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On the effect of microalloying on the mechanical properties of metallic glasses

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Abstract

"Microalloying", which refers to the addition of small concentrations of a foreign metal to a given metallic glass, has been used extensively in recent years in attempts to improve the mechanical properties of these glasses. The results are haphazard and nonsystematic. In this paper we provide a microscopic theory of the effect of microalloying, exposing the delicate consequences of this procedure and the large parameter space which needs to be controlled. In particular we consider two very similar models which exhibit opposite trends for the change of the shear modulus, and explain the origins of this difference as displayed in the various microscopic structures and properties.

Keywords: Microalloying; Amorphous solids; Mechanical properties; Metallic glasses; Shear modulus

1. Introduction

Bulk metallic glasses have attracted considerable attention due to their high strength compared to their crystalline counterparts [1]. On the other hand, these promising materials exhibit catastrophic brittle fracture and strain softening; these undesired properties seriously limit their uses as engineering materials [2,3]. In recent years many laboratories have tried to improve the mechanical properties of metallic glasses by adding small concentrations of a foreign metal [4,5]. A theoretical attempt has been made to explain the effect of microalloying by adding pinned particles to the glass-forming system [6]; such a procedure can only increase the observed shear modulus as well as the toughness. It turns out that in experiments the actual effect of "microalloying" is hardly predictable, and large efforts are necessary to try out different additives at different conditions with haphazard results concerning the observed mechanical properties. Thus, for example, in Ref. [7] one found a decrease in the mechanical modulus, whereas in Ref. [8] the opposite was found. The aim of this paper is to go beyond the ideal model of pinning, and to understand, based on a microscopic theory, the origin of these highly nonuniversal consequences of microalloying.

For simplicity and concreteness we will focus in this paper on simple model glasses in two dimensions at zero temperature. The reason for this choice is that at $T = 0$ and for quasistatic strain protocols we possess an exact theory for the mechanical properties and in particular the shear modulus that we analyze below [9,10]. The exact theory allows us to probe the precise reasons for the changes in shear modulus upon the addition of the foreign particles, exposing the very large parameter space that needs to be controlled. Choosing randomly foreign particles whose interactions with the present ones in a given glass are not precisely characterized can lead to changes in the shear modulus that are highly unpredictable. In Section 2 we present the two models used in this paper. Section 3 presents the results of microalloying in terms of the observed

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stress vs. strain curves and the shear modulus. Section 4 discusses the microscopic theory and explains the observed results. In Section 5 we offer a summary and conclusions.

2. The models

2.1. The basic model glass

We select as our model glass (before microalloying) the well-studied [6] model of a binary 50–50 Lenard–Jones mixture contained in a periodic box and whose potential energy for a pair of particles labeled i and j has the form:

$$U_{ij}(r_{ij}) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6} + A_0 + A_2\left(\frac{r_{ij}}{\sigma_{ij}}\right)^{2} + A_4\left(\frac{r_{ij}}{\sigma_{ij}}\right)^{4} + A_6\left(\frac{r_{ij}}{\sigma_{ij}}\right)^{6}\right]. \quad (1)$$

Depending on whether particles i and j are "small" (S) or "large" (L), the length parameters σ_{ij} take on the values σ_{SS}, σ_{LL} and σ_{SL}, chosen to be $2\sin(\pi/10), 2\sin(\pi/5)$ and 1, respectively. σ_{SL} is also referred to as simply σ and it acts as the fundamental scale. Thus the potential is cut-off at $r/\sigma = 2.5$. We ensure that this cut-off is smooth with two smooth derivatives, and this is the function of the parameters A_0, A_i $(i = 2, 4, 6)$. Finally, the energy parameters are $\epsilon_{SS} = \epsilon_{LL} = 0.5, \epsilon_{SL} = \epsilon_{LS} = 1$. Below ϵ_{SL} acts as the energy scale in units for which the Boltzmann constant is unity.

2.2. Modeling microalloying

In order to model microalloying we replace a small percentage of "small" particles by marked particles, designated below as "M". Then the mixture contains Small, Large and Marked particles. Importantly this substitution is made in the liquid state before the quench to an amorphous solid. We believe that this is in accordance with the laboratory procedure of microalloying. Note that we are not trying to model a particular experiment of microalloying, but rather to understand the observed high sensitivity to particular choices of added metals. Obviously, one can choose the marked particles in many ways, each contributing to a change in the mechanical properties of the mixture. For example, we can choose any of the interaction length-scales $\sigma_{MM}, \sigma_{ML}, \sigma_{MS}$ differently, as well as the corresponding energy parameters. This opens up a six-parameter phase space even for the very simple models that we discuss here. Other possibilities include three-particle interactions, angle-dependent interactions, etc. For concreteness we will examine only two models, not touching the range of interaction, taking for the ranges the same values for "M" as the small particle "S" that it replaces. The only difference will be in the energy parameters that determine the depth of the potential. In both models considered below we perform a standard quenching protocol from the melt to the amorphous solids at $T = 0$. The quench of a liquid with 5625 particles started at temperature $T = 1.2$ at a rate of 3.2×10^{-6}. All the simulations are done in NVT ensemble with a density $\rho = 0.976$.

Model A: The presence of marked particles increases the potential depth between the marked and the small particles. The interaction parameter between the marked and glass-forming particles have the values: $\epsilon_{MM} = 0.5$, $\epsilon_{SM} = 2.5, \epsilon_{ML} = \epsilon_{LS} = 1$. The other parameters remain the same as for the original glass-forming mixtures. With this choice of energy parameters there will be a tendency for small particles to aggregate and cluster around the M particles.

Model B: In the second model it is assumed that a marked particle attracts any large particles present in the mixture. To take this into account we have chosen the interaction parameters as $\epsilon_{MM} = 0.5, \epsilon_{LM} = 5.0$, $\epsilon_{MS} = 0.5, \epsilon_{LS} = 1$. Note that here the choice means that large particles will aggregate and cluster around the M particles.

While these differences in choice seems slight, we will see below that they lead to strong and opposite trends in changing the mechanical properties of the resulting glass.

3. Observed results of microalloying

The mechanical properties of the resulting mixtures are observed by straining the material at $T = 0$ under quasi-static shear with Lees–Edward boundary conditions [9] to preserve the volume. This means that after every infinitesimal change in the external strain γ the system is relaxed by gradient energy minimization to the nearest inherent state. The raw available data are the stress vs. strain curve as shown in Fig. 1 for both models A and B at six different concentrations of the marked particles M including zero concentration. It can easily be seen that the shear modulus decreases significantly in model A, about 30% with the addition of 5% M particles. In model B we observe the opposite trend, with about 12% increase in shear modulus for the same percentage of M particles.

One can attempt to figure out why these changes are occurring by looking directly at the structure of the resulting glasses. These are shown for the two models in Fig. 2 for a concentration of 5% of marked particles. The images show clearly the tendency of clustering in the two models: in model A small particles aggregate around the marked particles, whereas in model B we have the opposite—large particles aggregate around the marked particles. In both cases we see some crystalline order in these clusters. To make this fact more obvious we show in Fig. 3 the same pictures but with a Voronoi map. This kind of clustering has been observed in experimental microalloying [7], leading to a decrease in the Young's modulus. It is interesting to note that the effect of clustering cannot be seen in the standard two-point correlation function $g(r)$. This function is shown in Fig. 4 upper panel for both model A and model B, at 5% concentration of the marked particles. No new peak appears compared to the pure glass. On the other