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Jordan Hu

Washington University in St. Louis

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Observing microstructural heterogeneities in bulk metallic glass

Jordan Hu, Katharine M. Flores[a,b]

[a] Washington University in St Louis, Institute of Materials Science & Engineering, One Brookings Drive, St Louis, MO 63130, USA

[b] Washington University in St Louis, Department of Mechanical Engineering & Materials Science, One Brookings Drive, Campus Box 1185, St Louis, MO 63130, USA

Abstract

A Zr-based bulk metallic glass (BMG) was investigated to using dynamic modulus mapping (DMM) to explore spatial variations of mechanical properties. Elastic modulus patterns were determined using storage modulus maps at different positions on the sample. We partially re-confirmed the existence of a heterogenous directionally aligned elastic microstructure network in a Zr-based BMG. A K-means clustering algorithm was applied to the appropriate modulus maps, to divide the data into stiff, intermediate and compliant regions, however data on several of the maps was inconclusive.

Introduction

Although BMGs are amorphous and appear homogenous and isotropic when tested with conventional characterization techniques, such as electron microscopy and x-ray diffraction, deformation behavior can vary drastically with processing and alloy composition [1]. Recent studies have reported a nanoscale heterogeneous structure in metallic glasses, which has implications for the macroscopic mechanical properties [1]. BMGs are known to be heterogenous by definition, but heterogenous structures beyond atomic clusters are less obvious [1].

A number of papers have worked to further clarify and understand the properties and characteristics of intrinsic atomic level heterogeneities of bulk metallic glass using a variety of testing methods. Methods for studying and analyzing BMG nanomechanical properties are still being discussed. An understanding of the strengths and weaknesses of testing methods is vital to obtain effective conclusions on nanomechanical properties

A study conducted by Karuppasamy et al studied the elastic modulus and hardness at nanoscale of a Zr-based bulk metallic glass, (Zr-BMG, $Zr_{65}Cu_{15}Al_{10}Ni_{10}$) using the Berkovich Tip and Oliver-Pharr method and investigated the effect of loading rate and peak and cyclic loads on the mechanical properties of the BMG to analyze the indentation size effect [3]. Nanoindentation was conducted at three different indentation modes; standard single indentation with a linear loading rate, progressive multi-cyclic indentation and sinus mode indentation [3]. The study observed that the loading rate had significant effects on serration flow [3]. The report concluded that the results are in contradiction with the Oliver-Pharr method, which states that hardness is peak-load dependent and elastic modulus increases with load [3]. Thus, Karuppasamy et al concluded that due to this contradiction, the Oliver-Pharr method may not be suitable for Zr-based BMG's [3]. Based on these conclusions, any additional studies centered around Zr-based metallic glasses should use caution for selecting indentation and analysis methods. As Zr-based metallic glasses are relatively common due to their high glass-forming ability, it is important to make sure that proper methods are selected [3].

Another study conducted by Wagner et. al used atomic force acoustic microscopy (AFAM), which measures the resonances of atomic force cantilevers with the tip contacting the specimen surface to detect variations in the stress state that are otherwise undetectable using global ultrasound methods [4]. The study compared AFAM results between PdCuSi metallic glass and its crystalline counterpart and concluded that the glass expressed homogeneity on a scale less than 10nm, void of long-range order [4]. As the study by Karuppasamy et al noted that using the Berkovich Tip and Oliver-Pharr method may have reliability issues, AFAM techniques could be considered as an alternative for investigating heterogeneities in Zr-based BMGs.

Microhardness indentation is another method that has been previously used to study heterogeneities in BMGs. In a study by Vincent et. al, hardness testing was performed at four different loads of 100, 200, 300 and 500g in different regions of the rod to investigate microstructure dependent deformation behavior on a drop casted BMG [5]. Following hardness testing, indentation was performed. Testing was conducted on Zr-based BMG ($Zr_{60}Cu_{10}Al_{15}Ni_{15}$) rods[5]. The study found that there was a fully glassy region, composite regions and a crystalline region of the rod, their formation all dependent on cooling rate, and that the highest hardness was associated with the crystalline region [5]. The study also confirmed the existence of shear band propagation [5]. Methods and explanations detailed in this paper could be useful in further experiments attempting to further understand the nature of shear bands and the relationship between hardness and moduli in BMGs.

