Jerzy Morgiel
Institute of Metallurgy and Materials Science
Polish Academy of Sciences, Kraków

DEVELOPMENT, PROPERTIES AND APPLICATIONS OF STRUCTURAL BULK METALLIC GLASSES

Key words

bulk metallic glasses, melt spinning, glass forming ability

Abstract

The paper is centered on Zr-based metallic glasses. It discusses ways used in elaboration of new structural metallic glasses and techniques used in their characterization. Some results obtain in this area from author own laboratory are presented. Finally, the most important properties of metallic glasses as well as possibility of their applications are summarized.

Streszczenie

Opracowanie jest nakierowane na szkła metaliczne na bazie cyrkonu. W jego ramach przedyskutowane zostały problemy z zakresu opracowania nowych szkieł metalicznych, jak też charakteryzowania ich parametrów i struktury. W tej części przedstawiono również wyniki uzyskane w tej dziedzinie w laboratorium autora. Kończąc, omówiono wybrane własności szkieł metalicznych i perspektywy ich zastosowań.

1. Introduction

The amorphous metallic material was by the first time prepared by Clement, Willens and Duwez [1] from the Au – Si system using rapid solidification technique already in 1960. Due to the high cost of such alloys, novelty of the casting technique and ultra small thickness of the received ribbons it was, at that time, treated rather as scientific curiosity, than the discovery having any perspectives of practical application. The interest in this field was renewed not until more than twenty years later, when amorphous ribbons from less exotic system like Ti – Cu –Zr [2, 3] were produced and steered even more, when Kui, Greer and Turnbull [4] obtained first bulk amorphous material in the form of ingot of a several centimeter in diameter from PdNi (P,Si) alloy, i.e. solidifying in amorphous state at low cooling rates.

The concentrated effort of number of research teams, which followed next, allowed elaborating a few group of alloys for specific applications. One of the most successful was Inoue from Tohoku University obtaining metallic glasses from MgLnM (M = Ni, Cu, Zn) in 1988, LaAl(TM) in 1989, Zr-Ti-TM-Be alloys in 1993 and Fe-(Nb,Mo)-(Al,Ga)-(p,B,Si) in 1995 in the form of rods of 10, 30, 25 and 3 mm respectively [3].

Less active but famous for their 1990 record 50 mm thick glassy ingot from ZrTiCuNiBe called Vitreloy1™ was Johnsons laboratory from CalTech [5]. In the following years new metallic glasses of improved properties were developed, but none came near in diameter to Vitralloy1™.

Investigation of many multi-component systems allowed producing metallic glasses of different properties. They may be roughly divided into three groups [6], i.e. "light" including those based on magnesium or aluminium for aviation industry, "structural" including Zr-, Ti-, Cu-, Ni-based for all applications where strength and super-elasticity is at premium and "magnetic" both soft and hard Fe-, Co- or a Ni-based all with boron additions. Some other metallic glasses are also developed, but they either fall into one of the above specified group, like the Zr-based for hydrogen storage purposes or do not amount to make their own group yet.

The aim of this paper is to introduce the reader with ways used in elaboration of new structural metallic glasses including efforts made in author own laboratory, summarize their most important properties and discuss briefly possible applications.

2. Concept of amorphous material

The development of amorphous material inevitable rise question what it really means. The Greeks word *amorphous* was used to describe anything without shape (shapeless) or generally unclassifiable. Transferred to present day materials science, it defines solid material with atoms packed in tight but random way. The random in this case should be understood as the one precluding a drawing any type of lattice even in a distance of a few atomic distances. The scheme presented in Fig.1 shows, that depending weather material is classified using number of crystals per unit volume or through its grain size, than the amorphous

one will be placed either at the origin or at the end of the "material world". One should also notice, that the finer the grain size the more amorphous is the material (broken line) and the transfer from nano-crystalline to amorphous state is gradual.
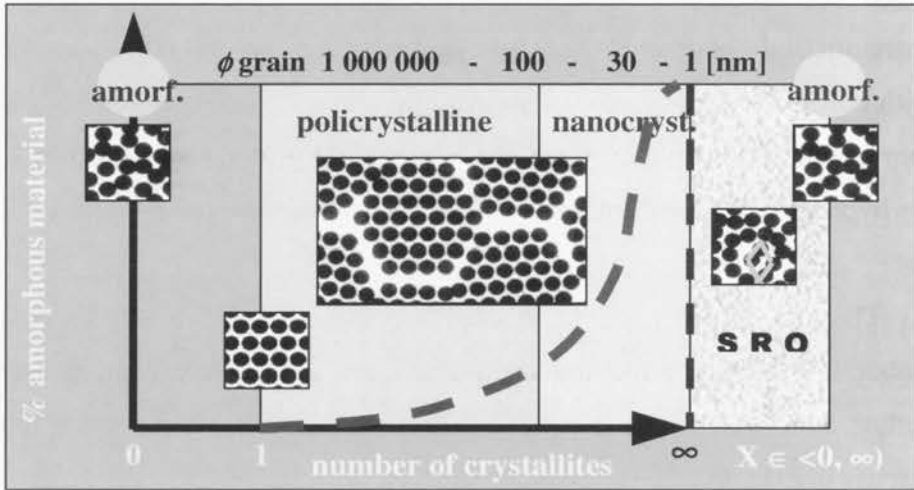

Fig. 1. Scheme of volume % of amorphous matter in crystalline material [7]

The border between these two states will be drawn in different places, depending what characterization technique one may have at his disposal. Additionally, it is safer to leave some space behind this borderline for amorphous material with presence of short range order (SRO), i.e. ordered arrangement in first and second coordination sphere of atom, which is neither crystalline nor amorphous state.

The most natural way to obtain amorphous material is just by freezing the random atoms movements in the liquid. Such fast cooling lowers the free energy of liquid close to crystalline state (Fig.2), making the Gibbs free energy smaller that the nucleation barrier. The temperature

range, at which all movements of atoms are stopped, except minor atomic position adjustments at distances much below their spacing, is called supercooled liquid region. During further cooling, at glass transition temperature (T_g), even this small adjustments are stopped.

