1. Introduction

Bulk metallic glasses (BMG) have been proposed as wear-resistant materials for a range of applications [1]. For example, BMGs were proposed as coating materials in dry (i.e., unlubricated) bearings for use in space. Togashi et al. [2] observed that the durability of a motor with BMG microgears exceeded the durability of bearings for use in space. Sliding wear behavior of a copper-based bulk metallic glass (Cu50Hf41.5Al8.5) was investigated for both as-cast and annealed samples. The wear resistance increased during isothermal annealing near the glass transition temperature. Nanocrystals developed during the annealing for annealing times up to 300 min. A linear relation between hardness and wear resistance was observed during the early stages of devitrification, but at longer annealing times the wear resistance increased less than the hardness. For the as-cast sample and a sample that was structurally relaxed, nanocrystallites developed during sliding and the wear resistance improved for longer sliding distances when the nanocrystals developed. The transmission electron microscopy analysis of the annealed samples suggests that the deviation from the linear hardness vs. wear resistance relation occurs at a critical volume fraction of the nanocrystals. The improvement in wear resistance with sliding appears to result from an increased surface temperature rather than directly from the sliding-induced nanocrystal formation.

The potential as an ultra-wear-resistant material led to several studies and reviews of the wear behavior of metallic glasses [5]. Whether it is despite or because of the wealth of investigations, the literature on the wear behavior of metallic glasses is riddled with apparent contradictions and incongruence. For example, hardness has at some occasions been demonstrated to correlate with wear behavior [6]. Other results show that a simple correlation between sliding or abrasive wear resistance and hardness does not exist [7,8]. Friction-, wear-, and surface chemistry studies of ferrous-based amorphous alloys were conducted in the early 1980s [1,9–13] and it was found that tribological contact, under some circumstances, induce a transformation of the material from the amorphous to the crystalline state. Friction and wear of a Zr-based metallic glass under dry and lubricated conditions were conducted by Blau [14], in which no sliding-induced transformations were detected by X-ray methods, whereas Fu et al. [16] observed that for devitrified glass, the sliding process caused the near surface to re-amorphize. Some studies report that metallic glasses have higher wear resistance than their crystallized states [16,17]. By contrast, there are results indicating that the wear performance of metallic glasses is inferior to the fully devitrified samples [17].

The differences in the literature results obtained for the wear behavior of metallic glasses could result from the multitude of input parameters, including the metastable nature of amorphous materials and thus their thermal history. The current study addresses the sliding wear behavior of a Cu50Hf41.5Al8.5 bulk metallic glass (BMG). Cu-based BMGs have been drawing increasing interest due to their lower material cost, high compressive fracture strengths of the order of 1900–2500 MPa and, in some cases, large plastic strain before failure (as large as 18%) [18,19]. Aside from their potential for applications, Cu-based glasses can be synthesized reproducibly and without much difficulty. The Cu-based glass used in the current study reveals a thermal behavior that approximately coincides with the thermal behavior of an amorphous Cu50Hf42.5Al7.5 alloy [20]. A large supercooled liquid region enables annealing treatments for the controlled synthesis of devitrified nanocrystal/amorphous bulk composites. Upon focusing on one composition only and systematically varying the annealing conditions, the wear behavior is examined for amorphous as well as partially devitrified samples. A particular emphasis is placed on the occurrence of dynamic effects such as sliding-induced crystallization and their role for the wear behavior of the glass.
2. Experimental procedure

