Chapter 6

SUMMARY AND FUTURE DIRECTIONS

SUMMARY

This thesis has attempted to elucidate the origins of toughness in bulk metallic glass from a few different angles, reflected in the titles of its four subject chapters: an exceptionally damage-tolerant glass, influence of configurational disorder on the intrinsic fracture toughness of metallic glasses, the dependence of fracture toughness on the configurational state of metallic glass, effect of microalloying on the toughness of metallic glass, and investigation of cavitation in glass-forming liquids. The multiple approaches taken were a necessity, as we do not have the knowledge to perfectly explain any of the fracture toughness phenomena that we have observed. The common thread between the chapters is the fundamental competition between the mechanisms of shear banding/toughening and cavitation/cracking. We hope that this central issue and the physical observations surrounding it in this thesis serve as experimental guideposts for the research to follow. It is clear that we still have much more to learn about this interesting class of materials. We will discuss some of the open questions of toughness in the future directions section that follows, but will continue here to summarize the main findings of this thesis.

In chapter 2, an exceptionally damage tolerant glass, we introduce a Pd-based glass that displays a level of damage tolerance, the combination of strength and toughness, that is unprecedented for monolithic bulk metallic glass and is in fact one of the most damage tolerant materials known. From observing the fracture of this very tough glass we see the intrinsic mechanisms of toughening at work: shielding and blunting of the crack tip by extensive shear banding, crack deflection, and perhaps interactions between shear bands ahead of the crack tip. The intrinsic toughening mechanisms allow for this alloy to tolerate significant stable growth of a subcritical crack, and exhibit a rising R-curve, a phenomenon not seen in any monolithic metallic glass at that time. The majority of monolithic bulk metallic glasses fail catastrophically as soon as a crack is initiated, which we believe is due to cavitation in the sliding shear bands ahead of the crack tip. We also note that the measurement of this tough glass was enabled only through the employment of nonlinear fracture mechanics, specifically the crack-tip opening displacement method. This technique will be critical in metallic glass fracture toughness as it may be impossible to form any of these tough glasses at thicknesses large enough to satisfy linear-elastic fracture mechanics specimen size constraints.

In chapter 3 we explore the fracture toughness of a moderately tough Zr-based glass by linear-elastic fracture mechanics, in hopes of establishing a valid K_{Ic} for the material. Our results were surprising, and not simple to interpret. We found that the frequency- and temperature-dependent relaxation modes of a dynamically vitrifying glass cannot be ignored as part of the processing history of the glass. If the glass is relaxed to an equilibrium well-defined configurational state, we find that the fracture toughness is consistent and correlates strongly with the average configurational properties of the glass, such as the shear modulus G. For as-quenched specimens, with a complex configurational state consisting of a broad spectrum of unrelaxed modes and thus more configurational disorder, they exhibit a large variance in their fracture toughness that cannot be correlated with the measured average configurational properties of the glass. This implies that the fracture process of a specimen with an atomically sharp crack tip is a local process that is sensitive to the local configurational environment of the crack tip. Relaxing the configurational modes of the glass reduces the variability in fracture toughness by reducing the configurational disorder at the crack tip.

In chapter 4 we investigate the effect of minor alloying additions (≤2%) on the configurational state and notch toughness of a Cu-based glass. In the previous chapter we manipulated the configurational state of the glass through its processing history, but in this chapter we take a close look at the how changing the chemical composition of the glass affects toughness. The same general trend of toughness correlating with the shear modulus is found to hold for minor additions of substitute elements. In fact, the combination of minor additions and tightly controlled processing could be used to fine-tune the absolute value and variance in the fracture toughness of metallic glass.

In chapter 5 we present a study on the nucleation of cavities in glass-forming liquids due to the dynamic application of negative hydrostatic pressure. This work was born out of the desire to understand the mechanism that competes with shear banding to limit the toughness of metallic glass, the cavitation (or opening) of the liquid inside a shear band into a crack. Shear banding during mode I fracture toughness tests is abundantly clear, but the only proof of a cavitation mechanism is seen in the veined and dimpled patterns seen on the fracture surfaces after failure [1]. If we could measure the barrier to cavitation in a glass-forming liquid, perhaps it would correlate strongly with fracture toughness. We found that a variety of glass-forming liquids are all metastable to negative pressure on laboratory timescales. Cavities can nucleate heterogeneously in the liquid at low negative pressures, or homogeneously at greater negatives pressures. The heterogeneous nucleation of cavities from trapped inclusions in the glass could play an important role in limiting fracture toughness. Ultimately, we found that Vitreloy 1 liquid is metastable on laboratory timescales at negative pressures, and nucleates homogeneously on laboratory timescales at pressures of –100 to –500 MPa.