It should be pointed here, that the metallic glass is an amorphous material, which was obtained by first cooling of the liquid metal or alloy.
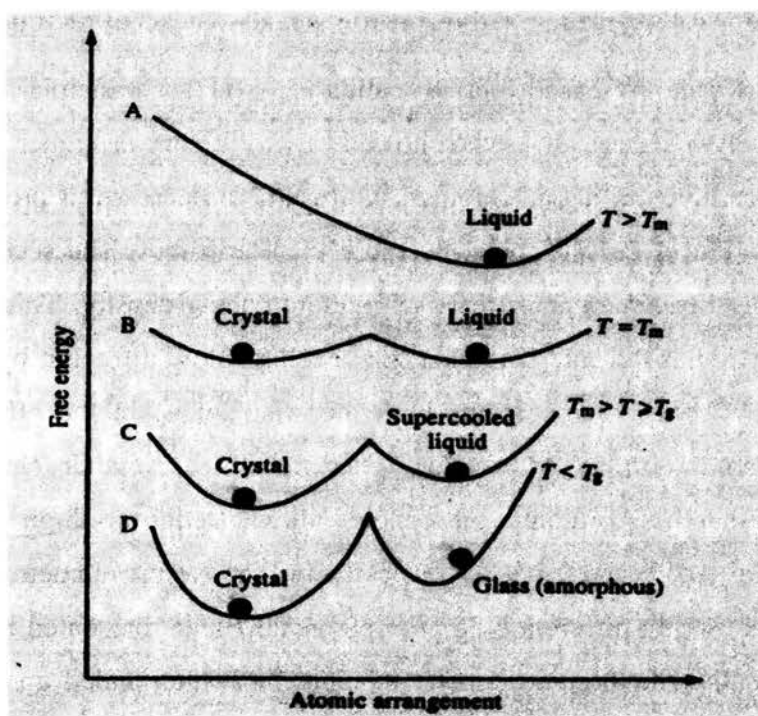

Fig. 2. Schematic changes of system free energy and resulting atomic arrangements with lowering temperature during fast cooling [3]

3. Rules for elaboration of metallic glasses

Analysis of already developed metallic glasses allowed Inoue [8,9] to propose three empirical rules, which should be satisfied simultaneously, to produce new metallic glasses, i.e.:

- alloy should be based on multi-component system (≥3 elements)

- additions should show significant atomic size mismatch exceeding 12%

- main alloying elements should show negative heats of mixing

The first rule is based on so called "confusion principle" treated extensively by Greer [10], who showed that for binary or higher element alloys introduction of still another one results in decrease of probability of formation of crystal nuclei by more than ten times. The second and third rules are aimed at increase of random pacing density. This should raise liquid – solid interface energy as well as slow diffusion by filling openings between large atoms with the small ones. In the effect, the crystallization of $Zr_{55}Al_{10}Ni_5Cu_{30}$ glass results in smaller change of density than the ordinary amorphous alloys (requiring high cooling rates), i.e. ~0.5% and 0.1-0.2% respectively. The atomic diameters of the elements used in different bulk amorphous alloys are presented in Fig.3. Additionally, the atomic diameter of elements which added up to form the Vitralloy™, i.e. the alloy which allowed casting the largest glassy ingot so far, are shown as well. One may see that the presence of beryllium in that case is of critical importance as only this element may fit the openings left between bigger atoms.

Having chosen a multi-component system, which fulfills all three Inoue rules, it is next necessary to search for low melting eutectic (Fig. 4) or at least avoid high melting Laves phases. Actually, it was not established as yet whether the largest glassy ingots are obtained exactly at eutectic, but one have to be close to it at least.
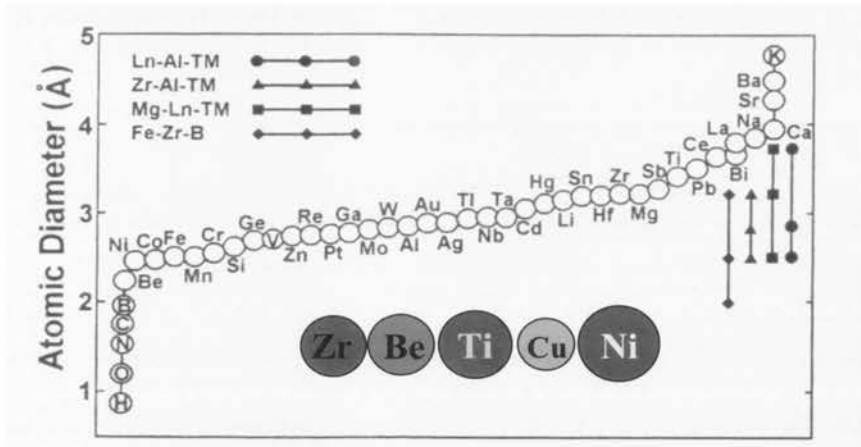

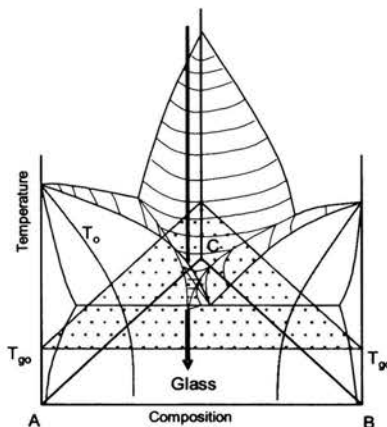*Fig. 3. Atomic diameters of elements used in bulk amorphous alloys [3]*

Fig. 4. Schematic presentation of position of good glass forming composition at ternary system [11]

