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Review

Thermal and Thermomechanical Analysis of Amorphous Metals: A Compact Review

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Abstract: Metallic glasses are amorphous metals that are supercooled to a frozen, glassy state and lack long-range order, in contrast to conventional metal structures. The lack of a well-ordered structure largely contributes to the unique properties exhibited by these materials. However, their synthesis and processability are defined and thereby constrained by a plethora of thermal and mechanical parameters. Therefore, their broader utilization in the scientific field and particularly in the related industry is somewhat hindered by the limitations related to preparing them in higher amounts. This may be overcome by changing the approach of metal glass formation to a bottom-up approach by utilizing solid-state plasma techniques, such as spark plasma ablation. Another important aspect of amorphous metals, inherently related to their non-equilibrium metastable nature, is the necessity to understand their thermal transformations, which requires unconventional thermal analysis methods. Therefore, this minute review aims to highlight the most important conceptual parameters behind configuring and performing conventional and advanced thermal analysis techniques. The importance of calorimetry methods (differential and fast scanning calorimetry) for the determination of key thermal properties (critical cooling rate, glass-forming ability, heat capacity, relaxation, and rejuvenation) is underscored. Moreover, the contributions of thermomechanical analysis and in situ temperature-dependent structural analysis are also mentioned. Namely, all of the mentioned temperature-dependent mechanical and structural analyses may give rise to the discovery of new glass systems with low critical cooling rates.

Keywords: thermal analysis; thermomechanical analysis; amorphous metals; fast scanning calorimetry

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1. Introduction

1.1. Amorphous Metals: Structure and Properties

Amorphous metals, also known as metallic glasses or bulk metallic glasses (BMGs), are a class of materials that have been researched for the past few decades due to their unique non-crystalline atomic structure. Unlike the conventional crystal structure of a metal, amorphous metals lack long-range atomic order, resulting in a disordered, glassy structure [1]. These materials possess remarkable properties that make them highly attractive for various applications.

One of the main advantages of amorphous metals is their superior mechanical strength. In contrast to crystalline metals, which can deform through dislocation movement along specific crystallographic planes, amorphous metals are far superior as their long-range order does not exist and therefore they do not possess any specific slip planes [2]. As a result, they can achieve higher strengths [3], often exceeding those of their crystalline counterparts by orders of magnitude. The yield strength, combined with their high elastic limit and plastic strain [4], makes amorphous metals suitable for applications where a high degree of mechanical performance is needed, such as in sports equipment [5], aerospace components [6], and sensing instruments [7].

Another important property of amorphous metals is their excellent resistance to corrosion [8]. Due to their lack of grain boundaries and the absence of crystalline defects,

amorphous metals exhibit superior resistance to chemical attacks and corrosion compared to their structural counterparts within a certain composition range [9]. This property makes them attractive for use in harsh environments, such as in marine applications [10] and medical implants [11].

These materials also possess unique magnetic properties. Amorphous alloys, like those based on Fe [12] and Co [13], exhibit soft magnetic behavior, making them suitable for applications in transformers, electrical motors, and magnetic shielding [14]. Other amorphous alloys, such as Nd-based materials, exhibit hard magnetic behavior, finding applications in permanent magnets and magnetic recording media [15,16].

1.2. Amorphous Metals: Preparation Techniques

Despite their exceptional properties, the production of amorphous metals presents a significant challenge. To achieve the desired amorphous structure, rapid cooling from the molten state is required, typically at rates exceeding 10^6 K s^{-1} [2]. This rapid solidification prevents the formation of crystalline phases and allows the retention of the disordered atomic structure [17]. Various techniques, such as melt spinning [18], vapor deposition, and thermal spraying [19], are employed to produce amorphous metal ribbons, coatings, and thin films [20]. The development of bulk metallic glasses (BMGs) has further expanded the potential applications of amorphous metals [21] due to overcoming the limitations of conventional amorphous metal ribbons and thin films. This was mostly achieved by tuning the composition and improving the glass-forming ability of some systems and reducing the critical cooling rate to numbers as low as 10 K s^{-1}. This achievement has opened up new opportunities for structural applications [22], biomedical implants [23], and advanced engineering components [24]. The numerous advantages and potential applications of bulk metallic glasses and amorphous metals have placed them in the forefront of research and development [25], with ongoing efforts to optimize their compositions [26], glass-forming ability [27], and production processes [28], and explore their diverse applications across various industries.

1.3. Amorphous Metals: Preparation by Ablation Techniques

One of the more interesting methods to produce metals with a highly disordered structure is ablation, induced either by laser or spark [29]. The approach to material synthesis here is bottom-up, where the target material is sublimated by high-energy plasma, which is also in some cases able to ionize the metallic vapor itself. The vapor then condensates, solidifying into primary particles of good local nanohomogeneity, and depending on the cooling rate of the particles, they either aggregate and crystallize or are frozen in the glassy state [30]. Laser ablation is usually performed in strong vacuum systems ($<10^{-3}$ Pa), while spark ablation can be performed under atmospheric conditions with a carrier gas. This carrier gas can be used to achieve a wide range of cooling rates, which is an obvious advantage for the synthesis of metallic glasses [31,32]. Nowadays, plasma techniques such as laser or spark ablation are proving highly useful for laboratory studies of new systems. Spark ablation shows promising potential for scaling up and advancing research into industrial applications, such as coatings [33,34], powders [35], and possibly even working parts, as evident by the already utilized spark plasma sintering [36].

