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# AMORPHOUS METALS: PHYSICS AND APPLICATION

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## Abstract

The unique combination of the metallic bond and glassy structure makes amorphous metals very useful for various applications. However, in order to harvest the maximum benefit from the new materials, their physical properties must be throughly understood. This is not an easy task for the amorphous solids, hence the applications of amorphous metals usually precede their detailed understanding. Here, instead of giving an extensive review of the present and potential applications of amorphous metals we focus our attention to the question why these properties. In particular we use our recent results for the magnetic and mechanical properties of Fe-Ni base alloys in order to discuss the nature of their magnetism. We also point out their exceptional frequency characteristics and discuss a possible future developments in the research and applications of amorphous metals.

## 1. Introduction

Ten years passed from the first systematic appearence of the amorphous metals on our condensed matter conferences /1/. The worldwide research into the properties of amorphous metals has intensified considerably over these ten years. This has been result of the need for new materials, the development of new fabrication methods, and the fact that fundamental ideas about the properties of highly disordered materials in general can be tested by a variety of experimental methods. The amorphous metals are already used in numerous applications: the exploitation of soft ferromagnetism in Fe-B type metallic glasses being the most notable example.

The research into the properties of amorphous metals has also progressed considerably in our country. The pioneering work of Zagreb group /1/ has been continued and expanded by several research teams throughout Yugoslavia. The range of research topics has also been brodened and presently includes the preparation conditions, the formation and stabillity (including relaxation), almost all physical and some chemical properties (corrosion resistance). Except for the local ones (such as NMR and the Mössbauer effect) almost all other experimental techniques are presently employed in these investigations. Various forms of collaboration with about twenty well known laboratories from Europe, USA and Australia have also been established. The Yugoslav contributions to the research of amorphous metals have been published in over 200 scientific papers.

The space allowed for this paper is not sufficient in order to describe the main results of the above research. Because of that we give here only a brief account of our contemporary research into the selected physical properties of Fe-Ni base metallic glasses. Since these alloy systems are already exploited in the applications of soft ferromagnetism we start with the short discussion how the favourable properties and the simplicity of making the final product affect the applications of metallic glasses. Static magnetic and mechanical properties of FeNiBSi amorphous alloys are discussed in parallel and the clue for their understanding given. We also present some very recent results for the dynamical magnetic properties (core loss, coercive field and remanence) of these alloys, which are crucial for their technological applications. Finally, we try to indicate some research topics which could be of particular importance for the future understanding and technological applications of amorphous metals.

## 2. Basic properties and the efficiency of production

Amorphous metals are nonequilibrium (metastable) metallic solids with the structure similar to that of glass. When prepared by the rapid solidification (quenching) from the melt they are usually called metallic glasses or glassy metals. In amorphous metals, the interplay of the amorphous (glassy) structure and of the metallic bond often yields a unique combination of favourable properties of metals and glasses as illustrated in Table 1. We emphasize here that it is the combination of properties (rather than a single property) which makes the amorphous metals so useful for various applications. In particular (Table 1) some amorphous alloys may have very high yield strength, hardness, breaking limit and ductility, and to be, at the same time, extremely soft ferromagnets (a narrow hysteresis loop) with a rather high resistivity and corrosion resistance. In the case of metallic

Table 1: Comparison between the properties of Metals, Glasses and Amorphous Metals /2/

| PROPERTY | METAL | GLASS | AMORPHOUS METAL |
|---|---|---|---|
| Structure | Crystalline | Amorphous | Amorphous |
| Bonding | Metallic | Covalent | Metallic |
| Yield Stress | Non-ideal | Almost ideal | Almost ideal |
| Workability | Good,Ductile | Poor,Brittle | Good,Ductile |
| Hardness | Low to High | Very High | Very High |
| U T S | Low to High | Low | High to Very High |
| Corrosion Res. | Poor to Good | Very Good | Very Good |
| Optical Trans. | Opaque | Transparent | Opaque |
| Thermal Cond. | Very Good | Poor | Good |
| Resistivity | Very Low | Very High | Low |
| Magnetic Prop. | Various | Non-exsistent | Various |

glasses the efficiency of their production has also beneficial effect on their applications.

