Developments and Applications of Bulk Glassy Alloys in Late Transition Metal Base System

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We review our recent results of the formation, fundamental properties, workability and applications of late transition metal base bulk glassy alloys which have been developed after the first synthesis of Fe-based bulk glassy alloys by the copper mold casting method in 1995. The late metal transition base bulk glassy alloys were obtained in Fe–(Al,Ga)–(P,C,B,Si), Fe–(Cr,Mo)–(C,B), Fe–(Zr,Hf,Nb,Ta)–(B, Fe–Ln–B(Ln=lanthanide metal), Fe–B–Si–Nb and Fe–Nd–Al for Fe-based alloys, Co–(Ta,Mo)–B and Co–B–Si–Nb for Co-based alloys, Ni–Nb–(Ti,Zr)–(Co,Ni) for Ni-based alloys, and Cu–Ti–(Zr, Hf), Cu–Al–(Zr, Hf), Cu–Ti–(Zr, Hf)–(Ni, Co) and Cu–Al–(Zr, Hf)–(Ag, Pd) for Cu-based alloys. These bulk glassy alloys exhibit useful engineering properties of high mechanical strength, large elastic elongation and high corrosion resistance. In addition, Fe- and Co-based bulk glassy alloys have good soft magnetic properties which cannot be obtained for conventional amorphous and crystalline type magnetic alloys. The Fe- and Ni-based bulk glassy alloys have already been used in some application fields. These late transition metal base bulk glassy alloys are promising as new metallic engineering materials.

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Keywords: synthesis, applications, bulk glassy alloys, late transition metal base, mechanical properties, soft-magnetic properties

1. Introduction

Since the first syntheses of bulk glassy alloys in metal-metal alloy systems without metalloid elements through stabilization of supercooled liquid4–3 for several years between 1988 and 1992, great efforts have been devoted to search for new bulk glassy alloy systems with high glass-forming ability and useful functional properties and to clarify the origins for high stability of supercooled liquid against crystallization and for the appearance of unique properties for bulk glassy alloys.4–7) A majority of studies on bulk glassy alloys have been focused on early transition metal base alloys in Zr-, Ti- and Hf-based systems, lanthanide metal (Ln) base alloys, simple metal base alloys in Mg- and Ca-based systems and noble metal base alloys in Pd- and Pt-based systems.4–7)

Considering some basic factors such as novel properties, material cost and material deposits on the earth for future development of bulk glassy alloys as advanced engineering materials, it was extremely important to find a late transition metal base bulk glassy alloy which had not been synthesized before 1995. Under the above-described severely limited situation of bulk glassy alloy systems, we succeeded in fabricating Fe-based bulk glassy alloys in Fe–Al–Ga–P–C–B system in 1995.8) Since then, we have also synthesized a variety of Fe-based bulk glassy alloys,9–13) followed by Co-based bulk glassy alloys,14–16) Ni-based bulk glassy alloys17–19) and then Cu-based bulk glassy alloys20–24) through alloy searches on the basis of the three empirical component rules for stabilization of supercooled metallic liquid.4–6) It has subsequently been found that the late transition metal base bulk glassy alloys exhibit various unique properties which have not been obtained for any kind of crystalline alloys. The novelty of various properties for late transition metal base bulk glassy alloys has enabled us to use as engineering materials and their application fields have a tendency to be extended widely. This paper intends to review our recent results on the formation, properties, thermal stability, workability and applications of late transition metal base bulk glassy alloys.

2. Features of Alloy Components in Late Transition Metal Base Bulk Glassy Alloys

It is well known that the first synthesis of late transition metal base bulk glassy alloy containing more than 50% late transition metal was made for Fe–(Al,Ga)–(P,C,B) system in 1995,8) followed by Co–Ga–(Cr,Mo)–(B,C,P) in 1996,13) Ni–Nb–(Zr,Ti,Hf)–(Co,Fe,Cu,Pd) in 199925) and then Cu–(Zr,Hf)–Ti in 2001.20) It is thus noticed that all the late transition metal base bulk glassy alloys were developed for the last one decade after 1995.

