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AMORPHOUS METALS: MATERIALS AND APPLICATIONS

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Abstract. A survey is given of the alloy design criteria, fundamental structure-property relations, present materials and main applications of amorphous metals.

Introduction

Amorphous metals can be produced by various processes such as vapour deposition, sputtering, galvanic deposition and others. But the recent advances in forming amorphous metal ribbons, wires and powders by rapid solidification processing have increased both scientific and technological interest considerably because amorphous metallic material is available now in a wide variety of compositions and in sufficient quantity. Amorphous metals thus produced are commonly called metallic glasses or glassy metals. These new materials are just at the threshold of becoming industrial products because they exhibit outstanding properties and can be produced economically. Although the present paper pertains primarily to amorphous metals formed by rapid solidification, most of its contents can be applied to amorphous metals formed by other methods as well because it has been found that their structure is qualitatively the same even though quantitative differences do exist, particularly in the as-formed state.

The pertinent literature is vast and is growing rapidly. Two triannual international conference series, "Rapidly Quenched Metals" [1] and "Liquid and Amorphous Metals" [2], and practically all current conferences on solid state physics, magnetism, physical metallurgy, glass science and many others are covering the subject.

In this paper the criteria for selecting particular materials, the requirements for their production from the melt and some fundamental structure-property relations are treated first, followed by a discussion of the main field of present materials and applications, i.e. soft magnetism.

Criteria of alloy selection for amorphous metallic materials

As with other alloys the basic components are chosen according to their atomic solid state properties such as magnetic moment (e.g. Fe,Co,Ni), high melting point and corresponding stabilisation and strengthening of the glass structure (e.g. Nb, Ta,Mo,W), propensity to form passivating surface films(e.g.Cr,P)etc.

Next the so-called glass-forming ability (GFA) of the alloy has to be established. This is essentially achieved by choosing alloy compositions with a high viscosity immediately above the liquidus temperature T_l and a low driving force to form simple crystal structures. Little is known about the GFA from first principles, but a number of useful empirical rules have been found, relating to

- atomic size ratio [3]
- valency electron concentration,
- electrical resistivity and its temperature coefficient,
- thermodynamic bulk properties [4],
- phase diagrams [5], etc.

In the important group of binary and multicomponent transition metal - metalloid (T-M) amorphous alloys it has been found that (i) B, C, Si and P are strong glass formers (as in silicate glasses), (ii) low eutectic temperatures relative to the melting points of the constituent elements (or nearest stable phases) are indicating ranges of good glass-forming ability, and (iii) such eutectics occur preferentially near compositions $T_{70-90}M_{30-10}$ (subscripts mean atom-%). Other alloy systems such as binary and multicomponent systems involving T-T, T-B, B-B and noble metal component combinations are also found to form metallic glasses in certain combinations and composition ranges.

The third aspect of alloy design is the resulting amorphous structure which, however, is practically unknown for all amorphous alloys of technical interest and rather incompletely known even for those binary alloys which have been studied structurally [1,2]. This is a considerable disadvantage compared to crystalline alloys because the structure - in combination with its composition, temperature and relaxation dependent variations - determines a number of essential features of the material such as:

- structure dependent properties,
- variability of isotropic short range order,
- propensity to the formation of anisotropic short range order,
- propensity to decomposition,
- propensity to crystallisation,
- kinetics of irreversible structural relaxation,
- kinetics of reversible structural relaxation,
- kinetics of stress relaxation.

As an example the two-dimensional atomic arrays shown schematically in Fig. 1 indicate three possible configurational variants which have effects as listed above.

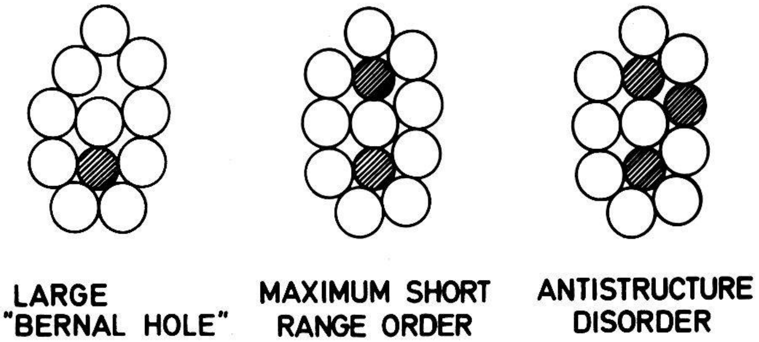

Fig. 1. Schematic representation of structural features affecting properties and kinetics of atomic displacements.