4. Characterization of glass forming ability (GFA) of alloys

The most important parameter describing glass forming ability (GFA) of an alloy is its critical cooling rate R_c, i.e. the lowest cooling rate allowing to avoid detectable fraction of crystals in quenched metallic liquid [12]. The achieved cooling rate $\dot{T}$ may be evaluated by taking into account a total time τ required to cool a sample from temperature T_m to Tg as:

$$\dot{T} = dT/dt \tag{1}$$

as $dT \sim (T_m\text{-}T_g)$ and $dt \sim \tau$, than

$$\dot{T} = (T_m\text{-}T_g)/\tau \tag{2}$$

however, $\tau \sim (r^2/\kappa)$, where r is the copper mold radius and κ is thermal diffusivity of alloy, which might be expressed as $\kappa = K/C$, where K is thermal conductivity and C is heat capacity per unit volume, so eventually:

$$\dot{T} = K(T_m\text{-}T_g)/C \cdot r^2 \tag{3}$$

Assuming that usually $(T_m\text{-}T_g) \sim 400K$, $K \sim 0.1$ W/cm·s^{-1} and C ~4 J/cm^3·K^{-1} (both values being typical of a molten alloy) the critical cooling rate $\dot{T}_{critical}$ expressed later as R_c may be estimated from the largest radius r_c of the ingot solidifying without formation of crystallites as:

$$R_c \ (K/s) = 10/r_c^2 \ (cm) \tag{4}$$

As the critical cooling rate R_c is inversely proportional to the square of ingot radius (4), so casting ingot ten times thicker, i.e. increase from 1 to 10 mm, requires development of new alloy with hundredth times lower R_c.

The alloys used for casting glassy ingots may be characterized also by their glass transition temperature T_g, the crystallization temperature T_x, and the melting temperature T_m (liquidus temperature T_l is occasionally used instead). All of them are defined as points of cross-section of respective tangential lines as marked in Fig.5. The heating of glassy metal above T_g results in shallow endothermic effect connected with resumption of small adjustments of atomic positions stopped by cooling. This process is continued until the start of crystallization signaled by strong exothermic effect. In case the crystallization proceeds in two stages or more a splitting of the peak is observed. Finally, usually after some stabilization of base line, the strong endothermic effect from melting is recorded.
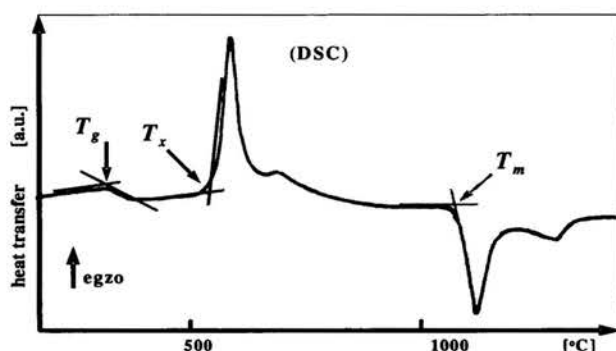

Fig. 5. Determination of metallic glass characteristic temperatures T_g, T_x and T_m with the help of differential scanning callorimetry (DSC)

It was soon found out, that for given composition of alloy the maximum thickness of an ingot which still remain fully amorphous is proportional both to the alloy supercooled liquid range expressed by difference between crystallization and glass transition temperature ($\Delta T_x = T_x - T_g$) and to the ratio of glass transition to melting temperature, i.e. the so called reduced glass transition temperature ($T_{gr} = T_g/T_m$) shown in Fig. 6 and 7 respectively. These empirical relationships helped to connect alloys characteristic temperatures, which could be easily measured using melt spun ribbons, with the critical cooling rate determined only through much harder to perform ingot casting experiments. Therefore, the glass forming ability (GFA) of alloys could be compared either directly by their R_c, or non directly by their ΔT_x and T_{gr} parameters.
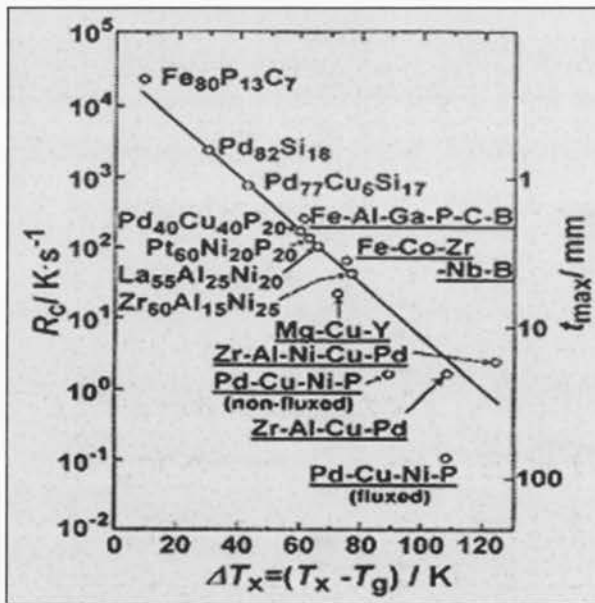

Fig. 6. Critical cooling rate R_c (max. thickness of amorphous alloys t_{max}) as function of ΔT_x (underlined alloys developed at Tohoku University) [3]
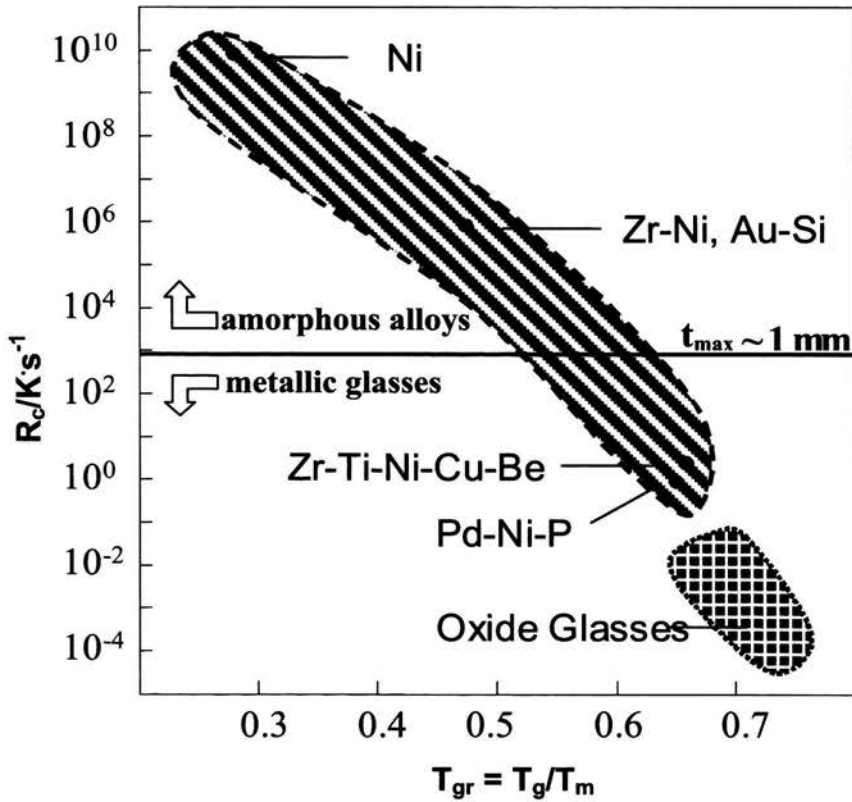
Fig. 7. Critical cooling rate Rc (max. thickness of amorphous alloys t_{max}) as function of T_{gr} [3, 11]