The Cu-based amorphous alloy with a nominal composition of Cu$_{50}$Hf$_{41.5}$Al$_{8.5}$ (at.%) was prepared by arc melting the mixture of 99.9% Cu, 99.9% Hf and 99.9% Al metals under a Ti-gettered argon atmosphere. The alloy ingots were melted several times to ensure compositional homogeneity. BMG rods with 3 mm diameter were then prepared by suction casting into a water-cooled copper mold. The amorphous nature of the alloy was confirmed using a Bruker GADDS X-ray diffractometer (XRD) with a chromium source, with a Perkin-Elmer Diamond differential scanning calorimetry (DSC), and transmission electron microscopy (TEM, Technai T12 at 120 kV). DSC measurements were performed under an ultra high pure argon atmosphere, calibrated with melting transition of indium and zinc. A heating rate of 60 K/min was used for all experiments. The amorphous alloy was vacuum sealed in a quartz tube and annealed at 510°C for different durations (15, 30, 60, 150, and 300 min) and then furnace cooled at a linear cooling rate of 1 K/min. For complete crystallization of the alloy, the samples were annealed at 750°C for 300 min. The amorphous-crystalline nature of the heat treated samples was again examined with the aid of XRD, DSC and TEM. Thin foils of the samples for TEM were prepared by twin jet electropolishing (Tenupol 5) in a solution of 33% nitric acid and 67% methanol at −25°C and 10V. Micro-hardness measurements were performed using a Vickers diamond indenter with an applied load of 1 kgf and a dwell time of 15 s. Linear reciprocating wear experiments were conducted on as-cast, annealed samples, and on 304 stainless steel (SS) as a reference material. A SiN sphere of 3.2 mm in diameter was used as counter material. SiN pins were used as a counter material to limit wear to the metallic glass surface. Irrespective of the annealing condition of the metallic glass, the SiN sphere surface remained smooth during the wear tests, without any evidence of wear. The load of 1.3 N and the sliding speed of 1.2 mm/s were selected to limit nominal heating of the metallic glass surface during sliding. Moreover, the load of 1.3 N induces a contact stress in the metallic glass that remains below the nominal yield strength of the metallic glass. Localized flash heating and plastic deformation can, however, not be ruled out with these parameter values. The sliding experiments were conducted in air and at room temperature to reflect the environmental conditions that can be expected for wear applications of metallic glasses. The average surface roughness of the specimen before wear testing was measured using a Zygo optical interferometer. The wear volume loss ($V_w$) is obtained from the line scan and the length of the wear track. The line scan provides the profile across the wear scar, which is used to determine the area of the wear scar at a particular position along the scar. The area of the wear scar is then multiplied with the scar length to obtain the wear volume. The wear track was analyzed using the Zygo optical interferometer to calculate the wear volume loss for different sliding distances. TEM samples after sliding were prepared using a micro-shield (lacquer) on the wear track and electropolishing the sample from the bottom side. Once the electron transparent region formed, the micro-shield was removed and the samples were plasma cleaned before analyzing them in TEM. Measurements of elastic constants were conducted with cylindrical samples and a RU-Spec resonant ultrasound spectrometer. The sample densities were determined from buoyancy measurements using terephtalate as a liquid.

3. Results

Following the objective of this work, it is important to characterize the metallic glass at the different annealing conditions. The microstructural and thermal characteristics of the metallic glass are highlighted in the next paragraph. Next, the sliding behavior is examined as a function of the sliding distance for a fixed sliding load and counter material. TEM analyses reveal microstructural characteristics...
changes that occur during sliding and are highlighted at the end of this section.

3.1. Microstructural and thermal characteristics of BMG samples

X-ray patterns of as-cast and annealed alloys are shown in Fig. 1. The X-ray pattern of the as-cast alloy in Fig. 1 reveals that the BMG was X-ray amorphous, showing a broad and diffuse peak. While the X-ray pattern does not reveal sharp peaks a small volume fraction of nanocrystallites could exist that cannot be detected with X-ray diffraction and thus the as-cast sample is considered to be “X-ray amorphous”. The sample remains X-ray amorphous after annealing for 15 min, since the corresponding X-ray pattern is indistinguishable from the pattern of the as-cast sample. The sharpening of the broad peak after an annealing time of 30 min indicates a crystallization reaction. The observation of two small but distinct peaks in the X-ray pattern after 30 min annealing suggests that the crystalline volume fraction has become significant. The X-ray pattern of the alloy annealed at 750 °C for 300 min reveals sharp diffraction peaks, indicating a fully crystalline state. The XRD spectrum for the crystallized sample reflects a mixture of three phases, including Hf14Cu51, AlCuHf, and Cu8Hf3 phases. The comparison between the X-ray patterns for increasing annealing times suggests that the crystalline phases transform to new crystalline phases during the isothermal annealing treatment since at least some peaks in the patterns change position or vanish for longer annealing times.

