Discovery of Critical Oxygen Content for Glass Formation in $\text{Zr}_{80}\text{Pt}_{20}$ Melt Spun Ribbons

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Abstract. $\text{Zr}_{80}\text{Pt}_{20}$ alloys may form meta-stable quasicrystals either during devitrification of an amorphous phase or directly upon cooling from a liquid depending on processing conditions. To date, little attention has been given to the role of oxygen on the glass formation or devitrification behavior of Zr-Pt and similar alloys. This study reveals that oxygen content during melt spinning indeed strongly influences the formation of the as-quenched structure. A critical amount of oxygen was found to be required to form amorphous ribbons at a fixed quench rate. At lower oxygen levels (i.e., <500 ppm mass), a fully crystallized is formed; the structure is composed mainly of meta-stable β -Zr with a small fraction of a quasicrystalline phase. At higher oxygen levels, the as-quenched structure transitions to a fully amorphous structure (~1000 ppm mass), and with further oxygen addition forms a mixture of amorphous and quasicrystalline (~1500 ppm mass) or crystalline phases (>2500 ppm mass). Details regarding the structure of the meta-stable β -Zr phase in the low-oxygen ribbons are provided along with a discussion of the structural similarity between this phase and the quasicrystal structure that formed in this alloy.

Introduction

Oxygen has been frequently demonstrated to profoundly influence both glass formation and subsequent devitrification pathways in metallic alloys. For example, oxygen contamination during synthesis of a metallic glass can severely limit the glass formability of a particular alloy. The role of oxygen in this situation is likely to serve as heterogeneous nucleation sites (e.g., insoluble oxide phase) that effectively increase the cooling rate required to achieve an amorphous structure [1]. Oxygen may exhibit a more innocuous effect by altering the transformation pathway during crystallization of a metallic glass. In particular, numerous reports discuss the connection between oxygen content and the formation of meta-stable devitrification phases such as quasicrystals (QC). Köster's observation of QC formation in Zr-Cu-Ni-Al bulk glasses [2-4] was later confirmed to be associated with a particular oxygen level [5,6]. Prior crystallization studies with the same alloy with lower oxygen levels did not produce the same meta-stable QC phase [7]. Further studies by Murty et al. [8,9] continued to examine the relationship between oxygen and QC formation in rapidly solidified Zr-based glasses, in contrast to the pioneering work of Köster that primarily examined bulk forming glasses. Murty's data [8,9] show that $\text{Zr}_{65-x}\text{Cu}_{27.5}\text{Al}_{7.5}\text{O}_x$ melt spun ribbons transform from an amorphous structure either directly to a stable $\text{Zr}_2(\text{Cu}, \text{Al})$ tetragonal phase or to an icosahedral QC phase at oxygen levels of $x = 0.14$ or $x = 0.43$, respectively. This specific result (i.e., QC formation is not stabilized by oxygen at levels around 1400 ppm atomic) is often used to support arguments for other mechanisms (e.g., icosahedral short-range order in the amorphous phase) leading to meta-stable QC devitrification phases. Saida et al. [10-12] frequently claim that the oxygen contents they obtain in Zr-Pd and Zr-Pt melt spun ribbons (e.g., 400-700 ppm mass) are sufficiently low to ignore the influence of oxygen impurity on QC formation. Similar claims were made by Murty [9] for amorphous Zr-Pd and Zr-Pt ribbons containing <1000 ppm atomic; however,

in that report neither specific details about measured oxygen values nor the analysis method were provided. In our opinion, extending the results from Zr-Al-Cu alloys directly to other systems such as Zr-Pd and Zr-Pt may not be completely appropriate. This paper examines the as-synthesized structure and devitrification behavior of $Zr_{80}Pt_{20}$ melt spun ribbons having oxygen contents ranging from <200 to approximately 5000 ppm mass. The first ever observation of the inability to form amorphous $Zr_{80}Pt_{20}$ ribbons with very low oxygen contents is presented.

Experimental Procedures

$Zr_{80}Pt_{20}$ alloys were prepared by arc melting high purity crystal bar Zr (O <50 ppm mass) and Pt (O <35 ppm mass). Additional arc melted alloys with the nominal oxygen contents listed in Table I were prepared by adding ZrO_2 . Buttons were re-melted several times to increase the homogeneity of the added oxygen impurity. Ribbons of the alloys were produced by single roller melt spinning using a linear wheel surface velocity of 25 m/s; ribbon cross sections were approximately 0.04 x 2 mm. Graphite crucibles were used to contain the molten alloys during melt spinning to eliminate oxygen impurities typically introduced by conventional fused silica crucibles. However, one ribbon was produced using a fused silica crucible to separate any artifacts that might arise from carbon contamination (see Table I). Melt spun ribbons were examined by X-ray diffraction (XRD) using $Cu-K_{\alpha}$ radiation and by transmission electron microscopy (TEM). Near free-side surface TEM specimens of the lowest oxygen content ribbon were prepared using unidirectional ion-milling. Devitrification behavior was examined using differential scanning calorimetry (DSC) with a Perkin Elmer Pyris 7 unit. Oxygen and carbon contents were measured using inert gas fusion and combustion chromatography, respectively; three measurements of each ribbon were made.