It was generally accepted that alloy compositions allowing to cast ingots or ribbons of at least 1 mm thick would be named <u>bulk metallic glasses</u> (BMG). The zirconium based alloys, like ZrTiNiCuAlCo, which produce amorphous ingots up to a few millimeter thick are characterized by $T_{gr} = 0.55 \div 0.65$ and $\Delta T_x \sim 100°C$ [3, 6].

5. Casting of metallic glasses

The solidification of metallic glasses is usually preceded by preparation of small classically vacuum cast ingot (Fig. 8), pieces of which are later re-melted in quartz tube and ejected on rotating copper wheel (Fig. 9a), between two rotating copper wheels (Fig. 9b) or into cylindrical copper mold (Fig. 10). In two former cases one may obtain amorphous ribbons (Fig.11a) of thickness in the range of tens of micrometers and fraction of millimeters respectively. In case of single wheel a liner speed up to 10-30 m/s liner speed is achieved giving cooling rates of 10^4 -10^6K/s, while in the second case 0.5 – 5 m/s speed is used giving cooling rates only around 10^2 -10^3K/s. In the case of copper mould bulk metallic glass ingots of diameter of up to a couple of millimeters could be produced (Fig.11b). A stepped diameter is applied to use opportunity of different cooling rates. A proper small under pressure is necessary to fill in the mold.

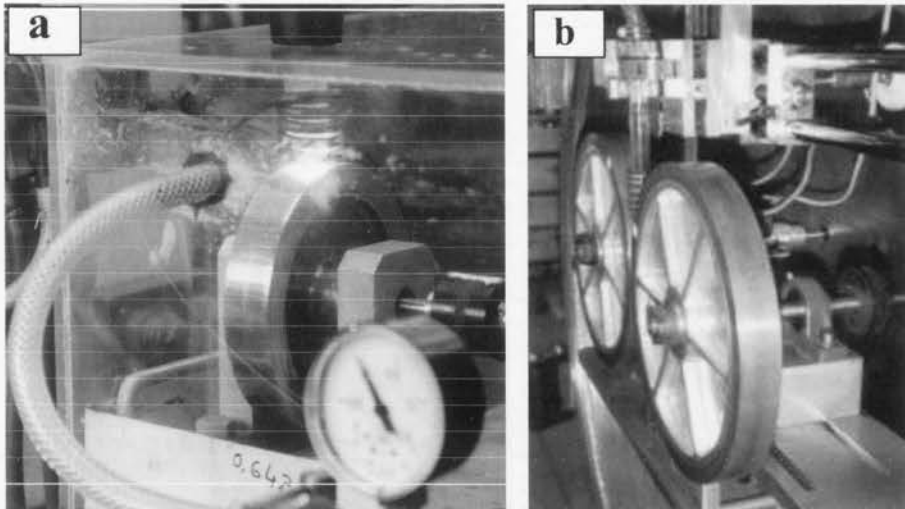*Fig. 8. Induction melted vacuum cast zirconium based ingot [13]*

Fig. 9. One (a) and two (b) wheel arrangement used for casting amorphous metallic ribbons [13, 14]
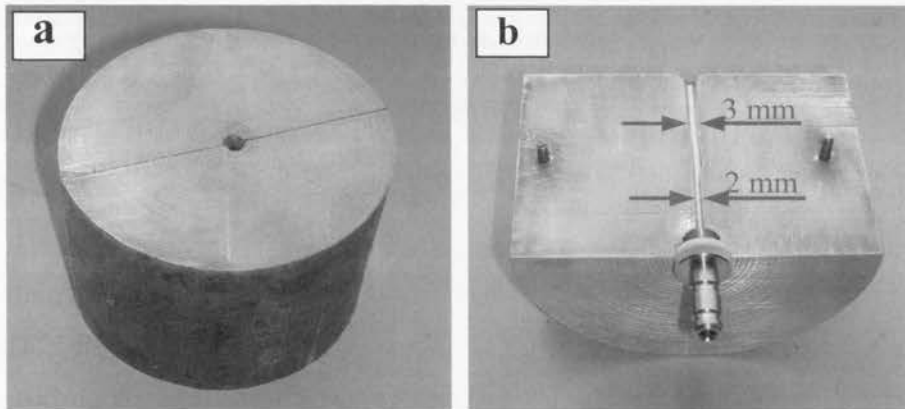

Fig. 10. One (a) and two (b) wheel arrangement used for casting amorphous metallic ribbons [13]

