

ROLE OF THERMAL ANNEALING DURING PROCESSING OF METALLIC GLASSES

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ABSTRACT

Methods of rapid cooling are surveyed and discussed from the point of view of pre-annealing effects during the preparation of metallic glasses. Types of relaxation processes induced by thermal treatment are analysed and flash annealing by heat pulses is discussed. The use of $T-T$ diagrams is shown for some characteristic cases of temperature-controlled crystallization.

INTRODUCTION

Metallic glasses are non-crystalline materials prepared by rapid cooling of melts with structures resulting from the freeze-in of a disordered distribution of atoms in undercooled melts. Metallic glasses are in the state of constrained, thermodynamic instability and/or structural-mechanical metastability, which tends to transform to the more stable state that becomes available on annealing. The most frequently used method for the production of metallic glasses is the continuous or discontinuous melt-quenching process, exhibiting characteristic cooling rates of 10^3 – 10^7 K s⁻¹. Because of the finite quenching rate and its possible inconstancy during the whole course of freezing, such a cast alloy should be regarded as partly annealed. In fact, it is the first stage of an as yet uncontrolled thermal treatment which is often responsible for the difference in physical properties indicated experimentally for various as-quenched alloys of identical composition. Intentionally controlled annealing may consequently lead to substantial improvements of the desired properties of glass and may, finally, effect the course of crystallization. This explains why a knowledge of the processes that occur on annealing is so crucial and worthy of more detailed analysis.

Reactions that may take place in a non-crystalline alloy on heat treatment can be of the following types [1–6]:

(i) Relaxation processes, involving the rearrangement of constitutional species below the crystallization temperature yet preserving the non-crystalline structure. They can be further divided into processes proceeding far below, just below and just above the glass transition temperature.

(ii) Nucleation processes, covering the segregation of embryos capable of consequent growth if nuclei of critical radius are present; it takes place on cooling and is usually difficult to observe.

(iii) Crystallization processes, occurring at higher temperatures (regularly above the glass transition temperature) and able to proceed under any temperature regime applied.

(iv) Chemical processes, taking place over the whole temperature range, usually associated with oxidation. This point will not be discussed here in more detail, although selective oxidation and the segregation induced may create concentration gradients at or near the surface, which strongly influence the local thermal stability by acting as preferred nucleation sites (e.g., in the glassy $\text{Fe}_{x/2}\text{Ni}_{x/2}\text{B}_{1-x}$ alloy the nickel concentration near the surface may increase owing to the preferred oxidation of iron, thus reducing locally the crystallization temperature).

