Some Aspects of Melt Spinning Technique in making Amorphous Metallic Alloys : Fe - B, & Gd - Y - Ag Systems

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ABSTRACT

The methods of preparation of metallic glass having unusual properties that can be exploited technologically is described with special emphasis on Chill-block melt-spinning technique, which has been applied by the author to make ribnons of Iron-based and Gadolinium based amorphous magnetic alloys.

The criteria for glass formation including thermodynamic, kinetic and process factors are discussed. The exact determination of the cooling rate, inspite of its crucial importance in the making of amorphous metallic alloys, is very difficult. The present discussion is therefore mainly emperical and qualitative.

Important experimental aspects for the optimal production of ribbons is reported.

The structural characteristics, stability and relaxation process connected with the preparation of metallic glass are outlined.

The potential applications of metallic glasses and the prospect of persuing research in this field is pointed out.

1. Introduction :

The term "glass" in the original sense denoted noncrystalline solid lacking long range order, produced by quenching the liquid at rates high enough to bypass crystallization and thus retaining the random arrangement of the atoms corresponding to the liquid state. Metals or its alloys invariably crystallize when cooled from the liquidous to solid state at rates for which non-metallic liquids form glasses.

In fact it was not believed that metals can exist in other than crystalline form when solidified, before 1950, when Brenner et al(1) for the first time reported to have made amorphous nickel-phosphorus alloys by electrodeposition and observing one broad diffuse peak in the X-ray scattering pattern. It is now proved that by drastic quenching methods such as vapour condensation, electrodeposition, chemical deposition and liquid quenching, at rates approaching million degrees per

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second. Some metallic alloys, if not pure metals, can be produced and retained in the amorphous state.

Although the expression "metallic glass" is often reserved only for the non-crystalline metals produced by the cooling of a melt and amorphous metals are referred to as those obtained by atomic condensation, it is very difficult to distinguish structurally, or by other properties, between the amorphous metallic alloys of the same composition made by different methods. We can, therefore, use the terms metallic glass and amorphous metals as equivalent for most purposes. The present enormous interest in metallic glass is largely due to Duwez et al(2) who in 1960 reported two new methods of achieving very rapid cooling of the melt by propelling liquid alloy drops on to cold metal surface, where it would form thin films and thus rapidly solidify due ro thin geometry of the melt and the high conductivity of the metal substrate and the intimate contact between the two.

However, the great technological interest in this new material developed through the report of Pond and Roddin (3), who in 1969 introduced the method of preparing Metallic glass in large quantities in a continuous way and at low cost by directing a molten stream of the alloy onto the surface of a rapidly rotating drum.

Although the different methods used in preparing amorphous metallic alloys will be mentioned here. the present paper will mainly deal with the chill—block melt spinning technique (CBMS) used by the author in preparing amorphous Fe-B and Gd-Ag alloy systems in the form of ribbons.

It is to be noted that inspite of the large amount of literature available on amorphous metals, the making of metallic glass ribbons is still much of an art, because a straight forward application of the principle as exist in the literature, without some trial and practical innovation, will almost invariably lead to a display of fire work rather than an amorphous ribbon. This is quite understandable because a large number of variables involving thermodynamic, kinetic and processing factors needs to be optimized, and these again are different for different alloy compositions.

Some of the practical aspects of our applied techniques discussed here, will apparently look contrary to general principle for producing glass state. This, the author hopes, will add to the cumulative knowldge and understanding of the actual process of making glassy metals This is particularly because, the preparation of amorphous Gd-Ag system by melt-spinning technique, other than by atomic deposition, does not seem to have been reported before.

2. The Structure of an amorphous metal :

An amorphous material is analogous to a liquid in that, there is no periodicity in the arrangement of atoms, although there may be some short range order in the sense that certain values of the interatomic distance r are more common than others. However, a metallic glass is distinct from a liguid and solid, because of its deviation from thermodynamic equlibrium. While both a melt and its corresponding crystalline phase have their free energy F at a minimum for a given condition, an amorphous material because of its non-equilibrium state is at a higher value of F.