Continuous heating DSC curves for an as-cast sample and a sample that was annealed for 15 min are highlighted in Fig. 2(a). The signal for the as-cast sample shows a temperature range between about 325 and 510 °C with an exothermic DSC signal followed by glass transition (Tg) and a supercooled liquid temperature range of approximately 50 K prior to the onset of crystallization (Tc) at 600 °C. The slight exothermic behavior of the DSC signal prior to Tg and an endothermic heat behavior at the upper end of the glass transition region has been rationalized based upon structural relaxation of as-cast amorphous alloy [21]. Fig. 2(b) shows the DSC scans for the as-cast, annealed, and crystallized sample conditions. A decrease in free volume is achieved below Tg onset with isothermal annealing and an increased annealing time leads to an increase of the endothermic effect between Tg onset and Tc end. The small exothermic signal for the sample annealed for 300 min at about 480 °C is an artifact. The reduced heat release during the crystallization reaction of the sample that was annealed for 300 min indicates that following an annealing time of 300 min at 510 °C the crystalline phases are in near metastable equilibrium with the amorphous matrix.

The results of micro-hardness measurements are summarized in Fig. 3. The annealing treatment gradually raised the hardness from 585 VHN in the as-cast alloy to 695 VHN in the alloy annealed for 300 min at 510 °C. A marked increase in hardness...
to 740 VHN occurred in the fully crystallized alloy. By comparison, the micro-hardness of the 304 SS alloy at the same applied load is 340 VHN. The optical micrographs of the micro-indenters are shown in Fig. 4. The majority of the shear bands (which represent the primary mechanism of plastic deformation in metallic glasses [22,23]) is confined to one end of the indent in the as-cast sample and the sample annealed for 15 min as seen in Fig. 4(a) and (b), respectively. There is also at least one edge, typically the edge opposite to the edge surrounded by shear bands that lacks any shear bands. Because of the deformation, the shear band surrounded edge appears curved or pin-cushioned whereas the shear band free edge is straight. The other two connecting edges show either sporadic shear band activity or none at all. These features are common in many micro-indentation studies on different types of BMGs [24–26]. It is believed that this asymmetry in deformation occurs as a result of the strain softening exhibited by metallic glass and is seemingly unlikely that these features are experimental artifacts. Qualitatively, the shear band density was found to be much larger in the as-cast alloy with a path that appears to be tortuous. The flow lines for the amorphous alloy that was annealed for 15 min were found to be much smoother with a decrease in the density of shear bands. Fig. 4(c) and (d) show indents for the 300 min annealed and crystallized samples, respectively. It is evident that there is no shear band propensity or cracking for the 300 min annealed sample which implies that with gradual increase in annealing the propensity of shear band formation decreased.

3.2. Sliding wear analysis

The two parameters that were changed systematically to investigate the sliding wear behavior of the metallic glass were the sliding distance and the annealing time at an annealing temperature of 510 °C. The wear volume loss decreases for a given sliding distance with increasing annealing time as long as the metallic glass is not completely crystallized. Fig. 5 clearly shows the improvement in wear behavior with annealing for an as-cast, annealed, and a fully crystallized sample, and for a 304 stainless steel reference sample. The wear resistance improves in the following order of sample conditions for all sliding distances: as-cast, annealed for 15, 60, and 300 min. The fully crystallized sample reveals a much higher wear volume loss than all other samples. The stainless steel sample reveals a wear volume loss that is lower than for the as-cast sample but higher than for the annealed amorphous samples. Included in Fig. 5 are error bars for the sample annealed for 300 min. The error bars are nearly identical for the other samples and are not included in the figure for clarity. From a statistical viewpoint, the differences in the wear volume loss between the samples annealed for 60 and 300 min are insignificant, however, the wear volume loss differences between the samples annealed for 15 and 300 min are statistically significant. This shows that the improvement in the wear volume with annealing time at the annealing temperature of 510 °C is indeed a real effect.

