

CHAPTER 1. INTRODUCTION

1.1. Historical background and development of bulk metallic glasses

Glass is any material that can be cooled from a liquid to a solid without crystallizing. Most metals do crystallize as they cool, arranging their atoms into a highly regular spatial pattern called a lattice. But if crystallization does not occur, and the atoms settle into a nearly random arrangement, the final form is a metallic glass. In recent years, production of new metallic glasses in bulk form is getting popular because of their superior strength, elasticity and magnetic properties [1].

Metallic glasses were discovered over forty years ago when rapid quenching methods were first applied to Au-Si system. This discovery is carried out the first worked on the technique known as “splat cooling” which achieves cooling rates in the range 10^6 - 10^8 °C/s as liquid alloy is solidified. In this technique, liquid droplets of the alloy are shot from a carbon dioxide gun onto a cooled Cu or Ag block to produce solid “splats”. This amorphous structure was metastable and could be converted into a metastable crystalline phase by annealing. [2,3]

Suppressing the crystallization, one of the crucial step to get low critical cooling rate for bulk metallic glasses has enabled with the discovery of new compositions. The glass forming ability (GFA), combination of large differences in atomic size of the constituent elements and negative heat of mixing hinder local atomic rearrangements in the undercooled liquid state are other important thermodynamic and kinetic criteria to get bulk metallic glasses.

During the past several years, advances have been made in this field as a result of the discovery and development of several families of alloys with substantially improved glass forming ability. Whereas previous metallic glasses were generally formed by cooling the melt at rates of 10^5 – 10^6 K s⁻¹, the more recently developed alloys require cooling rates of only 1–100 Ks⁻¹ or less. As such, the new materials can be cast from the molten state into glassy objects with dimensions up to several centimeters as compared with maximum thickness or diameter of 10–100 μm for rapidly quenched ribbons and powders. These new alloys are referred to as ‘bulk glass formers’ or ‘bulk metallic glasses’.

The work of the David Turnbull and his group in the early 1960s was another critical contribution to the subject [4]. This work illustrated the similarities between metallic glasses, ceramic glasses and silicates. Specifically, Turnbull, Chen, and other later collaborators clearly demonstrated the existence of a glass transition in rapidly quenched Au-Si glasses as well as the other Pd-Si and Pd-Cu-Si glass forming alloys synthesized initially by the Duwez group [5].

The field of metallic glasses gained momentum in the early 1970’s when Allied Chemical Corporation developed continuous casting processes for commercial manufacturing of metallic glass ribbon and sheets [6]. During the same period, Chen and collaborators used simple suction casting method to form millimeter diameter rods of ternary Pd-Cu-Si alloys at significantly low cooling rates in the range of 10^3 K/s [7]. The synthesis of metallic glasses in a bulk form (with thickness >1 mm) was successfully achieved in Ni₄₀Pd₄₀P₂₀ alloys in 1976 [8].

During the late 1980s, Akihisa Inoue and his coworkers in Sendai, Japan, found exceptional glass forming ability in the rare-earth rich alloys [9], e.g. La-Al-Ni and La-Al-Cu. By casting the alloys into copper molds, they fabricated fully glassy rods and bars with cast thickness of several mm. From there, they studied similar quaternary and quinary materials (e.g. La-Al-Cu-Ni) and developed alloys that formed glass at cooling rates under 100 K/s with critical casting thickness ranging upward toward 1 cm [10].

A similar family of alloys, with the rare-earth metal partially replaced by the alkali earth metal Mg were also developed along with the parallel family of multi component Zr-base alloy (e.g. Zr- Cu-Ni-Al) [11]. The work opened the door to develop of the other broad classes of bulk metallic glasses. Building on the Inoue work, Peker and Johnson [12] developed a family of ternary, quinary and higher order glass formers based on higher order alloys of Zr, Ti, Cu, Ni, Be (also combined with other transition metals, TM). One extensively studied example, referred to as Vitreloy 1, has a composition of $(Zr_3Ti)_{0.55}(Cu_5Ni_4)_{0.225} Be_{0.225}$. Critical cooling rate for glass formation are 1 K/s. The alloys were cast in the form of fully glassy rod with diameters ranging up to 5–10 cm. The alloys require no fluxing or special processing treatments and form bulk glass by conventional metallurgical casting methods [5].

Since 1988, bulk glass formation has been reported in various alloys based on Cu, Ti, Fe, Nd, and Pr. But these alloys generally have small supercooled regions and their critical sizes for glass formation are generally smaller than that (30 mm) of Zr based alloys. However, with attention back to Pd based alloys recently, large glass formation by water quenching using B_2O_3 flux has been reported in $Pd_{40}Cu_{30}Ni_{10}P_{20}$ alloy with

diameter up to 72 mm [13], which is the largest size of bulk metallic glasses reported so far [14].

Table 1.1 summarizes the critical cooling rates and section thickness for glass formation in chronological order and bulk glass formation in different alloy systems respectively.

Table 1.1 Critical cooling rates and section thicknesses for glass formation of bulk glass forming alloys in chronological order.