The state of maximum short range order can be associated with an extremum in structure dependent properties and a minimum in rates of atomic displacements. The structures with a deficiency or an excess of the minor alloy component may alter properties that depend on atomic configuration considerably and will, also, contribute to a higher atomic mobility. Indications that such structural variations do occur and give rise to the respective effects have been observed in numerous cases. However, for lack of concise structural information correlations of this kind are still tentative

Producing Metallic Glasses

In any process to produce metallic glasses two conditions have to be satisfied

- the alloy must exhibit a high GFA,
- the cooling rate must be sufficient to suppress crystal nucleation.

On cooling below the liquidus temperature T_l the rate of nucleation increases first, due to the increase in free enthalpy difference between melt and crystallizing phase, and decreases again due to the decrease in diffusion constant. This classical nucleation behaviour is shown for some glass forming alloys and for pure Fe in Fig. 2 [6].

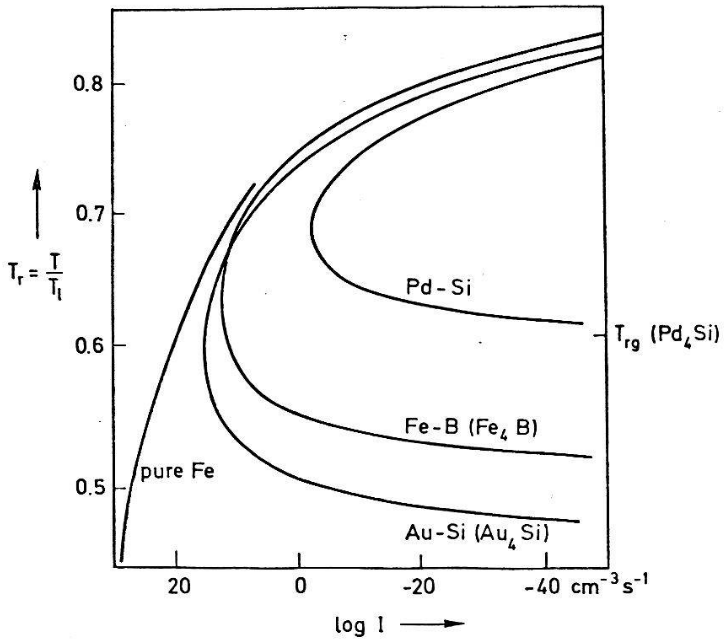

Fig. 2. Rate of Crystal Nucleation in Glas Forming Alloys [6].

A characteristic temperature to be taken into account regarding the formation of metallic glasses is T_g, the glass transition temperature, which is associated with a shear viscosity of $\eta \simeq 10^{13}$ poise, and which corresponds to the threshold temperature below which the undercooled melt does not acquire its thermodynamic equilibrium and crystallizes extremely slowly. The condition for the present procedures to produce amorphous metal ribbons is that the relative glass transition temperature $T_{rg} = T_g/T_l \gtrsim 0.5$. If this relation is satisfied, quenching processes associated with maximum cooling rates $10^5 \lesssim dT/dt \lesssim 10^6$ Ks^{-1} are suitable to form metallic glasses. The most common procedure of this kind used both for laboratory experiments and industrial production is the casting of a ribbon through a suitable nozzle onto a rapidly rotating cooling wheel, invented over 75 years ago. Resulting ribbons range from about 15 to 100 µm in thickness, essentially limited by conditions for laminar flow and heat conduction, and 1 to several 100 mm in width, depending on requirements and equipment design.

Basic Relations between Structure and Properties of Amorphous Alloys

Even though metallic glass structures can be analysed and described very incompletely only, some features are common to all and basic to their properties:

- the high degree of disorder imparted by the melt,
- the presence of short range order and its tendency, in many cases, to increase irreversibly given sufficient thermal activation,
- the propensity to reversible changes in degree of isotropic and anisotropic short range order by heat treatments, and
- the instability of extended, high energy structural defects such as the equivalent of crystal dislocations.