Table 1 summarizes typical bulk glassy alloy systems containing more than 50 at % late transition metal as a main constituent component. These alloy systems can be divided into two groups of metal-metalloid and metal-metal types. The former type alloys were mainly obtained in Fe-, Co-, Ni-, Pd- and Pt-based systems, while the main latter type alloys were synthesized in Ni- and Cu-based systems. It is also noticed that Ni-based bulk glassy alloys can be formed rather easily in both alloy types. When we focus on main ternary systems in Fe-, Ni- and Cu-based alloys which can be regarded as important engineering systems, one can see Fe–(Al,Ga)–metalloid, Fe–(Cr,Mo)–(C,B), Fe–(early transition metal)–B, Fe–Ln–B, Fe–(B,Si)–Nb, Ni–Nb–(Ti,Zr,Hf), Cu–Ti–(Zr,Hf) and Cu–Al–(Zr,Hf) systems. Table 1 also indicates that a more variety of bulk glassy alloys can be fabricated by adding fourth and fifth elements to the basic ternary alloys. On the other hand, the metal-metal type alloys in Fe- and Co-based alloy systems do not have high glass-forming ability and their critical diameters lie in the range of 1.0 to 1.5 mm. The future development of Fe- and Co-based alloys with various alloy components in the metal-metal type is important for further extension of application field of bulk glassy alloys.

The feature of three metallic components in the basic ternary alloy systems can be divided into five groups, as summarized in Table 2. Group I consists of late transition metal, simple metal and early transition metal as exemplified for Cu–Zr–Al and Cu–Hf–Al systems, group II includes late
transition metal, metalloid and early transition metal or Ln such as Fe–(B,Si)–Nb, Fe–(Zr,Hf,Nb)–B, Fe–Ln–B and Fe–(Cr,Mo)–(C,B) systems, group III is composed of Fe, metalloid and Al or Ga, group IV is exemplified for Ni–Nb–Ti and Cu–(Zr,Hf)–Ti systems and group V consists of Ni–Pd–P and Cu–Pt–P systems. Considering that bulk glassy alloys are formed in all types of the basic ternary systems, it can be said that the atomic size mismatch factor is more dominant for stabilization of supercooled liquid as compared with the negative heat of mixing factor.

Table 3 summarizes the features of glass-forming ability, temperature interval of supercooled liquid and reduced glass transition temperature for late transition metal base bulk glassy alloys. The glass-forming ability is the highest for Pd- and Pt-based alloys, followed by Cu-, Ni-, Fe- and then Co-based alloys.
There is a tendency for glass-forming ability to increase with decreasing liquidus temperature of their ternary alloys. In addition, we can notice a rather close relation between glass-forming ability and $T_g = T_l/C_1$, though their orders do not agree completely.

Table 4 also summarizes the features of mechanical fracture strength ($\sigma_f$) and compressive ductility ($\varepsilon_f$) for the late transition metal base bulk glassy alloys. All the late transition metal base bulk glassy alloys in metal-metalloid type have good elastic ductility as is evidenced from the achievement of 2% elastic strain. On the other hand, the 2% elastic strain property for the metal-metal type alloys is limited to Ni- and Cu-based alloy systems. The 2% elastic strain property has been also recognized for other bulk glassy alloys such as Zr-based alloy systems and is an essential factor for the achievement of high fracture strength.

As is evident from the development history of Fe- and Co-based bulk glassy alloys, only a few alloy systems of (Fe,Co,Ni)–Nb–(B,Si) and Co–Fe–Ta–B were developed for the last three years after the RQ11 conference held in 2002. Therefore, we will describe firstly the formation and fundamental properties of these new Fe- and Co-based bulk glassy alloys in the next two chapters.

### 3. Formation and Fundamental Properties of Fe- and Co-based Bulk Glassy Alloys in (Fe,Co,Ni)–(B,Si)–Nb System

We have found that the addition of small amounts of Nb to (Fe,Co,Ni)–(B,Si) alloys is very effective for the increase in glass-forming ability through the increase in the stability of supercooled region against crystallization. The glass transition phenomenon can be observed over the whole composition range in $[(\text{Fe}_{1-x-y}\text{Co}_x\text{Ni}_y)_{17.5}\text{B}_{0.2}\text{Si}_{0.05}]_{0.56}\text{Nb}_4$ alloys. Figure 1 shows the compositional dependence of glass transition temperature ($T_g$) for the (Fe,Co,Ni)–(B,Si)–Nb system.
The supercooled liquid region ($\Delta T_g$) defined by the difference between $T_g$ and crystallization temperature ($T_x$) shows a maximum value of about 65 K in the range of 0.50–0.65Fe, 0.35–0.45Co and 0 to 0.15Ni and keeps rather high values of over 60 K in the Ni content range up to about 0.35Ni, as shown in Fig. 2. In the alloy composition range, we can obtain high reduced glass transition temperatures above 0.61 as well as high glass-forming ability leading to the formation of bulk glassy alloys with diameters up to at least 5 mm by the copper mold casting process, as shown in Fig. 3. Considering that no glass transition is observed in Fe–Co–Ni–B–Si system, we can notice again the importance of the addition of the small amount of Nb as the third element leading to the satisfaction of the three empirical component rules for stabilization of supercooled liquid. As an example, Fig. 4 shows the outer shape and surface appearance of the cast Fe–Co–Ni–B–Si–Nb alloy rods with diameters up to 5 mm. These alloy rods have smooth outer surface and shiny metallic luster and no crystalline peaks are recognized even for the 5 mm rod.