The second parameter that was systematically studied was the sliding distance. Many materials reveal an approximately linear relation between the wear volume loss and the sliding distance, and the linear behavior is captured in Archard’s wear law [27], $V_w = K(N/H)$, where $V_w$ is the wear volume loss per unit sliding distance, $N$ is the total normal load, $K$ is the dimensionless wear coefficient, $H$ is the yield pressure for the asperities on the metallic glass surface, which is usually approximated with the indentation hardness [28,29]. The wear loss is approximately linearly proportional to the sliding distance for the fully crystallized sample, the stainless steel sample, and the amorphous samples that were annealed for 60 and 300 min. For the samples that were annealed for less than 60 min, i.e., the sample annealed for 15 min as well as the as-cast sample, the linear relation between wear volume loss and sliding distance holds true for the first 300 m, but for the last 100 m a deviation is observed from linearity as shown in Fig. 5. To capture the change in linearity better, the dimensionless wear coefficient, $K$, is shown in Fig. 6 for an as-cast sample, a sample annealed for 15 min, and a sample that was annealed for 300 min at 510 °C as a function of the sliding distance. Fig. 6 shows that the wear coefficient decreases for any sliding distance with increasing annealing time. This behavior corresponds to the decrease in wear volume loss for a given sliding distance with an increase in annealing time. The decrease in the value of the wear coefficient is more pronounced within the first 15 min of annealing than for the extension of the annealing time from 15 to 300 min. If the wear coefficient is evaluated as a function of the sliding distance, the data shows a decrease in the value of the wear coefficient with sliding distance for the as-cast sample for the last 200 m after an initial increase of the wear coefficient. The sample that was annealed for 15 min reveals an overall tendency of a slight decrease in the value of the wear coefficient, i.e., an improvement in the wear resistance with sliding distance. The wear coefficient of the fully devitrified sample remains nearly constant throughout the sliding process. For the evaluation of Fig. 6, however, it must be considered that the wear coefficient is not measured directly, but is obtained as a function of wear volume loss, hardness, load, and sliding distance. Each of these four variables is associated with statistical errors, either
due to precision or due to accuracy. With realistic errors for each of the four variables the error in the wear coefficient is considerable, i.e., the variation in the wear coefficient values for the as-cast sample, for example, is statistically non-significant. The main error in the wear coefficient stems from the error for the wear volume loss. A repetition of the wear experiment for the as-cast sample showed that the precision, obtained from the standard deviation, is 4.

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The main error in the wear coefficient stems from the error for the wear volume loss. A repetition of the wear experiment for the as-cast sample showed that the precision, obtained from the standard deviation, is 4. In other words, the value of the wear coefficient of the as-cast sample between 200 and 400 m might not decrease at all as suggested by the trend in the average values. On the other hand, repeating the wear experiment for the as-cast sample, the decrease in slope for the last 100 m of sliding is reproduced and thus appears to be a real effect and not a statistical fluctuation.

In general, surface profiles of wear scars can reveal details of the wear mechanisms. To compare the wear tracks of as-cast and annealed samples, surfaces were examined of an as-cast sample and a sample that was annealed for 300 min following a sliding distance of 400 m for both samples. Surface profiles of the wear scars are shown in Fig. 7(a) and (c) resulting from the sliding of the SiN sphere over as-cast and annealed samples, respectively. Line scans across these wear scars are shown in Fig. 7(b) and (d). The edges of the wear scar are flat implying that there is no pile up. An SEM image of a wear track after sliding for 400 m is highlighted in Fig. 8(a) for an as-cast sample and for a sample that was annealed for 300 min in Fig. 8(b).

The wear track of the as-cast sample reveals linear grooves as well as bright patches. The surface resembles wear tracks observed for other metallic glasses that were exposed to sliding wear in air. Similar bright patches have been identified as oxygen rich particles in the literature [15]. The SEM images of the annealed sample indicate that a higher area fraction of the wear scar is covered with oxygen patches. While the annealing treatment suggests that an oxygen layer develops during annealing, the depth of the wear scar that is about 15 μm shows that the oxygen patches observed in the SEM images after the wear tests must have developed during the test and are not remnants of an initial, thick oxygen layer. The partial oxygen pressure during the annealing treatment is about 10⁻⁶ atm and the volume of the quartz tube for the annealing treatment is about 0.1 l. Assuming ideal gas behavior, the number of oxygen molecules in the quartz glass is about 10⁻⁷ mol. Assuming furthermore that the oxygen atoms form a continuous layer with an average atomic distance of 5 Å the thickness of the oxygen layer on the 3 mm diameter sample would be on the order of 10 nm and thus much thinner than the depth of the wear scar.