A qualitative understanding of the basic properties of metallic glasses is rather simple. The amorphous structure (the absence of translational invariance or long range order) combined with the metallic bond (strong and isotropic) makes the metallic glasses uniquely homogeneous and isotropic solids. Indeed these properties alone can explain most of the properties of metallic glasses depicted in Table 1. In particular, good mechanical and corrosion resistant properties arise from their homogeneity (for example, high yield strength and the absence of pitting corrosion are due to a lack of the well defined extended defects, such as the grain boundaries and specific dislocations), whereas the soft magnetism arises from their isotropy (the absence of the magnetocrystalline anisotropy). Similarly the disorder alone explains well the qualitative features of their transport properties /1/: rather high resistivity and its low temperature coefficient arise from frequent scattering of the conduction electrons on structural (frozen-in) disorder.

A more detailed, quantitative understanding of the properties of amorphous metals is however very difficult to achieve. This arises from the disorder (a lack of periodicity) which makes both the techniques for the determination of their structure (x-ray and other diffractions) and the usual methods of the theoretical solid state physics (based on periodicity) less effective. Therefore a detailed and systematic experimental investigation is the main way of increasing the knowledge and understanding of metallic glasses.

The economy considerations (for example the cost of raw materials and the efficiency of production) play often a decisive role in the applications of the new materials. The materials (therefore their costs) depend on the specific application and are often practically the same both for crystalline and corresponding amorphous alloys. For example, the main constituents of crystalline soft ferromagnets are Fe, Co, Ni and to some extent Mo, Cr, Mn, Cu, Zn, Al, Si, P and C. In the case of amorphous ferromagnets the only addition to this list is some percentage of B. Therefore, rather high initial prices of amorphous ferromagnets were not due to cost of materials and are infact steadily decreasing with time as shown in Fig.1. The price of a larger quantity of amorphous ferromagnet (lower bound in Fig.1) is expected to reach that of the silicon steel in 1990.

A speed and simplicity of production often play a decisive role for the application of new materials. Although manufacturing of metallic glass (melt spinning) employes new, high technology way of making thin metallic sheets /3/, it is basically less complicated than the conventional process of making e.g. the nonoriented or grainoriented silicon steel. Fig.2 shows material processing flow chart for making silicon steel and amorphous ferromagnets both for the transformer core applications. We note that elaborate process involving six different operations for conventional materials is reduced to two operations only for the amorphous ones.

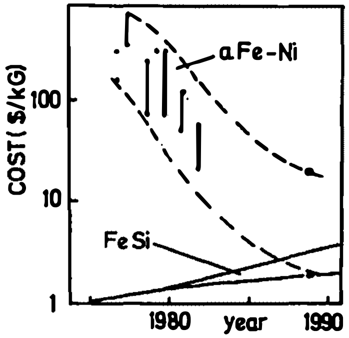


Fig.1 Estimated price range for amorphous metal and silicon steel. Allied Metglass prices. /4/

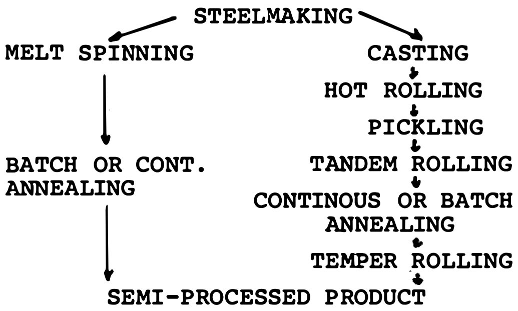


Fig.2 Processing flow chart for. amorphous alloy and silicon steel.