Figure 5 shows the compositional dependence of compressive fracture strength of the cast Fe–Co–Ni–B–Si–Nb alloy rods produced by the copper mold casting method.

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Figure 5 shows the compositional dependence of compressive fracture strength of the cast Fe–Co–Ni–B–Si–Nb alloy rods. The high strength of over 4000 MPa is obtained in the wide composition range of 0–1.0Co and 0–0.7Ni and the further increase in Ni content causes the decrease in strength to about 3700 MPa. In the case of the same composition of B, Si and Nb elements, the fracture strength is the highest for the Fe-based alloy, followed by the Co-based alloy and then the Ni-based alloy. In addition to the high strength, the Fe–Co–Ni–B–Si–Nb alloy rods also exhibit distinct plastic strains up to about 0.5% before final fracture as exemplified in Fig. 6. The alloy rod subjected to the plastic strain up to 0.3% shows a distinct shear band along the maximum shear stress plane. Besides, we can observe the trace of viscous flow deformation on the shear band, indicating the significant increase in temperature in the shear band.

These Fe–Co-based glassy alloys also exhibit good soft magnetic properties, i.e., rather high saturation magnetization reaching 1.3 T in the Fe-rich composition range above 0.8 and low coercivity of 1.0 to 2.5 A/m in the wide composition range of 0.25–1.0Fe and 0–0.6Ni. Thus, the appearance of ferromagnetic property at room temperature is dependent on Ni and Fe contents. The decrease of coercivity with increasing Co content has been recognized to originate from the reduction of saturation magnetostriction.\textsuperscript{26)}

Figure 7 shows the relationship between coercivity and electrical resistivity for Fe-based bulk glassy alloys in Fe–B–Si–Nb and Fe–Ga–P–C–B base systems, together with the data of amorphous and nanocrystalline alloys which require high cooling rates of over $10^5$ K/s for preparation as well as Co$_{43}$Fe$_{20}$Ta$_{5.5}$B$_{31.5}$ bulk glassy alloy. It is characterized that

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the Fe- and Co-based glassy alloys have better combination of lower coercivity and higher electrical resistivity among all soft magnetic metallic alloys. The lower coercivity is presumably due to the smaller magnetic anisotropy and lower internal stress. We examined in more details the contribution of internal stress to coercivity. It has previously been reported that the coercivity is proportional to the ratio of saturation magnetostrictive ($\lambda_s$) to saturation magnetization ($J_s$), i.e., $H_c = \Delta V \cdot J_s \cdot (\rho_d / J_s)$, and hence the slope is related to the volume and density of internal defects considering mainly of free volumes in the glassy structure. Figure 8 shows good linear relations between $H_c$ and the ratio of $J_s$ for Fe-based glassy and amorphous alloys. It is also noticed that their slopes are clearly distinguished between the glassy type alloys and the amorphous type alloys and the slope is much smaller for the glassy type alloys. This difference indicates that the structure of the glassy alloys is distinguished from that of amorphous type alloys and includes much lower volume and density of internal defects. The formation of the more homogenized disordered atomic configurations is concluded to be the origin for the lower coercivity for the glassy type alloys as compared with the amorphous type alloys including crystalline nuclei and density fluctuations.

We have reported that Co–Fe–Ta–B base bulk glassy alloys exhibit a large supercooled liquid region above 70 K before crystallization and the stabilization of the supercooled liquid enables the formation of bulk glassy alloy rods with diameters up to at least 2 mm. It has subsequently been reported that the Co–Fe–Ta–B base bulk glassy alloy rods exhibit very high yield strength of about 5200 MPa at room temperature as well as high elevated temperature strength of over 2000 MPa in the wide temperature range up to 585 °C, as shown in Fig. 9. In addition to the high strength, the Co-based glassy alloy in a ring shape form of 1 mm in thickness, 10 mm in outer diameter and 5 mm in inner diameter exhibits excellent soft magnetic properties, i.e., extremely high maximum permeability reaching 500000 and very low coercivity of 0.26 A/m.