1.4. Amorphous Metals: Characterization Techniques

Some of the crucial tools that have been employed to closely monitor the development of BMGs and amorphous metals every step of the way are state-of-the-art characterization techniques. These include thermal characterization techniques, such as differential scanning calorimetry and fast scanning calorimetry; mechanical analysis techniques, which involve the measurement of any kind of mechanical property (strain, hardness, deformation, etc.) with respect to the applied mechanical stress [37]; and structural analysis methods, such as electron and neutron diffraction and scattering. Additionally, spectroscopy methods, such as Fourier transform infrared spectroscopy and Raman spectroscopy, have been employed

as helpful tools in resolving the complex structural challenges that metallic glasses present. Moreover, microscopy has always provided good insight into systems from a morphological viewpoint, and has thus been used consistently, both in the past and present day [38]. These techniques have revealed and enhanced the understanding of many mechanisms and kinetic processes involved in glass formation. Advanced structural analysis has been used to link varying compositions to their physical and chemical properties [39], and mechanical analysis is obviously important, as it speaks to the application potential of newly developed materials, but out of all of them, thermal analysis seems to play a pivotal role in the modern development of new materials. This is because in recent decades, thermal analysis has expanded into a whole new range of techniques with newfound precision and sensitivity, such as fast scanning calorimetry [40]. Thermomechanical analysis, as a family of techniques focused on the study of the interplay between thermal and mechanical properties of the material, has witnessed a great improvement with upgraded sensing and temperature modulation equipment. With the rapid development and broadening of research techniques, it is important to summarize and give a simplified overview of the technical improvements, which have helped overcome many challenges that this class of materials poses. It is also important to highlight the versatility to which modern science has had to resort in order to resolve some of these issues. For example, nowadays one might even consider resolving the structure of materials in situ with a temperature-dependent thermal analysis; thus, it has become important to discern between a plethora of methods and their impact on research in the field.

In this work, we will review the most important thermal analysis methods, which have contributed and continue to add to the development of amorphous metals and bulk metallic glasses. Moreover, in situ structural analysis under temperature control will also be discussed.

2. Thermal Characterization of Amorphous Metals

2.1. A Brief Overview of Conventional Technology

2.1.1. Differential Scanning Calorimetry of Metallic Glasses

Conventional thermal analysis implies differential thermal analysis (DTA) and differential scanning calorimetry (DSC), both of which are methods that measure heat flux differences between a reference sample and the measured sample. The main difference lies in the collected signal; for DTA, that is the temperature difference between a reference sample and the measured sample, while for DSC, that is the direct heat flux difference between a reference sample and the measured sample. For DSC, this commonly involves different power outputs being applied to the heaters to keep the reference and measured samples at the same temperature. On the other hand, DTA is capable of simultaneous thermogravimetric analysis (TGA), which is the measurement of the sample's mass, while DSC is not. Calorimetry methods use a flat heater and a crucible in which the sample is deposited, which can achieve an average cooling rate of around 50 K min^{-1} and a maximum heating rate of 200 K min^{-1} [41]. It is a standard method of analysis for amorphous metals, primarily for the determination of the glass transition temperature [42] and critical cooling rates, which, along with the melting point of the alloy, define the metal's glass-forming ability (GFA), best described by Equation (1) [43]:

$$\gamma_m = \frac{2T_x - T_g}{T_l} \quad (1)$$

where T_x, T_g, and T_l stand for crystallization onset, glass transition onset, and liquidus temperature, respectively. The best glass-forming ability criterion has already been discussed and studied systematically, and was shown to be the one presented in Equation (1) due to the physical definitions of the parameters and the range of applicability. For further insight into all the proposed GFA criteria and their correlation with critical cooling rate, as well as their validity, we highly recommend the work of Guo et al. [43], as it will not be discussed further in the scope of this work. Critical cooling rate R_c is measured in

many ways, depending on the studied system. One of the most common methods is the continuous cooling method, where a number of discrete cooling rates are applied until a fully amorphous structure is obtained. It is quite easy but requires a substantial amount of experimental work [44]. The Colmenero and Barandiaran (CB) method requires fewer experiments and involves measuring T_l at a constant heating rate and the temperature of solidification T_{xc} at varying cooling rates [45]. Another important method is the time–temperature–transformation (TTT) curve method, which relies upon constructing a TTT diagram that defines the time required at any temperature to form a volume fraction of crystallized species. The critical cooling rate is defined as the slope that nearly reaches the TTT curve:

$$R_c = \frac{T_m - T_n}{t_n} \quad (2)$$

where T_m is the melting temperature, and T_n and t_n are temperature and time from the TTT curve [46].