The fabrication and processing of amorphous ferromagnets (metals in general) is also less time and energy consuming. As shown in Fig.2 the as-obtained amorphous ferromagnet needs some thermal and possibly strain or magnetic field treatment in order to obtain the best characteristics. This arises because of sensistivity of the magnetic properties on the atomic short range order (SRO) which can be modified by a suitable treatment. Furthermore, annealing reduces internal strains induced during the fabrication (rapid quenching) which greatly improves the soft magnetic properties of magnetostrictive alloys. The annealing temperatures for the amorphous ferromagnets are however much lower and the annealing times shorter than those required in processing of silicon steels.

By necessity, the amorphous metal transformer foils are several times thinner than conventional Fe-Si core material. This is beneficial for the high frequency applications but poses some problems in designing large power transformers which require new engineering solutions. Inspite of that the substitution of the conventional distribution transformers with those with the amorphous metal core has already started in U.S.A. A more detailed account of these and other present and potential applications of amorphous metals can be found elsewhere /5,6,7/.

## 3. Band structure and properties of FeNiBSi glasses

The electronic band structure is also modified by disorder and the sharp features in the electronic density of states (DoS) are smeared out in amorphous metals. This often results in a smooth variation with concentration of the physical properties in a given amorphous alloy system. As an example we show in Fig.3 the variation of residual resistivity for crystalline $Fe_xNi_{1-x}$ and amorphous $(Fe_xNi_{1-x})_{80}B_{18}Si_2$ alloys with x. A sharp maximum occuring around 70% of Fe (permalloy) in crystalline alloys is absent in the amorphous ones /8/. As shown below smooth variations with Fe content are characteristic for all properties of Fe-Ni base amorphous alloys.

In order to obtain amorphous Fe-Ni base alloys an addition of about 20% metalloid(s) is neccessary. The metalloid, in addition to lowering the quenching rate required for the formation of glassy state, directly affects structure (SRO) and properties of these alloys. Initially it was thought that metalloid atoms fill the empty sites between randomly distributed metal atoms. More recently it is found that metalloid atoms determine the chemical short range order (CSRO) in these alloys and local atomic arrangements similar to those in corresponding intermetallic compounds ($Fe_3B$, $Fe_3P$, $Ni_2B$ etc.) have been detected /9/. Therefore the effect of metalloids is not merely dilution of ferromagnets atoms and moreover a simple charge transfer picture (in which the s- and p-electrons of metalloid fill the d-band of transition metal) is probably not correct. The more appropriate description of diverse effects of the same metalloid in different alloys /10/ is probably provided in terms of hybridisation of valency electrons of the metalloid and transition metal /11/. However, the calculations along these lines are rather involved and their results rather uncertain. Therefore the understanding of amorphous ferromagnets depends primarily on intuition and systematic research.

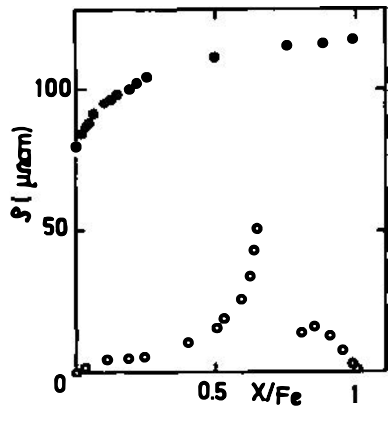


Fig.3 Residual resistivity of amorphous $(Fe_xNi_{1-x})_{80}B_{18}Si_2$ and crystalline $Fe_xNi_{1-x}$ alloys vs x.

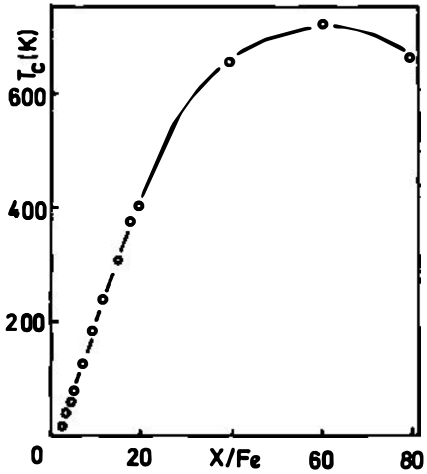


Fig.4 Curie temperatures of amorphous $Fe_xNi_{80-x}B_{18}Si_2$ alloys.