Considering that the extremely soft magnetic properties originate from highly homogeneous magnetic domain structure in the cast alloy ring, we tried to fabricate a soft magnetic glassy thin film exhibiting unique soft magnetic properties...
through the control of the structure-sensitive magnetic domain by a sputtering technique. The Co–Fe–Ta–B glassy alloy film with a thickness of 2.6 μm deposited at 298 K had a fine perpendicular type domain structure with a spacing of about 1700 nm and the domain structure changes to an in-plane type for the film deposited at 473 K, accompanying the significant change in the magnetic properties, as shown in Fig. 10.28) The success of synthesizing the glassy alloy thin film having the fine perpendicular type domain structure even at a large thickness of 2.6 μm is promising for future development as a new type of perpendicular type information recording material because the previous magnetic thin film thickness with the perpendicular domain structure is limited to less than several hundreds nm.29)

We have previously reported that the Fe- and Co-based bulk glassy alloys belonging to the metal-metalloid type have a unique network-like atomic configuration in which distorted trigonal prisms of Fe or Co and B are connected with each other in edge- and face-shared configuration modes through glue atoms of Ln, Zr, Hf, Nb or Ta.5,6) This network-like short-range ordered atomic configuration can suppress effectively the long-range rearrangement of the constituent elements which is necessary for the progress of crystallization, leading to the stabilization of supercooled liquid. Reflecting the formation of the network-like short-range ordered atomic configuration, all the Fe- and Co-based bulk glassy alloys in metal-metalloid alloy system have a unique primary crystallization phase of complex fcc (Fe,Co)23B6 having a large lattice parameter of about 1.2 nm and including 96 atoms in a unit volume.13,15) This phase is different from the primary crystalline phase consisting of the mixture of α-Fe, Fe2B, Fe3B and Fe3Si equilibrium phases for Fe-based amorphous type alloys which require high cooling rates for amorphous phase formation.30)

4. Ni- and Cu-based Bulk Glassy Alloys

Following the Fe- and Co-based bulk glassy alloys, we introduce recent progress in Ni- and Cu-based bulk glassy alloys developed in our group. Figure 11 shows stress-strain curves of Ni-based bulk glassy alloys in tensile and compressive deformation modes. The tensile fracture strength is as high as 2700 MPa for the metal-metal type alloy,18) while the metal-metalloid type alloy exhibits rather high compressive fracture strength of 1800 MPa as well as large compressive plastic strain of 7.5%.31) The high tensile strength of the Ni-based metal-metal type alloy is believed to be the highest for all the bulk glassy alloys, though much higher strength has been obtained under a compressive deformation mode. It is therefore concluded that the metal-metal type Ni-based bulk glassy alloys are appropriate for structural materials which require simultaneously high strength and high ductility.

The Ni-based bulk glassy alloys containing Nb or Ta as solute element exhibit high corrosion resistance in extremely severe circumferential condition which is required for fuel cell applications, i.e., in pH 2 H2SO4 at 353 K and in pH 2 H2SO4 containing 500 ppm NaCl or NaF at 353 K. As exemplified in Fig. 12, the addition of Ta causes the increase in anodic potential and the decrease in corrosive current density, resulting in a much better corrosion resistance as compared with SUS316L.
Figure 13 shows tensile and compressive stress-strain curves of Cu-based bulk glassy alloys in Cu–Zr–Ti and Cu–Hf–Ti systems. The Cu-based alloy rods exhibit high tensile strength of 2000 to 2100 MPa and have plastic strains of about 1.5% under a compressive deformation mode. It has previously been reported that the tensile fracture strength of the Cu–Zr–Ti alloy increases further to about 2500 MPa for the more multi-component Cu-based alloys caused by the addition of Be or Y. A very large supercooled liquid region with the temperature interval above 100 K is also obtained for the Cu–Hf–Al base alloys containing 5 at %Ag or Pd and the largest ΔTs reaches as large as 110 K which is the largest value for all late transition metal base bulk glassy alloys.

