



AFRL-AFOSR-UK-TR-2021-0016

The Local Structure and Chemistry in Marginal Glass Forming Alloys

Kalay, Eren
ORTA DOGU TEKNİK UNIVERSITESI
UNIVERSITELER MAHALLESİ, 1
DUMLUPINAR BULVARI
ANKARA, , 6800
TUR

06/24/2021
Final Technical Report

DISTRIBUTION A: Distribution approved for public release.

Air Force Research Laboratory
Air Force Office of Scientific Research
European Office of Aerospace Research and Development
Unit 4515 Box 14, APO AE 09421

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 24-06-2021		2. REPORT TYPE Final		3. DATES COVERED (From - To) 15 Mar 2020 - 14 Sep 2020	
4. TITLE AND SUBTITLE The Local Structure and Chemistry in Marginal Glass Forming Alloys				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER FA9550-17-1-0216	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Eren Kalay				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) ORTA DOGU TEKNİK UNIVERSITESI UNIVERSITELER MAHALLESİ, 1 DUMLUPINAR BULVARI ANKARA, 6800 TUR				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) EOARD UNIT 4515 APO AE 09421-4515				10. SPONSOR/MONITOR'S ACRONYM(S) AFRL/AFOSR IOE	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-AFOSR-UK-TR-2021-0016	
12. DISTRIBUTION/AVAILABILITY STATEMENT A Distribution Unlimited: PB Public Release					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT Research objectives met; deliverables received.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON JASON FOLEY
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U			19b. TELEPHONE NUMBER (Include area code) 555-555-5555

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

Grant Number: FA9550-17-1-0216

Research Title: The Local Structure and Chemistry in Marginal Glass Forming Alloys

P.I. Names: Yunus Eren Kalay (METU)

Ilkay Kalay (Cankaya University)

Period of Performance: 15 March 2017-14 September 2020

Table of Contents

List of Figures	2
Summary	5
1. Introduction	6
2. Methods, Assumptions, and Procedures	7
3. Results and Discussion	12
3.1 Levitation Melting Experiments	12
3.2 EXAFS modeling	15
3.3 Short-range order analysis	21
3.4 Cluster analysis	26
3.5 Mechanical analysis	32
4. Conclusions	36
5. References	38
6. List of Symbols, Abbreviations, and Acronyms	42
7. Project Outputs	44

List of Figures

- Figure 1. From our experiments at SOLEIL DIFFABS Beamline showing the experimental hutch. **8**
- Figure 2. CirPAd detector of Diffabs beamline in Soleil Synchrotron. **9**
- Figure 3. From our experiments at CLÆSS beamline. The inset depicts the path of the X-ray beam for both fluorescent and transmission mode, together with the sample insertion aperture. **9**
- Figure 4. (a) The heating curve of $\text{Al}_{88}\text{Sm}_{12}$ metallic alloy recorded during levitation melting. **13**
(b) The real-time photo of the levitated material upon heating. The red circle shows the formation of oxides on the surface of the metal.
- Figure 5. The real-time video frame of levitated Al-Sm amorphous alloys from room temperature (a) to 805 °C (f). **13**
- Figure 6. HEXRD patterns of $\text{Al}_{92}\text{Sm}_8$ at (a) room temperature, (b) 550 °C, (c) 700 °C and (d) 805 °C. **14**
- Figure 7. Normalized X-ray absorption spectra of $\text{Al}_{90}\text{Tb}_{10}$ melt-spun ribbons at L3 edge of Tb measured in transmission mode at several temperatures. **15**
- Figure 8. K3-weighted $\chi(k)$ graphs of $\text{Al}_{90}\text{Tb}_{10}$ melt-spun alloys at 30°, 250°C, 300°C, and 350°C, respectively. **16**
- Figure 9. Q space data in real space of $\chi(q)$ of $\text{Al}_{90}\text{Tb}_{10}$ melt-spun alloys at 30°, 250°C, 300°C, and 350°C, respectively. **17**
- Figure 10. 3D atomic rendering of the Al-Tb crystal data used in XAFS fitting. Al (pink) and Tb (gray) are color-coded with their respective atomic sizes. **18**
- Figure 11. Experimental EXAFS data (Tb L3 edge) and fit results for $\text{Al}_{90}\text{Tb}_{10}$ melt-spun ribbons at 30°C (a), 250°C (b), 300°C (c), and 350°C (d). The comparison shows the magnitude and the real part of the Fourier-transform. The fitting range is indicated. **20**
- Figure 12. K3-weighted $\chi(k)$ graphs of $\text{Al}_{90}\text{Tb}_{10}$ melt-spun (transmission mode) and magnetron sputtered (fluorescence mode) alloys at 30°, 250°C, 300°C, and 350°C, respectively. **21**
- Figure 13. Total X-ray structure factors of melt-spun ribbon and magnetron sputtered thin-film. **22**

Figure 14. a) Total X-ray structure factor experimental and RMC fit for ribbon, b) EXAFS data and RMC fit for ribbon, c) Total X-ray structure factor experimental and RMC fit for thin-film, and d) EXAFS data and RMC fit for thin film. **23**

Figure 15. (a) RMC simulation box after fitting, (b) close up view of triple $\langle 0,3,6,4 \rangle$ Voronoi cell interacting with each other, and (c) same clusters with face and intercross sharing. **23**

Figure 16. Fifteen most populated Voronoi cells of melt-spun ribbon and magnetron sputtered film for (a) Al centered cells, and (b) Terbium centered cells, Coordination number distribution of melt-spun ribbons and magnetron sputtered films around (c) Al atoms and (d) Tb atoms, most populated Voronoi cells categorized under the structures that they resemble of for (e) Al centered and (f) Tb centered atoms. **25**