In what follows we briefly summarize some results relevant to understanding of the electronic band structure (thus of magnetism) of amorphous $Fe_xNi_{80-x}B_{18}Si_2$ alloys ($0<x<80$). The results obtained for these alloys are typical for all amorphous Fe-Ni base alloys (including those applied in industry), thus the conclusions reached by our study apply to all these alloy systems.

The magnetic phase diagram of FeNiBSi alloys (represented by the variation of the Curie temperature ($T_c$) with Fe content) is shown in Fig.4. We note a strong depression of $T_c$ on Ni-rich side which results in paramagnetism of alloys with less than 2,5% Fe /12/. Analogous behaviour but with somewhat different critical Fe content ($x_c$) is observed in all Ni-base glasses. The paramagnetism of Ni-base metallic glasses with >18% of metalloid contrasts sharply with ferromagnetism of crystalline Ni and is not properly understood at present. Some empty d-states of Ni around the Fermi energy ($E_F$) indicate that this paramagnetism is not due to charge transfer only. The onset of ferromagnetism ($x_c$) introduces a wealth of new phenomena, first observed in these alloys /12/. However, we concentrate here on homogenous ferromagnetic alloys ($x>x_c$) which are of technological interest ($T_c>300$ K). The Curie temperatures of the amorphous Fe-Ni base alloys are strongly reduced (thus the exchange coupling J is also reduced) in respect to those of their crystalline counterparts. (This has however no effect on their applications since magnetization depends only weakly on temperature for $T<0,5\ T_c$ which is above room temperature for most of these alloys.) We also note that their $T_c$'s (thus J) saturate and even decrease a little at Fe-rich side.

Like their crystalline counterparts the alloys in this range are itinerant (band) ferromagnets /8,10,11,13/. However in crystalline Fe-Ni alloys the type of magnetism (weak or strong) changes with changing composition. This change is accompanied with anomalies in electrical (Fig.3), magnetic and mechanical properties /14/ in the invar region. The obsence of these anomalies in amorphous Fe-Ni alloys probably indicates no change in type of magnetism. Therefore it remains to be seen whether the magnetism of amorphous Fe-Ni alloys is of strong (like in Ni) or weak (like in Fe) type. There is no unique answer to that question at present. We will show however that the properties of FeNiBSi alloys (and probably of all Fe-Ni alloys with >20% of metalloids /8/) are described the best in terms of a strong ferromagnetism.

The variation of magnetization with Fe content in FeNiBSi alloys is shown in Fig.5. A linear variation for Fe contents above 30% with a slope corresponding to the Bohr magneton per valency electron reflects the d-band filling and is consistent with strong magnetism (one d-subband full). (The temperature dependence of magnetization in these alloys /15/ also supports that view.) A rapid decrease of magnetization for Ni-rich alloys reflects the instability of magnetism in amorphous Ni alloys, as discussed earlier. As for other Fe-base metallic glasses the saturation magnetization of FeBSi (Fig.5) is about 20 pct. lower than that of silicon steel. However this has no effect on their application in power transformers, since thir operating inductions (1,2-1,4 T) are below that value.

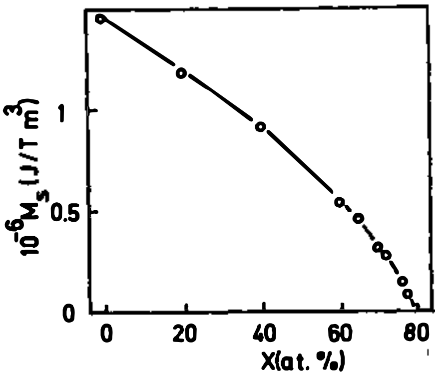


Fig.5 Saturation magnetization of amorphous $Ni_xFe_{80-x}B_{18}Si_2$ alloys at 4K.