We further measured fatigue strength of the Cu–Zr–Hf bulk glassy alloy rod with high tensile strength of 2000 MPa under a uniaxial tension-tension applied load. The fatigue endurance limit defined by the ratio of applied tensile amplitude stress (σa) to tensile fracture strength (σB) after the cycles of 10⁷ is 0.24 for the Cu-based alloy, as shown in Fig. 14. The fatigue limit is much higher than those for Ti-based crystalline alloys and Zr-based bulk glassy alloys. The fatigue crack initiated at the defect site which was located on the outer surface of the rod specimen and propagated into the inner region, accompanying distinct striation patterns. The final fatigue fracture region consisted of a well-developed vein pattern. Although the fatigue strength of the Cu–Zr–Ti glassy alloy is relatively high, it is expected that the elimination of surface defects caused by the decreases of inclusions and casting-introduced pores results in further improvement of fatigue strength.

The fracture toughness of the Cu–Zr–Ti bulk glassy alloy sheets was also evaluated by using the test specimen including fatigue pre-crack which satisfies the ASTM E399 criterion for the size and dimension. The fracture toughness was measured to be about 68 MPam²/2 which was slightly higher than that (40–60 MPam²/2) for Zr-based bulk glassy alloys. It is thus noticed that the Cu–Zr–Ti bulk gassy alloy exhibits high tensile strength, high ductility, high fatigue strength and high fracture toughness and all these mechanical properties are superior to those for Zr-based bulk glassy alloys.

By adding Ta element, which is immiscible to Cu, to Cu₆₀Hf₃₅Ti₁₅ alloy, we can obtain a mixed phase alloy consisting of homogeneously dispersed bcc-Ta rich dendrite...
phase with a size of about 15 μm embedded in a glassy matrix. When the volume fraction of the bcc-Ta phase was about 11%, the dendrite-dispersed Cu-based alloy exhibited high yield strength of 2100 MPa and large plastic strain of 34% which was much larger than that (1.6%) for the glassy single phase alloy. We can observe a high density of shear bands on the outer surface and the fracture occurs along the maximum shear stress plane. The significant increase in compressive plasticity is presumably due to easy generation of shear bands at the glass/dendrite interface through the increase in the stress concentration at the interface caused by the difference in the mechanical strength between the two phases.

5. Pd- and Pt-based Bulk Glassy Alloys

For the Pd- and Pt-based bulk glassy alloys, we developed a Pd–Cu–Ni–P bulk glassy alloy with an extremely low critical cooling rate of the order 0.01 K/s in 1996. Very recently, we also succeeded in finding another type of bulk glassy alloys with extremely high GFA in Pd–Pt–Cu–P alloy system without Ni. The critical cooling rate was lower than 1 K/s and the maximum sample thickness was larger than 50 mm. This is concluded to be the second alloy system in which bulk glassy alloys have large critical sizes above 50 mm and low critical cooling rates below 1 K/s.

6. Correlations Among Fundamental Properties of Late Transition Metal Base Bulk Glassy Alloys

Figure 15 summarizes the relationship between tensile or compressive fracture strength and Young’s modulus for the late transition metal base bulk glassy alloys, together with the data of conventional crystalline alloys. One can see a good linear relation. The strength and Young’s modulus increase in the order of Pt-, Pd-, Cu-, Ni-, Fe- and Co-based alloys. The strength value at the same Young’s modulus is about three times higher than that for crystalline alloys. The slope of the linear relation corresponding to elastic strain limit is 2% which is about three times larger than that (0.65%) for crystalline alloys. Also, the deformation and fracture behaviors of the bulk glassy alloys are independent of alloy component and strength level. The similar linear relation is also recognized between fracture strength and \( T_g \) or \( T_l \) for the late transition metal base bulk glassy alloys, indicating that the strength is dominated by the bonding nature among the constituent elements.

As shown in Fig. 16, we also scarcely recognized the correlation between the critical sample diameter (\( D_{\text{max}} \)) and the reduced glass transition temperature (\( T_g/T_l \)) or the supercooled liquid region (\( \Delta T_c \)) for the late transition metal base bulk glassy alloys, though there are significant scatterings. The correlation suggests that the high glass-forming ability is due to the combination of these two factors, i.e., steep increase in viscosity of supercooled liquid with decreasing temperature and high resistance of supercooled liquid against crystallization.

