Oxidation and crystallization of Zr-based bulk metallic glass due to machining

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Abstract

Bulk metallic glass was subjected to extreme deformation conditions during machining operation. The flash temperature, oxidation and crystallization within chips from a Zr-based bulk metallic glass were investigated. A near-infrared spectrometer was used to capture the light emission from the tool-chip interface allowing the calculation of the temperature. Very high temperatures in the 2400–2700 K range were observed and associated with the light emission and oxidation in the chips. X-ray diffraction analysis revealed oxidation of chips machined at high cutting speeds. Optical micrographs of polished and etched chip cross-sections showed a dendritic pattern due to crystallization. Using a field emission gun SEM, amorphous and crystalline regions were analyzed. This study demonstrates the oxidation and crystallization of bulk metallic glass during machining.

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1. Introduction

Bulk metallic glasses are amorphous alloys with no long-range periodic lattice structure, which exhibit unique mechanical, thermal, and magnetic properties. As shown in Table 1, Zr-based bulk metallic glass possesses a very high ultimate tensile stress (1900 MPa), high elastic strain limit (2%) and low thermal conductivity (4 W/m-K) compared to other crystalline metals. A variety of solidification techniques with rapid cooling are used to produce bulk metallic glass [1]. Recent development of new multi-component alloy groups has focused on slow cooling rates to enable the production of bulk metallic glass components with thick cross-sections. The bulk metallic glass investigated in this study is Zr_{52.5}Ti_{15}-Cu_{17.9}Ni_{14.6}Al_{10} [2,3], hereafter denoted as BMG.

Although casting is the most commonly used method for mass-producing BMG parts, machining is an important process for fabricating precision BMG components with high dimensional accuracy. During the chip formation in machining, the work-material is subjected to high temperature and high strain-rate conditions. This has made machining a novel way to investigate the response of BMG under extreme deformation conditions. The low thermal conductivity of BMG facilitates very high temperatures and subsequent surface oxidation, which generates spectacular light emissions [4]. This study used a near-infrared spectrometer to measure the flash temperature under different cutting speeds and integration time settings. Detailed analysis of the chip cross-section was performed to study the crystallization and microstructure in the BMG chips.

The mechanical properties of BMG depend strongly on its microstructure. The presence of any crystalline phase can significantly embrittle BMG [5]. The dispersion of nano-crystalline particles with an amorphous structure increases the elastic modulus [5], hardness [5–7], and tensile strength [8]. Wang et al. [9] quantified the effect of crystallization on hardening in
high temperature deformation of BMG. Zhang et al. [10] observed that, after full crystallization of the Zr48Nb8Cu14Ni12Be18 BMG, the material demonstrated a 40% increase in hardness, 20% increase in elastic constant, 6.7% increase in thermal expansion coefficient, and 1.6% increase in density. Fan and Inoue [11] observed the plastic strain to failure increased with volume fraction of nanocrystals.

In this study, the crystallization and oxidation in the BMG chips and machined surface were investigated. Experimental setups for the lathe turning of BMG, infrared spectrometer temperature measurement, and sample preparation are first introduced. Radiation thermometry and results of BMG chips flash temperature measurement are then 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.

## 2. Experimental setup

### 2.1. Machining

The machining experiments were conducted in an EMCO PC Turn 125 CNC lathe using a TiN coated WC-Co insert (Seco CCMT 09T304) with 0.4 mm tip radius and 5° rake angle. The configuration of the experimental setup is illustrated in Fig. 1(a). The cutting insert was moved across a 6.35 mm diameter BMG rod, which was prepared by melting and casting in a Cu mold. The diameter of the rod after cutting was 5.35 mm, i.e., the depth of cut \( d \) was 0.5 mm. Turning tests were conducted at three cutting speeds: 0.38, 0.76 and 1.52 m/s. The machine controller maintained the same feed per revolution, \( f_c \) at 50 \( \mu \)m in order to have the same undeformed chip geometry at all three cutting speeds. The cutting was conducted without using coolant.