The bulk amorphous materials might be also produced by consolidation. In that case, amorphous powders obtained though mechanical synthesis [15] are later hot extruded in supercooled liquid region.
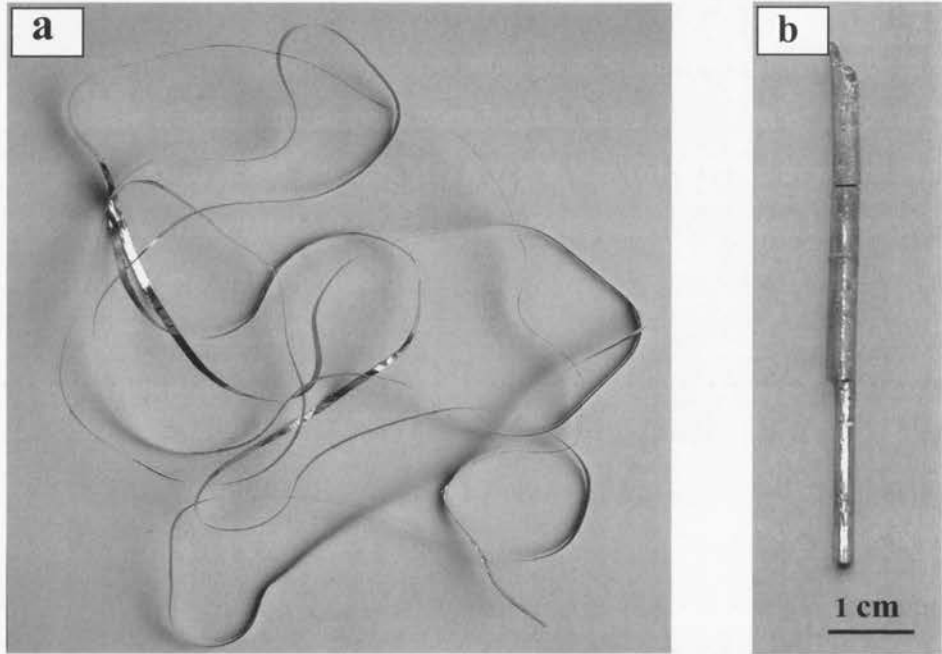
Fig. 11. Melt spun ribbon (a) and ingot from stepped copper mould (b) from ZrTiNiCu alloy

6. Microstructure characterization of metallic glasses

The most frequently used technique for confirming amorphous character of both ribbons and small ingots is X-ray diffractometry. The diffractograms obtained from amorphous material show just one broad maximum at the 2θ corresponding to average spacing between nearest neighbors, while in case of presence of some crystallites like β phase in TiZrNi alloys some sharp peaks are presents (Fig. 12). The cross-section scanning electron microscopy (SEM) or plan-view transmission electron microscopy (TEM) microstructures like those presented in Fig. 13 are also useful in characterization of such materials. TEM/EDS mapping

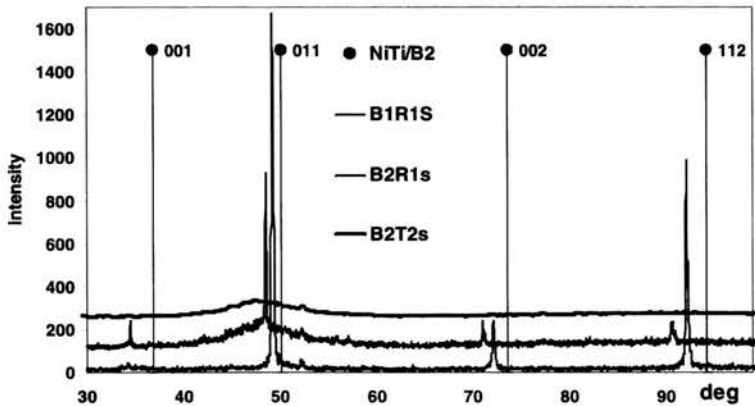(EDS) showed that the large β crystallite nucleate preferentially at zirconium oxide (Fig. 14).

Fig. 12. X-ray diffractograms of TiNiZr10 (B1 alloy) and TiNiZr20 (B2 alloy) cast at around 8 (R1 casting speed) and 16 m/s (R1 casting speed) [16]
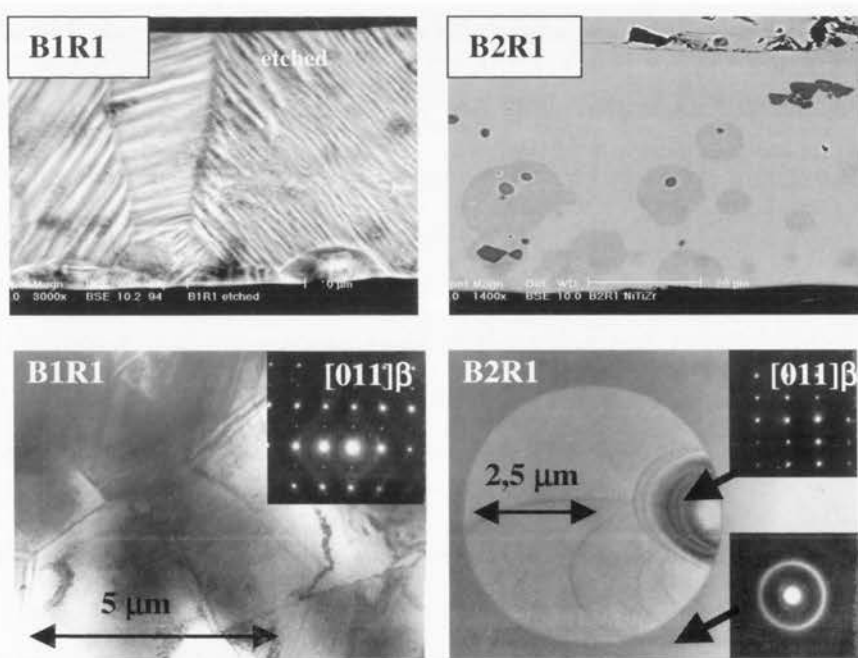