7. Applications

Table 5 summarizes the features of fundamental properties of the late transition metal base bulk glassy alloys. Typical fundamental properties of Fe-, Co-, Ni- and Cu-based bulk glassy alloys were demonstrated in previous sections. In addition, it is important to point out that the Pt–Pd–Cu–P bulk glassy alloys have very useful combination of low \( T_g \) of about 500 K, a large supercooled liquid region of over 90 K...
The Ni-based glassy alloy sensor. At present, one automobile diameter for the conventional standard sensor to 5.0 mm for the miniaturization of the pressure sensor from 8.5 mm in have much higher sensitivity than that for SUS630. The use of pressure sensors made of Ni- and Zr-based bulk glassy alloys vapor deposition technique. It has been confirmed that the surface of the diaphragms by the low temperature chemical die casting process and made the strain gauge pattern on the glassy alloy balls have been commercialized as shot peening production ability reached 20 tons per month. These Fe-based alloy powders with sizes ranging from 0.1 to 2 mm and its technique which enabled the production of Fe-based glassy alloy has much higher tensile strength, much lower core losses as compared with Sendust and high durability by using the high-strength Ni-based bulk glassy alloy through the resolution of various technical difficulties, as shown in Fig. 17.43) The constructing parts of the 1.5 mm diameter geared motor cannot be made by any mechanical machining techniques, though the 2.4 mm diameter geared motor can be scarcely constructed by mechanically machined SK-4 steel parts. It is noticed that the durability of Ni-based glassy alloy gears in the 2.4 mm diameter geared motor increased by 313 times as compared with the SK-4 steel gears. Even after the rotation number of 1875 million, the Ni-based glassy alloy gear keeps the original shape, being in good contrast to the significant wear loss of the steel gear after 6 million rotation numbers. Besides, we succeeded in making the 1.5 mm micro-geared motor using Ni-based glassy alloy gear parts such as shaft with carrier, planetary gear and carrier with sun-gear. It was confirmed that the micro-geared motor had high-rotating torques of 0.1 mNm at 2 stages stacked gear-ratio reduction system and 0.6 mNm at 3 stages which were 6 to 20 times higher than the vibration force for conventional geared motor with a diameter of 4.5 mm in mobile telephones. These micro-geared motors are expected to be used in advanced medical equipments such as endoscope, micro-pump, rotator and catheter for thrombus removal, precision optics, micro-industries, micro-factory and so on.

Fe-based soft magnetic glassy alloys in Fe–Co–Ga-metalloid and Fe–Co–B–Si–Nb systems have been commercialized as consolidated magnetic cores for power supplies such as choke coils, common mode and noise filter.5,6) The really commercialized magnetic cores exhibit very good soft magnetic properties, i.e., nearly constant relative permeability in a wide frequency range up to several MHz, good linear relationship between permeability and DC bias field, and much lower core losses as compared with Sendust and Permalloy. These Fe-based glassy alloys in Fe–Co–Ga–P–C–B–Si and Fe–Co–B–Si–Nb systems with very high effective permeability above 100000 at 1 kHz and rather high $H_i$ of 1.2 to 1.3 T in a thick sheet form have been tested as the yoke material in precision positioning linear actuators in which the wiring pitch for circuit process unit can be controlled on a scale of 10 to 30 nm. The linear actuator using Fe-based glassy alloy yoke sheets exhibits higher Lorentz force of 0.35 N in a frequency range of 20 to 40 Hz as compared with those for other soft magnetic alloys, indicating that the linear actuator is appropriate for small, large force, fast drive and energy-saving types.

By the recent rapid development of nano- and micro-scale working process techniques using ion beam, electron beam and high corrosion resistance which are suitable for viscous flow working treatments on a nanometer scale in the supercooled liquid region. By the combination of these unique features, the late transition metal base bulk glassy alloys have already gained various application fields. Their application examples will be briefly explained in this section.

We developed a mass-production type water atomization technique which enabled the production of Fe-based glassy alloy powders with sizes ranging from 0.1 to 2 mm and its production ability reached 20 tons per month. These Fe-based glassy alloy balls have been commercialized as shot peening balls.41) It has been demonstrated that the shot penning effect leading to the generation of compressive residual stress field on the surface of material is much superior to that for conventional crystalline shot penning balls, in addition to the much longer endurance time for the Fe-based glassy alloy balls.