2.1.2. Possibilities of DSC for Metallic Glasses

Liu et al. studied the influence of composition on the properties of $Pd_{79}Cu_{6-x-y}Au_xAg_ySi_{10}P$ glassy ribbons using conventional DSC at heating and cooling rates of 0.33 K s^{-1}, and they found that there exists an optimal ratio for the addition of Ag and Au glass formers, which stands at 2% and 1%, respectively [47]. It is also possible to calculate the crystallization activation energy in order to gain insight into the kinetic processes [48]. Frey et al. investigated the kinetics of Mg-based glasses [49], while Mandal et al. researched the crystallization kinetics of $Cu_{60}Zr_{25}Ti_{15}$ and $(Cu_{60}Zr_{25}Ti_{15})_{95}Ni_5$ bulk metallic glasses using the Arrhenius and Avrami models to calculate activation energy and kinetic parameters, respectively [50].

2.1.3. Challenges of Conventional Calorimetry Methods for the Case of Amorphous Metals

However, conventional DSC methods cannot produce very high heating and cooling rates, which would be representative of the kinetic processes during metal glass formation [51]. Namely, in a regular DSC configuration, the samples are placed inside a crucible, which reduces the heat transfer from the heater to the sample and from the sample to the sensor, ultimately limiting the detection limit and time response of the measured parameters. For decades, studying and determining glass formation parameters for bulk metallic glasses, which vitrify rapidly through quenching, has been a persistent challenge. These issues have impeded important discoveries regarding the mechanisms of glass formation in various promising systems.

2.2. Fast Scanning Calorimetry of Amorphous Metals

2.2.1. Configuration Considerations

To overcome the challenges that the conventional calorimetry methods face when aiming to describe the amorphous metals, fast scanning calorimetry (FSC) has risen as one of the most prominent methods to study these processes. It is a modified variation of DSC that surpasses the physical and practical limits of its predecessor [52]. First off, the samples are placed directly on a micro-electromechanical system (MEMS) dual sensor chip with a ceramic frame, which holds two silicon nitride membranes: one acting as a reference and the other as the sample. Silicon nitride is widely recognized for its excellent mechanical properties, and studies have indicated that it does not affect measurement accuracy or sensitivity [53]. Direct contact of the sample to the sensor allows for better heat transfer during heating and cooling and provides an ultrafast and sensitive sensor response, making it possible to study samples that undergo subtle transformations, degrade quickly, or are unstable [54]. Two kinds of sensors are used, depending on the temperature range needed: MultiSTAR UFS1 sensor (Mettler, Toledo, OH, USA) for temperatures up to 450 °C and the MultiSTAR UFH1 sensor (Mettler, Toledo, OH, USA) for temperatures up to 1000 °C. The difference in execution of the MEMS chip lies in the area of the sample and reference: 500 and 80 µm for the UFS and UFH sensors, respectively [55]. The UFH sensor is ideal for

analyzing bulk metallic glasses, but the area is much smaller. FSC has proven that at high heating and cooling rates, complex composite systems, such as BMGs, often undergo only one crystallization instead of multiple transitions (Figure 1).

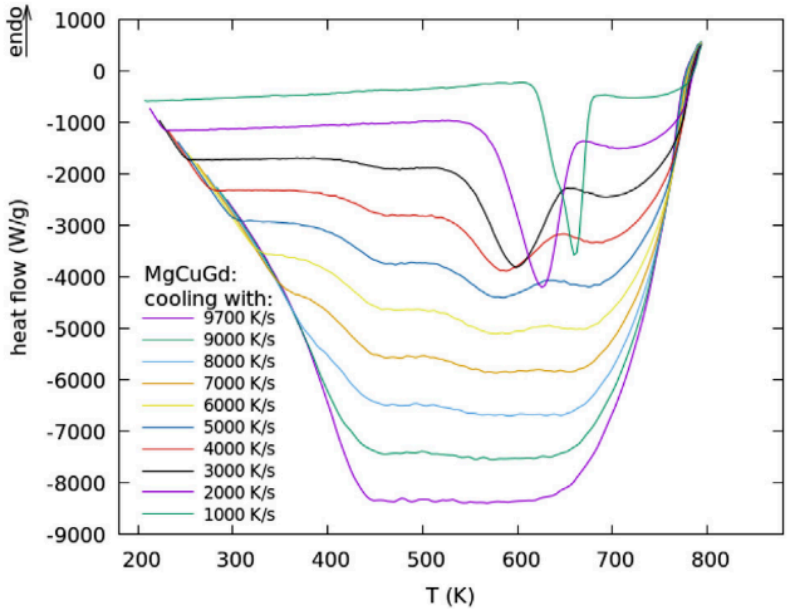


Figure 1. Fast scanning calorimetry of MgCuGd glasses at different cooling rates. A distinct peak (glass transition) diminishes at high cooling rates, indicating a shift in the glass formation mechanism (reprinted with permission via CC Attribution 4.0 License) [56].