Table I gives a survey of how these basic structural features affect principal properties

Table I. Basic Structure - Property Relations

Structural Feature	Property			
	electrical	magnetic	mechanical	chemical
disorder, non-periodic structure	high residual resistivity ρ_0, low or negative $d\rho/dT$	absence of crystal anisotropy ($K_1=0$), low eddy current p_W and hysteresis losses p_h	low elastic constants E,G,K; viscous flow	high surface activity, high rate of passivation high solubility of H
short range order, irreversible increase on annealing			high yield stress σ_0 embrittlement	
reversible and anisotropic short range order		hysteresis loop B(H) adjustable in wide limits, low hysteresis losses p_h		
instability of structural defects			high yield stress σ_0, low work hardening ratio $d\sigma/d\varepsilon$	high perfection of passivating films

Application Related Magnetic Properties

Due to the intrinsic soft magnetic properties and their superior magnitude compared to the properties of conventional permalloys and ferrites [7], the ferromagnetic metallic glasses lend themselves to a number of applications in electronics [8] and for power electric devices such as transformers [9, 10].

The absence of crystal anisotropy and of strongly interacting crystal defects leads to weak interactions between domain rotation and domain wall motion with the amorphous structure. This means that a low coercive field and high permeability values can be attained. Moreover, the magneto-elastic anisotropy which is proportional to the product of elastic stress and magnetostriction constant λ_s can be minimized by stress relaxation annealing or by choosing an alloy composition for which $\lambda_s = 0$, e.g. in certain Co base alloys.

Furthermore, it is desirable that uniaxial magnetic anisotropy K_u can be induced by annealing in a magnetic (or stress) field. The propensity of amorphous metals to reversible anisotropic short range ordering leads to $K_u \lesssim 8 \cdot 10^3$ Jm^{-3} in suitable alloys and states of heat treatment, comparable to the magnitude of K_u attainable in permalloys. This permits to induce by heat treatment hysteresis loops in widely variing shapes which are desired for different applications.

Finally, low power losses during magnetization reversal are required for most applications. The total losses are essentially given by the sum of the static or hysteresis losses p_h and the eddy current losses p_w. The high permeability and low H_c inherent in metallic glasses lead to a low magnitude of p_h. The second term $p_w \sim (d^2/\rho)(B \cdot f)^2$, where d = thickness and ρ = electrical resistivity of the material, B = induction and f = frequency, is favourably small due to two properties of amorphous metal ribbons: their low "natural" thickness d and their high resistivity ρ, which exceeds that of comparable Fe-Ni and Fe-Si crystalline alloys by a factor of about 3. Therefore, power losses of amorphous metals can be lower than those of ferrites even at high frequences [7].

The magnetic properties of some typical transition metal-metalloid metallic glasses presently in use are listed in Table II.

Table II. Magnetic Properties of Typical T-M Metallic Glasses Presently in Use

Alloy	J_s T	H_c mA/cm	μ_i (50 Hz)	μ_{max} (50 Hz)	p_{Fe} (20kHz 0,2T) $W \cdot kg^{-1}$	loop1)
$Fe_{81}(Si,B,C)_{19}$	1.6	35	-	260 000	30	Z
		60-80	8 000	-	10	F
$(Fe,Ni)_{78}(Mo,Si,B)_{22}$	0.75-0.85	6-12	-	300 000	25	Z
		10-40	10 000	-	8	F
$(Co,Fe,Mn)_{70..76}(Mo,Si,B)_{30..24}$	0.55	3- 5	-	600 000	6	Z
	0.8	3-5	50... 100 000	-	4	F

1) Z:Rectangular Loop, F: Flat Loop

As an additional aspect of magnetic applications it should be noted that not only the magnetic properties as such but also other, concomitant properties render amorphous metals suitable for particular and often innovative applications. Thus, e.g., their high yield stress, high corrosion resistance (if alloyed with Cr or P) and low ribbon thickness are utilised specifically in a number of cases.

Magnetic Applications

Table III gives a rather comprehensive list of potential magnetic applications, but obviously a few typical examples only can be dealt with in the present context regarding the particular reasons and advantages of employing metallic glass materials

Power Distribution Transformers. In power distribution systems with rather small mains transformers, e.g. in the 35 kVA range, leading to individual homes etc., the core losses under load and, in particular under no-load conditions, can take up a substantial fraction of the energy supplied.