### 2.2. Optical fiber and infrared spectrometer

The spectrometer used was an Ocean Optics USB2000 spectrometer, which analyzes radiation in the near-infrared range from 0.72 to 0.92 \( \mu \)m. This spectrometer uses charge-coupled discharge (CCD) arrays to acquire the thermal radiation light spectrum over a specified sampling integration time. The light signal is collected by an optical fiber and transmitted to the spectrometer. A so-called cosine corrector, which is transparent in the near-infrared range, is used to protect the optical fiber tip from the hot flying BMG chips. Fig. 1(c) shows a picture of the setup for temperature measurement in machining BMG.

### 2.3. Sample preparation

The collected chip specimens were mounted in an epoxy and then cut and polished using metallographic techniques to generate cross-sections. During mounting, the chips were carefully positioned so the polished cross-section surface was perpendicular to the cut surface. One micrometer size alumina paste was used as the final lapping compound. The surface was immediately etched after polishing in a solution of 40 ml HNO3 with 0.12 ml of HF for about 2–3 s prior to examination using an optical microscope.

### 2.4. X-ray diffraction and microscopy analysis

A Scintag 4-axis goniometer using copper radiation, parallel beam optics and liquid N2-cooled Ge detector was employed for the X-ray diffraction analysis of the BMG chips and the machined surfaces. An optical microscope, Nikon Epiphot 300, was first used to examine the cross-sectional surface of the chips. A field emission gun SEM, Philips Model XL-30, was used to examine the etched surface to spot Kikuchi patterns and polished surface (without etching) to identify different crystalline regions. Electron backscatter diffraction technique and secondary electron technique were used to do these analysis respectively. Spatial resolution was 15 nm for field emission gun SEM. Electron backscatter diffraction (EBSD), also known as backscatter Kikuchi diffraction, were used in the field emission gun SEM. The most attractive feature of EBSD is its unique capability to perform rapid, automatic diffraction analysis to give crystallographic data and imaging with good spatial resolution [12]. The EBSD technique depends on

### Table 1

Comparison of properties of Zr-based bulk metallic glass (BMG) and other metals

<table>
<thead>
<tr>
<th>Material</th>
<th>Elastic modulus (GPa)</th>
<th>Poisson ratio</th>
<th>Ultimate tensile stress (MPa)</th>
<th>Percent of elongation to fracture</th>
<th>Thermal conductivity (W/m-K)</th>
<th>Fracture toughness (MPa.m(^{1/2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr41.2Ti13.8Cu12.5Ni10.0Be22.5 BMG</td>
<td>96</td>
<td>0.36</td>
<td>1900</td>
<td>2 (all elastic)</td>
<td>4</td>
<td>40–55</td>
</tr>
<tr>
<td>Ti-6Al-4V (annealed)</td>
<td>114</td>
<td>0.34</td>
<td>880</td>
<td>14</td>
<td>6.7</td>
<td>75</td>
</tr>
<tr>
<td>Inconel 718</td>
<td>200</td>
<td>0.28</td>
<td>1370</td>
<td>25</td>
<td>11.4</td>
<td>20</td>
</tr>
<tr>
<td>Aluminum 6061-T6</td>
<td>69</td>
<td>0.33</td>
<td>310</td>
<td>12</td>
<td>167</td>
<td>29</td>
</tr>
<tr>
<td>AISI 4340 steel Q + T</td>
<td>205</td>
<td>0.32</td>
<td>1250</td>
<td>14</td>
<td>45</td>
<td>50</td>
</tr>
<tr>
<td>316 stainless steel (annealed)</td>
<td>200</td>
<td>0.30</td>
<td>550</td>
<td>60</td>
<td>16</td>
<td>80</td>
</tr>
</tbody>
</table>

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positioning the electron beam at a shallow incident angle, typically 20°, to impinge on the specimen surface. Because of the shallow angle, the proportion of back-scattered electrons able to undergo diffraction and escape from the specimen surface is enhanced. The resulting diffraction pattern can be captured and the software can be used to distinguish the orientation of each diffraction pattern and crystalline structure.