As the understanding of heterogeneities in BMGs has become more refined, several studies have tried to observe mitigate the shear bands and inherent brittleness of MGs by introducing long-range order without compromising the advantages presented by BMGs.

In a study by Vincent et Al, a melt spun glassy ribbon sample was annealed at supercooled liquid region (**Δ**Tx), offset of first crystallization (Tx1) and offset of second crystallization temperature (Tx2) [6]. The glassy ribbon was a Cu-based BMG (Cu_{60} $Zr_{20}Ti_{20}$) and the annealed samples were analyzed using X-ray diffraction and transmission electron microscopy [6]. The objective of the study was to study the correlation between crystallization and processing on microstructure [6]. The report concluded that crystallization from by annealing in the supercooled liquid region and at the onset of first crystallization peak temperature produced the hardest sample [6]. However, the report also noted an upper limit of hardness, after which the sample was prone to fracture [6]. This study was conducted only on a Cu-based BMG, and additional research could be conducted on a different variety of BMGs, and potentially at different sizes.

Another study claims to have manipulated BMGs to be plastic at room temperatures. The report by Liu et al studied a variety of BMGs of various compositions all containing Zr, Cu, Ni, and Al [7]. The report manipulated elastic microstructure by controlling for the exact compositions Zr, Cu, Ni and Al [7]. In microstructural analysis, the report concluded that their most plastic BMG, which underwent a true strain of 160%, was comprised of regions of high stiffness surrounded by soft regions [7]. This study has many implications for BMG manufacturing as the study claims to have created a BMG with plasticity with no processing after formation. The scope of the study could be further expanded to include a wider variety of glass-forming elements to see if this is repeatable or practical for manufacturing.

Intensive power ultrasound has also been identified as a possible method of BMG treatment to mitigate brittleness. A report by Zhai et al used intensive power ultrasound at 20 kHz to treat Zr-based ($Zr_{46.75}Cu_{46.5}$ $Al_{6.5}$) BMG rods to incite atomic rearrangement [8]. The results showed that ultrasound was capable of forming $Cu_{10}Zr_7$ nanocrystals, which increased the compressive plasticity and yield strength of the BMG [8]. The report notes that intensive power ultrasound techniques are relatively easy to procure and non-destructive [8]. This research could be further expanded to compare other known processes used to strengthen BMGs. Additionally, more testing could be conducted at different settings for ultrasound.

In this work we applied dynamic modulus mapping of $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ bulk metallic glass samples to explore spatial variations of mechanical properties. The collected data partially confirms previously discovered modulus maps [2]. Additionally, we reviewed existing research on bulk metallic glass heterogonies and methods of mitigating the intrinsic weaknesses of metallic glasses.

Experimental methods

$Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ specimens were prepared by arc melting elemental feedstock with minimum purities of 99.9 at% in an argon atmosphere and casting the resulting ingots into 1mm diameter rods. The ingots were flipped and re-melted 3 times to ensure homogeneity before casting. The rod was then sectioned into a disk, which was polished with colloidal silica. DMM was then performed on the circular cross section at the center of the disk, then at the north, east, south, and western positions of the disc, which were determined by a marking on the mount. Before indentation, the sample was sonicated in acetone and methanol to remove surface contaminants. DMM mapping applies a sinusoidal load function and maintains contact between the diamond Berkovich tip and the BMG surface during the experiment. DMM was conducted with a load frequency of 200 Hz and a load amplitude was chosen to get a tip displacement between 1 and 2 nm [1]. Because the tip has a sinusoidal load applied, we analyze indentation storage modulus, which represents the elastic structure's energy [9]. Indentation storage stiffness is calculated using the following equation

$$k' = \frac{F_D \cos(\phi)}{d_D} + m_T \times \omega^2 - k_T$$

Where F_D is the dynamic load, d_D is the dynamic displacement, ϕ is the phase shift, m_T is the mass, ω is the angular frequency, and k_T is the stiffness [2]. k' can be then used to calculate the storage modulus

$$E'_r = \sqrt{\frac{(k')^3}{6F_D r}}$$

Where r is the curvature of the tip for small displacements [2].