TEM analyses were conducted to rationalize the wear volume loss behavior of the different samples. In Fig. 9 TEM images are highlighted for the amorphous alloy after different annealing times and an annealing temperature of 510 °C. The as-cast sample did not reveal crystallites, neither in the bright field (BF) image, Fig. 9(a), or the dark field (DF) image, Fig. 9(b). After 15 min of annealing the amorphous phase still did not reveal any crystallites and the diffraction pattern (DP) that is shown in the inset to Fig. 9(c) is very similar to the DP of the as-cast sample in Fig. 9(a). The amorphous nature of the as-cast sample and the sample that was annealed for 15 min agrees with the XRD results in Fig. 1 that only revealed one broad peak. Crystallization is observed in the sample annealed for 60 min. The BF image along with the DP in Fig. 9(e) and the DF image in Fig. 9(f) reveal very fine crystallites distributed in the amorphous matrix with a size range of 10–20 nm. After annealing for 300 min the size of the crystallites did not increase much compared with the sample that was annealed for 60 min and remained well below 100 nm. The small holes of about 200 nm which can be seen in Fig. 9(g) and (h) are electropolishing-induced artifacts.

TEM DF micrographs of as-cast samples after 200, 300, and 400 m of sliding are shown in Fig. 10(a)–(c). The inset in these images shows the DP. Fig. 10(d)–(f) are the DF images for the samples after annealing for 15 min and sliding at distances of 200, 300, and 400 m. The DF images indicate that the sliding induces nanocrystals for samples in the as-cast condition and after a pre-wear annealing of 15 min. The largest nanocrystals are on the order of 10 nm in size. The DP show an increasingly pronounced ring structure with increasing sliding, which could result from an increase in the density of the nanocrystals with sliding, but further studies are necessary to elaborate on the details of the sliding-induced crystallization process.
4. Discussion

A longstanding issue for wear studies of metallic glasses is the correlation of hardness with wear resistance. It has been suggested that the wear behavior correlates with the hardness of metallic glasses, although opposite opinions have been expressed as well. The hardness of metallic glasses changes due to structural relaxation and devitrification processes. A hardness-wear resistance correlation would then amount to a link between the wear behavior, structural relaxation, and devitrification. In the following, the hardness evolution with annealing time is discussed first, followed by a discussion of the wear/hardness correlation and sliding-induced crystallization.

4.1. Hardness as a function of annealing time

Within the first 15 min of annealing at 510 °C, structural relaxation occurs without crystallization and the hardness of the amorphous alloy improves. The increase in hardness, however, is not linear for longer annealing times. Fig. 3 indicates that the hardness increase is less pronounced after 15 min annealing than for the first 15 min of annealing. After reaching a near plateau in hardness between about 15 min of annealing and 60 min the hardness then increases rapidly with time after 60 min of annealing. The hardness behavior reflects the changes in the amorphous phase due to structural relaxation and crystallization. Within the first approximately 30 min structural relaxation is the main factor in the hardness increase. The improvement in hardness with structural relaxation has been demonstrated for a wide range of metallic glasses [30,31]. For longer annealing times, the devitrification process contributes to the hardening. The rapid increase in hardness after 60 min of annealing is reminiscent of the hardness increase in a Ag–Al2O3 nanocomposite beyond the percolation threshold of the softer Ag phase, i.e., at volume fractions of more than 50–60% of the harder Al2O3 phase [32]. It was pointed out frequently that nanocrystals crystallizing from amorphous precursor phases were defect free and thus revealed strength levels near the theoretical limit [33] although more recent, detailed studies suggested the presence of twins in primary Al nanocrystals and twins, stacking faults, and dislocations in primary Ni nanocrystals.
[34]. At rather low volume fractions of nanocrystals, load transfer to the nanocrystals does not occur. The precipitation process, however, changes the solute content of the amorphous matrix and the solute enrichment was demonstrated to help increasing the hardness of partially devitrified amorphous alloys [35]. For the current amorphous Cu50Hf41.5Al8.5 alloy, however, primary crystallization is not observed and the volume fraction of the nanocrystals following 300 min of annealing could indeed reach the percolation threshold. The hardness would then increasingly be controlled by the nanocrystallites, which are still well below 100 nm in size. Further studies are necessary, however, to analyze the exact origin of the hardness increase after 60 min of annealing.

