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$M_{80}S_{20}$ metallic glass powder and its explosive consolidation

JINYUAN ZHANG, BAOREN AI, TONGXIA ZHANG*, CHUNLAN LIU,
GUEYAN WUAN, RUIZHEN ZHU
Central Iron & Steel Research Institute, 13 Taipingzhuang, Beijing, China

The factors influencing metallic glass forming ability (GFA) are discussed. An alloy of the general formula $M_{80}S_{20}$ which can easily be atomized into amorphous powder by conventional nitrogen gas-atomization techniques has been developed. The explosive consolidation and devitrification of $M_{80}S_{20}$ powder are described.

1. Introduction

A glass state, as a first approximation, can be regarded as a frozen undercooled melt. The formation of glasses from the melt is substantially due to the factors which can effectively impede nucleation and growth of crystalline phases during the quenching process. Among all the factors, cooling rate and composition of the alloy are two critical factors. It is well known that the initial crystallization temperature of a melt T_{c_1} is much more sensitive to the cooling rate $\dot{T}$ than the glass transition temperature T_g. Hence, in theory, it should always be possible to lower T_{c_1} below T_g as long as $\dot{T}$ is high enough. In other words, for a given alloy there exists a critical cooling rate $\dot{T}_{cr}$ and whenever $\dot{T} > \dot{T}_{cr}$ the alloy will be solidified into the glassy state. However, the critical cooling rates required for different alloy compositions to form amorphous phases from melts are quite different (e.g. from 10^2 to $10^{12}\,\mathrm{K\,sec^{-1}}$) depending on their glass forming ability (GFA).

It is of practical importance to develop alloy systems with high GFA. Based on experimental trials and theoretical analysis, we have developed an alloy which can be easily atomized into amorphous powder by conventional nitrogen-atomization techniques, and the amorphous state is easily retained during consolidation processing.

2. Metallic glass powder with high GFA

The question of the GFA is just as complex as that of the formation conditions of crystalline phases. Several papers describing the GFA in metallic melts have been published [1–4]. Up till now, there is no complete empirical law or theoretical principle with which we can quantitatively evaluate the GFA of alloy melts and some experiments have indicated that the GFA for a given alloy is also in many ways related to the quenching technique used [5]. However, several factors have been recognized as being associated with the metallic glass formability. In general a deep eutectic is thermodynamically favourable for glass formation because at this point the free energy difference between the undercooled melt and the crystalline alloy is minimal, and therefore only a small driving force exists for crystallization of the equilibrium phases. On the other hand, the crystallization process based on this concentration is related to sharp local composition changes and long range diffusion in order to coincide with the compositions of the corresponding crystalline phases, which is also favourable to glass formation. The atomic size effect is also one of the most significant factors for GFA in metallic alloy systems. Shuji Ueno and co-workers [4], have summarized an empirical approach to correlate the atomic volume mismatch with the minimum solute concentration required to form a glassy phase from the melt. Large electronegativity differences between the alloying elements are frequently tied to strongly negative values for the enthalphy of mixing, and hence are conducive to glass formation. At the phenomenological level there are also several factors, such as the ratio of crystallization temperature to the melting point of alloy [6], activation energy for crystallization [7], heat of compound formation, etc, which are also connected in some way with GFA.

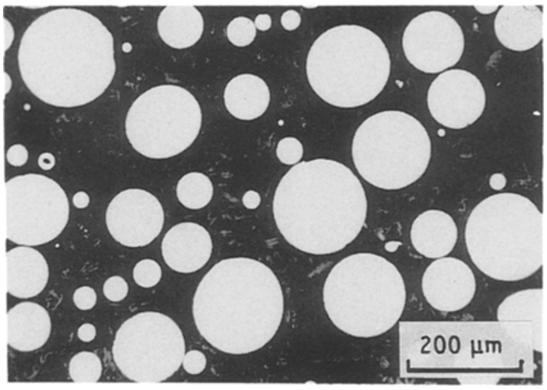

Figure 1 Optical micrograph of polished and etched sections of $M_{80}S_{20}$ powder.

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*Present address: Institute of Mechanics Research, Academina Sinica, Beijing, China.