Results

Figure 1 below shows the topography of the sectioned disc at the location of indentation.

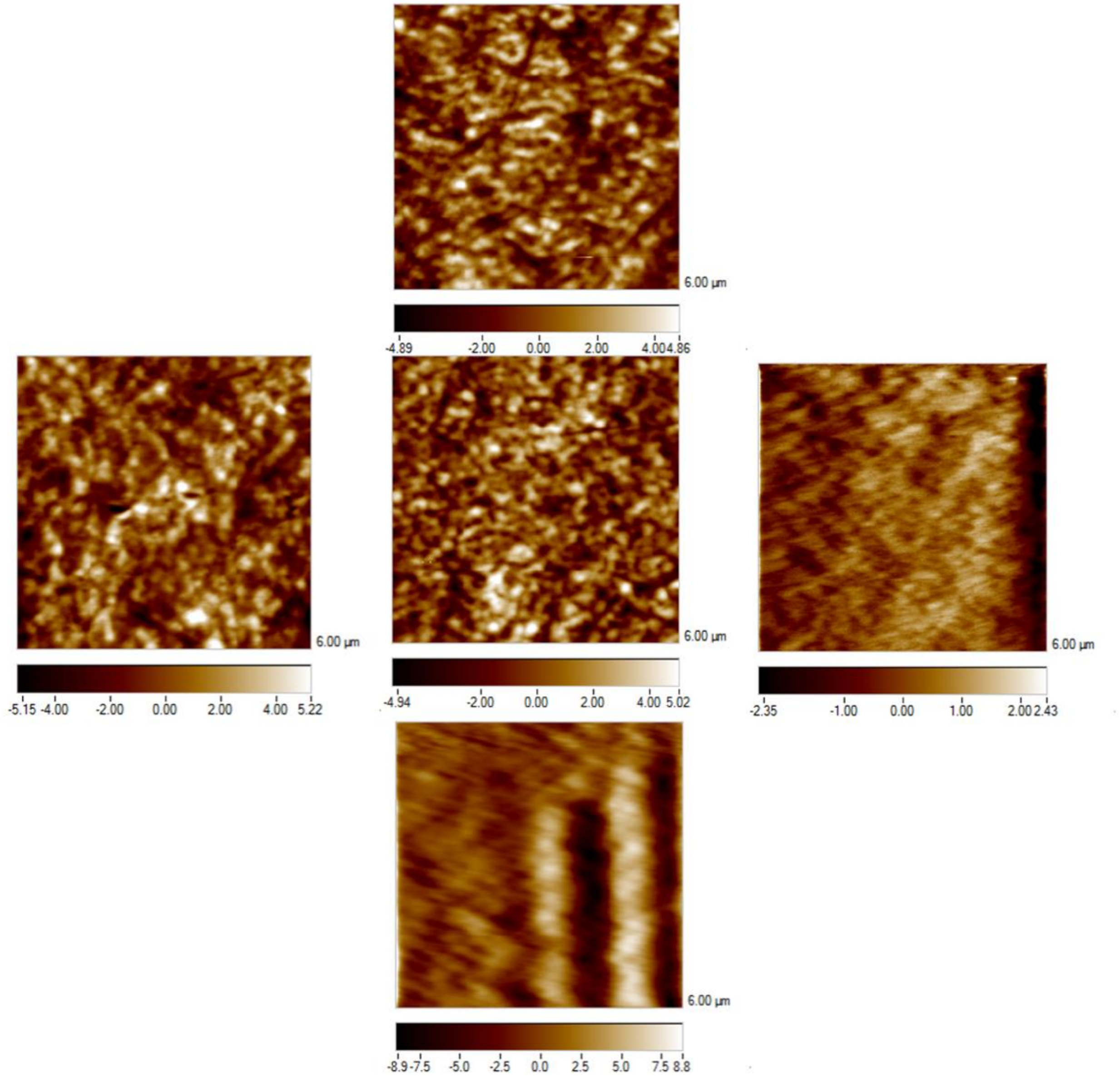

Fig. 1 Surface topography maps.