3. BMG chips flash temperature measurement using infrared thermometry

A distinctive characteristic observed during machining of BMG at 0.76 and 1.52 m/s cutting speeds was the intense emission of visible light from the tool-workpiece contact area. Due to the low thermal conductivity of BMG, the chips remained hot and the light emission continued for an extended period of time, as shown in Fig. 1(b). This phenomenon was not observed during the machining of other metals. An infrared spectrometer was used to capture the light emission spectrum and the spectrum was used to calculate the chips flash temperature.

Light emission during fracture of BMG was observed previously [3,4,13,14]. Gilbert et al. [13] applied infrared spectrometers and a nonlinear least-squares regression method to analyze the light emission during rupture of BMG. Flash temperatures of ~3175 K in air and ~1400 K in nitrogen on the fracture surface were observed. This indicates that the intense light emission in air was associated with the oxidation of fresh BMG material exposed during rupture. Since the cutting was conducted in air, the high flash temperature and oxidation of the BMG chips were expected.

The relative intensities at different wavelengths of the spectrometer, \( R(\lambda) \), were scaled to match the blackbody emission curves \( E_B(\lambda, T) \), to determine the effective source temperature [15]. \( E_B(\lambda, T) \) can be expressed as:

\[
E_B(\lambda, T) = \frac{c_1}{\lambda^5 \left( e^{c_2/\lambda T} - 1 \right)}
\]

where \( c_1 = 8\pi hc = 4.99 \times 10^{-24} \text{ Nm}^2 \), \( c_2 = hc/k = 14390 \mu\text{mK} \), and \( h, k, \) and \( c \) are Planck’s constant, Boltzmann’s constant, and the velocity of light, respectively. For graybody spectrum radiation at temperature \( T \) from a source of emissivity \( \epsilon \) passing through a material with transmissivity \( \tau \) into a spectrometer with an aperture constant \( a \), the spectrometer output \( R(\lambda) \) would be
\[ R(\lambda) = \frac{aeTc_1}{\lambda^2(\sigma^2 - 1)} \]  

Eq. (2)

Assuming \( \epsilon, \tau, \) and \( \alpha \) are independent of wavelength over the measurement range, a scaled spectrometer output function based on Eq. (2) can be written as

\[ SR(\lambda) = E(\lambda, T) = \frac{1}{\lambda^2(\sigma^2 - 1)} \approx \frac{e^{-\frac{\lambda}{\lambda_T}}}{\lambda_T} \]  

where \( S \) is the adjustable scale factor accounting for the unknown constants. For source temperatures less than about 2500 K and wavelengths less than 1 \( \mu \)m, the approximation in Eq. (3) is valid since the term \( \exp(-c_2/\lambda T) \ll 1 \) [15]. Taking natural logarithms of both sides of Eq. (3) and rearranging gives

\[ \ln\left(\frac{1}{\lambda^2 R(\lambda)}\right) = \frac{c_1}{T} + \ln S \]  

where \( T \) is the temperature. For a spectrometer measurement of relative intensity, \( R(\lambda) \), a plot of \( \ln(1/\lambda^2 R) \) vs. \( 1/\lambda \) should be a straight line. Using a linear least-squares fit over the 0.72 \( \mu \)m \( \leq \lambda \leq 0.92 \) \( \mu \)m wavelength measurement range used in this study, the temperature \( T \) can be obtained from the slope \( (= c_2/T) \).

As shown in Table 2, four sets of BMG cutting temperature experiments were conducted at 0.76 and 1.52 m/s cutting speed. Integration time is defined as the duration of time that the shutter is open for the spectrometer to receive the thermal radiation light emission from the optical fiber. The effect of integration time at 2, 5, and 10 ms was investigated at 1.52 m/s cutting speed and 2 ms at 0.76 m/s cutting speed. Four tests were conducted at each cutting speed and integration time combination. In total, 16 cutting tests were conducted for temperature measurement.

