

**UNDERSTANDING PLASTICITY IN BULK
METALLIC GLASS AND ITS COMPOSITES
USING THE INDENTATION TECHNIQUE**

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by

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to the



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Dedicated to
My parents

Certificate

This is to certify that the thesis entitled “**UNDERSTANDING PLASTICITY IN BULK METALLIC GLASS AND ITS COMPOSITES USING THE INDENTATION TECHNIQUE**” is being submitted by **Ms. PRIYANKA SAINI** to the Indian Institute of Technology Delhi for the award of the degree of **DOCTOR OF PHILOSOPHY**. This is a record of bonafide research work carried out by her under my supervision and guidance. The matter presented in this thesis has not been submitted, in part or in full to any other University or Institute for the award of any degree or diploma.

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PRIYANKA SAINI

Abstract

Bulk Metallic Glasses (BMGs) are multi-component metallic alloys that exhibit superior strength and elastic strain compared to conventional engineering alloys and can be processed to near-net shapes close to their glass transition temperature, T_g . However, their use in structural applications is discouraged as they exhibit nil tensile ductility owing to unhindered propagation of shear bands in the featureless matrix. Determination of the mechanical properties of BMGs is a critical endeavour for improving their plasticity. The indentation technique is commonly opted to assess the mechanical behaviour of BMGs primarily due to its ease of sample preparation and reliable data acquisition from small specimen volumes. Another pivotal aspect is that during the indentation of BMGs, a substantial number of shear bands are formed due to the constrained deformation conditions. Therefore, in pursuit of deciphering the mechanical behaviour of BMGs using indentation, we commence this thesis by examining the role of free volume on the mechanical properties of BMGs. Owing to the disordered nature of atomic packing in BMGs, the shear strength is statistically analysed in the subsequent study to extract quantitative and qualitative information on the evolution of shear bands. Finally, we discuss the shear band interaction with the crystalline phase in bulk metallic glass composites (BMGCs) and yielding criteria in terms of hydrostatic stress or pressure sensitivity, using constraint factor as a proxy measure, with temperature.

In the first study, the free volume content of Zr-based BMG is varied through short-term annealing treatment. This process involved heating BMGs above and below the glass transition temperature, T_g , for the short-term, followed by quenching to preserve the randomness of the structure. The temperature to which the sample is heated is called fictive temperature, T_f , as it refers to the temperature at which structure of equilibrium liquid is similar to structure of solid glass. It is found through differential scanning calorimetry (DSC) that the sample with the highest T_f possesses the highest free volume content owing to entropic considerations. Subsequently, 100 spherical indentation tests are conducted to facilitate a comprehensive study of heterogeneity in free volume throughout the material. The investigation revealed that local shear yield strength, τ_y , and

plasticity rise with T_f . Microscopic deformation models are employed to explain the variations in strength and plasticity.

Note that the local shear yield strength, τ_y , of BMGs, is measured from the load at which first pop-in occurs, P_{FP} , in the load, P , vs. displacement, h , curve during spherical-tip nanoindentation. τ_y exhibits significant heterogeneity owing to the disordered nature of atomic packing in BMGs. Statistical analysis of τ_y is carried out in existing studies to extract quantitative and qualitative information on the microscopic carriers of plasticity in the material. The literature review has shown that the 3-parameter Weibull model best describes the dispersion in τ_y as yielding in BMGs initiates at structural weak links, which are regions with lower atomic packing or higher free volume. Our study further revealed that the 3-parameter Weibull model is the best fit for 2nd pop-in event as well. Additionally, it is observed that the distribution becomes bimodal when indenters with larger radii are used or when the loading rates of the test are relatively higher. The distribution becomes unimodal when the structural state changes from as-cast to structurally relaxed. This is rationalized on the basis of the availability of the number of shear band paths operating at different stresses. It is then concluded that the strength of shear bands is approximately 8–11% and 15–17% lower than the strength of the undeformed BMG in the as-cast and structurally relaxed conditions, respectively.