Figure 17. (a) and (b) cluster analysis of $\langle 0,2,8,5 \rangle$ Voronoi cells, (c) and (d) network clusters, (e) and (f) separate clusters for melt-spun ribbon and magnetron sputtered film respectively (Clusters were color-coded). Pure Al clusters in the structure for (g) melt-spun ribbon and (h) magnetron sputtered films, fcc-like cluster atoms (red) others (blue). **27**

Figure 18. (a, b) Bright-field images and corresponding SAD patterns (in-sets), (c, d) bright-field images, and (e, f) SAD after initial crystallization of as-quenched ribbon and thin-film $\text{Al}_{90}\text{Tb}_{10}$, respectively. SAD indexing represents fcc-Al reflections. **30**

Figure 19. (a) Continuous DSC traces for melt-spun ribbons and sputtered thin-films collected at 40 K/min heating rate (b) Kissinger and (c) Ozawa plots. **31**

Figure 20. Differential scanning calorimetry traces of $\text{Al}_{90}\text{Tb}_{10}$ samples. Inset showing the annealing temperatures in the first fcc-Al crystallization and second the intermetallic compound formation. **32**

Figure 21. $\text{Al}_{90}\text{Tb}_{10}$ fully amorphous (a) Stress-strain diagram of 4 samples, (b), (c), (d), and (e) SEM images of micropillars and fracture surfaces. **33**

Figure 22. $\text{Al}_{90}\text{Tb}_{10}$ 241 °C heat-treated (a) Stress-strain diagram of 3 samples, (b), (c) and (d) SEM images of micropillars and fracture surfaces. **34**

Figure 23. $\text{Al}_{90}\text{Tb}_{10}$ 251 °C heat-treated (a) Stress-strain diagram of 4 samples, (b) and (c) SEM images of micropillars and fracture surfaces. **35**

Figure 24. $\text{Al}_{90}\text{Tb}_{10}$ 259 °C heat-treated (a) Stress-strain diagram of 3 samples, (b) and (c) SEM images of micropillars and fracture surfaces. **35**

Figure 25. $\text{Al}_{90}\text{Tb}_{10}$ 263 °C heat-treated (a) Stress-strain diagram of 6 samples, (b) and (c) SEM images of micropillars and fracture surfaces. **36**

Summary

In this project, structural and corresponding mechanical properties of marginal metallic glass-forming alloys were studied. $\text{Al}_{90}\text{Tb}_{10}$ system exhibits unique devitrification features due to Al nanocrystals' exceptional primary crystallization products with populations reaching up to 10^{24} m^{-3} . A full agreement on how this abnormal nucleation event occurs is still lacking. Our previous studies on Al-RE (RE: rare-earth element) have shown that two different amorphous precursors prepared using melt-spinning and magnetron sputtering techniques showed apparent differences in phase selection hierarchy upon continuous heating. It is considered that this difference is originated from the medium range ordered structure, which exists in the as-quenched melt-spun ribbon, which is inherited from its molten state. In this study, the local structure, chemistry, and any possible higher-order correlations were investigated by performing critical high energy synchrotron X-ray Diffraction (HEXRD), Extended X-ray Absorption Fine Structure (EXAFS), ab-initio, and Reverse Monte Carlo (RMC) modeling. RE atoms were found to be highly correlated with Al atoms, which results in the formation of a network dividing the amorphous matrix, resulting in abnormal crystallization behavior. The nanocrystals' effects on mechanical properties were investigated via micropillar compression tests, nanoindentation and transmission electron microscopy (TEM). Embedding nanocrystals on the amorphous matrix increased the fracture stress and ductility simultaneously. A further increase in the heat treatment temperature beyond the first crystallization caused the formation of intermetallic compounds, which decreased the ductility while improving the fracture stress.

Keywords: Metallic Glasses, Nanocrystals, Crystallization, Synchrotron XRD, EXAFS, RMC, Micropillar Compression Testing, TEM

1. Introduction

Attributed primarily to its superior properties, metallic glasses have been considered promising materials for engineering applications^{1–8}. On the other hand, applications of metallic glasses are limited because of their near-zero ductility^{8–11}. Due to the formation of highly localized strain during deformation, metallic glasses fail catastrophically after yielding. Metallic glass/nanocrystal composites, on the other hand, have shown improved ductility over the monolithic metallic glasses. Such composite materials can be either prepared through direct solidification^{12,13} or partial crystallization of metallic glasses by heat treatment or deformation^{14,15}. Among the metallic glass/nanocrystal composites, Al-RE (RE: rare-earth element) alloys have remarkable significance. Partial devitrification of the Al-RE marginal metallic glasses results in the unusual number of nanocrystals, on the order of $10^{21-23} \text{ m}^{-3}$, embedded in the amorphous matrix^{16–19}. Despite the volume of the research, an exact explanation for the mechanism underlying the formation of highly populated nanocrystals is still missing^{18,20,21}.

So far, attempts to explain this high nucleation density speculate around several models such as "quenched-in nuclei"^{19,22}, "phase separation in the amorphous state"^{23–25}, and "heterogeneous nucleation"²⁶. "Quenched-in nuclei model" is stating that some small fractions of crystallites nucleate initially during cooling. Their development is prevented by rapidly increasing viscosity with continued cooling near glass transition temperature (T_g). Upon reheating a sample with preexisting crystallites, rapid crystallization ensues at T_g , and these preexisting crystallites grow to nanocrystals. "Phase separation in the amorphous state" relies on phase separation similar to spinodal decomposition resulting in heterogeneous nucleation at the phase boundaries. According to this approach, time-dependent homogeneous nucleation occurs due to the formation of Al-rich and Al depleted zones with a length of 74 to 126 nm²⁵. The other hypothesis to describe the observed high nucleation densities of nanocrystals is the possibility of an extremely large number of heterogeneous nucleation occurring on either impurity site, such as nanoscale oxides²⁷ or clusters of inhomogeneously distributed atoms²⁶. This hypothesis is only observed for a few multi-component amorphous systems. It is still under question since impurities' population usually orders magnitudes lower than the number of nanocrystals formed during devitrification. Other recent studies suggest that during undercooling specific atomic arrangements called "motifs" like ordered icosahedral structures forms and increase in amount as undercooling increases. These regions interact with each other and have different mobility. Therefore, these regions can reach higher undercooling²⁸. When devitrification of the Al-Sm system was analyzed under SAXS/WAXS, the formation of certain metastable and intermetallic phases were confirmed. Moreover, these phases seemed to compete with one another and are highly composition-dependent^{29–31}. Consequently, there is still no agreement on the mechanism of highly populated nanocrystal formation in marginally metallic glass-forming alloys.