Figure 2 shows the storage modulus results of DMM mapping. The maps are oriented relative to how they were taken on the sample and labeled center, north, south, east, and west.

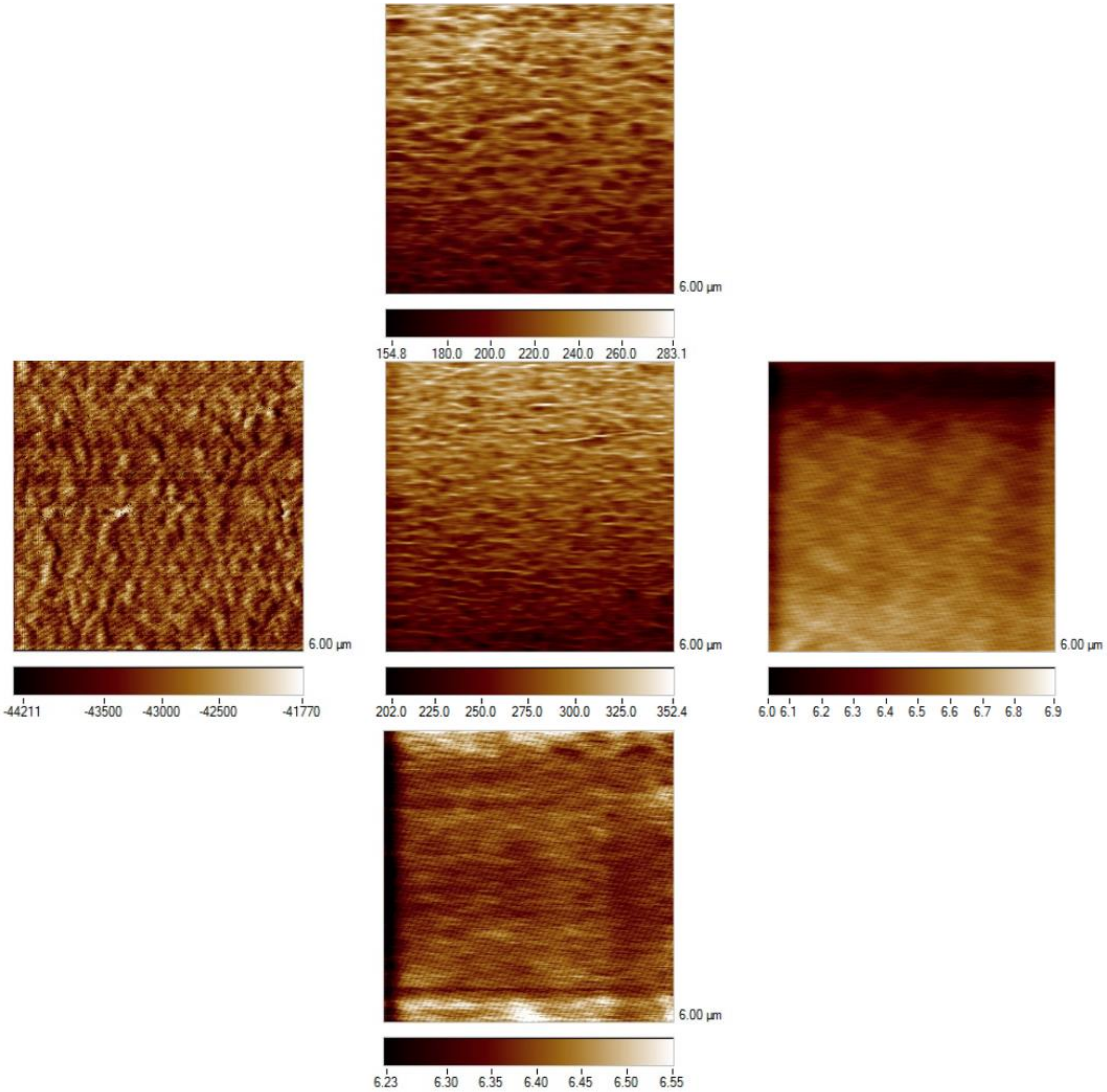

Fig. 2 Modulus Maps Obtained from DMM. Selected 6µm by 6µm storage modulus maps collected from different locations on the circular cross-section

Discussion

Figure 3 shows the western storage modulus map after processing using K-means clustering. K-means is an unsupervised machine-learning technique which we used to separate the data into three categories; stiff, intermediate, and compliant regions. This is translated into colored regions on the map, with the darkest, the brown region, and the lightest region being the most compliant, intermediate, and stiff regions, respectively. K-means was only deemed appropriate for the western modulus maps due to image clarity and quality.