Fig. 2(a) and (b) shows the spectrometer measured relative intensity, \( R(\lambda) \), for 0.76 m/s cutting speed with 2 ms integration time and 1.52 m/s cutting speed with 10 ms integration time, respectively. The \( \ln(1/\lambda^2 R) \) vs. \( 1/\lambda \) is presented in Fig. 2(c) and (d). Fig. 2(c) and (d) also shows the least-squares fit (solid line) of the data points. Very good fit of a straight line was obtained, which demonstrated the feasibility of using the infrared spectrometer for temperature measurement in this study. The slope of the least-squares regression was used, according to Eq. (4), to calculate the temperature.

Results of the temperature for all 16 cutting tests are summarized in Table 2. Under the same 2 ms integration time, the difference in temperature at 0.76 and 1.52 m/s cutting speed is not significant. Both show high flash temperature at about 2400 K. At the longer integration time (5 and 10 m/s), the calculated temperature slightly increased to around 2600 and 2700 K. Results in Table 2 indicate that a high flash temperature, around 2400–2700 K, exists on the surface of the chips during machining of the BMG. This measured temperature is further validated in Section 4 by comparing it with the adiabatic flash temperature estimated using an analytical approach.

### Table 2

<table>
<thead>
<tr>
<th>Cutting speed (m/s)</th>
<th>0.76</th>
<th>1.52</th>
</tr>
</thead>
<tbody>
<tr>
<td>Integration time (ms)</td>
<td>2, 5, 10</td>
<td>2, 5, 10</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>Test 1: 2452, 2399, 2699, 2526</td>
<td>Test 2: 2524, 2380, 2782, 2645</td>
</tr>
<tr>
<td>Test 3: 2397, 2467, 2756, 2734</td>
<td>Test 4: 2420, 2380, 2673, 2713</td>
<td></td>
</tr>
<tr>
<td>Average temperature (K)</td>
<td>2448</td>
<td>2407</td>
</tr>
<tr>
<td>Deviation of temperature (K)</td>
<td>55.3</td>
<td>41.3</td>
</tr>
</tbody>
</table>

4. Analytical prediction of chips temperature

An analytical approach using the energy generated from oxidation of Zr to ZrO\(_2\) to heat the layer of BMG in the chips was developed to estimate adiabatic flash temperature. This estimated chips temperature could be used to validate the experimental temperature measurements.

The thickness of the oxide layer on the chip surface is about 5 \( \mu \)m, as will be shown later in the chip cross-section micrographs in Figs. 7 and 8. The energy generated by oxidation of the surface layer on the chips was estimated by the standard enthalpy of formation of ZrO\(_2\), denoted as \( \Delta H_{\text{ZrO}_2} \), which is 1100 kJ/mol [16]. Under adiabatic conditions, this energy raises the temperature on the chips surface by \( \Delta T \), which is the adiabatic flash temperature. The balance of energy is:

\[ \Delta H_{\text{ZrO}_2} = C_p \Delta T \]  

where \( C_p \) is the heat capacity of Zr-based BMG, which is 55 J/K-mol [3]. Based on the known \( \Delta H_{\text{ZrO}_2} \) and \( C_p \), the \( \Delta T \) can be calculated. \( C_p \) and \( \Delta H \) values are given per unit mol; therefore total weight of the remaining BMG and the formed oxide layer were converted to molar equivalents based on a rectangular cross section, which is of unit length and surrounded by a 5 \( \mu \)m oxide layer. The outer and inner radius of cross section were determined by the depth of cut, and feed rate, which were 0.5 and 0.05 mm, respectively. The calculated total area was \( 5.40 \times 10^{-9} \) mm\(^2\) for the oxide layer and \( 1.5 \times 10^{-9} \) mm\(^2\) for the BMG chips. Atomic weight and density values were taken from references [16,17] as 123 g/mol and 6100 kg/m\(^3\) for ZrO\(_2\) and 73 g/mol and 6100 kg/m\(^3\) for BMG, correspondingly. Using these values, the weights of the total formed oxide layer and produced chips were calculated as \( 2.68 \times 10^{-4} \) and \( 13.15 \times 10^{-4} \) mol, respectively.
According to Eq. (5), the adiabatic flash temperature created during the turning of Zr-based BMG was estimated at 2400 K, which agrees well with the measured values.