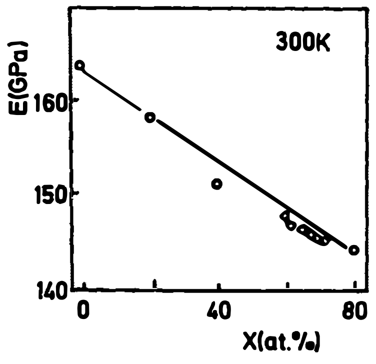


Fig.6 Young's modulus of amorphous $Ni_xFe_{80-x}B_{18}Si_2$ alloys at 300 K.

Recently, the above findings about the band structure and inter-electronic correlations (J,U) in amorphous FeNiBSi alloys have also been confirmed by the measurements of their mechanical properties /16/. Fig.6 shows the variation of the Young modulus (E) in FeNiBSi alloys with Fe content. E increases almost linearly with Fe content. The relative change in E is about 15 pct. and agrees well with that observed in other Fe-Ni base glasses /17/. This indicates that variation of E is determined by Fe/Ni ratio (thus filling of the d-band) and not by the content or type of metalloid.

Smooth variation of E with the effective number (Z) of d-electrons resembles that expected /18/ for the cohesive energy ($E_c$) and the bulk modulus (B) of transition metals. (It is not due to magnetic energy $\sim M_s^2$ as erroneusly suggested /19/.) Indeed, strong cohesion of transition metals is largely due to d-electrons and for isotropic metal (such as metallic glass) E is proportional to B. Whereas in crystalline 4d- and 5d- transition metal series $E_c$ varies as expected ($\sim Z(10-Z)$), in 3d- metals $E_c$ is strongly reduced and the specific atomic volume incresed towards the middle of series /20/. Indeed both B and E of crystalline Fe are lower than those of Ni /14,20/. This is due to correlations between d-electrons (U,J) which are particularly strong in 3d-metals. The correlations (Coulomb repulsion, exchange interaction and spin-orbit interaction) in general decrease the cohesive energy, hence increase the atomic volume and decrease elastic moduli (E,B).

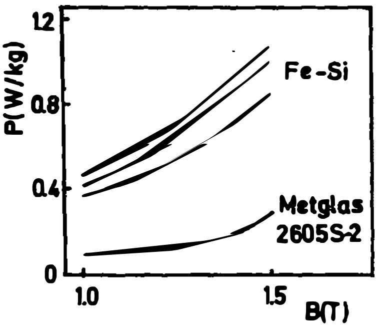
The increase of E with Fe content in FeNiBSi glasses apparently shows that correlation effects are less strong than in corresponding crystalline alloys. This is consistent with the observed (Fig.4) lower Curie temperatures (thus smaller J) and with a smaller change of the specific atomic volumes /21/ in amorphous FeNiBSi alloys. Furthermore, the absence of the anomalies in E does not support a change in the type of magnetism in these alloys.

It is interesting to note that the microhardness ($H_v$) of amorphous FeNiBSi alloys varies with Fe content /16/ in a similar way as E. A simple correlation between E and $H_v$ (also observed for other metallic glasses) is surprising since plastic properties ($H_v$) of crystalline metals are associated with defects and microstructure of a given sample. Hence $H_v/E$ is not well defined for a crystalline metal or alloy. In amorphous metal however the absence of well defined extended defects enables the nature of bonding to show up also in plastic properties.

## 4. Soft ferromagnetic properties

Basic magnetic properties ($M_s$,$T_c$) of amorphous ferromagnets are inferior to those of silicon steels. However for the soft ferromagnetic materials the easy of magnetization (narrow hysteresis loop) outweighs small difference in $M_s$. (Moreover the present-day power transformers are designed to work at 1,2-1,4 T which is well within the reach of metallic glasses, $B_s$<1,8 T.) Soft ferromagnets dominate the world market for the magnetic materials and their sale amounts to several billions of US dollars per year.