This can also be observed in other studies, such as the work of Zhao et al., who proposed the existence of three regimes, varying from deeply undercooled to slightly undercooled liquids. They found that for the highly undercooled liquid (high heating and cooling rates), the energy of activation was independent of the heating rate as opposed to the slightly undercooled liquid [57,58]. Generally, it can be said that in the deeply undercooled regime, crystallization is controlled only by pre-existing nuclei [59,60]. Furthermore, the true values of the critical cooling rate can be measured with ease, and it has been shown that the critical cooling rate and general crystallization kinetics depend on the sample mass. However, the sample mass needs to be in the range of $<10^1$ µg and loaded onto a sensor chip, which complicates sample preparation [53] (Figure 2). Schawe et al. showed that there are various critical cooling rates, which can lead to different glasses for the same material. In their work, they utilized FSC for the analysis of two glasses, one cooled at 500 K s^{-1} (self-doped glass) and the other at 20,000 K s^{-1} (chemically homogeneous glass), and their findings concluded that there are various nucleation mechanisms that govern glass formation [61].

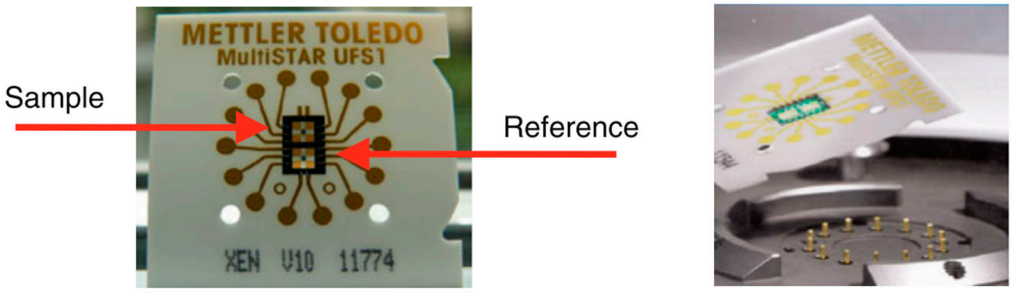


Figure 2. MultiSTAR UFS 1 MEMS chip sensors for sample loading: sample and reference sensor sites are on the left, while the 14 connectors of the Flash DSC (fast scanning calorimetry instrument by Mettler Toledo) are on the right (reprinted with permission via CC Attribution 4.0 License) [54].

2.2.2. Expansion of Measurable Transitions by Utilizing FSC

The utilization of this method extends to the study of rejuvenation processes in amorphous alloys. Annealing metallic glasses above their T_g followed by rapid cooling potentially increases their enthalpy, ΔH [62,63]. The magnitude of the material's rejuvenation has been found to depend on the ratio of effective cooling (Φ_c) and post-annealing cooling rates (Φ_i), whereas experimental evidence of rejuvenation saturation with long enough annealing time has also been revealed [64]. Rejuvenation, a structural change that is usually obtained thermally or mechanically, plays an important role in the mechanical properties of amorphous metals in their glassy state, and it is often described as a process where the glass undergoes heavy internal strain in order to introduce structural disorder, which improves the desired properties related to amorphous structures. FSC has significantly improved the cooling rate, which allows for the determination of the change in enthalpy under plastic deformation, ultimately providing information on the relaxation processes in ribbon-like melt-spun metallic glasses [65] and thin films [66]. BMGs also seem to show a sub-T_g shadow glass transition at very high heating rates, correlated to the heterogeneity of the glass, which increases with aging.

2.3. Improvements to the Temperature Control—Temperature Modulation

Furthermore, one of the key aspects of FSC that has proven to be essential for distinguishing and studying the metastable phases, which appear during the vitrification, process [67] is the ability to determine the heat capacity of each of these phases in comparison to conventional DSC, where the measurement is much slower and a lot of the data on the short-lived phase changes cannot be appropriately collected. Temperature-modulated DSC (TMDSC) with the stochastic modulation of temperature (TOPEM) is being used for the highest accuracy of results [68]. It is a technique of DSC where stochastic temperature modulation is superimposed on a conventional DSC program, in comparison, to TMDSC, which superimposes a sinusoidal heating/cooling rate. Additionally, it does not need a reference sample and shows better repeatability and more representative results [69]. Sample mass is usually determined by conventional DSC through measuring the heat capacity or enthalpy of a known substance. Manoel et al. investigated two differently thermally modified $Pd_{40}Ni_{40}P_{20}$ metallic glasses obtained by different thermal cycling treatments for the purposes of measuring and identifying β- and α-relaxation modes, which correspond to the shadow glass transition and enthalpy recovery, i.e., rejuvenation, respectively. Using TOPEM DSC coupled with a structural analysis of medium-range order (MRO), they found that MRO in glasses can be influenced by sub-T_g quenching and annealing, which could lead to new properties of bulk metallic glasses [70].