5. X-ray diffraction analysis of chips and machine surfaces

The high temperature generated during machining can initiate the crystallization of BMG work-material. Fig. 3 shows the X-ray diffraction results on the as-received BMG, machined surfaces, and chips. Fig. 3(a) shows the typical X-ray diffraction pattern with one set of broad peaks at $2\theta = 37.8$ and $\sim 65^\circ$ for the as-received BMG material. As shown in Fig. 3(b) and (c), the same broad peaks were observed for all machined surfaces at three cutting speeds and for the chips machined at the lowest cutting speed (0.38 m/s). These broad peaks in the X-ray diffraction pattern have been reported for amorphous BMG by Liu et al. [2] and Wang et al. [5]. Fig. 3(d) and (e) shows the diffraction peaks in the BMG chips surface machined at 0.76 and 1.52 m/s cutting speeds, respectively. The visible light emission observed at the two higher cutting speeds is associated with the diffraction peaks. For the chips cut at 0.38 m/s, there was no visible light emission and no distinguishable diffraction peak in the chips surface [Fig. 3(c)].

The analysis of diffraction peaks showed the crystalline phase in the of chip material is monoclinic ZrO$_2$ (Fig. 4), which confirmed that oxidation is associated with machining.

6. Crystallization analysis

Since the BMG chips undergo high temperature and high strain-rate deformation during cutting, it might also crystallize. Optical microscopy and field emission gun SEM were used to investigate the possibility of oxidation and crystallization.

6.1. Optical microscopy

Fig. 5 shows optical micrographs of polished cross-sections of the BMG chips machined at two cutting speeds: 0.38 and 1.52 m/s. No chemical etching was performed on these two polished surfaces. In the chips cut at 1.52 m/s, in Fig. 5(b), a dark oxide layer, is visible...
all around the chips and associated with the light emission during machining. No such oxide layer is observed in the chips cut at 0.38 m/s [Fig. 5(a)].

Fig. 6 shows the four optical micrographs of polished and etched cross-sections of a BMG chip machined at 1.52 m/s. Various microstructural regions in these machined chip cross sections are illustrated in Fig. 6(a)–(d). Chemical etching reveals the oxide layer on the outside surface of the chip and the dendritic pattern inside the chip. The dendritic pattern is crystallization of the BMG. Fig. 6(a) shows the inception of a dendritic pattern near the oxide layer. Fig. 6(b) shows crystalline and amorphous microstructures in the same chip cross-section. Crystallization inside the chip is not homogenous, as indicated in Fig. 6(a) and (b). The cross-section in Fig. 6(c) has a more dendritic pattern than in the first two micrographs. Growth of the dendritic structure may match the direction of maximum cooling rate during the chip cooling. Some of the growth directions of dendrite branches are pointed out with arrows in Fig. 6(c). The dendritic structure has fully grown in the chip cross-section shown in Fig. 6(d).

6.2. Scanning electron microscopy

Electron back scattered diffraction analysis conducted on the etched samples of BMG chips cut at 1.52 m/s resulted in several different Kikuchi patterns. These patterns did not index with known phases of Zr-based BMG, by using SEM analysis software. This could be
due to the high deformation characteristics of the machining process. High deformation increases strain and this strain causes weak Kikuchi patterns that can not be identified. Nevertheless, these patterns demonstrated that the machined chips had crystallized during machining.

The field emission gun SEM micrographs of the polished, un-etched cross-sections of the BMG chips cut at 1.52 m/s are shown in Figs. 7 and 8. Fig. 7 shows a region with mixed crystalline and amorphous structure. Fig. 8 illustrates a fully crystalline chip. Using the field emission gun SEM, different gray level regions represent material with different crystalline structures. Energy dispersive spectroscopy (EDS) analysis verified that regions with different contrast have different chemical compositions and, in the same way, regions with the same contrast have identical chemical compositions.