We consider that fcc-like medium-range order (MRO) structures inherited from the parental liquid state plays a crucial role in abnormal nanocrystallization of Al-RE (and possibly in other Al-

RE-TM) (TM: transition metals) metallic glass alloys³². To further prove that MRO might be originated in the liquid form, we have produced amorphous Al-RE with the same composition but using different processing techniques. The first set of Al₉₀Tb₁₀ was produced using melt-spinning, and the second set with the same composition was produced using DC magnetron sputtering³³. The phase selection hierarchy of these glassy alloys produced by two different techniques was investigated. Although the fcc-Al nanocrystals were observed as the primary devitrification product in both specimens, the morphology, the average size, and the nucleation density were substantially different. Further investigation also showed that ribbons devitrifies with a metastable hexagonal phase and transforms into a metastable cubic phase. In contrast, the sputtered thin-film suppresses the hexagonal phase and directly changes into the cubic phase upon crystallization. The difference between the crystallization of as-sputtered and as-spun of Al₉₀Tb₁₀ was also detected in thermal analysis results. It was claimed that these differences might be associated with the degree of topological and chemical order within the amorphous precursors. According to this hypothesis, chemical separation up to some degree has already been established in the ribbons that were quenched from the liquid state. We consider that this separation was inherited from the liquid state in the melt-spun ribbons^{32,33}. Some recent molecular dynamics (MD) simulations on fragile binary metallic glasses have shown the existence of first-order freezing transition from liquid (L) to metastable heterogeneous solid-like phase, denoted as the G-glass³⁴, upon isothermally holding below the melting point. This is considered as a metastable non-crystalline phase and indicates the possible existence of ordered structure in the liquid state³⁵. On the other hand, a full description of amorphous structures in melt-spun ribbon and sputtered thin-film via advanced characterization techniques are still missing.

In this project work, high energy X-ray Diffraction (HEXRD) and X-ray absorption fine structure (EXAFS) experimental methods coupled with Reverse Monte Carlo (RMC) simulations and Voronoi tessellation were used to examine the atomic structures formed in melt-spun ribbon and magnetron sputtered film Al₉₀Tb₁₀ alloys. Short-range order (SRO) and MRO in resulting structures were revealed by first neighbor shell and cluster analysis. TEM analyses were conducted to demonstrate the fundamental structural difference in ribbons and thin-films in early crystallization periods. These findings were supported by Kissinger and Ozawa-Matusita thermal analysis methods. The hypothesis of liquid state inhomogeneity resulting in different devitrification paths was attempted to be revealed by liquid state, levitation melting HEXRD experiments. Finally, melt-spun ribbons were analyzed mechanically by Focused Ion beam milling micropillars and performing compression tests. Effects of nanocrystals on mechanical properties and optimum heat treatment temperatures were revealed.

2. Methods, Assumptions, and Procedures

In this project, the samples were produced by arc-melting, melt-spinning, and magnetron sputtering. The major characterization methods used in this study can be summarized as; synchrotron-based X-ray diffraction and X-ray absorption fine structure, transmission electron microscopy, scanning electron microscopy differential scanning calorimetry, focused ion beam milling, and micropillar compression testing. Computational methods used include Reverse Monte Carlo modeling with Voronoi Tessellation and Extended X-ray absorption fine structure modeling. Finally, for thermal analysis Kissinger and Ozawa-Matusita methods were used.

Sample production:

Ingots of Al₉₀Tb₁₀ were produced by arc-melting from highly pure Al (99.99 wt. %) and Tb (99.9 wt. %) elements in an argon atmosphere and re-melted three times for chemical homogeneity. A single copper block jet melt-spinner produced amorphous melt-spun ribbons of 25 μm thickness and 12mm width by quenching from 1423 K at a tangential wheel speed 30m/s. Amorphous thin-films of 10 μm were created by direct current magnetron sputtering on liquid nitrogen cooled copper. Further details on production are provided elsewhere^{30,36}. Compositions of the samples were confirmed as 90.3 and 90.6 at-% with electron dispersive spectroscopy (EDS) for ribbon and thin-film samples.

HEXRD experiments:

X-ray diffraction experiments were performed at BL04-MSPD beamline of ALBA synchrotron facility in transmission mode using a wavelength of 0.4136 Å with a double Si monochromator. The diffraction data were collected in the Q-range ($Q = 4\pi\sin(\theta)/\lambda$) where θ is the Bragg's angle, and λ is the wavelength of X-ray radiation) of 0.83–7.5 Å⁻¹ using a Mythen array detector system. Intensity versus Bragg angle data was first corrected for background, polarization, absorption, and multiple Compton scattering, then converted into a total X-ray structure factor using pdfgetX3 software³⁷.