2.4. Challenges of the Advanced Calorimetry Methods for the Case of Amorphous Metals

Regarding the calorimetric analysis of metallic glasses, most of the advancement has been shown to be a consequence of the shift in the practical approach, that is, the execution of the instrumental setup. However, certain drawbacks are still present for bulk metallic glasses, such as depositing a representative sample onto an 80 × 80 μm surface when analyzing, e.g., the formation of more complex systems consisting of multiple solid precursors. In the future, methods that achieve nanoscale homogeneity, such as laser or spark ablation combined with aerosol direct writing, could potentially be used to prepare representative samples.

3. Thermomechanical Characterization of Amorphous Metals

3.1. Introduction to Conventional Measurements

The thermal analysis of all solid materials has always been closely followed by mechanical and thermomechanical analysis (TMA), which is a method where deformation (elongation) is measured as a function of temperature [37]. However, in modern times, the definition and application have expanded somewhat to include a range of techniques in order to determine, to the full extent, the temperature dependency of mechanical properties,

such as the Young and shear modulus, the degree of plastic deformation, and hardness [71]. Moreover, the wide range of techniques that can fit into this extended category may also be utilized to apply mechanical load or stress in order to determine and analyze various thermodynamic parameters, such as glass transition temperature, thermal expansion coefficients, softening, and structural behavior [72], including relaxation processes due to internal stress [37]. The transition to viscous flow has been experimentally determined and modeled by measuring elongation with increasing temperature. TMA has also been utilized to determine the viscosity and fragility indexes in the glass transition region, where Jiang et al. observed an increase of almost an order of magnitude within the T_g/T range of 0.9–1.02 [73].

3.2. Possibilities of TMA for Metallic Glass Analysis

Meylan et al. studied the effects of the uniaxial compression of $La_{55}Al_{25}Ni_{20}$-based glasses under three different loads and analyzed the relaxation processes using FDSC by varying the time after deformation at which the analysis was performed. They concluded that under plastic deformation, the enthalpy of the material increases, but only by a fraction of the mechanical work applied to the samples (~3%), and while this is not unusual for the glassy state of amorphous metals, it is still low compared to, e.g., polymers in their glassy state, which can store, on average, an order of magnitude more energy than glassy metals. By performing stability measurements, they also observed that the stored energy is lost after ~24 months in all the samples. However, they proved that mechanical rejuvenation can be as effective as thermal rejuvenation following their previous work [65] (Figure 3).

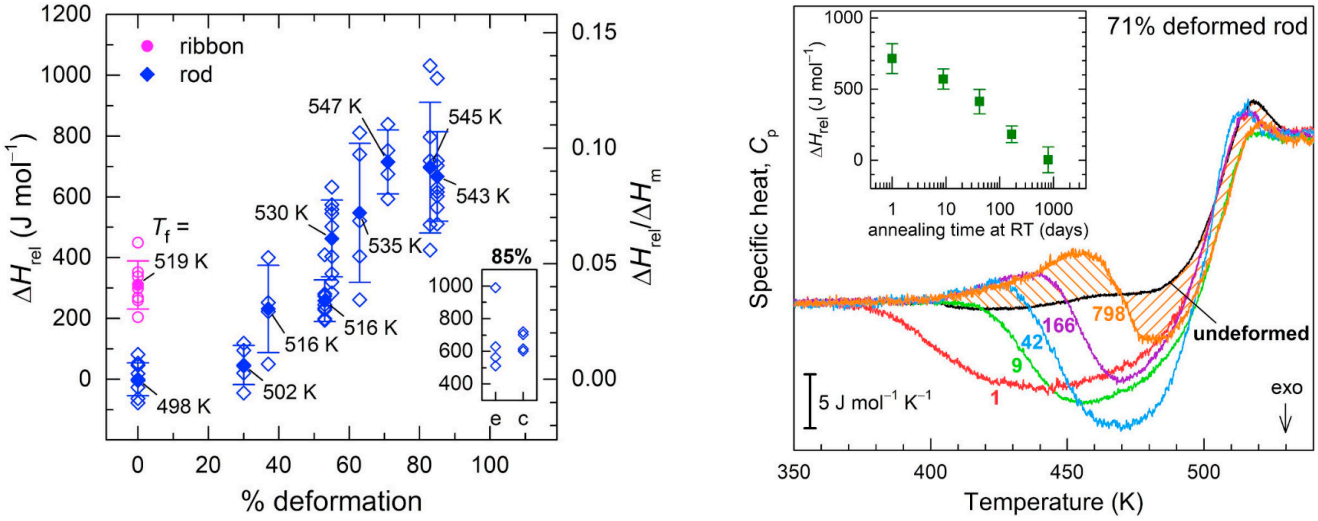
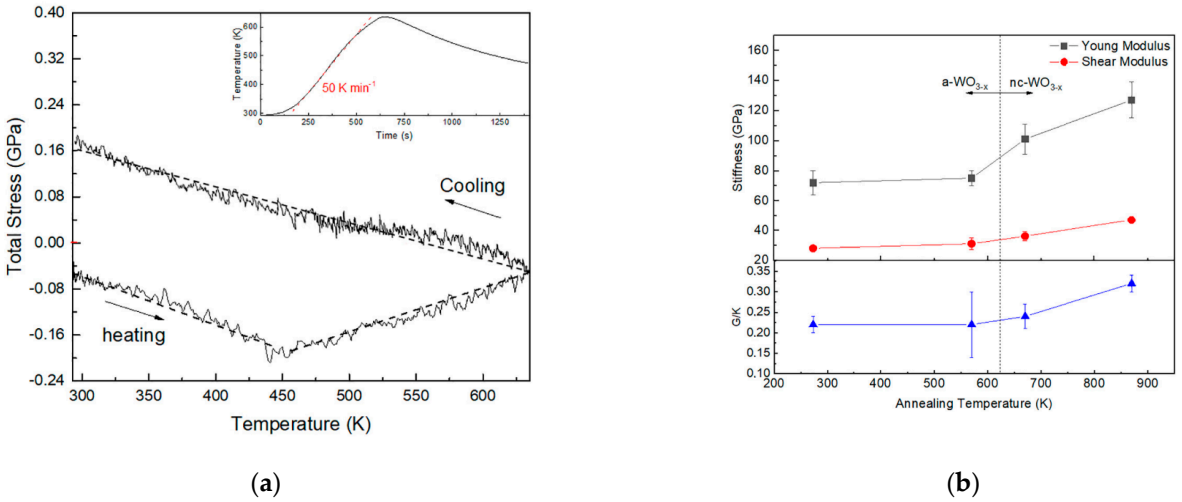