Fig. 13. Cross-section SEM (upper row) and plan-view TEM microstructures (lower row) of ribbons from alloy TiNiZr10 (B1) and TiNiZr20 (B2) [16]
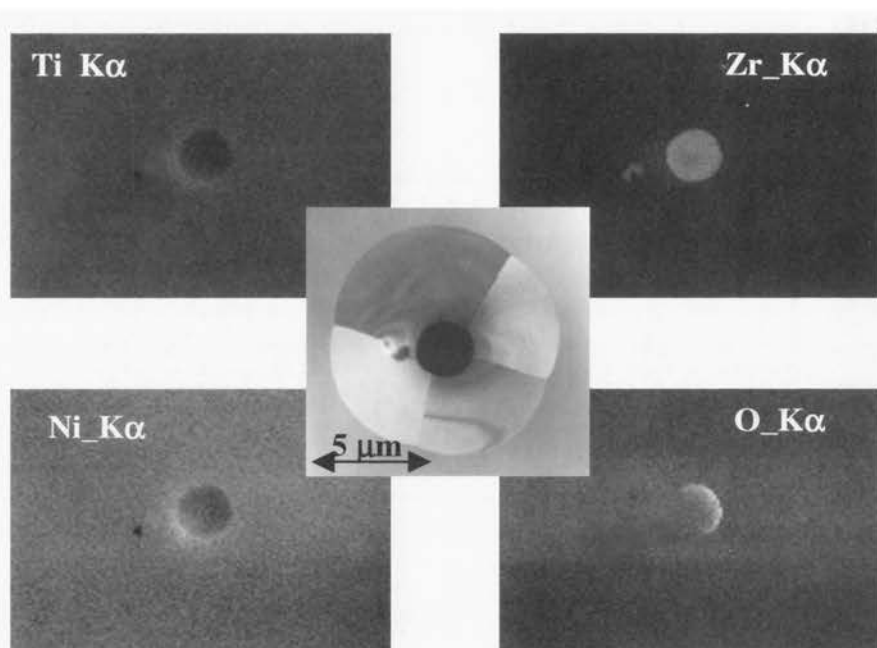
*Fig. 14. TEM microstructure (centre) and EDS maps of Ti, Zr, Ni and O
pointing at zirconium oxide contamination as nucleation sites for β phase [16]*

Detection of very fine crystals in amorphous matrix like in ZrTiNiCuAg alloys the high resolution electron microscopy (HREM) has to be used (Fig. 15a, b). It helps to describe shape, density and even phase composition (through analysis of symmetry and lattice spacing) of nano-crystals down to a few nanometers. In present case, it proved that the precipitates are of silver solid solution. Fully glassy material shows no contrast during standard TEM observations, but produces characteristic texture like contrast in HREM (Fig. 15c, d). The characterization of still smaller microstructure features like clusters or presence of the short range order (SRO) still other even more specialized techniques like anomalous X-ray scattering technique basing on which

radial distribution function (RDF) [8, 17] is estimated or field ion microscopy (FIM) [18].
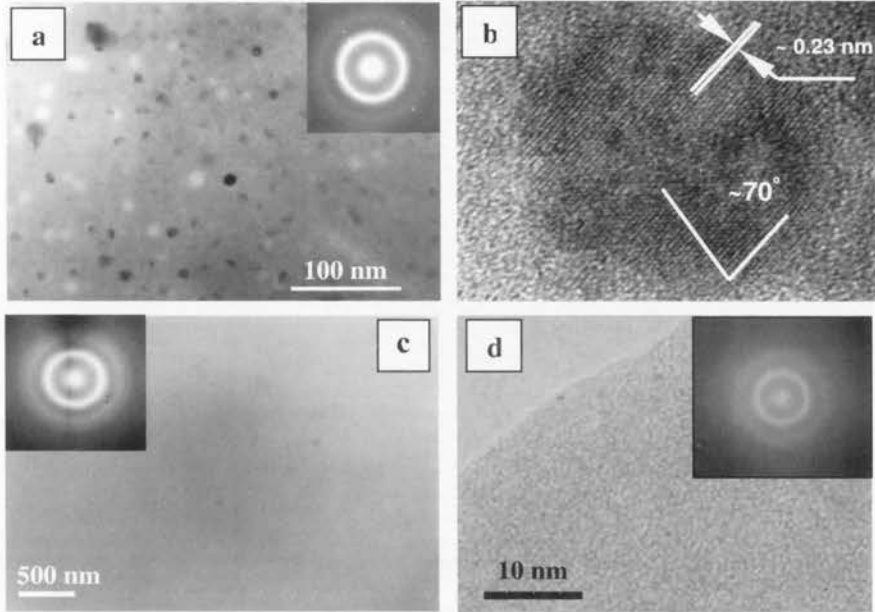

Fig. 14. TEM and HREM microstructures of as spun ribbons from ZrTiNiAg alloy (a, b) and TiZrNiCu alloy [19, 20]

7. Mechanical properties of metallic glasses

The bulk metallic glasses stirred great interest not only because their importance in the field of basic science, but also due to unparalleled by any other crystalline material combination of mechanical properties. One of the most striking thing is their both relatively low elastic modulus ranging from 40 to 100 MPa and high tensile strength from 1 GPa to 4 GPa (similar situation is with hardness) depending on alloy composition

(Fig. 15). It is worth to note, that while Young's modulus is close to that of Duraluminium™, though the strength of zirconium based glasses is at the level characteristic for high strength steels.
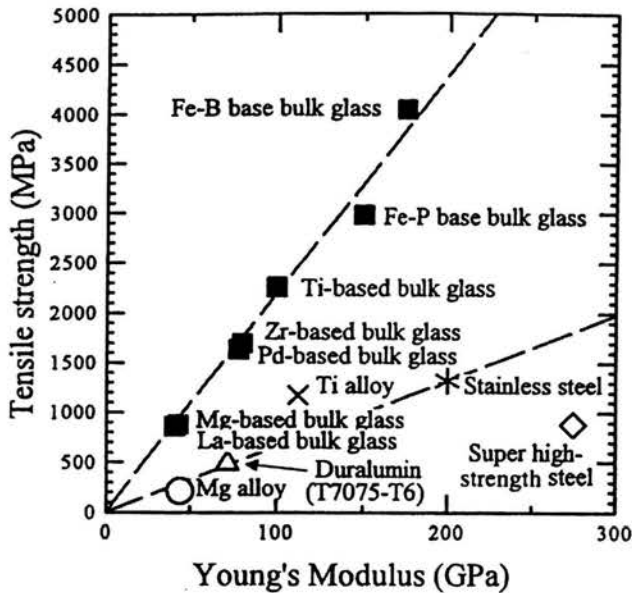

Fig. 15. Tensile strength against Young's modulus for various materials including metallic glasses [3]

The describe above unique combination of low Young modulus and high strength and hardness is of course possible only because metallic glasses are characterized by roughly ten times larger elastic elongation limit of 2%, while crystalline materials rarely exceed 0.2% (Fig.15). This superelasticity and directly connected with it large elastic energy of metallic glasses results in material excellent energy storing ability. The latter is frequently compared through density of recoverable energy

(Table I), which in present case is just density of the stored elastic energy E_{el} equal:

$$E_{el}/V = (Y \cdot \varepsilon^2) / 2 \qquad (5)$$

Y- Young's modulus, V – unit volume, ε - elastic strain

Table I. Average elastic elongation limit and elastic energy density for aluminium, stainless steel and bulk metallic glass

material	elastic elongation limit [%]	max. elastic energy density [MJ/m3]
Al. 20024	0.1	0.07
Stainless Steel	0. 11	0.23
Vitralloy 1	2	37

The metallic glasses inherited unfortunately characteristic for classical oxide glasses absence of distinct plastic elongation at ambient temperatures, but show some small plastic deformation of up to 1 % at compression (Fig. 16). A significant improvement in this field is possible through controlled "introduction" of small amounts of fine crystalline phases like ZrC [21].