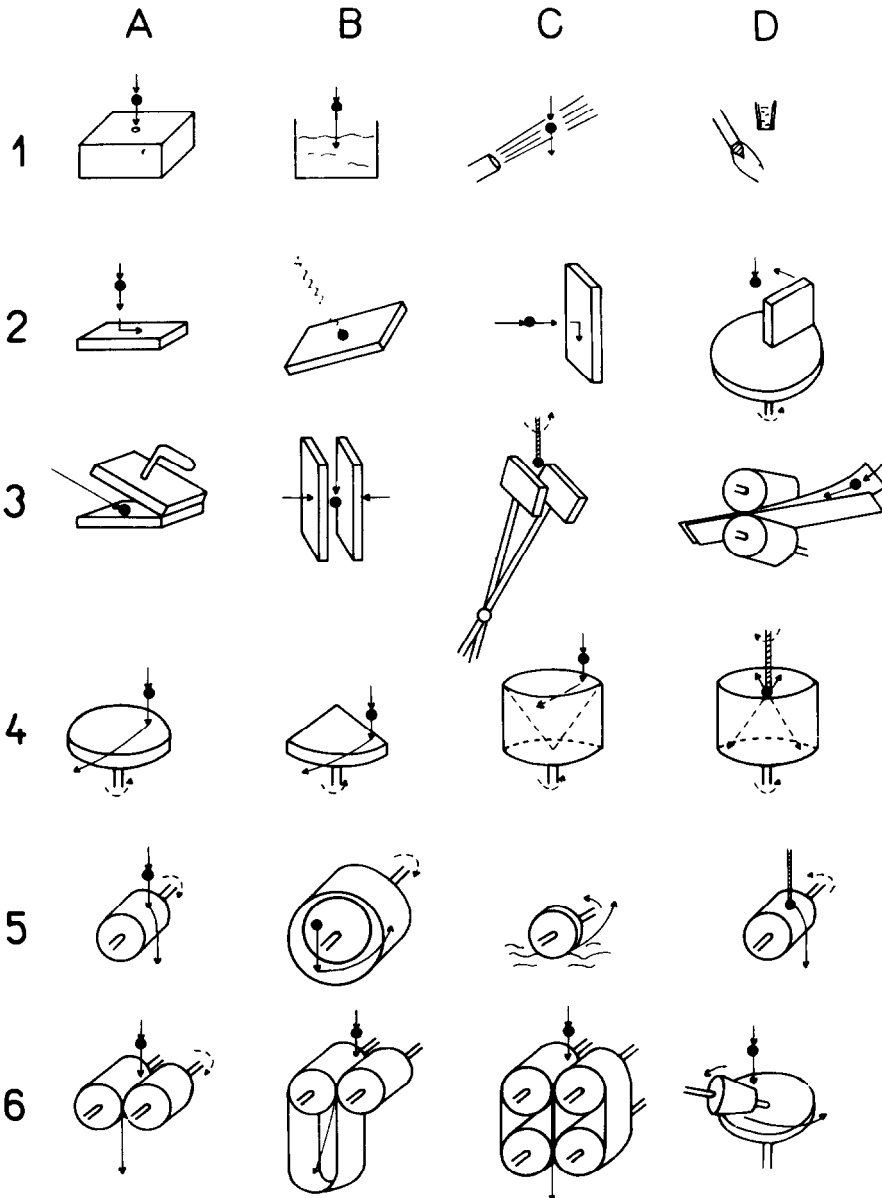
PREPARATION METHODS AND INHERENT DEGREE OF ANNEALING

Figure 1 illustrates the most common techniques employed for the acceleration of cooling rates. They can be classified from different points of view but the essential thing is the continuous or discontinuous and/or the one-sided or both-sided method of sample cooling. Some aspects are evident,

Fig. 1. Survey of methods for rapid cooling of metallic melts (cooling rate regions a, b and c for 10^{-10^4} , 10^3-10^6 and 10^5-10^8 K s^{-1} , respectively).

- (1) Filamentary casting (A-a), cooling by fluid media (liquid immersion, B-a; gas blowing, C-a) and drop powder melting (D-b) or spray quenching.
- (2) Cooling by contact with a single stationary (A, C) or cyclically moving (swinging wing method, D-b) surface using simple pouring (A-a) or shooting (C-c) melt or laser surface glazing (B-c).
- (3) Stationary cooling between two surfaces operated manually (A-a) or mechanically (piston-and-anvil method, B-c), pendant drop pressing by scissors (C-b) and melt pressing between two movable foils (D-b).
- (4) Continuous cooling on to horizontally moving surfaces, rotating disc (A-b) or cone (B-b) or its inside (C-b), and melted sample centrifugation into tiny drops (D-c).
- (5) Continuous cooling on vertically moving surfaces by melt spinning and/or casting (A-b) on to rotating wheel and/or inside tilted tip of drum (B-b), by surface melt extraction (C-b) or pendant drop melt extraction (D-b).
- (6) Continuous cooling between two moving surfaces by two rotating wheel method (A-b), one (B-b) or two (C-c) belt running method and by rotating disc with a cone (D-b).

e.g., one-sided cooling creates unequal surfaces with more pronounced gradients across the sample thickness but it is technically more easily constructed, particularly with respect to the desired continuous production of ribbons. Most important is the different extent of pre-annealing achieved during the quenching procedure, which can be generally located within the