Levitation melting experiments:

In-situ levitation melting experiments under synchrotron XRD were conducted in DIFFABS beamline at SOLEIL, France. This work's main motivation was to develop a comprehensive atomic model of the liquid alloys within metallic glass formation composition. For this purpose, our levitation study involved critical experiments investigating the structural ordering in Al-RE with respect to temperature in a molten state. It is difficult to use conventional furnaces for high-temperature experiments as physical contact of the liquid sample with the container can cause contamination and unwanted structural properties modification. Such problems encouraged the development of containerless techniques, powerful tools to study the solidification of undercooled melts and the molten state's structures. Various types of levitation melting include

electromagnetic, acro-acoustic, electrostatic levitation, optical, and aerodynamic levitation. In our experiments, we used aerodynamic levitation in DIFFABS beamline, SOLEIL. For aerodynamic levitation, gas pressure is adjusted to levitate the specimen. We have prepared high purity $\text{Al}_{1-x}\text{Sm}_x$ ($x=0.08, 0.10$ and 0.12), $\text{Al}_{1-x}\text{Tb}_x$ ($x=0.9$ and 0.10) within the glass formation range. We used laser heating and levitating chamber setup to collect high-quality data between 800°C and 2000°C .



Figure 1. From our experiments at SOLEIL DIFFABS Beamline showing the experimental hutch.

In levitation melting experiments, firstly, spherical samples were fixated with Ar flowing nozzle before the chamber's vacuum sealing. Chamber was then vacuum sealed down to 10^{-3} mbar pressure and re-filled and swept with Ar gas during the experiment by the Ar flowing nozzle. Samples were levitated with Ar flow during investigations, and they were heated by a laser focused on the specimen by two mirrors attached to the experimental setup. Approximate sample temperatures were collected by a pyrometer and recorded to plot heating and cooling curves for each experiment. Real-time videos of levitating molten samples were captured at the same time to monitor macroscopic changes in the sample appearances. Incident high energy X-ray was bombarded on the molten specimens to collect HEXRD patterns as soon as the intended temperatures were attained.

The second experiment was conducted with experimental conditions in the same beamline with the new two-dimensional CirPAD detector shown in Figure 2. This detector decreased the data acquisition times to an instant since it consists of 20 smaller detectors that can collect data from a 140° range as a snap. These 20 smaller detectors are hybrid pixel array detectors, which are engineered so that the dead zones between them are reduced to only 7 pixels out of a total of 1.3 million pixels with a size of $130 \times 130 \mu\text{m}^2$ ³⁸.



Figure 2. CirPAD detector of Diffabs beamline in Soleil Synchrotron.

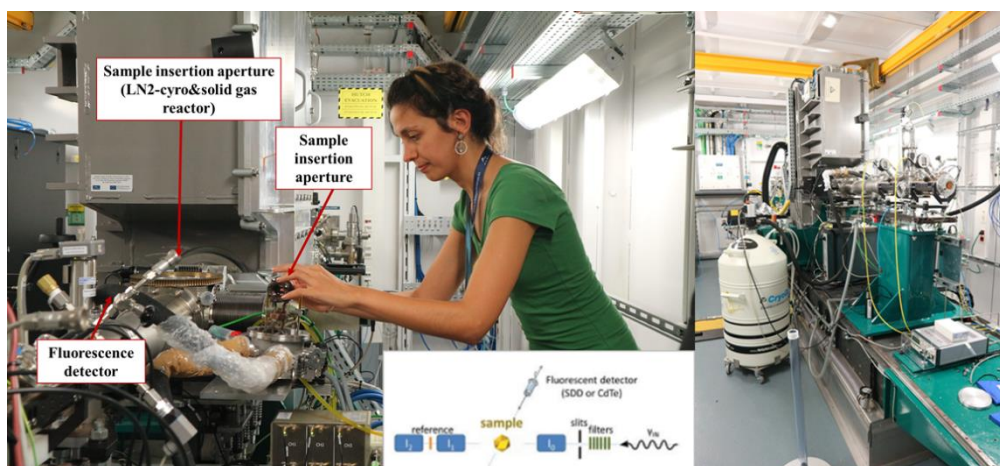


Figure 3. From our experiments at CLÆSS beamline. The inset depicts the X-ray beam's path for both fluorescent and transmission mode, together with the sample insertion aperture.

XAFS experiments:

XAFS measurements were performed at CLAESS beamline of ALBA using a double-crystal Si (1 1 1) monochromator at Terbium L3 edge. Ionization chambers were filled with N₂, He, and Kr gasses. Silicon-drift and CdTe single-channel fluorescence detectors were used to collect data in transmission, and fluorescence modes for melt-spun ribbons and magnetron sputtered films, respectively. Co is used as an energy reference and simultaneously measured with the samples.

Three different scans were performed, and data obtained simultaneously from different channels were averaged to form the XAFS spectrum. DEMETER software was used for data processing and model fitting³⁹. A crystal structure of Al-Tb with similar atomic environments to its amorphous counterpart was used for EXAFS modeling. Tb atom at the atomic site of Tb1 with Frank-Kasper 15 vertex and Al atom at the atomic site of Al11 with icosahedron atomic environments have proved useful.

RMC Simulations:

RMC simulations were initiated using the RMC_POT package with RMC_Multi implementation with a 30,000 atoms cubic simulation box of ~83 Å edge length with periodic boundary conditions. RMC was constrained by density, cut-off distances obtained from ab-initio molecular dynamics (AIMD), and XRD, EXAFS experimental data. Calculated coherent structure factor $S(Q)$ from X-ray diffraction data and calculated $\chi(k)$ data from EXAFS were fitted to their observed values. Due to its nature, $\chi(k)$ data contain larger noise signals, which can be detrimental to the RMC fitting. Therefore while XRD data were fitted as is, EXAFS data is imported in k space then filtered via the Savitsky-Golay method to avoid degrading peaks while reducing noise levels^{40,41}. The difference between experimental and calculated values for $S(Q)$ and $\chi(k)$ are calculated and minimized according to

$$\chi_i^2 = \frac{\sum_k (S_i^C(Q_k) - S_i^E(Q_k))^2}{\sigma_i^2} \quad [1]$$

and

$$\chi_i^2 = \frac{\sum_j (a_i E_i^E(k_j) + b_i - E_i^C(k_j))^2}{\sigma_i^2} \quad [2]$$

respectively where $S_i^C, S_i^E, E_i^E, E_i^C$ are computed and experimental structure factors and EXAFS data, respectively. Whereas σ contains the weight of the data set used in the fitting procedure^{42,43}.

