solution of Co. Analogically, after heating to a temperature above peak II, X-ray diffraction indicated a phase Co_2Si and above peak III additionally a phase Co_2B . Upon annealing of the fully crystalline material to 1000 K the amount of phase Co_2Si particularly increased. The lack of a shift of X-ray reflections, as compared with the data given in the ASTM cards, indicated that the crystalline phases formed during the decomposition of the amorphous phase did not perceptibly differ from the equilibrium phases. Moreover no other phases appeared, in particular no ternary compounds, in addition to the above mentioned ones. This was fully consistent with published results for Co–Si–B alloys in the equilibrium state [9]. Therefore, it seems surprising that other authors [6] have identified as many as 7 phases during crystallization of alloys of similar compositions.

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Comment on "Influence of surface potential on the kinetics of glass reactions with aqueous solutions"

The amount of alkali ion extracted from a unit area of glass sample on the effect of an aqueous solution is a function of time. Namely, a square root dependence prevails at the beginning of the attack while after a certain time a linear function can be observed provided that the rate of network dissolution is sufficiently fast. The network dissolution moderates and finally can stop the thickening of the surface layer formed by the ion exchange and interdiffusion of alkali ion and hydrogen ion. Thus the dissolution of network leads or may lead to a steady state in which the phase boundary is shifted toward the glass bulk with a constant velocity and the rates of all processes are constant. Consequently, the amounts of the products of both the ion exchange and network vary linearly with time.

Recently Mularie, Furth and Westwood [1] attributed the deviation from the square root dependence and the transition to the linear regime to the effect of an electric field present in the "near surface region" of the glass. These authors disregarded the fact of network dissolution [2] and the related explanation of the time dependence of alkali extraction [3]. (However, the respective publications are cited in their reference list.) Nevertheless their final conclusion is in accordance with

the experimental observation. This contradiction is the reason for discussing the treatment presented in the authors' paper.

The extended Fick's equation given by the authors are

$$J(x, t) = -D \frac{\partial N(x, t)}{\partial x} + vN(x, t) \quad (1)$$

and

$$\frac{\partial N(x, t)}{\partial t} = D \frac{\partial^2 N(x, t)}{\partial x^2} - v \frac{\partial N(x, t)}{\partial x} \quad (2)$$

where N is the mobile charge carrier concentration, J the flux of this ion, D the diffusion coefficient and v denotes the alkali ion velocity which is equal to mobility μ times the field strength E

$$v = \mu E \quad (3)$$

By attributing a constant value to E , a solution for Equation 2 and a formula for amount, Q , of extracted alkali have been obtained. Limiting cases of the latter are

$$\lim_{t \rightarrow 0} Q(t) \propto \sqrt{t} \quad (4)$$

and

$$\lim_{t \rightarrow \infty} Q(t) \propto t \quad (5)$$

in agreement with experiments.

Equations 1 and 2 apply, of course, when interstitial mechanism prevails. In this case the rate of an interdiffusion depends on self diffusion coefficients of both types of ion involved. Accordingly, the flux and the diffusion coefficient of hydrogen