Results and Discussion

Impurity Contents of $Zr_{80}Pt_{20}$ Melt Spun Ribbons. Table 1 lists the measured oxygen and carbon values of the melt spun ribbons. The reduced oxygen contamination samples A and B compared to sample C, which was made using a silica crucible, indicates that some oxygen is introduced from the silica during melt spinning. The good agreement between nominal and measured oxygen values for samples D-G illustrates that the ZrO_2 added during arc melting was completely melted and homogeneously distributed throughout the button. Carbon contents in ribbon from graphite crucibles are somewhat higher compared to sample C; the moderate level of carbon contamination with graphite crucibles may be associated with rapid formation of a passive ZrC layer during melt spinning.

Table 1. Oxygen and carbon contents of $Zr_{80}Pt_{20}$ melt spun ribbons

Sample Label	Crucible Material	Nominal Oxygen content (ppm mass)	Measured Oxygen content (ppm mass)	Measured Carbon content (ppm mass)
A	graphite	*	184±9	411±2
B	graphite	*	301±36	286±19
C	silica	*	414±40	147±4
D	graphite	1000	1053±64	187±11
E	graphite	1500	1547±85	209±16
F	graphite	2500	2690 ±30	239±63
G	graphite	5000	4737±233	289±10

*No ZrO_2 intentionally added during arc melting

Structure of $Zr_{80}Pt_{20}$ Melt Spun Ribbons. The astonishing result from this study is the absence of glass formation in $Zr_{80}Pt_{20}$ ribbons containing <500 ppm mass oxygen, Fig. 1; note, all ribbons were prepared with the same quench rate (25 m/s wheel speed). Samples A-C do not exhibit any indication of an amorphous phase, nor do they show typical peak broadening from a nano-grained structure. Carbon does not appear to be the cause of full crystallization during quenching; sample C prepared using a silica crucible shows the same behavior as A and B. The three strongest reflections in the XRD patterns in Fig. 1a match well with the (110), (220) and (330) planes of the bcc β -Zr structure. The data in Fig. 1a were obtained from the free-surface of the ribbons, and therefore, only reflect the top several microns of the ribbons. The fully crystalline, coarse-grained structure in ribbons A-C indeed are constrained to the free-surface regions of the ribbons, as illustrated by the XRD patterns from the corresponding wheel-side surfaces presented in Fig. 1b. As a result of increased quenching rates at the wheel surface, a much finer grained structure is developed. However, the patterns in Fig. 1b still show a β -Zr structure, but now with substantial peak broadening from the nanocrystalline structure. Melt spun ribbons with higher oxygen contents, which were achieved by adding ZrO_2 during processing, show a transition to amorphous structures (sample D) and mixtures of amorphous + QC (sample E) and amorphous + undetermined crystalline phases (sample F and G), Fig. 2. These XRD results are from the free-side surfaces of ribbons D-G; analysis of wheel-side surfaces is in process. The TEM results in Fig. 2 illustrate the typical amorphous and amorphous + QC structure found in samples D and E, respectively.

Fig. 1 XRD patterns of low-oxygen melt spun ribbons obtained from (a) free-side surface and (b) wheel-side surface.

Fig. 2 XRD and TEM results from melt spun ribbons containing >500 ppm mass oxygen.

Although samples A-C show a broad range of grain sizes throughout their cross section, Fig. 1, they do not contain a detectable amorphous phase. This cannot be determined unambiguously from the XRD results alone, but the DSC data in Fig. 3 further support this observation. No exothermic reaction can be seen in temperature range around 720 K frequently observed for the amorphous-to-QC transformation in $\text{Zr}_{80}\text{Pt}_{20}$ melt spun ribbons [10-12]. Instead, only a single DSC peak occurs at higher temperatures. The DSC data from ribbons containing >500 ppm mass oxygen illustrate the transformation of an amorphous phase, as evidenced by the initial exothermic peaks. The onset temperatures of the first crystallization reaction increase in ribbons with higher oxygen contents. In addition, the onset temperatures for the second exothermic peak decreases as oxygen content increases. These results suggest that oxygen stabilizes the amorphous structure, but decreases the stability of meta-stable phases (e.g., QC phase) that evolve from the amorphous phase. Others have suggested that oxygen stabilizes meta-stable QC phases in amorphous Zr-based alloys [8,13], and the results in this study for ribbons D-G continue to support this idea, while also showing that glass formation in these alloys is associated with oxygen content. The discovery that a critical amount of oxygen is necessary to achieve some degree of glass formation suggests that in the absence of sufficient QC stabilization throughout the system, crystallization rather than vitrification during quenching can be kinetically dominant. It is important to note that these results were all obtained at a fixed quench rate, so the critical oxygen level (i.e., ~ 500 ppm mass) below which no amorphous phase forms in the $\text{Zr}_{80}\text{Pt}_{20}$ melt spun ribbons is likely to be specific to the 25 m/s wheel speed used in this study.