The mechanical properties of metallic glasses start to change rapidly as they approach the supercooled liquid temperatures ($T_g < T < T_x$), at which they show extensive superplasticity (Fig. 17, 18). The strain rate sensitivity approaches 1 at strain rates from 10^{-2} to 10^{-3} s^{-1}, while overall elongation were from 200 to nearly 500% at 10^{-3} s^{-1} for different glasses.

The uniqueness of metallic glasses may be probably best appreciated through comparing their position against classical materials on one of Ashbe charts, i.e. those presenting strength and elastic limit of materials (Fig. 19).

It clearly shows that this new material has strength better than most steels and elastic limit within polymers range.
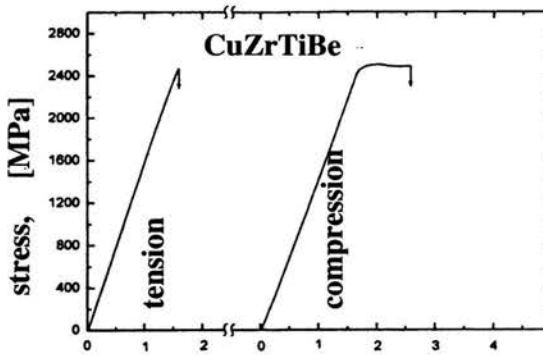

Fig. 16. Tension and compression tests performed at R.T. [9]
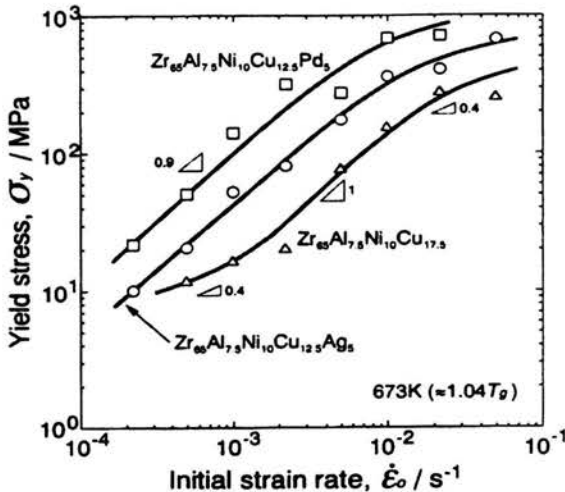

Fig. 17. Yield stress against initial strain rate for different metallic glasses measured within the supercooled liquid temperature range [22]
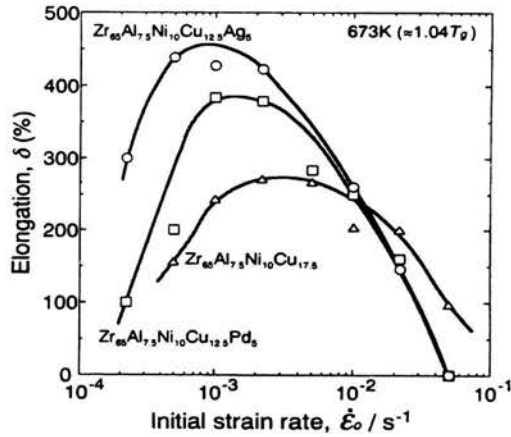
Fig. 18. Elongation against initial strain rate for different metallic glasses measured within the supercooled liquid temperature rage [22]
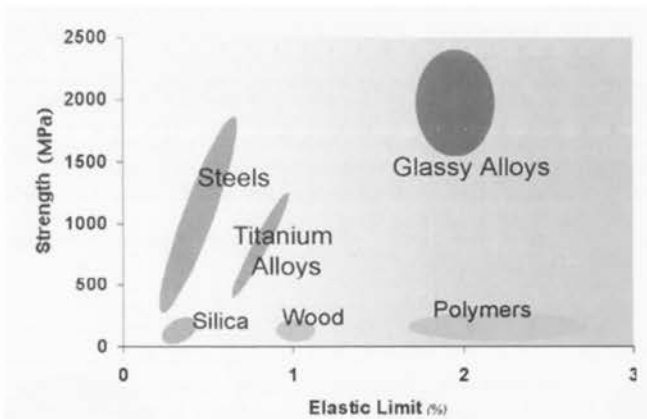

Fig. 19. Ashby chart comparing strength against elastic limit of traditional materials and metallic glasses [5]

8. Present and future applications

The unique combination of very good mechanical properties at room temperature of metallic glasses like high strength, high hardness and

large elastic limit do not make it automatically a good material for industry.

Fortunately, it is additionally backed with excellent cast ability and very low solidification volume change opening the road to applications, were near net shape castings might be used [6]. As one example of activity in that direction might serve laser mirrors produced at Tohoku University (Fig. 20), for which high luster of metallic glasses was of great advantage. Also specially formed ingots might fit cavities left for them in golf clubs adding range to golf balls [9, 23].