4.2. Correlation between hardness and wear resistance

Correlations between hardness and wear resistance have been proposed in the past and the diagram depicted in Fig. 11 shows indeed a linear relation between wear resistance and hardness for samples that were annealed for up to 60 min. For an annealing time of 60 min the amorphous alloy is already partially devitrified as shown in Fig. 9. This indicates that the early stage of devitrification that entails nanocrystal sizes of less than about 30 nm does not affect the linear hardness-wear resistance relation and the improvement in wear resistance at the early stage of devitrification is determined mainly by structural relaxation and the structural relaxation-induced hardness increase of the amorphous matrix. A linear relation between hardness and wear resistance has been observed, for example, for Al–Y–Ni amorphous and partially devitrified alloys for volume fractions of the primary Al phase of up to about 35% [36]. The linear relation between hardness and wear resistance does not continue for longer annealing times, though, for the Cu53.5Hf41.5Al8.5 glass. Fig. 11 reveals a deviation from the initial linear relation after an annealing time of 300 min; the hardness increase outweighs the increase in wear resistance at longer annealing times, resulting in a decrease in the slope in Fig. 11. One reason for the deviation from the initial linear relation could be that with increasing annealing time the opposing effects of hardness increase and embrittlement on the wear behavior — the former improving wear resistance, the latter deteriorating the wear resistance — tilt toward the effect of embrittlement on the wear resistance. To examine this idea in more detail, the Poisson ratio was measured for the amorphous alloy after different annealing treatments. It has been shown in previous studies that the brittleness of amorphous materials is reflected in the Poisson ratio [37,38]. For values of the Poisson ratio of less than 0.31–0.32, brittle behavior is observed while for values of the Poisson ratio of about 0.34 or more ductile behavior is observed although not in a conventional tensile ductility sense. Measurements of the Poisson ratio...
for different annealing times are highlighted in Fig. 12 along with the results of hardness measurements. For the as-cast amorphous alloy, the Poisson ratio is 0.34, decreasing after 15 min of annealing to 0.32 and to 0.31 after 30 min of annealing. These results indicate that the Poisson ratio is already in the “brittle” regime when the hardness-wear resistance relation is still linear. With further devitrification during longer annealing times, however, the brittleness increases, which is not necessarily captured in the change of the Poisson ratio. In the fully devitrified condition the alloy is indeed remarkably brittle. Boswell reported in among the earliest studies of wear of metallic glasses that at increasing annealing temperatures of a Pd75Cu55Si164 glass the hardness increased while the wear resistance decreased [39]. He attributed this observation to the dependence of wear resistance on hardness and crack nucleation and propagation [39]. In light of Boswell’s results and the current results, the linear correlation between hardness and wear resistance changes at a critical nanocrystal volume fraction and size distribution, but not at the onset of devitrification. Further work focuses on the toughness changes during devitrification. The rapid increase in hardness for long annealing times and similar results in Scanlon’s work [32] furthermore suggest that the deviation from the linear hardness vs. wear correlation behavior might occur at the percolation threshold of the hard phase. Much of the work on the wear behavior of partially devitrified amorphous alloys focused on Al-based alloys, for which the volume fractions of the primary crystallizing phase are limited to levels below the percolation threshold of the primary nanocrystals and thus the breakdown in the hardness/wear resistance correlation might not be observable at all for these alloys.

Tam and coworkers examined the wear behavior of a Cu0.6Zr0.4Ti1 metal glass [40]. The wear behavior of the Cu0.6Zr0.4Ti1 glass deteriorated after annealing compared to the as-cast sample. Moreover, the wear behavior of the metal glass samples was inferior to 304 stainless steel. Differences between this work and Tam’s work are the load, which is about one order of magnitude higher in [40], the sliding velocity, which was also about an order of magnitude higher than in this work, and the use of 400 grit SiC paper as a counter material compared to a polished SiN ball in this work.