Moreover, due to the unhindered propagation of shear bands, which generally results in failure of BMG immediately after yielding under uniaxial tension, various strategies to improve plasticity are consistently explored in the literature. Employing the composite approach, which introduces a microstructure impeding the propagation of shear bands in the BMG matrix, is the most effective method for enhancing plasticity. Among the numerous extensively studied BMGCs, those alloys that exhibit the crystallization of a β -Ti phase within the amorphous matrix upon solidification are particularly promising owing to their excellent combination of strength and ductility. While several studies have focussed on improving the ductility of these BMGCs, the pressure sensitivity of plastic deformation in these composites has not been addressed yet. With the aim to determine the pressure sensitivity of these alloys, we considered two Zr/Ti-based BMGCs, with the dendrite, in one case, transforming under stress to α'' -Ti and deforming by slip in the other. We initiated our study by determining their hardness, H , and yield strength, σ_y . Notably, the hardness values exceeded the compressive yield strength values, the ratio of

which is called constraint factor, C . Through an in-depth review of pertinent literature, we found that BMGs are particularly sensitive to hydrostatic stress, a feature distinct from crystalline materials, where yielding primarily occurs due to deviatoric stresses. This unique trait contributes to a C of ~ 3.28 , and a rising trend with temperature in BMGs. Our experimental study revealed that the C of the two BMGCs is 13-50% higher than that of the BMG at the lowest temperature of testing. Moreover, with increasing temperature, the constraint factor increases in the case of BMGC with non-transforming dendrites (BMGC-NT) but decreases in the one with transforming dendrites (BMGC-T). These variations are rationalized on the basis of the flow stress variations of the individual phases in the hardness and uniaxial compression test. Gaining insights into this specific aspect of plasticity holds significant importance for forming processes.

Overall, this thesis discusses the influence of structure on strength and plasticity, statistical analysis of the second ‘pop-in’ behaviour of the spherical tip nanoindentation of BMGs, and temperature dependence of pressure sensitive flow in BMG and BMGCs.

सार

बल्क मेटैलिक ग्लास (BMG) बहु-घटक धातु मिश्र धातु हैं जो पारंपरिक इंजीनियरिंग मिश्र धातुओं की तुलना में बेहतर ताकत और लोचदार तनाव प्रदर्शित करते हैं और उन्हें उनके ग्लास संक्रमण तापमान, T_g , के करीब नेट आकार में संसाधित किया जा सकता है। हालाँकि, संरचनात्मक अनुप्रयोगों में उनके उपयोग को हतोत्साहित किया जाता है क्योंकि फीचर रहित मैट्रिक्स में कतरनी बैंड के निर्बाध प्रसार के कारण वे शून्य तन्यता लचीलापन प्रदर्शित करते हैं। BMG के यांत्रिक गुणों का निर्धारण उनकी प्लास्टिसिटी में सुधार के लिए एक महत्वपूर्ण प्रयास है। इंडेंटेशन तकनीक को आमतौर पर BMG के यांत्रिक व्यवहार का आकलन करने के लिए चुना जाता है, मुख्य रूप से नमूना तैयार करने में आसानी और छोटे नमूना संस्करणों से विश्वसनीय डेटा अधिग्रहण के कारण। एक अन्य महत्वपूर्ण पहलू यह है कि BMG के इंडेंटेशन के दौरान, बाधित विरूपण स्थितियों के कारण पर्याप्त संख्या में कतरनी बैंड बनते हैं। इसलिए, इंडेंटेशन का उपयोग करके BMG के यांत्रिक व्यवहार को समझने की खोज में, हम BMG के यांत्रिक गुणों पर मुक्त मात्रा की भूमिका की जांच करके इस थीसिस को शुरू करते हैं। BMG में परमाणु पैकिंग की अव्यवस्थित प्रकृति के कारण, कतरनी बैंड के विकास पर मात्रात्मक और गुणात्मक जानकारी निकालने के लिए बाद के अध्ययन में कतरनी ताकत का सांख्यिकीय विश्लेषण किया जाता है। अंत में, हम थोक धातु ग्लास कंपोजिट (BMGC) में क्रिस्टलीय चरण के साथ कतरनी बैंड इंटरैक्शन और तापमान के साथ प्रॉक्सी माप के रूप में बाधा कारक का उपयोग करके हाइड्रोस्टैटिक तनाव या दबाव संवेदनशीलता के संदर्भ में उपज मानदंड पर चर्चा करते हैं।