Year	Alloy	Critical cooling rates (K/s)	Thickness (mm)	Method
1969	Pd-Cu-Si		1	Splat quenching
1978	Pd ₇₂ Cu ₆ Si ₁₆		0.9	Water quenching
1981	Pd ₇₈ Cu ₆ Si ₁₆	1000	1.5	Low gravity tube dropping
1981	Pd ₇₇ Cu ₆ Si ₁₇	125	0.75	Bridgman solidification
1982	Au ₅₅ Pb _{22.5} Sb _{22.5}		1.5	Liquid quenching
1984	Pd ₄₀ Ni ₄₀ P ₂₀	0.17	10	Casting with B ₂ O ₃ flux
1990	La ₅₅ Al ₂₅ Ni ₂₀	87	3	Metallic mold casting
1991	Mg ₆₅ Cu ₂₅ Y ₁₀	93	4	Metallic mold casting
	Zr ₅₇ Ti ₅ Al ₁₀ C ₂₀ Ni ₈		20	Mold casting
	Zr ₆₅ Al _{7.5} Ni ₁₀ Cu _{17.5}	1.5	7	Chill casting
1992	Mg ₆₅ Cu ₂₅ Y ₁₀	93	7	High pressure die casting
1993	Zr ₆₅ Al _{7.5} Ni ₁₀ Cu _{17.5}	15	16	Water quenching
	La ₅₅ Al ₂₅ Ni ₁₀ Cu ₁₀ Co ₅	55	> 9	High pressure die casting
	Zr _{41.2} Ti _{13.8} Ni ₁₀ Cu _{12.5} Be _{22.5}	0.9	14	Water quenching
1994	Nd ₆₀ Al ₁₅ Co ₁₀ Cu ₁₀ Fe ₅		> 6	Injection mold casting
1995	Fe ₇₃ Al ₅ Ga ₂ P ₁₁ C ₅ B ₅		1	Injection casting
1996	Pd ₄₀ Ni ₁₀ Cu ₃₀ P ₂₀	0.1	40	Water quenching
	Zr ₅₅ Al ₁₀ Ni ₅ Cu ₃₀	15	30	Suction casting
	Pd ₄₀ Ni ₄₀ P ₂₀	0.17	25	Water quenching
	Nd ₆₀ Fe ₃₀ Al ₁₀	12	15	Suction casting
1997	Pd ₄₀ Ni ₁₀ Cu ₃₀ P ₂₀	0.1	72	Water quenching

1.2. Overview of This Research

In this study, machining performance of $Zr_{52.5}Ti_5Cu_{17.9}Ni_{14.6}Al_{10}$ metallic glass under different turning and drilling parameters evaluated. Evaluation was not carried out only in the mechanics of machining but also characterization of BMG chips in the microstructural point of view. Chip light emission, chip morphology, cutting mechanics, tool wear, burr formation, oxidation and crystallization of Zr-based bulk metallic glass due to turning and drilling of Zr-based bulk metallic glass are studied throughout the research. These topics are going to be addressed in the following Chapter 2-6. Partial results have been covered in several publications [15-19].



Figure 1.1 Zr- based BMG button and ingot prepared by arc melting and drop casting in inert gas atmosphere

Figure 1.1. shows the Zr-based BMG button and ingot prepared by arc melting and drop casting in inert gas atmosphere in Oak Ridge National Laboratory (ORNL), the close collaborator of this research. BMG material was produced in the Metals and Ceramics Division and material characterization and drilling tests were conducted in the

High Temperature Materials Laboratory at ORNL. Metallic glass machining chips were characterized using the SEM, x-ray diffraction and nano-indentation in Chapter 2 and [15]. Above a threshold cutting speed, oxidation of the Zr produces high flash temperatures and causes crystallization. The chip morphology was unique and showed the presence of shear bands, void formation and viscous flow.

Chapter 3 and [16] are focused on the crystallization and oxidation in the BMG chips and machined surface. Experimental setups for the lathe turning of BMG, infrared spectrometer temperature measurement, and sample preparation are introduced. Radiation thermometry and results of BMG chips flash temperature measurement are presented. Results of x-ray diffraction, optical microscopy, and field emission gun SEM analysis of crystallization in the cross-section of BMG chips are discussed.

The goal of the Chapter 4 and [17] is to study the process conditions that trigger the light emission and analyze the cutting forces, chip morphology, surface roughness, and tool wear in lathe turning of Zr-based BMG. Four cutting tools with different coatings and substrate materials were investigated for turning the BMG material [6,7]. Two other work-materials, the aluminum 6061-T6 and AISI 304 stainless steel, were machined under identical cutting conditions. The chip morphology and cutting conditions that initiate chip light emission are studied. Cutting forces of BMG turning are analyzed. The machined surfaces and tool wear are presented to extract distinctive characteristics in machining the BMG.

In Chapter 5 and [18], the chip light emission, chip morphology, burr formation and machined surface in BMG drilling are investigated. The conditions that trigger the

chip light emission in drilling are discussed. The chip morphology and crystallization are analyzed and the burr formation of drilled holes is examined.

In Chapter 6 and [19], thrust force, torque, and tool wear are investigated. Study showed that, when feasible process parameters are selected, BMG could be efficiently drilled using either the HSS or WC-Co tool. The WC-Co tool with better mechanical and thermal properties is the choice of tool for drilling BMG. The chip light emission, which associated with high chip and tool temperatures, showed the detrimental effect on the drill life.

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