In comparison with SUS630 which has been used as conventional pressure sensor, the Ni–Nb–Ti–Zr–Cu–Co bulk glassy alloy has much higher tensile strength, much lower Young’s modulus and much better corrosion resistance. By use of these features, the Ni-based bulk glassy alloy is expected to be applied to a new type of pressure sensor having the features of the world smallest size of 1.5 mm, heavy loadable and high durability by using the high-strength Ni-based bulk glassy alloy through the resolution of various technical difficulties, as shown in Fig. 17.43) The constructing parts of the 1.5 mm diameter geared motor cannot be made by any mechanical machining techniques, though the 2.4 mm diameter geared motor can be scarcely constructed by mechanically machined SK-4 steel parts. It is noticed that the durability of Ni-based glassy alloy gears in the 2.4 mm diameter geared motor increased by 313 times as compared with the SK-4 steel gears. Even after the rotation number of 1875 million, the Ni-based glassy alloy gear keeps the original shape, being in good contrast to the significant wear loss of the steel gear after 6 million rotation numbers. Besides, we succeeded in making the 1.5 mm micro-geared motor using Ni-based glassy alloy gear parts such as shaft with carrier, planetary gear and carrier with sun-gear. It was confirmed that the micro-geared motor had high-rotating torques of 0.1 mNm at 2 stages stacked gear-ratio reduction system and 0.6 mNm at 3 stages which were 6 to 20 times higher than the vibration force for conventional geared motor with a diameter of 4.5 mm in mobile telephones. These micro-geared motors are expected to be used in advanced medical equipments such as endoscope, micro-pump, rotator and catheter for thrombus removal, precision optics, micro-industries, micro-factory and so on.

**Table 5 Features of fundamental properties for late transition metal base bulk glassy alloys.**

<table>
<thead>
<tr>
<th>System</th>
<th>Feature</th>
</tr>
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<tbody>
<tr>
<td>Fe-based</td>
<td>1. Soft Magnetism (Glass, Nano-crystal)</td>
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<tr>
<td></td>
<td>2. High Strength</td>
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<tr>
<td></td>
<td>3. High Corrosion Resistance</td>
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<tr>
<td></td>
<td>4. High Endurance against Cycled Impact Deformation</td>
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<tr>
<td>Co-based</td>
<td>1. Soft Magnetism</td>
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<tr>
<td></td>
<td>2. High Strength</td>
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<tr>
<td></td>
<td>3. High Corrosion Resistance</td>
</tr>
<tr>
<td>Ni-based</td>
<td>1. High Strength, High Ductility</td>
</tr>
<tr>
<td></td>
<td>2. High Corrosion Resistance</td>
</tr>
<tr>
<td></td>
<td>3. High Hydrogen Permeation</td>
</tr>
<tr>
<td>Cu-based</td>
<td>1. High Strength, High Ductility (Glass, Nano-crystal)</td>
</tr>
<tr>
<td></td>
<td>2. High Fracture Toughness, High Fatigue Strength</td>
</tr>
<tr>
<td></td>
<td>3. High Corrosion Resistance</td>
</tr>
<tr>
<td>Pd-based</td>
<td>1. High Strength</td>
</tr>
<tr>
<td></td>
<td>2. High Fatigue Strength, Rather High Fracture Toughness</td>
</tr>
<tr>
<td></td>
<td>3. High Corrosion Resistance</td>
</tr>
<tr>
<td>Pt-based</td>
<td>1. Very Low $T_g$</td>
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<tr>
<td></td>
<td>2. Very Low TL</td>
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<td></td>
<td>3. High GFA</td>
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<td>4. High Corrosion Resistance</td>
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<td></td>
<td>5. Good Nano-imprintability</td>
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and high corrosion resistance which are suitable for viscous flow working treatments on a nanometer scale in the supercooled liquid region. By the combination of these unique features, the late transition metal base bulk glassy alloys have already gained various application fields. Their application examples will be briefly explained in this section.

We developed a mass-production type water atomization technique which enabled the production of Fe-based glassy alloy powders with sizes ranging from 0.1 to 2 mm and its production ability reached 20 tons per month. These Fe-based glassy alloy balls have been commercialized as shot peening balls.41) It has been demonstrated that the shot penning effect leading to the generation of compressive residual stress field on the surface of material is much superior to that for conventional crystalline shot penning balls, in addition to the much longer endurance time for the Fe-based glassy alloy balls.