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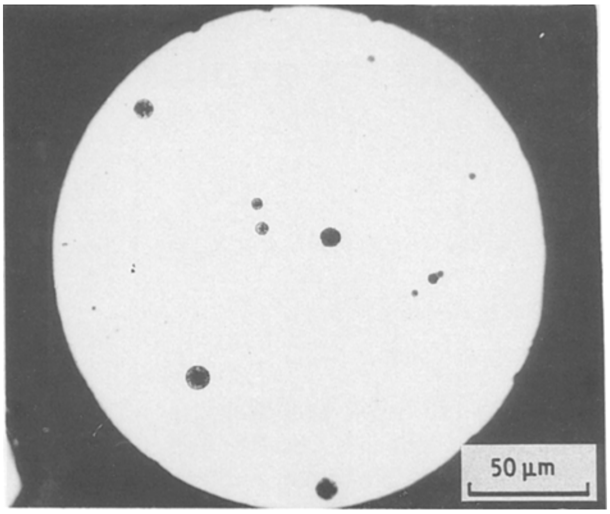

Figure 2 Optical micrograph of polished and etched section of 216 μm particle (etched by aqua regia).

During a study of self-fluxing alloy, we developed an alloy system which could be easily atomized into amorphous powder by using only conventional nitrogen-atomizing equipment operating under normal conditions (i.e. giving an average cooling rate $\sim 10^3$ K sec^{-1}). It is an octonary iron base alloy system, consisting of (Fe, Cr, Ni, W, Mo)$_{80}$ (B, Si, C)$_{20}$. The content of each element must be in a definite range (the range of each element (at%): (65–70)Fe-(3–5)Cr-(2–4)Ni-(2–4)W-(1–2)Mo-(10–14)B-(4–7)Si-(2–3)C and the atomic ratio of metal–metalloid is about 80 : 20 (so abbreviated as $M_{80}S_{20}$). The GFA of this alloy is so high that all powder particle sizes below 180 μm are totally amorphous as shown in Fig. 1. For larger particles, some are entirely amorphous (Fig. 2) some partially amorphous (Fig. 3). In many instances, the amorphous areas appear inside particles rather than on their surfaces. It is therefore implicit that concentration fluctuations and atomic aggregations have occurred within a particle before complete solidification. Some studies on structure relaxation, crystallization and phase transitions of $M_{80}S_{20}$ powder have been published earlier [8]. Its crystallization temperature T_{cs} is 858 K at 5 K min^{-1} heating rate, activation energy 118 Kcal mol^{-1}. Most of the particles are spherical and their true density is 7.81 g cm^{-3}, the average microhardness $H_v = 980$. In view of the high T_{cs} and low $\dot{T}_{cr}$ of this powder (indicating a low driving force for crystallization), it is easy to consolidate to amorphous bulk material.

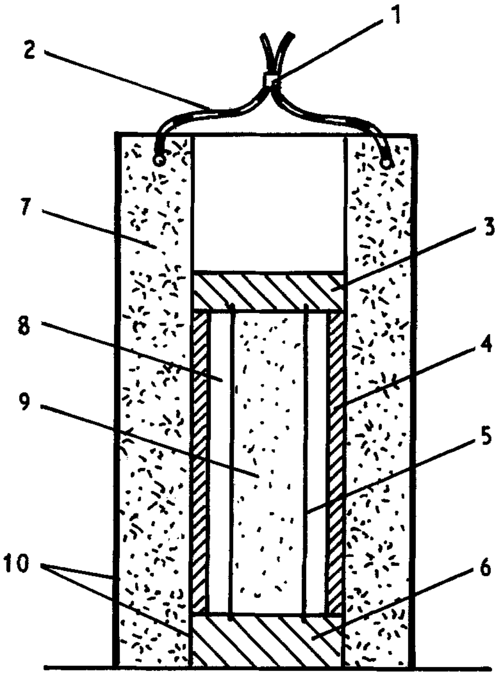

Figure 4 Schematic diagram of cylindrical converging explosive unit. (1) detonator, (2) blasting fuse, (3) partition board, (4) steel cylinder, (5) can (aluminium), (6) cushion block, (7) gun powder and sawdust, (8) gas gap, (9) amorphous powder, (10) paper chase.

3. Explosive consolidation of $M_{80}S_{20}$ powder

In recent years, several approaches have been found capable of consolidating powders into amorphous bulk parts [9–11]. The first reported successful consolidation of metallic glasses was achieved using an explosive technique.