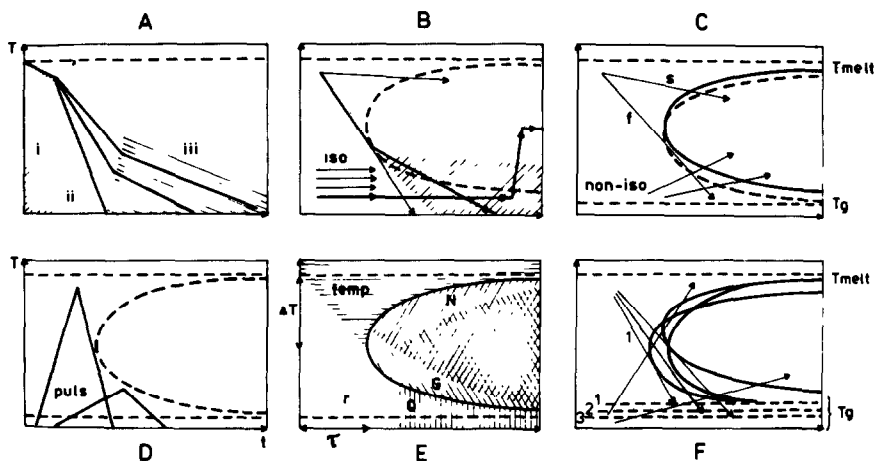


Fig. 2. Hypothetical temperature-time-transformation diagrams as a tool for establishing possible courses of thermal treatments.

(A) Approximate cooling lines in $T-t$ coordinates with three stages discussed in the text.

(B) Two-stage cooling (cf., Fig. 1, part 6-A) marked together with a $T-T-T$ boundary line (dashed) showing their intersection during the low-temperature (low-stage) cooling. Isothermal annealing (with common two-stage treatment to enhance nuclei formation during its first, low-temperature stage in the region of maximal nucleation, shaded area) is also marked.

(C) $T-T-T$ diagram with two overlapping crystallization processes illustrating the possibility of formation of two different phases on slow (s) and fast (f) cooling. Non-isothermal course of reheating is also marked.

(D) Flash annealing by heat pulses introduced in front of the nose of the $T-T-T$ curve or below it.

(E) $T-T-T$ diagram with the shaded areas marked for different rate-controlling processes, nucleation (N) and crystal growth (G) (their mutual positions in the temperature axis are then responsible for the final course of crystallization and consequent two-stage thermal treatment, B); quenched-in nuclei (Q), their formation being time dependent, and areas of dominant processes taking place during relaxation (r) and tempering (temp.). The extreme of the crystallization (solid) curve arises from the competition between the driving force for the crystallization (increasing with undercooling, ΔT) and the molecular mobility (viscosity, having an opposite trend to T) and represents the least time required to form a given degree of crystallinity, which provides an estimate of the critical cooling rate, $\phi_{\text{cnt}} = \Delta T/\tau$.

(F) Model of possible overlap of three crystallization curves of three phases with different degrees of metastability to show that the crystallization products can be affected by the different rates of cooling and reheating.

three major stages (cf., Fig. 2A):

(i) Fusing, tempering and transporting melt to the place of processing when the sample temperature is being controlled by self-cooling owing to the heat loss through radiation and convection.

(ii) Rapid cooling through heat conduction into the tempering support; this is time-limited by the duration of contact.

(iii) Free cooling after the termination of effective contact with a heat sink when the sample temperature is being controlled by self-cooling again.