### 4.3. Sliding-induced crystallization

The cyclic sliding on the metallic glass surface represents a continued energy input due to elastic and plastic surface deformation. This driven process clearly induces nanocrystals in the metallic glass as highlighted in Fig. 10. Nanocrystal formation during sliding wear was up to now reported for transition metal-metalloid amorphous alloy systems: Ni78Si18B14 [41], Co70.3Fe4.7Si15B10 [42], Fe68Cr18M02B12 [16], Fe57Co18B14Si1 [1], and it was suggested based on analysis of wear debris for Zr41Ti14Cu12.5Ni10Be22.5 bulk metallic glass (Vit 1) [43]. The interest in dynamically induced nanocrystallities centers usually on their impact on the wear behavior and the mechanism behind their formation. The value of the wear coefficient decreases when nanocrystals develop during sliding of as-cast samples. It is not a priori clear, however, if the wear behavior improves because of the nanocrystals, or because of other factors that induce nanocrystals and independently improve the wear resistance. A qualitative comparison between the TEM images of the amorphous alloy after annealing for 60 min and the as-cast alloy after 400 m of sliding reveals a similar nanocrystal number density and size distribution in both cases. Since it was concluded that the improvement in wear resistance during the initial stage of the thermally induced devitrification process is due to the structural relaxation-induced hardness increase, the conclusion can be drawn that the wear resistance during sliding of the as-cast sample does not improve because of the nanocrystals but because of effects that mimic annealing at the surface during sliding or because of an actual temperature rise at the surface during sliding.

When considering temperatures at surfaces during sliding, three different temperatures are usually considered, the surrounding temperature – usually room temperature – the average or bulk surface temperature, and the flash temperature. The flash temperature represents a local surface temperature at contacting asperities that exceeds both the average surface temperature and the surrounding temperature [44]. Fleury et al. [43] and more recently Kong et al. [45] calculated flash temperatures on the sliding surfaces of metallic glasses. Kong showed that the flash temperatures can reach several hundreds of degrees [45]. The highly localized flash temperatures lead to an overall increase in the surface temperature that is captured in the average surface temperature. Lim and Ashby developed an analytical expression for the average surface temperature during sliding [44]. While the equation for the surface temperature includes among others the thermal diffusivity and the thermal diffusion coefficient – both are not known for the Cu90Zr10Al0.5 glass in this work – even with a wide variation in the input data that includes values of thermal diffusivity and diffusion coefficient for several metallic glasses, the average surface temperature does not increase more than about 100 K above room temperature. Besides frictional heating, which occurs for any material during sliding, an additional surface temperature rise occurs for metallic glasses when shear bands develop in the surface region. Adiabatic heating in shear bands has been examined for metallic glasses and a wide range of temperature spikes were estimated [46]. During sliding wear of metallic glasses then a temperature distribution should develop with local temperature excursions or spikes due to flash heating and possibly adiabatic shear band formation. As a result, the local thermal history varies at the sliding surface of metallic glasses. Anis discussed the effect of flash temperatures on the surface crystallization during sliding [16]. Following Moreton’s earlier work [47], he proposed embrittlement to occur as a result of flash temperature heating. Due to differences in the local surface temperature histories, Anis’ argument might only hold true locally and not for the bulk of the surface. Following the argument of local differences in the thermal history, some regions in the worn surface of the metallic glass would at all times remain below the crystallization temperature and even below temperatures at which structural relaxation can occur. Other regions experience temperature spikes that have been associated with the formation of nanocrystals. If the conditions are sufficient to induce nanocrystals, these regions should be structurally relaxed and should have higher hardness values than the surface regions that remained at lower temperatures. In this scenario the overall wear behavior...
would improve, nanocrystals could form, but the average surface temperature would not increase substantially.

5. Summary

The results of this study thus show that the wear behavior of a metallic Cu50Hf41.5Al8.5 glass improves with isothermal annealing near the glass transition temperature range for increasing annealing time and surpasses the wear behavior of a 304 stainless steel if a nanocomposite microstructure is induced. A linear relation between hardness and wear behavior holds for the fully amorphous condition and the early stages of the partially devitrified condition even when the Poisson ratio of the metallic glass suggests a brittle behavior. Nanocrystals developed during sliding at ambient temperatures for an as-cast sample and a sample that was structurally relaxed without observable nanocrystals prior to the wear testing. Following the dynamic devitrification process, the wear behavior slightly improved for the as-cast samples. It was concluded that the slight improvement in the wear resistance during sliding resulted from surface temperature spikes and concomitant local structural relaxation rather than directly from the precipitation of the nanocrystals. The results of this study show that controlled annealing treatments of the Cu50Hf41.5Al8.5 metallic glass can optimize the hardness and sliding wear resistance to levels that far exceed those of, for example, stainless steel.

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