Fig. 3 DSC curves of melt spun ribbons. Arrows indicate approximate initial onset temperatures for crystallization of the amorphous phase.

Structure of Low-Oxygen $\text{Zr}_{80}\text{Pt}_{20}$ Melt Spun Ribbons. The crystal structure of the β -Zr phase that formed in ribbons A-C was examined more closely; TEM details from the free-side of the ribbon with 184 ppm O, sample A, are presented here. The bright field image in Fig. 4a reveals a coarse-grained structure, which agrees with XRD results in Fig. 1a. The selected area diffraction pattern (SADP), Fig. 4b, from the outer region in Fig. 4a can be indexed along the [111] direction in β -Zr. The six highest intensity reflections correspond to $\{110\}$ planes in β -Zr with a d-spacing of ~ 0.25 nm, which is very close to the expected value for β -Zr. Superlattice reflections are visible at approximately one-third spacings between center spot and the 110 reflections, implying an ordered substitution of Pt into the β -Zr structure resulting in β -Zr(Pt) superstructure with a d-spacing of approximately 0.75 nm. These superlattice reflections agree well with the low-angle peaks from low-oxygen ribbons shown in Fig. 4. These XRD reflections can be indexed as $1/3(110)$ and

1/3(220). Close examination of the superlattice spacings in the SADPs, Fig. 4b indicates that they are not exactly at one-third separations, but instead are slightly less or more than one-third. Thus, the superstructure of the free-side ribbon surface is a distorted bcc β -Zr structure.

Very strong structural similarities between the β -Zr and QC phases can be seen in comparing the diffraction results in Fig. 4. The SADP of the QC phase along the 2-fold direction, Fig. 4c, was obtained with nearly the same beam direction (i.e., $\sim 1^\circ$ difference) as in Fig. 4b. This reveals an orientational relationship of $[111]_{\beta\text{-Zr}} // 2\text{-fold}_{\text{QC}}$. Numerous examples of coexistence between these phases were observed in the free-side surface of this sample. The distortion in the β -Zr and QC phases currently precludes determining exact unit cell dimensions required to verify if the β -Zr phase is an approximant structure. Work is in process to establish both the orientational and structural relationships between these meta-stable phases. Additionally, further work is needed to determine if oxygen is preferentially constrained to a specific phase. For example, electron energy loss spectroscopy may be helpful to investigate if the QC phase has a higher oxygen level than the β -Zr phase, which would follow the suggestions of Murty [9] and Köster [13] that oxygen stabilizes the QC phase in Zr-based glasses. Speculatively, if the preceding experimental observation is realized, it might lead to the suggestion that at very low oxygen contents (e.g., <500 ppm mass), an insufficient quantity of QC domains are stabilized to favor glass formation in preference to crystallization.

Fig. 4 Low-angle XRD results from low-oxygen melt spun ribbons highlighting superlattice reflections and TEM data from free-side surface of Sample A (184 ppm mass oxygen) showing (a) bright field image coarse-grained structure and illustrating orientational and structural similarities between β -Zr and QC phases: (b) SADP along $[111]$ direction of β -Zr phase and (c) 2-fold direction of QC phase.

Conclusion

The oxygen content in $\text{Zr}_{80}\text{Pt}_{20}$ melt spun ribbons produced at the same quench rate influences the as-synthesized structure and devitrification behavior. At very low oxygen levels (i.e., <500 ppm mass) no amorphous phase forms and the resulting meta-stable structure is comprised predominantly of an ordered β -Zr superstructure with a small amount of a QC phase. Increasing the oxygen to around 1000 ppm mass yields a fully amorphous structure, while additional oxygen promotes a mixture of amorphous and QC or crystalline phases. The amorphous phase that forms in

the $Zr_{80}Pt_{20}$ system appears to be increasingly stabilized at higher oxygen contents. The coexistence of meta-stable β -Zr and QC phases in low-oxygen ribbons is characterized by strong orientational relationships and very similar structural similarities.

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