We have conducted a series of experiments utilizing $M_{80}S_{20}$ powder with a nominal particle size of < 100 μm

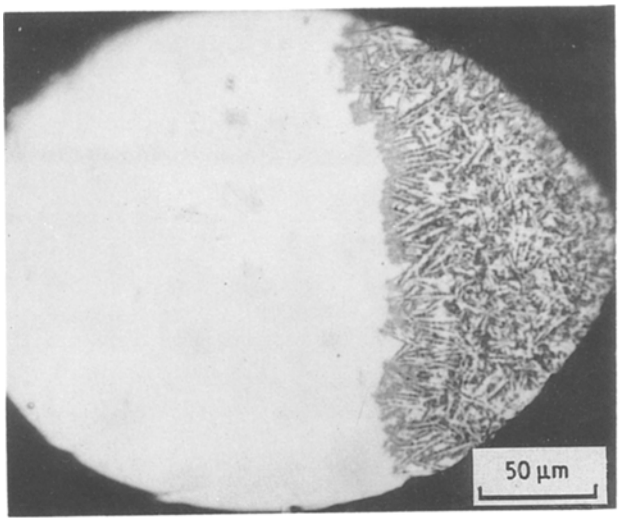

Figure 3 Optical micrograph of partially amorphous particle (etched by aqua regia).

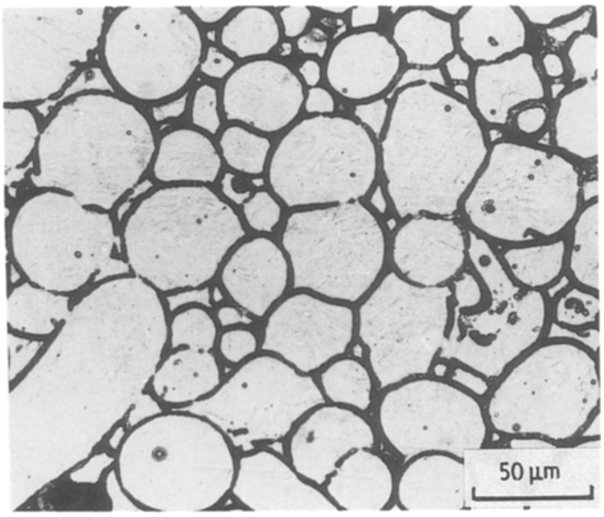

Figure 5 Optical micrograph of specimen section explosively consolidated from $M_{80}S_{20}$ powder (heavily etched).

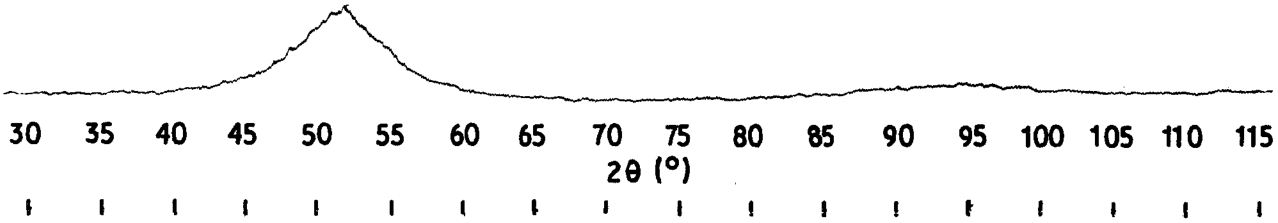

Figure 6 X-ray diffraction chart of the specimen explosively consolidated from $M_{80}S_{20}$ powder. CoKα 35 kV 30 mA 400 c.p.s.

containing 14% of $< 45\,\mu$m particles. A schematic drawing of the explosive unit is shown in Fig. 4. After ignition, the explosive shock waves produce an adiabatic compression of the amorphous powder. The friction between powder particles and the plastic deformation of particles themselves can result in local temperatures high enough to melt the particle surfaces and stick them together in a few microseconds. Because of the good conductivity of metals the molten zone will be rapidly quenched and the glassy structure recreated. Several metallic glass bars having dimensions up to 18 mm in diameter with a length of 50 mm have been prepared by the dynamic consolidation process.

Fig. 5 shows an optical micrograph of polished and heavily etched (using aqua regia) section of the explosively consolidated product. The particle boundaries and particle deformation can be clearly seen from this micrograph, but there is no evidence of crystalline grains. The retention of amorphism in the explosively consolidated product was confirmed by X-ray diffraction, as shown in Fig. 6.

The average density of the consolidated amorphous bars is $7.46\,\mathrm{g\,cm^{-3}}$, corresponding to 95.5% of theoretical density and the average microhardness is about 950 (H_v). Rather high residual stresses exist in the as-consolidated samples. To relieve these stresses, samples were annealed at 250° C for 2 h, then cut to form a toroid for magnetic measurements. Fig. 7 shows the magnetic hysteresis loop. It can be seen that the coercive force is quite small though the saturation magnetic induction is not so high.