When a melt is cooled too rapidly its viscosity and relaxation time increase to the point where the internal equilibrium can no longer be maintained and the equilibrium configurations become inaccssible.

Two basic models are usually used to describe metallic glass.

One is microcrystalline or nano caystalline model, in which it is assumed that there are regions of the order of 15 Å in which the atoms are ordered. However, this microcrystalline model is distinct from fine grain polycrystalline system in that, these are much smaller in size and are oriented at random, providng no surface to the microscopic regins.

The other one is the topologically disordered model in which the atoms are packed in a continuous liquid like fashion.

"Non-crystallographic cluster" model, intermediate between the above two models have also been considered recently. However, an unambiguous differentiation between these models is still not possible by X-ray diffraction data due to the well-known line broadening effect, which occurs as the crystals become progressively smaller.

3. Diffderent methods for synthesizing amorphous Metallic alloys

The different experimental techniques developed to produce metallic glass can be grouped into two. One is the atomic deposition and the other is the fast cooling of the melt. The atomic deposition methods include condensation of a vapour on a cooled substrate [4], Electordeposition [5], chemical deposition [6] and deposition by sputteritg [7].

The methods using the principle of fast cooling of melt include gun technique [8], hammer and anvil process [9], the twin roll technique [10], the melt spinning (3) and melt extraction technique. Other variations of these techniques are also there.

As mentioned before, amorphous metals can be obtained from the corresponding liquids only at relatively high cooling rates of the order of 10^6 K/sec. This can be attained, as first suggested by Duwez, by a cooling processes that provide both a sufficiently high heat transfer coefficient at the interface of the liquid metal and the cooling medium and an appropriate thin metal crosssection, so that the heat can be conducted out of the spread out melt in the short time required. All melt quenching techniques therefore involve a metal substrate and a mechanism for spreading a thin layer of the molten metal on to the substrate.

Only the CBMS technique which is a modification of the melt spinning technique and has been used by the author will be reported here at length.

4. CBMS Apparatus :

As shown in a schematic diaram in Fig. 1, the CBMS apparatus consists mainly of a copper roller, the induction heater and the crucible.

The roller was driven by a variable speed motor via a tooth belt. The angular velocity could be varied in the range 0 - 2000 rev./min. Use of cog wheel rotation enable one to vary the surface velocity continuously from 10 to over 60 m S^{-1}. The diameter of the copper roller was 15 cm. The use of copper for the roller material was choosen for its good conductivity and mechanical softness, which allowed cleaning and polishing to be carried out easily. For room temperature work at least, it showed that there was no contamination of the ribbon from the roller material, and the careful preparation of the suface was more important than the material of the roller.

In choosing the diameter of the wheel we had to consider that vibration of the roller should be well below the