Voronoi Tessellation:

Structural arrangements in the system analyzed using Voronoi tessellation with VORO++ software⁴⁴. Voronoi tessellation is a method to divide 3D space into Voronoi cells by creating shared planes with the center atom to neighbor atoms. Voronoi cells are formed with these planes, denoted by indices $n3, n4, n5, n6, n7, n8$, where n_i is the number of edges each Voronoi surface has^{3,45}. Radial Voronoi tessellation with periodic boundary conditions on a cubic simulation box is used due to the significant atomic size difference between Al and Tb atoms.

Transmission Electron Microscopy:

Specimens for TEM analyses were prepared using electropolishing with a solution of 25 vol.% nitric acid and 75 vol% methanol at 241 K.

Heat Treatment and Thermal Analysis:

Differential scanning calorimetry (DSC) measurements were performed at five different heating rates as 10, 20, 30, and 40 K/min from room temperature to 773 K under N₂ atmosphere on 1mg to 1.6 mg melt-spun ribbon samples. Empty Al pans are used as references. DSC traces were then used in Kissinger and Ozawa analyses to calculate the first crystallization event's activation energies for ribbon and thin-film samples. Kissinger and Ozawa's methods were used since the first method uses the change in transformation temperature used by different heating rates. The latter method assumes a constant degree of reaction where the relation becomes independent of the heating rate. Kissinger relationship for non-isothermal reactions is ⁴⁶;

$$\ln(\Phi/T_p^2) = \text{const.} (-E_c/RT_p) \quad [3]$$

where Φ is the heating rate, T_p is the peak temperature, E_c is the activation energy, and R is the gas constant. Whereas in the Ozawa method degree of reaction is assumed to be constant and independent from heating rate as in ⁴⁷;

$$\ln(\Phi) = \text{const.} (-1.052E_c/RT_p) \quad [4]$$

Activation energies of the first fcc Al crystallization for ribbons and thin-films were then obtained from the slopes of $\ln(\Phi/T_p^2)$ vs. $1/T_p$ and $\ln(\Phi)$ vs. $1/T_p$ plots.

Mechanical Testing:

Micropillars of 2.75 μm top surface diameter, 3 μm medium height diameter, and 3.25 μm bottom diameter were fabricated from melt-spun ribbons using focused ion beam milling (FIB). Compression tests were then performed on these micropillars in displacement-controlled mode with linear loading and unloading stages. Three different loading rates were applied, which correspond to strain rates around 10^{-2} , 10^{-4} , and 10^{-5} s^{-1} . Which yielded the corresponding stress-strain diagrams

3. Results and Discussion

3.1. Levitation Melting High Energy X-Ray Diffraction Experiments

In this part of the project, the liquid state structure was investigated in SOLEIL DIFFABS Beamline for the glass formation range's compositions. Levitated samples were heated with laser in Ar atmosphere. The specimen temperatures were recorded, and heating curves were plotted, as shown in Figure 4. Series of photos captured during heating and cooling by the laser beam is shown in Figure 5 (a) to (f). It is worth noting that the recoalescence was captured during the solidification of the melt. Recoalescence is a spontaneous rise in temperature occurring when

the supercooled liquid suddenly crystallizes, forming a solid but releasing heat in the process. This phenomenon can be observed from the temporary glow shown in Figure 5 (d) to (e).

Although all of the necessary equipment was present in the experimental setup, we encountered a severe oxidation problem during our experiments. Since the high-temperature experiments in DIFFABS beamline at Soleil have been carried out with the oxides and ceramics, unfortunately, the precautions they took were not enough for preventing the oxidations in metallic systems. The main problem is the fact that the vacuum leak rate for the chamber was poor. Although a turbomolecular vacuum pump was operating, it took 15-20 minutes to reach 10^{-3} mbar pressures. Having a high leak rate also caused oxidation to our samples during melting. Al-RE samples were getting oxidized at elevated temperatures before the X-ray diffraction procedure ends, which can be clearly observed on the levitated metal in Figure 4 (b). Oxidized parts were even visible in real-time videos that were captured. We could not manage to collect clean HEXRD data from our liquid samples because of the oxidation problems. All of our recorded diffraction patterns contained crystalline oxide peaks. Since our objective was to collect clean, high-quality HEXRD data to perform Reverse Monte Carlo simulations to investigate the liquid (amorphous) structure, oxide peaks and deteriorated structural data were not purposeful.

Figure 6 shows a series of representative XRD collected at various temperatures from $\text{Al}_{92}\text{Sm}_8$ alloy. As it can be seen in the Figure, the sample was liquidized at 805°C. Preliminary results indicate that specimen had been oxidized before reaching liquidus temperatures. Unfortunately, the oxidation problem cannot be avoided for any Al-RE specimens during levitation melting experiments.