4. Devitrification of explosive consolidated products

The metallic glass can be converted into a devitrified microcrystalline alloy by heat-treatment. Initially, the consolidated bars were heat treated in a hydrogen atmosphere at 550° C for 4 h. The heat-treated specimen was found, by X-ray diffraction, to be a mixture of the amorphous phase and metastable crystalline phases. Fig. 8 shows an optical micrograph of a polished and heavily etched section of the annealed specimen. It is clear from this micrograph that the microcrystalline phases are beginning to precipitate. Continuing with this heat treatment, the specimens are further annealed at 1000° C for half an hour. After that the specimens are fully densified and have a very high hardness ($H_v = 870$). Fig. 9 shows an optical micrograph of a specimen devitrified at 1000° C. The microstructure consists of fine homogeneously dispersed precipitates in a matrix which shows no evidence of the original particle boundaries.

5. Conclusions

(1) The $M_{80}S_{20}$ alloy possesses excellent Glass Forming Ability. It can be easily atomized into amorphous powder using conventional nitrogen-atomizing equipment operating under normal conditions.

(2) $M_{80}S_{20}$ metallic glass powder can be consolidated by an explosive technique into amorphous bulk material.

(3) The consolidated amorphous bulk alloy can be converted into devitrified microcrystalline material by heat treatment above the crystallization temperature. It has a very fine microstructure and very high hardness.

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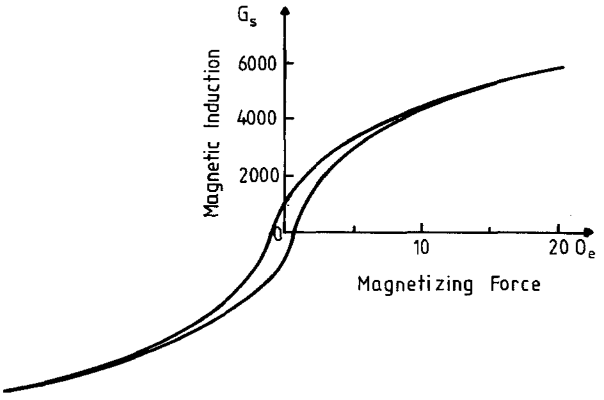

Figure 7 Magnetic hysteresis loop of specimen explosively consolidated from $M_{80}S_{20}$ amorphous powder and annealed 2 h/250° C.

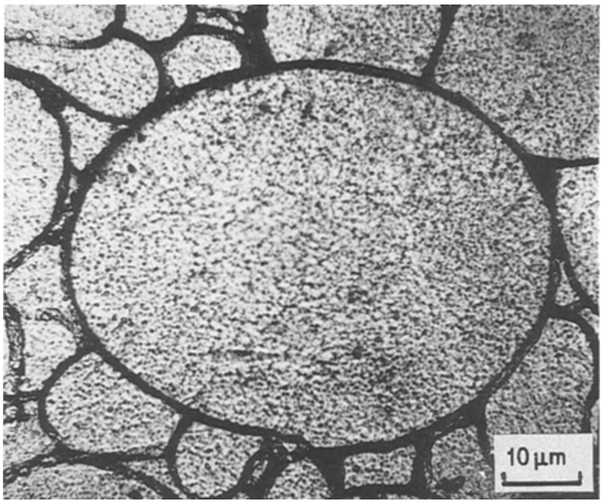

Figure 8 Optical micrograph of annealed (550° C, 4 h) specimen, etched by aqua regia.

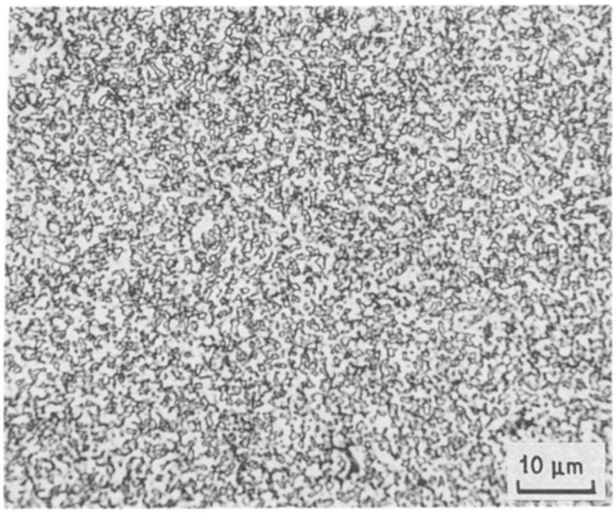

Figure 9 Optical micrograph of annealed (1000° C, 30 min) specimen, etched by aqua regia.

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