Discontinuous, both-sided cooling methods (see Fig. 1, Nos. 1–3) make it possible to maintain rapid cooling during the whole process of quenching (Fig. 2B), whereas, e.g., the popular continuous twin-roller technique (Fig. 1, part 6A), providing effective quenching only along the linear contact of wheels, yields two separate rates (not often considered as the reason for apparatus-induced recrystallization). This can certainly be removed (Fig. 1, parts 6B and C), but only with very sophisticated instrumentation. It follows that a deeper knowledge of operational factors during the quenching, with respect to the pre-assumed type of $T-T-T$ diagram, can be of great assistance in distinguishing the different modes of thermal pre-treatment of the samples.

The experimental methods for subsequent sample annealing on reheating will not be dealt with here in as much detail as the above, as they involve classical isothermal (Fig. 2B) and/or non-isothermal (Fig. 2C) heating using different types of readily available furnaces.

RELAXATION PROCESSES AND HEAT PULSE TREATMENT

Relaxation processes [7] in a non-crystalline structure can be defined as any thermally activated rearrangement of any constitutional species (single atoms or their groups) and can be of three types [2,3,5]:

(i) Topological short-range ordering, in which the structural defects are subject to relaxation and annihilation at temperatures close to T_g . It usually occurs as a collective movement of constitutional species and thus shows logarithmic-type kinetics of associated changes observed during measurement of a selected (representative) physical property during the heating. It is usually related to the atomic transport in glasses.

(ii) Compositional short-range ordering, in which chemically similar elements (e.g., Ni, Co and Fe) can mutually exchange their atomic positions, resulting in rearrangements of the nearest neighbours, revealing changes in the Curie temperature, magnetic field-induced anisotropy, etc.

(iii) Diffusional ordering, again connected with the existence of structural defects and thus dependent on the thermal history of the glass preparation, i.e., on the rate of structure freeze-in. The greater is the quenching the greater is the diffusion, thus permitting a higher rate of relaxation of mechanical stresses and deformations at relatively low temperatures (ca. 150°C), usually far below T_g .

Inoue et al. [8] and Chen et al. [9] considered the above classification to be too strict when analysing their calorimetric study of the anneal-induced relaxation of metal-metalloid glassy alloys (see Fig. 3), although they found two essential stages. Their relatively low activation energies, associated with a low temperature peak, reflect the occurrence of a local structural relaxation; they increase drastically to the values attributed to cooperative struc-

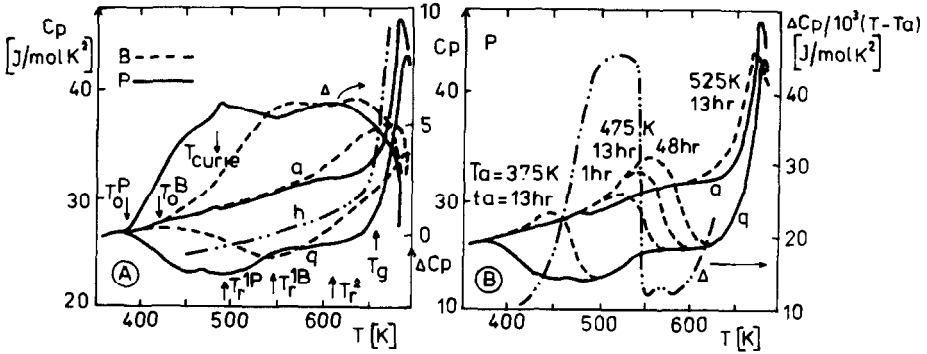


Fig. 3. Enthalpy relaxation behaviour of $(Fe_{0.5}Ni_{0.5})_{83}(P \text{ or } B)_{17}$ glassy alloys on annealing (after Chen et al. [9]).

(A) Heat capacity (C_p) versus temperature curves on reheating at 40 K min^{-1} for as-quenched (q) and annealed (a) samples and their differences (Δ) with the marked characteristic temperatures T_0 , T_{curie} , T_r^1 and T_r^2 , and T_g associated with the onset, Curie transformation, relaxation (1) and (2) and glass transformation, respectively. The inserted hypothetical curve (dashed-and-dotted) shows the possible behaviour of a sample quenched at a slower rate.