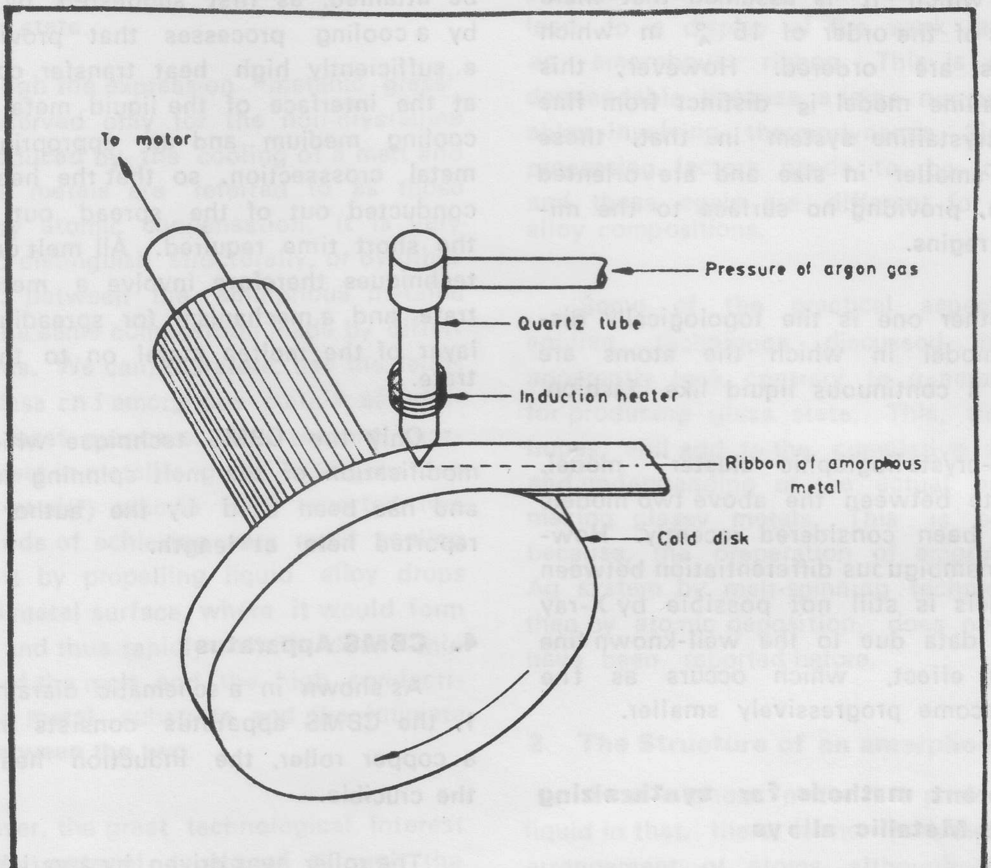

Fig. 1 Thin layer of molten alloy in intimate contract with the outer surface of metalic rotor is quenched in to ¢ amorphous

high frequency vibration of the melt puddle to avoid any influence of it on the geometry and uniformity of the ribbon, and to see that the ribbon does not remain in contact with the surface of the roller for a whole revolution and be hit from the back. A bigger diameter was thus prefered for the roller. The induction heater coil was made of hollow copper tubing which was cooled simultaneously by circulating water through its inner hole. The shape and diameter of the induction heater as also its winding were adjusted to produce proper temperature gradient. This was to avoid, sudden cooling of the melt in its way out of the crucible and blocking the nozzle. The crucible used was made of quartz tubing, having outer diameter 10 m. m. and narrowed down conically to 0.9 to 1.0 mm hole for the nozzle. The nozzle geometry was selected to minimize the contraction in the cross-sectional area of the molten zet as it leaves the nozzle orifice. Quartz crucible was suitable for repeated use in several successful runs and was transparent to make the melting process visible. It could withstand the sudden fast changes in temperature.

5. Experimental details

The master alloys were prepared in an Arc-furnace in an argon atmosphere. The buttons prepared were about 12 grams each. Care was taken to ensure thorough mixing and homogeneity of the alloy compositions, by turning over and remelting each button few times.

The mother alloys which were formed in the form of buttons in an arc furnace, were cut into small pieces, and for each run a single piece was introduced in the crucible. The crucible was connected from the top by rubber "O" rings and metal rings to the argon cylinder through a valve and a pressure gauge.

After proper cleaning of the roller surface and adjusting its speed to the desired value, as measured by stroboscope, the induction furnace was powered. When the melting temperature was reached as observed through a protective specticle, the injection pressure was applied by opening the pressure value. To avoid the turbulent of the wind, arising from the high speed of the roller in disturbing the melt puddle, cotton pad and metallic shield were used just beneath the roller. To avoid oxidation of the ribbon during its formation, an inert atmosphere was created around the roller by a slow stream of helium gas.

The speed of the roller, the volumetric flow rate, the orifice diameter, the substrate orifice distance, the injection angle etc. were adjusted by trial and error to get the best result in respect of the quality and the geometry of the ribbon.