Forming of bulk metallic glasses to predetermined shape is a challenging task, but at supercoold liquid temperature range possible. In that case forming operation should be performed just above glass transition temperature at which the material softens dramatically. Alloys with wider temperature range of supercooled liquid are at premium giving better safety margin against accidental crystallization eliminating plasticity.
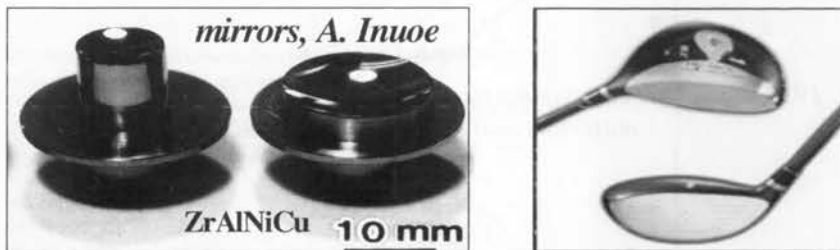

Fig. 20. Metallic glass laser mirrors from Tohoku University [9] and gof clubs produced by Liquidmetal® company

Even at those slightly adverse conditions, a forming of tiny gears from ZrCuNiTiBe metallic glass and similar nano-engineering experiments [9] was possible (Fig. 21a).
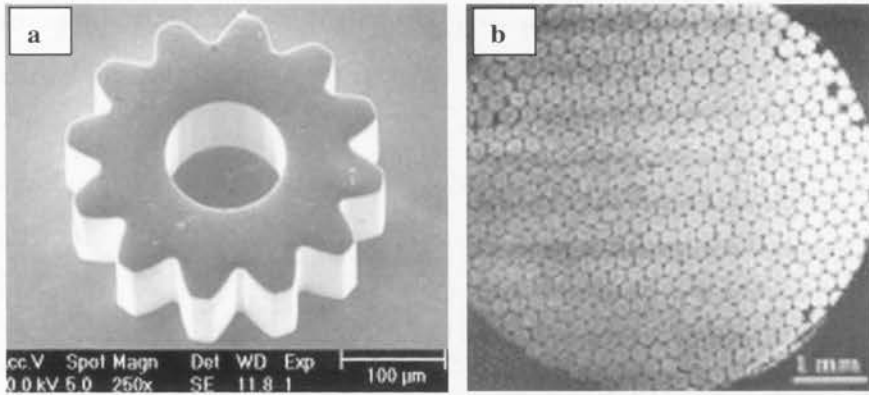

Fig. 21. Gear produced with silicon form at 380°C /5 MPa stress (a), and composite with glassy matrix filling in spaces between tungsten wires (b) [24]

A very impressive, as it concerns formability of metallic glasses, was also production of composite in which tungsten wires are held together by glassy matrix acting as glue (Fig. 21b). This application was aimed at using another, not discussed as jet property of metallic glass, which shows itself by so called self sharpening helpful in penetration of other hard objects. In the described composite the glassy matrix will control shear both of the matrix and crystalline rods, while presence of tungsten will guarantee proper weight needed for projectiles. Other interesting application from that area are aimed at using to advantage the strong rise of dynamic toughness with increasing loading rates, while in "normal" materials like steels this relation is reversed.

9. Summary

The difference in atom arrangement in metallic glasses as compared to crystalline metals and alloys resulted in presence of either unusual properties or unusual combination of generally available properties opening doors to application which require an overcoming of barriers imposed by classical materials. However, the majority of developed up till now so called "good glass forming" compositions allow producing amorphous ingots in the range of millimeters, while only a couple reach more "practical" size of a centimeters but under penalty of having poisonous beryllium as one of the alloying addition.

Therefore, the break through in wider scale applications will be possible only after development of new alloys securing production of beryllium less significantly thicker amorphous ingots.

References

1. Clement W., Willens R.H. and Duwez P., Nature 187 (1960) 869
2. Massalski T.B., Woychik C.G., and Dutkiewicz J., Metallurgical Transactions A19(1988)1853
3. Inoue A., Bulk Amorphous Alloys; Preparation and Fundamental Characteristics, Trans Tech Publications LTD, Switzerland, 1998
4. Kui H.W., Greer A.L., Turnbull D., Appl. Physics Letters, 45(1984)615
5. Johnson W.L., www.its.caltech.edu/~matsci/wlj/Johnson.html
6. Inoue A., Bulk Amorphous Alloys; Practical Characteristics and Applications, Trans Tech Publications LTD, Switzerland, 1999

7. Christodoulou L., Workshop on Structural Amorphous Metals, DARPA Program, Arlington, Virginia 2000, http://www.darpa.mil/dso/thrust/matdev/sam/html/presentations.html

8. Inoue A., Acta materialia, 48(2000)279

9. Inoue A., Takeuchi A., Materials transactions, 43(2002)1892

10. Greer A.L., Nature 366(1993)303)

11. Fecht H.-J., Johnson W.L., Metastability and thermodynamics of bulk metallic glass forming alloys, Proc. Conf. on Mathematical Modeling and Simulation of Metal Technologies, MMT-2000

12. Lin X.H., Johnson W.L., J. Applied Physics, 78(1995)6514

13. Morgiel J., Report: Development of bulk amorphous TiZrNiCuAlCoMn alloys, IMMS PAS, Kraków 2003 (*in Polish*)

14. Ochin P., http://www.cecm.cnrs.fr/

15. Eckert J., Materials Science and Engineering, A226-228(1997)364

16. Morgiel J., Dutkiewicz J., Proc. Conf. on Advanced Materials and Technology, Jurata 2000, *published in* Mat. Eng.,2001, no.5, p.651

17. Li J., Gu X., Hufnagel T.C., Microscopy and Microanalysis 2001, Supplement 2, p. 1260

18. http://physics.unipune.ernet.in/~fem/

19. Czeppe T., Rashkova V., Dobrev E., Latyńska L., Morgiel J., Labar J., Dutkiewicz J., Materials Science, A375-377(2004)260

20. Dutkiewicz J., Morgiel J. Czeppe T., Faryna F., Heinrich H., Kostorz G., Proc. XIth Electron Microscopy Conference on Solids, EMC 2002, *published in* Materials Chemistry and Physics, 81(2003)376

21. Chen F., Takagi M., Imura T., Kawamura Y., Kato H., Inoue A., Materials transactions, 43(2002)1892

22. Ishihara S., Inoue A., Materials transactions, 42 (2001)1517

23. Kakiuchi H., Inoue A., Onuki M.,Yamaguchi T., Materials transactions, 42 (2001)678

24. Dowding R.J., Workshop on Structural Amorphous Metals, DARPA Program, Arlington, Virginia 2000, http://www.darpa.mil/dso/thrust/matdev/sam/html/presentations.html