(B) Curve shifting (dashed) due to anneals at given temperatures (T_a) and times (t_a) with the superimposed collective curve (dashed-and-dotted) of the relaxation entity spectra showing two separable maxima coincident with the assumed two-stage relaxation mechanism.

tural relaxation over a longer range, exhibited by the second peak. In accordance with the percolation model conceived by Cyat [10], they confirm the appearance of an excess endothermic peak occurring above the temperature of annealing (cf., Fig. 3B) and evolved reversibly in a continuous manner [9]. Consequently, they divided the structural relaxation into irreversible/reversible processes consisting of (i) local and medium-range rearrangements, which occur by interactions involving only metal atoms and (ii) long-range regrouping, which occurs by interactions between metal and metalloid atoms.

Experimentally detectable effects on collectively measured changes of the given physical property can be of three types [3]: (i) varying linearly with the logarithm of the isothermal annealing time; (ii) changing reversibly when the annealing temperature is slowly cycled; and (iii) indicating a certain misfit, called a cross-over effect, when one annealing regime is switched to another.

A representative summary of experimental evidence on such relaxation phenomena was given by Gibbs et al. [11], showing, e.g., that Curie temperature [12], Young's modulus [12] and resistivity [13] can behave in either way. Theoretical models to describe relaxation processes were proposed by Egami et al. [15], using local parameters to express the freeze-in of structural defects, i.e., hydrostatic pressure, local shear stress, fluctuation density and the degree of ellipsoidal distortion, and by Gibbs et al. [11], proposing a certain distribution of activation energies of processes causing the relaxation

and available to contribute to the overall change of the measured property. The problem of stress relief of the glassy state was recently examined in detail by Taub and Luborský [16,17], providing a mathematical treatment on the basis of flow phenomena (homogeneous deformation) that acts to improve the soft magnetic properties by decreasing the stresses present in the magnetic glassy materials. For the stress relief fraction, $\xi = (\tau - \tau_0)/(\tau_{(0)} - \tau_0)$, where τ , τ_0 and $\tau_{(0)}$ are the shear stress, the threshold value (below which the material does not flow) and the initial stress, respectively, the structural change is expressed as a viscosity ratio, $\eta/\eta_{(0)}$, and is solved as a function of temperature at a constant value of ξ , i.e.,

$$\ln[\eta/\eta_{(0)}] = (3\dot{\eta}/\epsilon)\ln\xi$$

ϵ being the elastic modulus, of the order of 10^{11} Pa. A plot of this equation indicates that the higher is the annealing temperature, the lower is the degree of structural change for the same amount of stress relief. In other words, the structural relaxation is minimized during the stress relief anneal by operating at the highest temperature possible. In order to achieve the most advantageous performance of the anneal at higher temperatures, as high as possible a heating rate is required to ensure that the stress relief is occurring at the desirably highest temperature and not during the time of heating. This requirement was reflected through a new progressive technique called flush annealing, in which heat is delivered to the sample by distinct pulses [15,16,17]. In practice, such a treatment is basically accomplished in two ways:

- (i) Continuously, where the glassy ribbon is pulled under a constant tension from a supply spool so as to pass over a heated block and immediately cooled rapidly from both sides, usually by a jet of nitrogen.
- (ii) Discontinuously by resistivity heating with short d.c. or a.c. electric current pulses flowing directly through the ribbon conveniently immersed in the cooling medium (oil or liquid nitrogen; the latter, however, is much less effective than is usually assumed).

The first procedure provides heating rates of about 2 to 7×10^2 K s⁻¹ up to maximum temperatures of about 500°C, whereas the second appears to heat the sample as fast as 10^4 – 10^5 K s⁻¹, achieving temperatures of about 800°C (usually reaching above the critical temperature, T_{cr} , without causing undesirable crystallization of the sample). The cooling rates, however, are about an order of magnitude lower than those found during pulse heating. The assumed temperature course can be conveniently illustrated with a hypothetical T – T – T diagram (see Fig. 2D). In practice, this method is a more convenient and faster way of annealing the samples without the need for time-consuming heating in a classical furnace and provides relaxation spectra of a similar character [19] as to those shown in Fig. 3.