6. Optimal Production Condition :

To obtain the best conditions for the production of glassy metallic ribbon in the laboratory by a single jet CMBS techniquc, the following points should be considered from the practical point of view.

i) The surface of the roller should be thoroughly polished and cleaned.

ii) The melt puddle has to be maintained stable and the volumetric flow rate through the orifice kept constant.

iii) Super heating of the melt has to be avoidəd by choosing the proper time of applying the pressure. Use of solenoid valve is preferable, although in our case ordinary gas value was used and visually controlled by looking at the melt in the crucible.

iv) The other parameters are the orifice diameter, substrate orifice distance, the injection angle, the inner shape of the crucible etc.

v) The width of a quenched ribbon is limited by thə stability of the spread out sheet of liquid alloy. Our observed limit was 10 mm. For the injection angle = 90°, which we used, the width of the ribbon depends mainly on the verticle flow rate puddle and is not much affected by the losses from the puddle as droplets.

vi) The maximum thickness of the foil is determined by the physice of the process, and provided sufficient heat transfer is ensured to keep the ribbon glassy, the thickness is mainly dependent on the substrate velacity V_s.

A qualitative relation between the volumetric flow rate and the geometry of the ribbon can be written as

$$Q = A_R V_s = W\bar{t} \quad V_s, \qquad \ldots \qquad \ldots \qquad (1)$$

Where A_R is cross-section of the ribbon and w and $\bar{t}$ are ribbon width and average thickness respectively. More rigorous relations based on emperical results as suggested by Kavesh(11) are

$$W = C \frac{Q^{0.75}}{V^{0.25}} \quad \ldots \quad \ldots \quad (2)$$

$$\bar{t} = \frac{1}{C} \frac{Q^{0.25}}{V_s^{0.75}} \quad \ldots \quad \ldots \quad (3)$$

C = Constant.

However, the above relations do not seem to be strictly applicaable in all cases and we have used them only as guide lines.

Factors Contributing to glass formation

There are three interrelated factors that determine glass forming tendency. These are, thermodynamic conditions that favour the liquid phase relative to the crystalline phase, the kinetic conditions that inhibit crystallization and the process factors that arise due to experimental conditions.

Quantities defining the thermodynamic factor for glass formation are liquidus temperature Tm at which the the alloy melts, the heat of vaporization H_v, and the free energy of all the phases (12) that arise or could potentially arise during solidification process. Viscosity of the melt, the glass transition temperature T_g and the homogeneous nucleation rate belong to kinetic parameters. The glass transition temperature is defined as the temperature at which the supercooled liquid takes on the rigidity of a solid, or more specifically at which the viscosity becomes 14.6 poise. Because of the very rapid variatron of viscosity with temperature in this region, Tg is not sensitive to arbitrary choise of viscosity for defining glass, as might seem.

Processing parameters are the cooling rate, the heterogeneous nucleative rate and the super cool.ng temperature interval. The temperature of the glass transition is slightly dependent on the cooling rate. At each cooling rate the glass will freeze in a different state of internal energy. This is illustrated in Fig. 2.

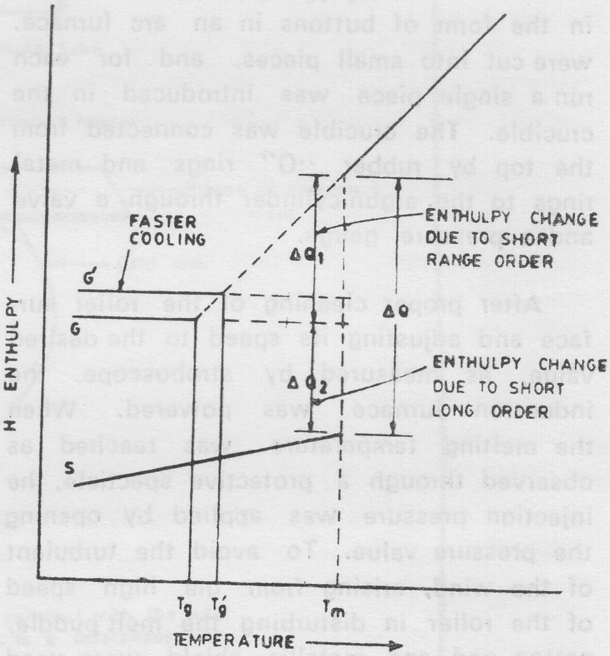

Fig. 2 Temperature dependance of Enthulpy H. G & G' corresponds to glass & S corresponds to Crystallin State.