Essentially, the fracture toughness of metallic glass shows a strong dependence on its composition and processing history, a complex blend of issues. If that wasn't enough to worry about, one cannot ignore the influence of any inhomogeneities in the production of the glassy samples. Shrinkage cavities, entrained gas bubbles, atmosphere contaminants, and hard inclusions are a sure shortcut to brittle, inaccurate results. The successful commercialization of metallic glasses will depend on accurately controlling for all of these factors, and those that are yet to be discovered.

FUTURE DIRECTIONS

The direction of future research on the toughness of bulk metallic glass should aim for a description of toughness that successfully incorporates both the toughest and most brittle metallic glasses, as well as the composition and processing history effects observed in the previous chapters. At this point we have a general understanding of some of the factors that can increase or decrease toughness, but we cannot accurately predict the toughness of any given alloy. We show in chapter 2 that the fracture toughness of an alloy can be related to the ratio of B to G and T_g, and that it may be a better way to correlate the toughness than the Poisson ratio. However, in chapter 3 we present results for an as-quenched Zr-based glass where the Poisson ratio cannot explain the measured toughness. Just within the past year, a Zr-Cu-Al-Ti glass with a modest Poisson ratio of ~0.37 was found to exhibit a rising R-curve [2], like the ~0.42 Poisson ratio Pd-based glass of chapter 2 [3]. Clearly, the entire story of toughness cannot be contained in the macroscopic average of the elastic constants of the glass. We have proposed that there is sensitivity to the local configurational makeup at the point of the crack tip, but this doesn't directly address why a particular composition of metallic glass can have such an unprecedentedly large toughness, no matter what the Poisson ratio is. At this point, two monolithic bulk metallic glasses have the ability to prevent a catastrophic stress instability at the crack tip until a toughness of ~150 MPa·m$^{1/2}$ is achieved. How is it that the shear bands in these two glasses grow and multiply with impunity while the liquid inside those shear bands experiences an opening force that would cause cavitation and crack growth in the vast majority of metallic glasses? These two glasses have an amazing insensitivity to flaws and configurational disorder, they easily shield any stress concentrators and do not display the large variation in toughness seen in the Zr-based glass of chapter 3. There is no particular descriptor of these two glasses that one could look at and predict their extreme toughness, yet they are incredibly tough.

Additionally, we showed in chapter 3 that the toughness of a glass relaxed to an equilibrium configurational state correlates strongly with the configurational enthalpy of that state. If this is carried to its logical conclusion, what is the limit of toughness in metallic glasses? Could it be determined solely by the amount of configurational enthalpy that can be stored in the glass? How much configurational enthalpy can even be successfully stored in a metallic glass such that it provides useful shear banding during fracture? Under these circumstances perhaps the barrier to cavitation and cracking will limit the upper bound of toughness, as opposed to the shear flow barrier. The work by Bouchaud et al. [1] shows the characteristic patterns of cavitation in the failure of metallic glass, and the recent molecular dynamics work in metallic glass-forming liquids by An et al. [4] and Murali et al. [5] show cavitation in action. Chapter 5 highlights the difficulty of studying cavitation directly in the laboratory, but we likely have a lot more to learn about cavitation that could be very helpful in understanding the variety of observed phenomena in metallic glass fracture toughness.

We have proposed that the toughness of a glass is dependent upon the local configurational disorder at the crack tip of a precracked specimen. If this proposal is true, we have not yet discussed an important consequence. When can one trust that their measurement of an as-quenched sample is the true intrinsic fracture toughness of the glass? Should we be discussing fracture toughness as more of a statistical quantity? Perhaps, one can only trust a measurement when the glass is relaxed to a well-defined configurational state at a known temperature. However, it is possible that the effect of configurational disorder only dominates the results for samples with sharp cracks; notched samples like those of chapter 4 could be exempt as the stress is distributed over a much larger volume and the crack must still be initiated. Recent computational works by Rycroft and Bouchbinder [6,7] have explored how the configurational modes of metallic glass can affect the fracture toughness. We hope that a carefully selected combination of modeling and experiments will eventually reveal the origins and determination of fracture toughness in metallic glasses.

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