Static magnetization hysteresis of a ferromagnet reflects the magnetic anisotropy (MA) arising from various intrinsic sources. The intrinsic origins of MA are primarily the structural anisotropy and the magnetostriction. Being macroscopically isotropic amorphous ferromagnets should have no magnetocrystalline anisotropy. However even in non-magnetostrictive metallic glasses there is some MA. It arises from the local anisotropy, associated with the atomic SRO, defects and local strains in magnetostrictive materials. As all these sources of MA can be effectively reduced by suitable post-preparation treatments, the amorphous ferromagnet can be made magnetically more soft than any other material. Consequently, the transformer core made from suitably selected and annealed metallic glass my have core loss several times lower than that made from silicon steel (Fig.7).



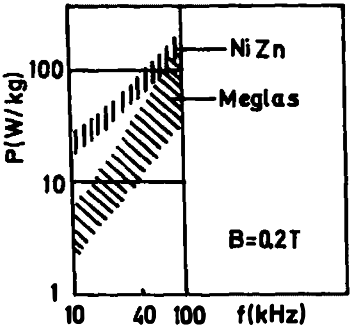


Fig.7 Core losses of Fe-Si steels and Metglas 26055-2 vs induction.

Fig.8 Losses of Ni-Zn ferrites and some Metglas alloys vs frequency.

The other advantages of metallic glasses are before mentioned simplicity of production of thin ribbons and foils, good mechanical and corrosion resistant properties, practically unlimited possibility of alloying (thus modifying their properties) and their high electrical resistivities. Since eddy current loss dominates already at power frequencies, lower thickness and higher resistivity are the main contributors to lower core losses of amorphous ferromagnets. These factors become particularly important at higher frequencies and enable metallic glasses to compete with ferittes as illustrated in Fig.8.

The potential of soft amorphous ferromagnets for the applications at elevated frequencies (starting with airborne transformers operating at 400 Hz) has been described in some detail elsewhere /5,6/. Recent results for the high frequency characteristics of FeNiBSi alloys can be found in these preceedings /22/. We note that these alloys are inferior to amorphous alloys which are allready used for high frequency applications, yet their frequency characteristics are close to those of permalloys. Therefore it is clear that systematic research in that field is highly relevant for the applications of metallic glasses.

## 5. Conclusions

Although the knowledge and understanding of some aspects of amorphous metals progressed considerably over the last ten years a detailed understanding is yet to be reached. In spite of that some amorphous metals have already important technological applications: the amorphous soft ferromagnets being the most notable example. In this paper we have given a qualitative explanation how some properties of amorphous metals arise and how the simplicity of manufacturing the metallic glasses in a form of ribbons or foils affects their applications (transformer cores, shielding cables flexible brazing materials etc.). We also used our recent results for amorphous FeNiBSi alloys (a prototype system of soft ferromagnetic alloys) in order to show a present-day understanding of their magnetic and mechanical properties. The potential of amorphous ferromagnets for the applications at elevated frequencies was also briefy discussed.

In what follows we briefly mention some areas of research and development which may be of particular interest for the future applications and understanding by amorphous metals.

i) Preparation. Except for mechanical alloying /23/ no new fabrication method has been developed for the last ten years. Single--roll melt-spinning, although simple, may appear impractical for the production over long periods, thus of large quantities. The use of belt instead of roller may solve that and some other problems /24/.

ii) Glass formation. Quenching rates ($T_{cr}$) for obtaining different amorphous metals range from $10^2$-$10^{10}$ K/s /25/. Large $T_{cr}$ values make fabrication complicated and result in thiner product. Thus, paper understanding of the amorphous metal formation may enable a vast increase in their applications.

iii) Relaxation and stabillity. Since amorphous state is not unique, the properties and thus applications of amorphous metals can be greatly affected by preparation conditions and additional treatments). The mechanism(s) of this as well as of stability of amorphous metals is still not well understood.

iv) Theory. The accurate theoretical description of disordered systems would be of largest importance for the future developments in the field of amorphous metals (materials in general). This however is a problem wich defies the efforts of the best theorists for over fifty years.

The above, non-exhaustive, list shows that amorphous metals will remain an active research field for a long period. The extent of this research will certainly affect their applications.

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