At the melting point Tm, the enthulpy H of a crystal includes latent heat of fusion due to long range order and that due to short range order. In the case of rapidly melt the energy decrease due to long range oreer do not take place, thus leaving the system at a higher energy state. Heat treatment, relaxation and stability are thus important considerations in metallic glass. One could look at the glass forming tendency from the atomic point of view such as size difference between the constituent elements (13). Thus, it appears that appreciable size difference between the components in the glassy alloy is a necessary condition for ready glass formation.

Valence difference may also be be important in favouring glass formation.

A single parameter that express glass forming tendency is the ratio of the glass transition temperature to the melting temperature defined as

$$T_{gr} = T_g / T_m$$

Higher values of T_{gr} obviously favour glass formation. For metallic glass to be formed by rapid cooling, Tgr should be greater than 0.45 [14]. Based on alloy compositions, there are two major groups that readily form glasses.

The first groups is rererred to as metal metalloid systems, where the metal is from M_n, F_e, C_o, N_i, Pd, or P_t and the metalloid is B, C, Si, Ge or p, our prepared Fe--B system belongs to this metal—metalloid group.

The other major group is referred to as intertransition metal systems. our Gd=Yt—Ag system belong to this group.

8. Examining the amorphosity :

The amorphous nature of the melt spun ribbons of Fe–B and Gd—Yg—Ag alloy systems were chequed by x—ray diffraction, using CuKα radiation. It was observed that the ribbons that showed broad diffraction maximum and no low angle scattering, were also ductile and could be bent with out breaking.

In those cases for which low angle scattering did appear and the broad diffraction peak were subdued, showing the presence of microcrystalline phase, the speed of the roller had to be increassed. This however, produced thinner ribbons. The maximum thickness of the amorphous ribbon that we produced were about 100 microns for F_e–B system .

The nature of the broad diffraction peak observed is shown in fig. 3.

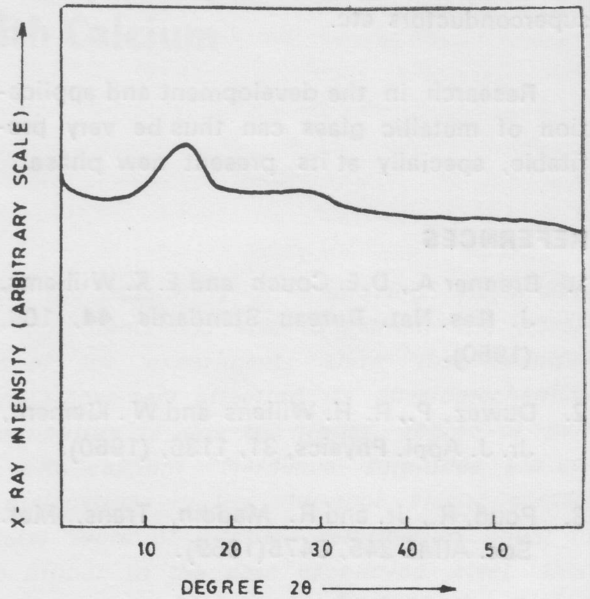

Fig. 3 X-ray diffraction from the top surface of Fe_{80} B_{20} Amorphous Ribbon.

9. Applications of Metallic glass :

The absence of crystallinity, lack of grain bounderies and line defects and also its chemical homogenity provide metallic glass with unusual mechanical, magnetic and chemical properties that can be technologically expoited [15].

Iron—base, copper–base and titanium base metallic glass can exhibit strengths in excess of those exhibited by forged materials. amorphous ferromagnets have interesting magneto--elastic coupling and magnetic softness due to absence of crystalline anisotropy. Glassy metals are unusually corrotion free because of the absence of local electrochemical potential differences. Thus by a recently developed technique called laser glazing, surfaces of expensive metallic equipments are made amorphous to avoid corrosion. Metallic glass has many other refined applications like development of magnetic bubbles for computer memory, amorphous superconductors etc.

Research in the development and application of metallic glass can thus be very profitabie, specially at its present new phase.

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