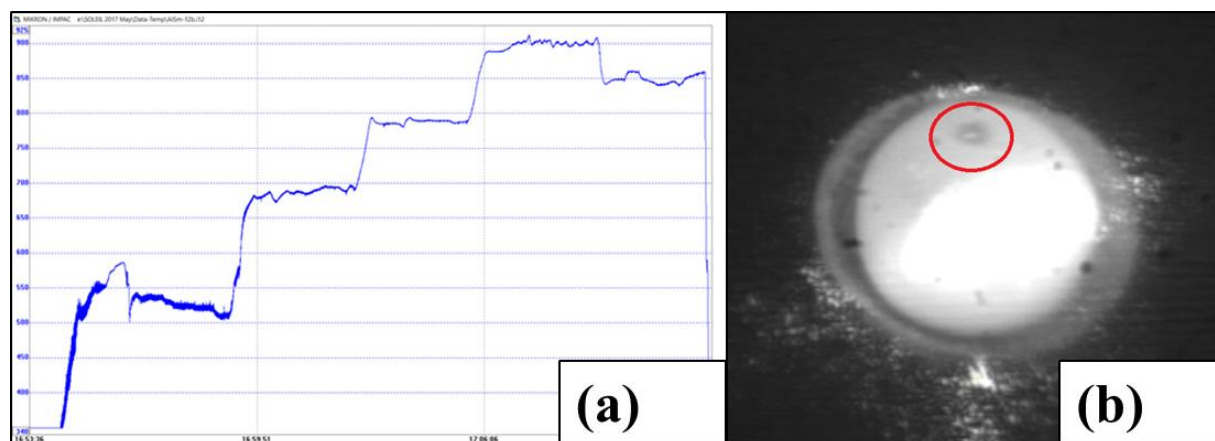


Figure 4. (a) The heating curve of $\text{Al}_{88}\text{Sm}_{12}$ metallic alloy recorded during levitation melting. (b) The real-time photo of the levitated material upon heating. The red circle shows the formation of oxides on the surface of the metal.

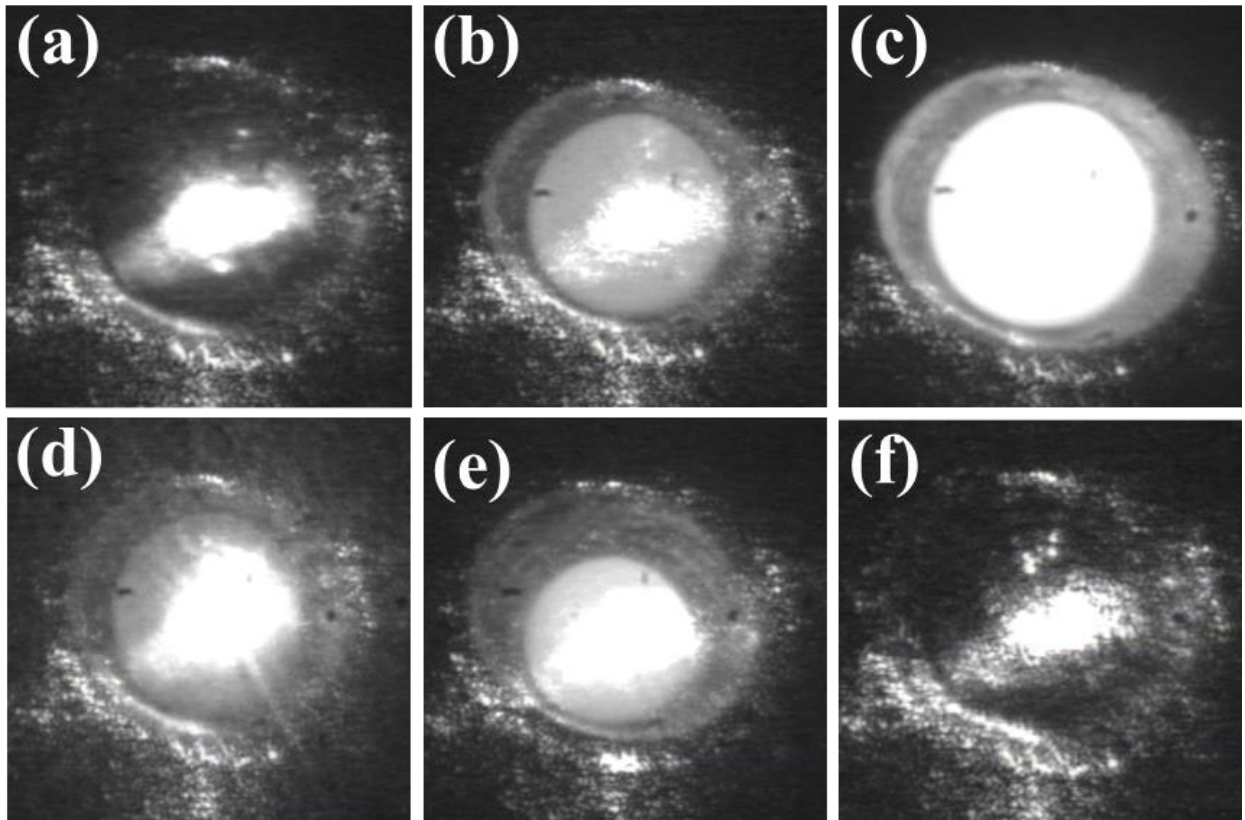


Figure 5. The real-time video frame of levitated Al-Sm amorphous alloys from room temperature (a) to 805 °C (f).