In comparison with SUS630 which has been used as conventional pressure sensor, the Ni–Nb–Ti–Zr–Cu–Co bulk glassy alloy has much higher tensile strength, much lower Young’s modulus and much better corrosion resistance. By use of these features, the Ni-based bulk glassy alloy is expected to be applied to a new type of pressure sensor exhibiting higher pressure capability and higher sensitivity.42) We produced Ni-based glassy alloy diaphragms by the resolution of various heavy loadable and high durability by using the high-strength Ni-based bulk glassy alloy through the resolution of various technical difficulties, as shown in Fig. 17.43) The constructing parts of the 1.5 mm diameter geared motor cannot be made by any mechanical machining techniques, though the 2.4 mm diameter geared motor can be scarcely constructed by mechanically machined SK-4 steel parts. It is noticed that the durability of Ni-based glassy alloy gears in the 2.4 mm diameter geared motor increased by 313 times as compared with the SK-4 steel gears. Even after the rotation number of 1875 million, the Ni-based glassy alloy gear keeps the original shape, being in good contrast to the significant wear loss of the steel gear after 6 million rotation numbers. Besides, we succeeded in making the 1.5 mm micro-geared motor using Ni-based glassy alloy gear parts such as shaft with carrier, planetary gear and carrier with sun-gear. It was confirmed that the micro-geared motor had high-rotating torques of 0.1 mNm at 2 stages stacked gear-ratio reduction system and 0.6 mNm at 3 stages which were 6 to 20 times higher than the vibration force for conventional geared motor with a diameter of 4.5 mm in mobile telephones. These micro-geared motors are expected to be used in advanced medical equipments such as endoscope, micro-pump, rotator and catheter for thrombus removal, precision optics, micro-industries, micro-factory and so on.

Fe-based soft magnetic glassy alloys in Fe–Co–Ga-metalloid and Fe–Co–B–Si–Nb systems have been commercialized as consolidated magnetic cores for power supplies such as choke coils, common mode and noise filter.5,6) The really commercialized magnetic cores exhibit very good soft magnetic properties, i.e., nearly constant relative permeability in a wide frequency range up to several MHz, good linear relationship between permeability and DC bias field, and much lower core losses as compared with Sendust and Permalloy. These Fe-based glassy alloys in Fe–Co–Ga–P–C–B–Si and Fe–Co–B–Si–Nb systems with very high effective permeability above 100000 at 1 kHz and rather high $H_i$ of 1.2 to 1.3 T in a thick sheet form have been tested as the yoke material in precision positioning linear actuators in which the wiring pitch for circuit process unit can be controlled on a scale of 10 to 30 nm. The linear actuator using Fe-based glassy alloy yoke sheets exhibits higher Lorentz force of 0.35 N in a frequency range of 20 to 40 Hz as compared with those for other soft magnetic alloys, indicating that the linear actuator is appropriate for small, large force, fast drive and energy-saving types.

By the recent rapid development of nano- and micro-scale working process techniques using ion beam, electron beam
and LIGA process etc., the importance of materials with homogeneous structure on a nanometer scale has significantly increased. In the case of metallic alloys, the alloys with such features are limited to glassy and nanocrystalline alloys. The glassy alloys have much homogeneous structure and can be deformed via viscous flow working even at much lower temperatures as compared with nanocrystalline alloys.

By applying the focused ion beam (FIB) technique to bulk glassy alloys, we have fabricated various complex patterns with smooth surface on a nanometer scale which cannot be obtained for conventional crystalline alloys.44) The controllable minimum size of the complex pattern by the FIB technique reached as small as 12 nm. We fabricated bulk glassy alloy surfaces having highly functional characteristics through the FIB working of Pt-based bulk glassy alloys to nanometer-scale controlled functional surface, as shown in Fig. 18.45) The Pt_{48.75}Pd_{7.75}Cu_{19.5}P_{22} bulk glassy alloy with low $T_g$ of 502 K and large $\Delta T_g$ of 85 K can be regarded as an ideal viscous flow working material on a nanometer scale. The low $T_g$ enabled the use of polyimide die supported with copper plate and only one cycle viscous flow pressing against the polyimide die in the supercooled liquid region produced complex micro-inductors. We have confirmed that the minimum pattern size caused by the viscous flow die forging process reaches as small as 22 nm, as is evidenced from the fabrication of the imprinted nano-data-pit patterns for next generation DVD recording storage material in Fig. 19.

8. Conclusions

The development of advanced metallic materials by use of the science and technology of supercooled metallic liquid has...
started around 1990 and the new research field on the basis of this concept is believed to become more and more significant in the near future.

REFERENCES

33) Metals Databook, (Japan Institute of Metals, Maruzen, Tokyo, 2004), p. 139.