Figure 3. (**a**) The increase in enthalpy (ΔH) after compression at varying degrees of deformation and (**b**) specific heat curves show a shift in thermal behavior of the material with increasing heating rate from 1 to 798 K min^{-1} (reprinted with permission via CC Attribution 4.0 License; multiple Figures were merged for a better overview of the authors' work) [65].

Greer et al., however, studied the effects of elastostatic load (EL) and cryogenic thermal cycling (CTC) on the ability to induce rejuvenation in $Pd_{43}Cu_{27}Ni_{10}P_{20}$ glasses. In their work, CTC was executed by cooling with nitrogen, while the EL measurements were performed at 85% of the components' yield stress. They observed that neither EL nor CTC have any effect on T_g, T_c, or enthalpy of crystallization. The experimental data indicated that both processing techniques result in an increase in stored energy. However, thermomechanical analysis revealed that this increase does not correspond to rejuvenation. This conclusion is drawn from the different correlations observed between enthalpy and density changes in samples processed using EL and CTC methods compared to conventionally prepared metallic glasses that underwent rapid quenching. Furthermore, they propose

that the mechanism of enthalpy increase is structurally driven, activated by the shear transformation zones, which possess locally increased entropy (because their deformation is thermodynamically favored) that draws in the heat upon mechanical deformation, resulting in increased stored energy within the material [74]. There are reports on thin films as well, where thermomechanical analysis has proven useful in identifying the best mechanical properties of metallic glass thin films for various applications under thermal load (photo- and thermophotovoltaic and sensing applications) where the interface and morphology play a crucial part in the proper functioning of the device [75,76]. Bessozzi et al. deposited thin films of tungsten oxide by laser ablation and studied the mechanical properties with annealing. Thanks to the versatility of laser ablation, they were able to reproduce various morphologies, which allowed them to observe the change in total stress as a result of grain growth and diffusion processes, leading to the shrinkage of the material, which can be observed as a change in the slope in Figure 4a. Figure 4b shows multiple moduli that can be monitored as a function of annealing temperature [77].



(**a**) (**b**)

Figure 4. (**a**) The change in total stress as a function of heating and (**b**) varying moduli as a function of annealing temperature for deposited tungsten oxide coatings. The blue line, *G/K* represents a shear to bulk modulus ratio, which is representative of the ductility of the material. It can be seen that the stiffness increases during crystallization and grain growth, followed by an increase in density. (reprinted with permission via CC Attribution 4.0 License; multiple Figures were merged for a better overview of the authors' work) [77].

3.3. Challenges of the Advanced Thermomechanical Methods for the Case of Amorphous Metals

Thermomechanical analysis has emerged as a crucial technique for processing and studying amorphous metals and metallic glasses, thanks to its capability to analyze materials across all solid configurations, including thin films. Since the sample size for these methods is inherently sufficient to represent the bulk, they do not encounter significant challenges in terms of measurement limitations. However, an intriguing approach to temperature control has emerged through modulated temperature techniques [74], which have also been applied to this method. This allows for distinguishing between reversible and irreversible changes [75], potentially enhancing the understanding of the crucial properties of metallic glasses, such as relaxation kinetics and rejuvenation mechanisms.