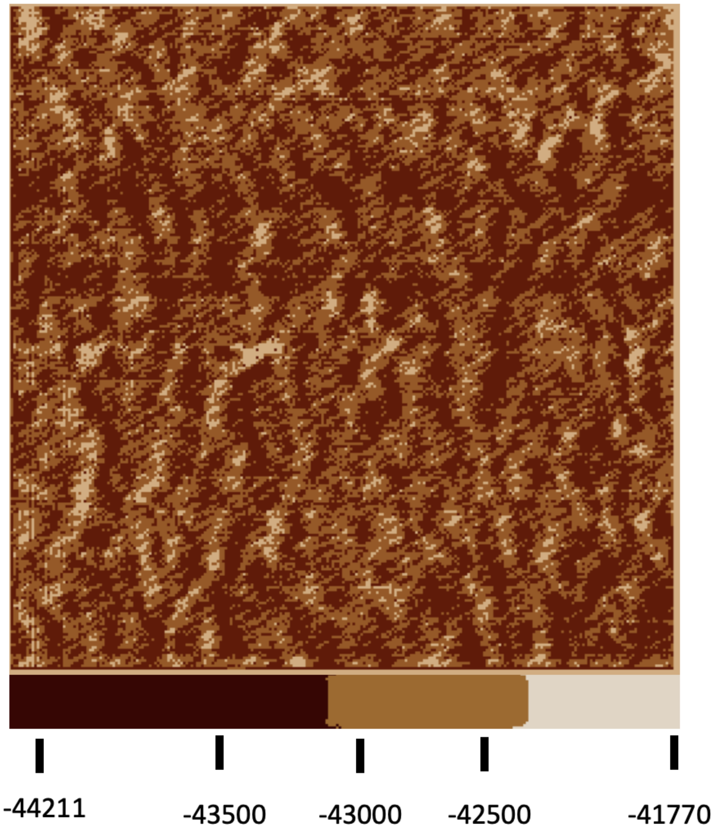

Fig. 3 Storage Modulus Map of the Western Edge of the Sample. Selected 6μm by 6μm storage modulus map with regions partitioned by K-means clustering.

Compared to the modulus maps in Tsai et. al the modulus maps exhibit similar patterns of heterogeneity [1]. Based on the northern, western, and center storage and modulus maps, we can clearly see a modulus network that is oriented based on the position each map was taken at. The southern and eastern modulus maps are inconclusive. The color gradient in the northern and eastern modulus maps that go from dark to light along the length of the map suggests that the sample was not sufficiently flat, and thus the modulus readings were incorrect. Because of this gradient, and a general lack of clarity, it was not appropriate to run K-means on these modulus maps.