पहले अध्ययन में, Zr -आधारित BMG की मुक्त मात्रा सामग्री को अल्पकालिक एनीलिंग उपचार के माध्यम से विविध किया गया है। इस प्रक्रिया में अल्पावधि के लिए ग्लास संक्रमण तापमान, T_g , के ऊपर और नीचे BMG को गर्म करना, इसके बाद संरचना की यादृच्छिकता को संरक्षित करने के लिए शमन करना शामिल था। जिस तापमान पर नमूना गर्म किया जाता है उसे काल्पनिक तापमान, T_f , कहा जाता है, क्योंकि यह उस तापमान को संदर्भित करता है जिस पर संतुलन तरल की संरचना ठोस ग्लास की संरचना के समान होती है। डिफरेंशियल स्कैनिंग कैलोरीमेट्री (DSC) के माध्यम से यह पाया गया है कि उच्चतम T_f वाले नमूने में एन्ट्रोपिक विचारों के कारण उच्चतम मुक्त मात्रा सामग्री होती है। इसके बाद, संपूर्ण सामग्री में मुक्त मात्रा में विविधता के व्यापक अध्ययन की सुविधा के लिए 100 गोलाकार इंडेंटेशन परीक्षण आयोजित किए जाते हैं। जांच से पता चला कि

स्थानीय कतरनी उपज शक्ति, τ_y , और प्लास्टिसिटी T_f के साथ बढ़ती है। ताकत और प्लास्टिसिटी में भिन्नता को समझाने के लिए सूक्ष्म विरूपण मॉडल का उपयोग किया जाता है।

ध्यान दें कि BMG की स्थानीय कतरनी उपज ताकत, τ_y , उस लोड से मापी जाती है जिस पर पहला पॉप-इन होता है, P_{FP} , लोड में, P , बनाम विस्थापन, h , गोलाकार-टिप नैनोइंडेंटेशन के दौरान वक्र। BMG में परमाणु पैकिंग की अव्यवस्थित प्रकृति के कारण τ_y महत्वपूर्ण विविधता प्रदर्शित करता है। सामग्री में प्लास्टिसिटी के सूक्ष्म वाहकों पर मात्रात्मक और गुणात्मक जानकारी निकालने के लिए मौजूदा अध्ययनों में τ_y का सांख्यिकीय विश्लेषण किया जाता है। साहित्य समीक्षा से पता चला है कि 3-पैरामीटर वेइबुल मॉडल τ_y में फैलाव का सबसे अच्छा वर्णन करता है क्योंकि BMG में उपज संरचनात्मक कमजोर लिंक पर शुरू होती है, जो कम परमाणु पैकिंग या उच्च मुक्त मात्रा वाले क्षेत्र हैं। हमारे अध्ययन से आगे पता चला कि 3-पैरामीटर वेइबुल मॉडल दूसरे पॉप-इन इवेंट के लिए भी सबसे उपयुक्त है। इसके अतिरिक्त, यह देखा गया है कि जब बड़ी त्रिज्या वाले इंडेंटर्स का उपयोग किया जाता है या जब परीक्षण की लोडिंग दरें अपेक्षाकृत अधिक होती हैं तो वितरण द्वि-मोडल हो जाता है। जब संरचनात्मक स्थिति एज़-कास्ट से संरचनात्मक रूप से शिथिल हो जाती है तो वितरण एकरूप हो जाता है। इसे विभिन्न तनावों पर संचालित होने वाले कतरनी बैंड पथों की संख्या की उपलब्धता के आधार पर तर्कसंगत बनाया गया है। फिर यह निष्कर्ष निकाला गया कि एज़-कास्ट और संरचनात्मक रूप से आराम की स्थिति में अपरूपण बैंड की ताकत विकृत BMG की ताकत से लगभग 8-11% और 15-17% कम है।