4. In Situ Temperature-Dependent Structural Characterization of Amorphous Metals

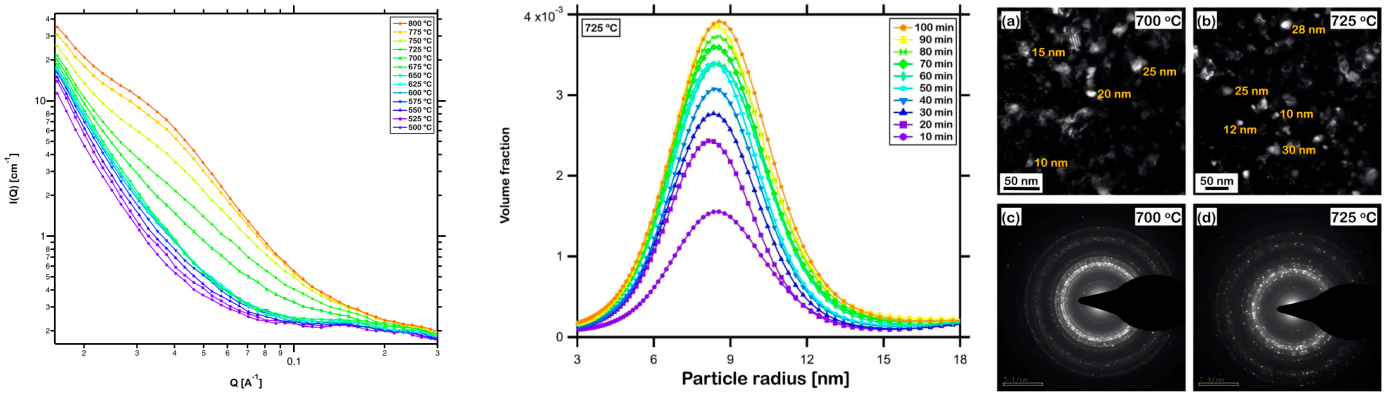
4.1. Possibilities of In Situ Structural Analysis

Although temperature-dependent structural analysis using X-ray and spectroscopic methods may not be conventional, it is valuable to explore the insights these techniques can provide. This exploration can help better understand the aspects and challenges involved in the development of amorphous metals and bulk metallic glasses [78]. These materials must

possess an amorphous structure, characterized by short-range order within the system. Therefore, diffraction techniques such as electron and neutron diffraction, applied to both bulk and thin film configurations, are typically used initially to confirm the absence of long-range order before any scientific investigation begins [79]. Gregoire et al. combined nanocalorimetry with synchrotron-grade X-ray diffraction to analyze the supercooled quenched metallic glasses, where they managed to vaguely correlate crystallization kinetics with glass-forming ability [80]. It is also possible to study application properties via X-ray diffraction, given that a good enough source is provided. Bednarcik et al. studied the in situ formation of nanocrystalline Fe metallic glassy alloys, and they tracked the shift in magnetic behavior with respect to the temperature at a constant heating rate. They also derived pair distribution functions (PDFs) to describe the crystallization kinetics [81]. Moreover, local atomic structure can be investigated by spectroscopic techniques such as FTIR and Mossbauer spectroscopy [82]. However, this short-range order can nowadays be determined accurately enough to show differences in structure during even subtle structural changes, such as relaxation and rejuvenation processes.

4.2. Medium-Range Order and Bridging the Gap between the Precursor Treatment and Application Properties

Mattern et al. studied the change in structure of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ metallic glass during thermal annealing in situ via synchrotron X-ray diffraction. They confirmed that in the glassy state, thermal expansion is accompanied by atomic rearrangements and an increase in larger interatomic distances [83]. Using small-angle neutron scattering combined with X-ray diffraction, Paul et al. studied the safe temperatures at which a $Fe_{48}Cr_{15}Mo_{14}Y_2C_{15}B_6$ bulk metallic glass can operate by spark plasma sintering the samples to up to 800 °C [84]. X-ray diffraction showed the appearance of $(Fe,Cr)_{23}C_6$ crystals, while the measured scattering intensity, which was fitted to a size distribution model based on the maximum entropy model, showed that the formed crystals were in the size range between 3 and 18 nm, and that they originated from already pre-existing nuclei formed during the rapid quenching process. This was concluded from a kinetics study, which was performed on behalf of the size distributions that were obtained from the measurements (Figure 5).



(**A**) (**B**) (**C**)

Figure 5. (**A**) Logarithm plot of in situ small-angle neutron scattering intensity measured over a small Q range at different temperatures; (**B**) the size distribution of newly formed particles during isothermal crystallization of the spark-plasma-sintered glass also confirmed by (**C**) TEM images of the formed crystals at (**a**) 700 °C and (**b**) 725 °C and selected area diffraction patterns of crystals formed at (**c**) 700 °C and (**d**) 725 °C (reprinted with permission via CC Attribution 4.0 License; multiple Figures were merged for a better overview of the Authors work) [84].