NUCLEATION AND CRYSTALLIZATION WITH RESPECT TO UNDERCOOLING

The precipitation of a crystalline phase is conditioned by the formation of embryos (nuclei) of a critical size capable of consequent growth [21,22]. The total Gibbs energy required to form a critical nucleus is proportional to the cube of the isotropic interfacial energy and the reciprocal of the square of the change in chemical Gibbs energy per mole of the phase (conveniently assumed to be proportional to the degree of undercooling). It follows that the nuclei that form first may not be the phase with the lowest change in chemical Gibbs energy but an alternative metastable phase that has, e.g., a lower interfacial energy. With decreasing annealing temperature the critical radius also decreases and with a very high degree of undercooling the total Gibbs energy becomes negligible with respect to the activation energy for the rate-controlling transport of atoms across the interface of a nucleus. It is believed that a steady-state concentration of embryos exists at all times. At the very beginning, however, there ought to be a finite period (cf., Fig. 2A) during which this steady state is being established, resulting in transient nucleation [2,21,23], which was predicted for the crystallization of high viscosity melts. This is also reflected in the decisive role of the thermal pre-treatment during the melting for molecules forming chains (cf., Fig. 2E). In a classical nucleation theory a homogeneous type of nucleation is assumed, which, however, can be superimposed by heterogeneous or athermal nucleation [2,3,24,25]. Any kind of interfaces is likely to catalyse the nucleation as the newly crystallizing phase replaces a portion of the surface, thus reducing the total surface energy and also accelerating the surface diffusion. As the energy of amorphous-to-crystalline interfaces is smaller than that of crystalline-to-crystalline interfaces, heterogeneous nucleation at interfaces is not as effective as is usually presumed, particularly in comparison with the analogous case of crystalline materials. Quenched-in embryos that were too small at higher temperatures to become nuclei could, however, become crystallization nuclei at lower temperatures, which is typical of annealing regimes effective just below the crystallization temperature. These quenched-in embryos may not always possess the right structure or may be ineffective when comparable to the unit cell size, or may need some time to become effective nuclei, or they can even dissolve during annealing at high enough temperatures. The number of quenched-in embryos for such athermal nucleation therefore depends, for a particular alloy, only on the quenching rate applied during the preparation. Temperature-dependent (oscillating) nucleation is also worth analysing [23].

The growth of nuclei can be controlled by either interface reactions or transport processes and is dependent on the kind of overall process governing the crystallization and so may or may not reveal the compositional gradients at the interface. Additionally, long-range diffusion should not be forgotten as it can cause phase separation ahead of the crystallization front.

Similarly to nucleation, the thermodynamic driving force for crystal growth is an increasing function with increasing undercooling and is compensated by the opposite effect of viscosity (usually assuming the validity of the Stokes–Einstein law). The overall crystallization process is then controlled by the overlap of these two elementary processes, conveniently illustrated in the form of T – T – T diagrams [21,22] (see Fig. 2E), and nucleation–growth kinetics are best described by the popular form of the Johnson–Mehl–Avrami–Yerofeev–Kolgomorov equation [21,22,26–29]. It is understandable that the individual system exhibits a characteristic positioning of boundary lines in T – T – T diagrams, which are responsible for the given phase formation [26,29] controlled by the course of sample cooling and reheating (cf., Fig. 2F). A number of such graphical representations, in some instances not very common ones, may be found useful for pre-determining the possible formation of metastable phases as a response to a particular heat treatment.

CONCLUSION

Different types of thermal treatment and their impact on glassy metals have been studied. Such procedures are best visualized by using T – T – T diagrams and belong, in fact, to a wider family of thermoanalytical methods dealing with unusual temperature measurements and thermal property engineering.

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