इसके अलावा, कतरनी बैंड के अबाधित प्रसार के कारण, जिसके परिणामस्वरूप आम तौर पर एकअक्षीय तनाव के तहत उपज के तुरंत बाद BMG की विफलता होती है, साहित्य में प्लास्टिसिटी में सुधार के लिए विभिन्न रणनीतियों का लगातार पता लगाया जाता है। समग्र दृष्टिकोण को नियोजित करना, जो BMG मैट्रिक्स में कतरनी बैंड के प्रसार को बाधित करने वाली एक सूक्ष्म संरचना का परिचय देता है, प्लास्टिसिटी को बढ़ाने के लिए सबसे प्रभावी तरीका है। बड़े पैमाने पर अध्ययन किए गए कई BMGCs में से, वे मिश्र धातुएं जो जमने पर अनाकार मैट्रिक्स के भीतर β -Ti चरण के क्रिस्टलीकरण को प्रदर्शित करती हैं, ताकत और लचीलेपन के उत्कृष्ट संयोजन के कारण विशेष रूप से आशाजनक हैं। जबकि कई अध्ययनों ने इन BMGCs की लचीलापन में सुधार पर ध्यान केंद्रित किया है, इन कंपोजिट में प्लास्टिक विरूपण की दबाव संवेदनशीलता को अभी तक संबोधित नहीं किया गया है। इन मिश्र धातुओं की दबाव संवेदनशीलता को निर्धारित करने के उद्देश्य से, हमने डेंड्राइट के साथ दो Zr/Ti -आधारित BMGCs पर विचार किया, एक मामले में, तनाव के

तहत α'' -Ti में परिवर्तित हो गया और दूसरे में स्लिप द्वारा विकृत हो गया। हमने अपना अध्ययन उनकी कठोरता, H , और उपज शक्ति, σ_y , का निर्धारण करके शुरू किया। उल्लेखनीय रूप से, कठोरता मान संपीड़ित उपज शक्ति मान से अधिक है, जिसके अनुपात को बाधा कारक कहा जाता है, C । प्रासंगिक साहित्य की गहन समीक्षा के माध्यम से, हमने पाया कि BMG विशेष रूप से हाइड्रोस्टैटिक तनाव के प्रति संवेदनशील हैं, जो क्रिस्टलीय सामग्रियों से अलग एक विशेषता है, जहां उपज मुख्य रूप से विचलन संबंधी तनावों के कारण होती है। यह अद्वितीय गुण ~ 3.28 के C और BMG में तापमान के साथ बढ़ती प्रवृत्ति में योगदान देता है। हमारे प्रायोगिक अध्ययन से पता चला कि परीक्षण के न्यूनतम तापमान पर दो BMGC का C BMG की तुलना में 13-50% अधिक है। इसके अलावा, बढ़ते तापमान के साथ, गैर-रूपांतरित डेंड्राइट (BMGC-NT) वाले BMGC के मामले में बाधा कारक बढ़ जाता है, लेकिन ट्रांसफॉर्मिंग डेंड्राइट (BMGC-T) वाले मामले में बाधा कारक कम हो जाता है। इन विविधताओं को कठोरता और एकअक्षीय संपीड़न परीक्षण में व्यक्तिगत चरणों के प्रवाह तनाव भिन्नताओं के आधार पर तर्कसंगत बनाया गया है। प्लास्टिसिटी के इस विशिष्ट पहलू में अंतर्दृष्टि प्राप्त करना प्रक्रियाओं के निर्माण के लिए महत्वपूर्ण महत्व रखता है।

कुल मिलाकर, यह थीसिस ताकत और प्लास्टिसिटी पर संरचना के प्रभाव, BMG के गोलाकार टिप नैनोइंडेंटेशन के दूसरे 'पॉप-इन' व्यवहार के सांख्यिकीय विश्लेषण और BMG और BMGC में दबाव संवेदनशील प्रवाह की तापमान निर्भरता पर चर्चा करती है।

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