To investigate the influence of transition metals on the formation of $Al_{85}TM_{10}Y_5$ amorphous alloys (where TM corresponds to Ni, Fe, Cr, and Cu) prepared by melt spinning, Babilas et al. also employed laboratory-source X-ray diffraction and performed in situ experiments up to 500 °C, correlated with differential thermal analysis (DTA) and dynamic

mechanical analysis (DMA). A negative impact on GFA with Cr addition was observed. They were able to distinguish the material with the best anticorrosive properties and determine that the precipitation crystallization of the YCrAl phase as well as the presence of Cu shows the better anticorrosion properties when compared to the homogeneous, completely amorphous samples. Their research shows the need for only a few techniques to completely describe and determine the processing parameters and range of stability (time and temperature related) [85].

4.3. Challenges of the Advanced In Situ Temperature-Dependent Structural Methods for the Case of Amorphous Metals

While these techniques are useful for linking processing to the resulting application properties, replicating quenching is challenging from both the standpoint of inducing rapid temperature changes and obtaining accurate time-resolved spectra. Another issue to overcome lies in the inaccessibility of the techniques, which are also spatially resolved and provide information fine enough to study the complex amorphous structure of these materials. The reason there are not many studies conducted in this nature most likely lies in the fact that the combination of in situ temperature control with state-of-the-art spectroscopy or diffraction techniques equipped with detectors and sensors that can detect the signal of the faint medium-range order is financially impossible for most groups, especially when considering that these studies usually only bring rise to discoveries for niche applications.

5. Conclusions, Perspective, and Outlook

Thermal and thermomechanical analysis supported by structural information is a powerful tool to describe the kinetic processes of glass formation as well as their operating range, conditions, and thermal and mechanical stability. Fast scanning calorimetry is shown to be the frontrunner of all the used techniques as its technical development has been followed by the rapid development of bulk metallic glasses as a research topic. It allows for the determination of all transition temperatures, enthalpy of formation, relaxation processes, rejuvenation, and specific heat capacity of very small samples. However, one must consider that the drawback of this method is the very small sample size, which can be detrimental to the repeatability of measurements for systems highly dependent on precursor homogeneity. Possibly, this can be overcome by utilizing bottom-up approaches to metallic glass formation, such as spark ablation.

Thermomechanical analysis offers valuable insights into the structural changes and their impact on mechanical properties, whether induced thermally, mechanically, or both. Advanced structural characterization allows for analyzing how various glass formers influence short- and medium-range order, and correlating these findings with the diverse application properties typical of this class of materials. It has been shown here that glass-forming ability is most significantly influenced by changes in short- and medium-range order, which can be influenced by chemical composition, making the idea of new systems resistant to crystallization even at low cooling rates viable. Even though the correct experimental GFA criterion is still being discussed, the general consensus that a BMG with excellent GFA will have a low critical cooling rate still stands.

It is probable that the combination of thermal, thermomechanical, and structural techniques will pave the way for the development of new amorphous alloys, glasses, and systems capable of forming at low cooling rates. This advancement could enable these materials to surpass size limitations and find applications across a broader spectrum of uses, ultimately providing long lasting, corrosion-resistant, hard materials with excellent durability (Figure 6).

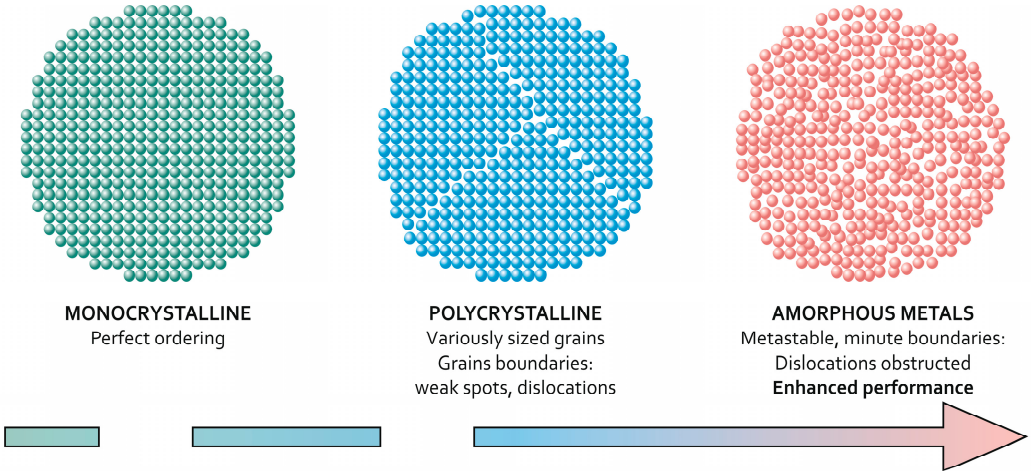


Figure 6. Scheme of how structural organization yields beneficial performance of amorphous metals.

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