In the western modulus map, we observe a pattern in which most of the area of the modulus map is categorized as the intermediate, with strands of complaint regions and isolated points of stiff regions. The compliant regions have a pattern in which the strands of compliant region run circumferentially. The distance between complaint and stiff regions varied, with the stiff regions generally having a buffer region of intermediate stiffness between compliant regions. The high stiffness regions generally only have a width of 0.1μm, while the compliant regions are much thicker. Although K-means was not run on the northern and center modulus maps, we can still determine that a pattern of directionally aligned darker and lighter bands are present for the north and center modulus maps.

As two out of the five modulus maps were not clear and four out of five of the modulus maps were unsuitable for K-means image analysis, we cannot make conclusions based on the eastern and southern modulus maps. More work can be done to ensure sample readiness for indentation. In the future, more advanced algorithms could possibly be written to account for surfaces that are not sufficiently flat and process the gradient observed in the north and center modulus maps.

Conclusion

In this work, we reviewed existing literature on testing methods to detect heterogeneities in BMGs as well as processing methods to reduce the inherent brittleness of BMGs. We also partially re-confirmed the existence of a heterogenous microstructure network in a Zr-based BMG and applied a K-means clustering algorithm to the appropriate modulus maps. The microstructure network appeared to be directionally aligned where visible and seems to agree with the observations of a circumferentially aligned elastic microstructure along the made by Tsai [1]. However, as two out of the five modulus maps were not clear and four out of five of the modulus maps were unsuitable for K-means image analysis, we cannot fully confirm the directionally aligned pattern observed by Tsai [1].

References

[1] Y.Q.Cheng,E.Ma,Atomic-level structure and structure-property relationship in metallic glasses, Prog. Mater. Sci. 56 (2011) 379e473.

[2] P. Tsai, K. Kranjc, K. Flores, Hierarchical heterogeneity and an elastic microstructure observed in a metallic glass alloy, Acta Materialia 139 (2017) 11-20

[3] Karuppasamy Pandian Marimuthu, Kwangmin Lee, Jungmoo Han, Felix Rickhey, Hyungyil Lee, Nanoindentation of zirconium based bulk metallic glass and its nanomechanical properties, J MATER RES TECHNOL. 2020;9(1):104–114

[4] Hannes Wagner, Dennis Bedorf, Stefan Küchemann, Moritz Schwabe, Bo Zhang, Walter Arnold1,2 and Konrad Samwer, Local elastic properties of a metallic glass Nature Materials 10 (2011) 439-442

[5] S. Vincent, B. S. Murty, M. J. Kramer and J. Bhatt, Micro and Nano Indentation Studies on Zr_{60} Cu_{10} Al_{15} Ni_{15} Bulk Metallic glass, Materials and Design, Volume 65, January 2015, Pages 98-103

[6] S. Vincent, Joysurya Basu, B.S. Murty, Jatin Bhatta, Micro indentation study on $Cu_{60}Zr_{20}Ti_{20}$ metallic glass, Materials Science and Engineering A 550 (2012) 160–166

[7] Yan Hui Liu, Gang Wang, Ru Ju Wang, De Qian Zhao, Ming Xiang Pan, Wei Hua Wang, Super Plastic Bulk Metallic Glasses at Room Temperature, SCIENCE VOL 315 9 MARCH 2007 1385-1388

[8] W. Zhai, L.H. Nie, X.D. Hui, Y. Xiao, T. Wang, B. Wei, Ultrasonic excitation induced nanocrystallization and toughening of $Zr_{46.75}Cu_{46.75}Al_{6.5}$ bulk metallic glass, Journal of Materials Science & Technology 45 (2020) 157–161

[9] Braun, Simon G. Ewins, David J. Rao, Singiresu S.. (2002). *Encyclopedia of Vibration, Volumes 1-3 - Equivalent Viscous Damping.* Elsevier. Retrieved from

https://app.knovel.com/hotlink/pdf/id:kt004QR113/encyclopedia-vibration/equivalent-viscous-damping