Table III. Major Magnetic Applications of Metallic Glasses

Presently in the Process of Introduction

Field of Application	Specific Application	Major Properties Used
electrical power supplies	50/60 Hz distribution transformers	low power losses
	400 Hz transformers	low power losses
	transformers, reactors transductors for switched mode power supplies	low coercivity, low power losses, variable hysteresis loop
	transformers and chokes for high repetition rate switching cascades	low power losses, highly rectangular hysteresis loop
magnetic cores and inductive components	various inductive components	low power losses, highly variable hysteresis loop
	audio, video, data magnetic heads	high permeability, low power losses, high wear resistance
	ground fault interruptors	high permeability
transducers and sensors	magneto-elastic force and displacement transducers, inductive press keys	high magneto-elastic effect, low coercivity, high permeability, high yield stress
	acoustic delay lines	high magneto-elastic effect
	personal identification and theft protection devices	low coercivity, high permeability
	bistable pulse generator devices	high permeability, high yield stress
magnetic shielding	flexible shielding wrap, flexible cable shielding	high permeability, high yield stress
	cassette shielding spring	high permeability, high yield stress
	temperature tranducer (based on ultrasound-transit time)	high magnetostriction, high yield stress
machinery	electric motors	low power losses
	high gradient magnetic separators	high saturation induction small radius of ribbon edges, possible low remanence, high corrosion resistance

Therefore, low loss core materials are in demand. At 50 and 60 Hz amorphous Fe base metals with losses 60 to 70 % lower than those of oriented silicon-iron alloys are attractive core materials. Developments of suitable materials, core and transformer designs, heat treatment and manufacturing technologies are presently underway, in particular in the USA and Japan, which are expected to lead to viable products in the late 1980s.

Inductive Components for Switched Mode Power Supplies. Standard mains power supplies are replaced increasingly by switched mode power supplies due to their superior performance. Their circuits for which components such as transformers, chokes and transductors are required, operate at frequencies in the 20 to 100 kHz range. The wide variety of hysteresis loops, low coercivity and low power losses of amorphous core materials permit to construct the required inductive components such as to yield higher performance, to generate less heat, to be smaller in size and to even be less expensive in a number of cases than comparable components incorporating conventional materials.

Magnetic Heads. Audio, video and data storage systems require magnetic head materials combining high permeability, low power losses and high wear resistance. Amorphous materials offer this combination and have been successfully tested as well as introduced commercially as one of the earliest applications.

Magneto-Elastic Transducers. The hysteresis loop of a soft magnetic material is distorted if an elastic stress is applied. This magneto-elastic effect cannot be utilized with most crystalline alloys because of their low elastic limit. But amorphous metals, having a high yield stress, lend themselves to be manufactured into force or displacement transducers, e.g. in ring form, which can be deformed and spring back purely elastically. Concomitant changes in induction can be converted into electrical signals either for analogue output or for switching functions.

Flexible Magnetic Shielding. Magnetic shielding of static or low frequency electro-magnetic fields requires a high permeability material and mumetal is commonly used. But its permeability is very sensitive to (i) elastic distortions, because its anisotropic magnetostriction constants λ_{100} and λ_{111} cannot be reduced to zero simultaneously, and to (ii) plastic deformation occuring at low stresses because of its low elastic limit. Amorphous metals, however, have an isotropic magnetostriction which can be adjusted to be practically zero by composition control and heat treatment; furthermore, their yield stress is high, so that they are much less sensitive to plastic deformation. Therefore, they can be utilized for flexible, magnetically and mechanically insensitive shields in the form of wrapping strip, woven mats and braided or helically wound cable shieldings.

Conclusions

Despite the limited scientific clarification of structure-property relations of amorphous metals, their development to technically useful and superior materials is well underway, in particular with regard to magnetic properties and applications. Other fields of application have not yet reached a comparable degree of development, mostly because competitive materials do exist both with regard to properties and cost. But the technology of rapid solidification processing, having been developed earlier and revided by the production of amorphous metals, is now beginning to be exploited for a variety of amorphous and crystalline metallic and non-metallic materials, leading to a wide field of high technology in which many questions to materials physicists remain to be solved.

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