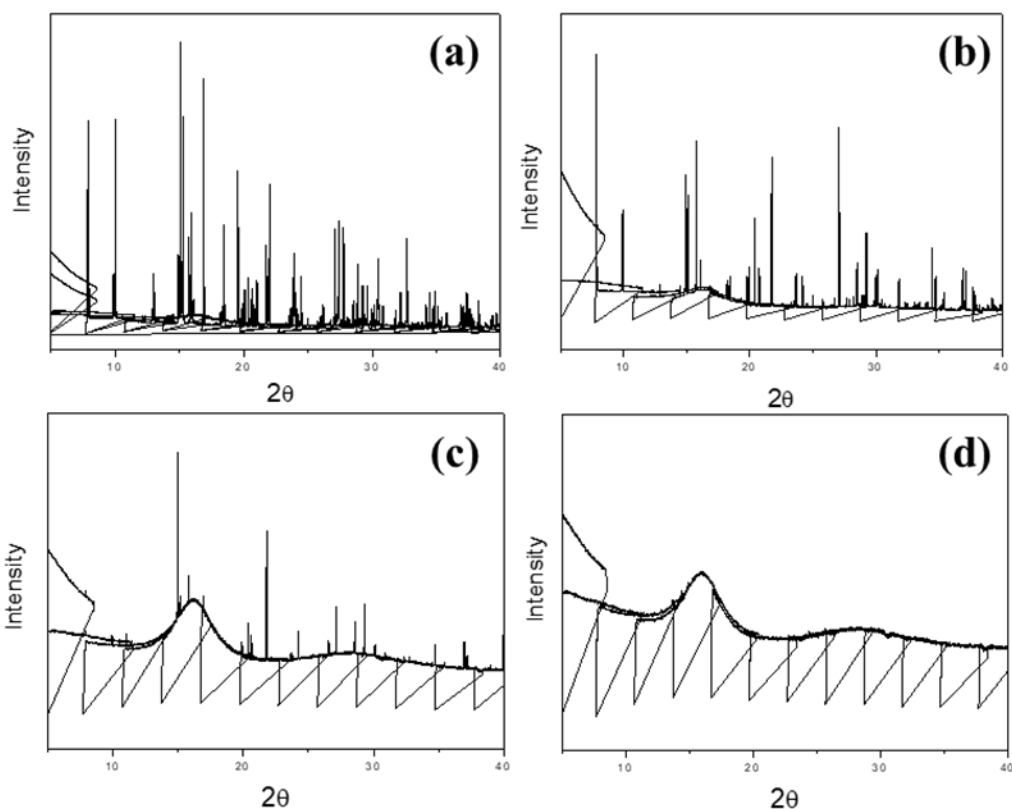


Figure 6. HEXRD patterns of $\text{Al}_{92}\text{Sm}_8$ at (a) room temperature, (b) 550 °C, (c) 700 °C and (d) 805 °C.

Diffabs beamline of Soleil synchrotron installed a new detector called CirPAD in 2019. This detector consists of 20 detection modules, enabling data acquisition in the 140° range in a single acquisition step. Vacuum conditions in the beamline were not improved; however, since data can be collected instantly, data collection before oxidation is considered possible. Our group was invited to repeat the experiment with a new setup for the first time in Diffabs beamline. However, due to the new detector's high background noise, only a part of the main amorphous peak was barely visible. Pre-peak in the structure, which corresponds to medium-range order, was drowned by noise background signals in the XRD data.

This experiment is crucial to understand the difference in devitrification behaviors of melt-spun ribbons and magnetron sputtered thin films since amorphous precursors were considered to have differences in the structure. Therefore, another experiment is planned to be conducted at I15- XPDF beamline on Diamond light source in London. This experiment aims to collect PDF data from high purity $\text{Al}_{1-x}\text{RE}_x$ (RE: Sm, Y, Tb and $x=0.04, 0.06, 0.08, 0.10$ and 0.12) alloys in liquid state. Compositions covered are within and out of the glass formation range, which will reveal the strange behavior observed in the Al-based marginal metallic glass formation range lying beyond the eutectic formation range, unlike other metallic glasses. In this experiment, Helios I.R. furnaces

will be used for heating the between 800°C (1073K) and 1100°C(1373K) while the structural changes will be monitored in the molten state. Samples will be sealed in carbon-lined quartz capillaries (Oxygen<400 ppm) to avoid previously encountered oxidation problems. This proposal was very well received and accepted in December 2019; however, due to breakdown at I15 Beamline, it was rescheduled to late April 2020. Afterward, the Diamond synchrotron halted all research from the outside country due to the Pandemic. This experiment is currently planned to be conducted remotely soon due to Covid-19 restrictions.

3.2. EXAFS Modelling

The X-ray absorption spectrum of the $\text{Al}_{90}\text{Tb}_{10}$ melt-spun ribbons at temperatures 30°, 250°C, 300°C, and 350°C are given in Figure 7. Normalization of the absorption spectrum is performed by background subtraction and removal of false signals by ATHENA software. E_0 values are chosen as the values closest to the absorption spectrum's inflection point but still out of the XANES region. The energy range of the measurement is 7400-8200 eV. The curves are highly similar, indicating a resemblance of the empty 5d states' local density responsible for the given energy spectrum's absorption behavior.

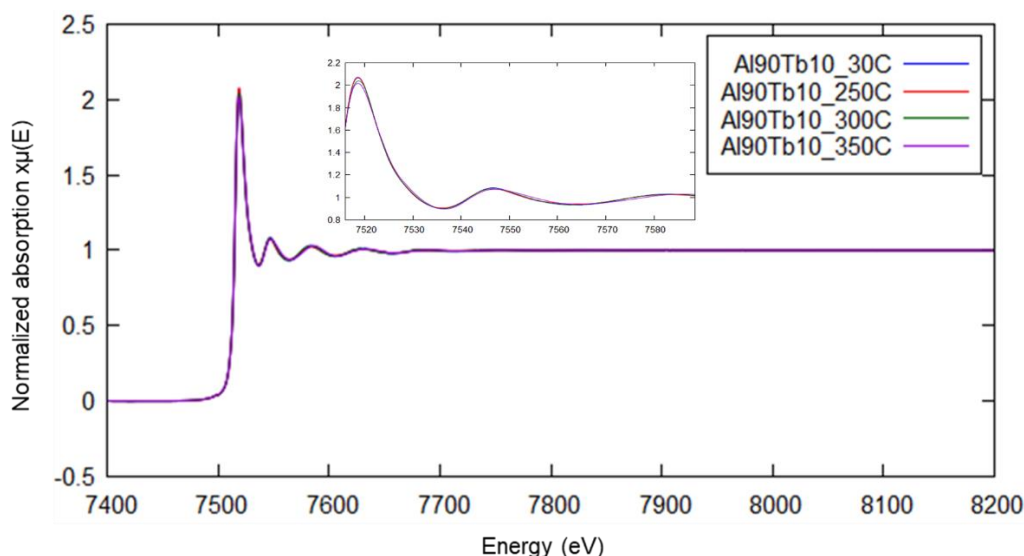


Figure 7. Normalized X-ray absorption spectra of $\text{Al}_{90}\text{Tb}_{10}$ melt-spun ribbons at L3 edge of Tb measured in transmission mode at several temperatures.