In general, four regions with different color contrasts can be identified in Figs. 7 and 8.

1. Oxide layer (O): Similar to the optical microscopy pictures, the oxide layer, marked by O, is surrounding the chips. The SEM adjustment in Fig. 7(a) is set to reveal the oxide layer,
Fig. 7. Field emission gun SEM micrographs of the chips cross-section with both eutectic and amorphous regions, (a) contrast adjusted to show the oxide layer surrounding the chips, (O) (b) contrast adjusted to show the inside crystalline and amorphous regions, (G) represents the gray leaf-shape crystalline region, and (c) close-up view of the box in (b) with the amorphous (A) to eutectic (E) crystalline transition.

Fig. 8. Field emission gun SEM micrographs of the fully crystalline chip cross-section, (a) overview of the fully crystallized chips, (b) close-up view of the box in (a), and (c) close-up view of the eutectic crystalline region [box in (b)].
2. Dark gray color crystalline phase (G): The leaf shape crystalline phase with dark gray color, marked by G, can be seen in Figs. 7(b) and 8(b).
3. Amorphous region (A): This region, marked by A, can be seen inside the chips in Fig. 7(b) and in the lower region of Fig. 7(c), and
4. Eutectic region (E): This is a crystalline region showing eutectic microstructure, as illustrated in the upper region in Fig. 7(c) and the close-up view in Fig. 8(c).

EDS was used to estimate the elemental composition in these regions. The BMG material used in this study contained five elements: Zr, Al, Ni, Cu, and Ti. To estimate the difference in elemental percentage in each region with different color contrast, a procedure using the EDS in the field emission gun SEM was conducted. First, by examining the overall chip cross-section, the average percentage of each of the five elements was obtained as the baseline. The SEM was then zoomed into the specific region with different color contrast, and the EDS analysis was performed once again. The element percentages in each region were compared with the baseline data. According to this procedure, the dark gray regions (G) have higher levels of Al, Ni and Cu content than the eutectic region (E) and about the same level of Ti. Gray river-like areas [Fig. 8(c)] between regions have less Al, Ni, Cu, Ti than any other region, which could indicate an amorphous structure. No significant amount of oxygen was detected in any of the phases.

7. Conclusions

This study investigated the flash temperature, oxidation and crystallization of chips during lathe turning of Zr-based BMG. X-ray diffraction showed no crystallization on the machined surface and chips cut at low cutting speed. Using a near-infrared spectrometer for radiation thermometry, a very high chip flash temperature in the 2400–2700 K range was estimated. An analytical method was developed to estimate the chips adiabatic flash temperature, which was in good agreement with the experimental measurements using infrared thermometry. At high cutting speed, the BMG chips were oxidized in the outside layer of chips. The oxidation is associated with the light emission during machining. Optical microscopy of the polished and chemically etched layer showed a dendritic pattern due to crystallization. Four different regions were observed in the cross-section of the chips: (1) oxide layer, (2) amorphous region, (3) fully crystalline regions, and (4) crystalline-amorphous transition region. The field emission gun SEM and EDS were further applied to analyze the crystallization regions in the chips. The X-ray diffraction peaks match the pattern for monoclinic ZrO₂, confirming the earlier hypothesis that oxidation is associated with light emission and high flash temperature. Although optical microscopy and SEM showed crystallization inside the chips, no additional diffraction peaks could be detected by X-ray diffraction. This could be due to the thick oxide layer. The average oxide layer thickness is about 5–10 μm and calculated average X-ray effective penetration depth value also has about the same level. The oxide layer blocks the X-ray from penetrating into the chips to reveal other crystalline structures in the chips.

This study demonstrates that it is feasible to use machining as a test method for investigating the behavior of BMG under extreme deformation conditions; i.e., large stress and strain, high strain-rate, and high temperature.

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