Fourier transform of the data is taken in a k (wavenumber $\text{\AA}^{-1}$) range primarily determined by the noise in the data as $3 \text{\AA}^{-1}$ to $10 \text{\AA}^{-1}$ for $\text{Al}_{90}\text{Tb}_{10}$ melt-spun alloy. In EXAFS fitting, depending on the number of absorption paths, there are many variables to calculate. These variables are floated in data with a limited number of independent points, which increases with the range of k . While the number of independent points must be large for an efficient fit noise in the data limits, this range and an optimum must be found as a trade-off. k space graphs of the data with k^3 weighting factor and their fits are given in Figure 8.

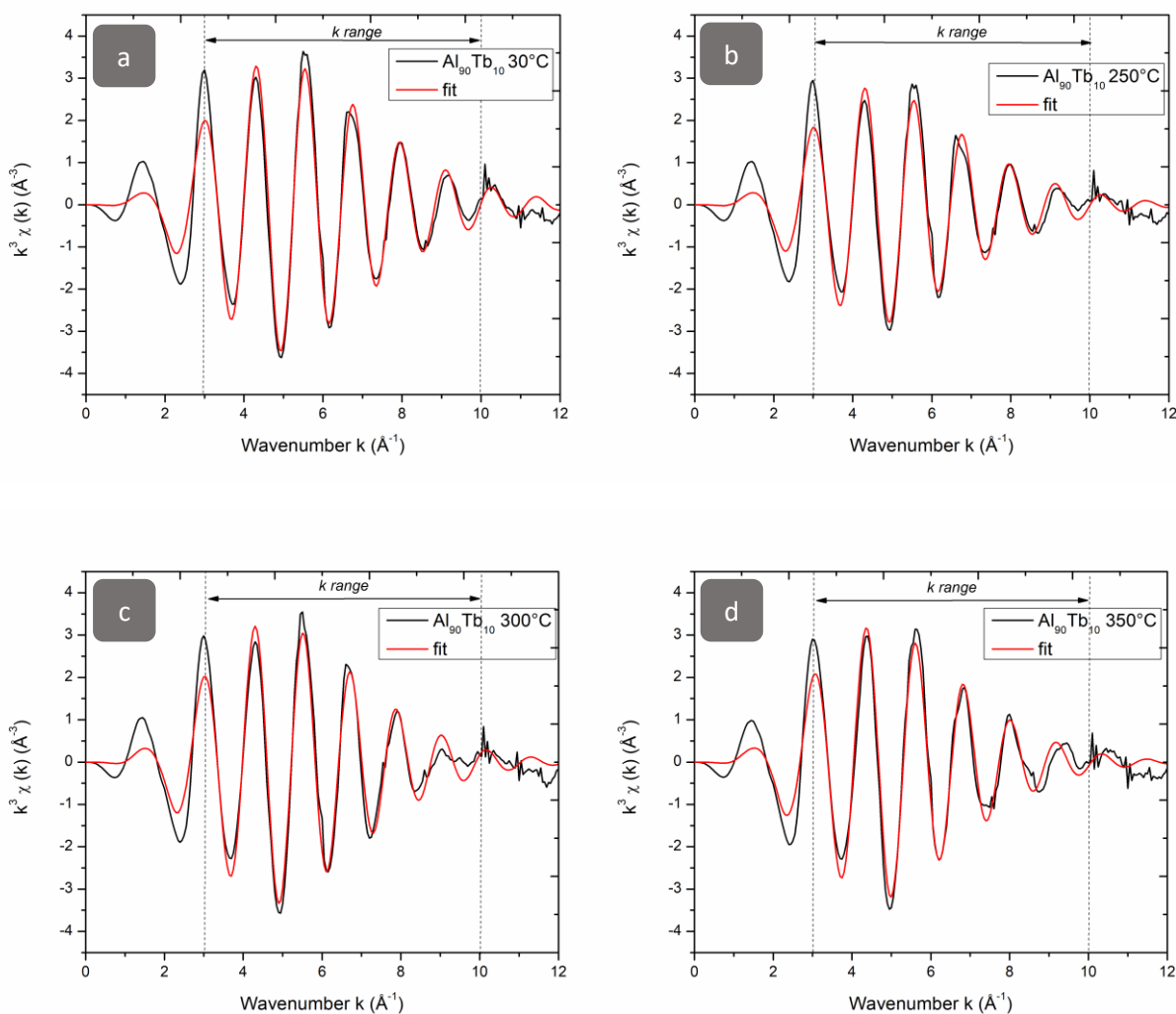


Figure 8. k^3 -weighted $\chi(k)$ graphs of $\text{Al}_{90}\text{Tb}_{10}$ melt-spun alloys at 30°, 250°C, 300°C, and 350°C, respectively.

Fourier transformed data in k space is reasonably clean in the determined k range; deterioration of the data by noise and false peaks starts after $10 \text{ \AA}^{-1}$. Sample in room temperature labeled a is in perfect synch with the model fitted even beyond the k range determined up to $11 \text{ \AA}^{-1}$. As the temperature increases, slight signs of synch loss start to appear in the higher k ranges. Similar behavior can be seen in q space ($\text{\AA}^{-1}$) data as well (Figure 9).

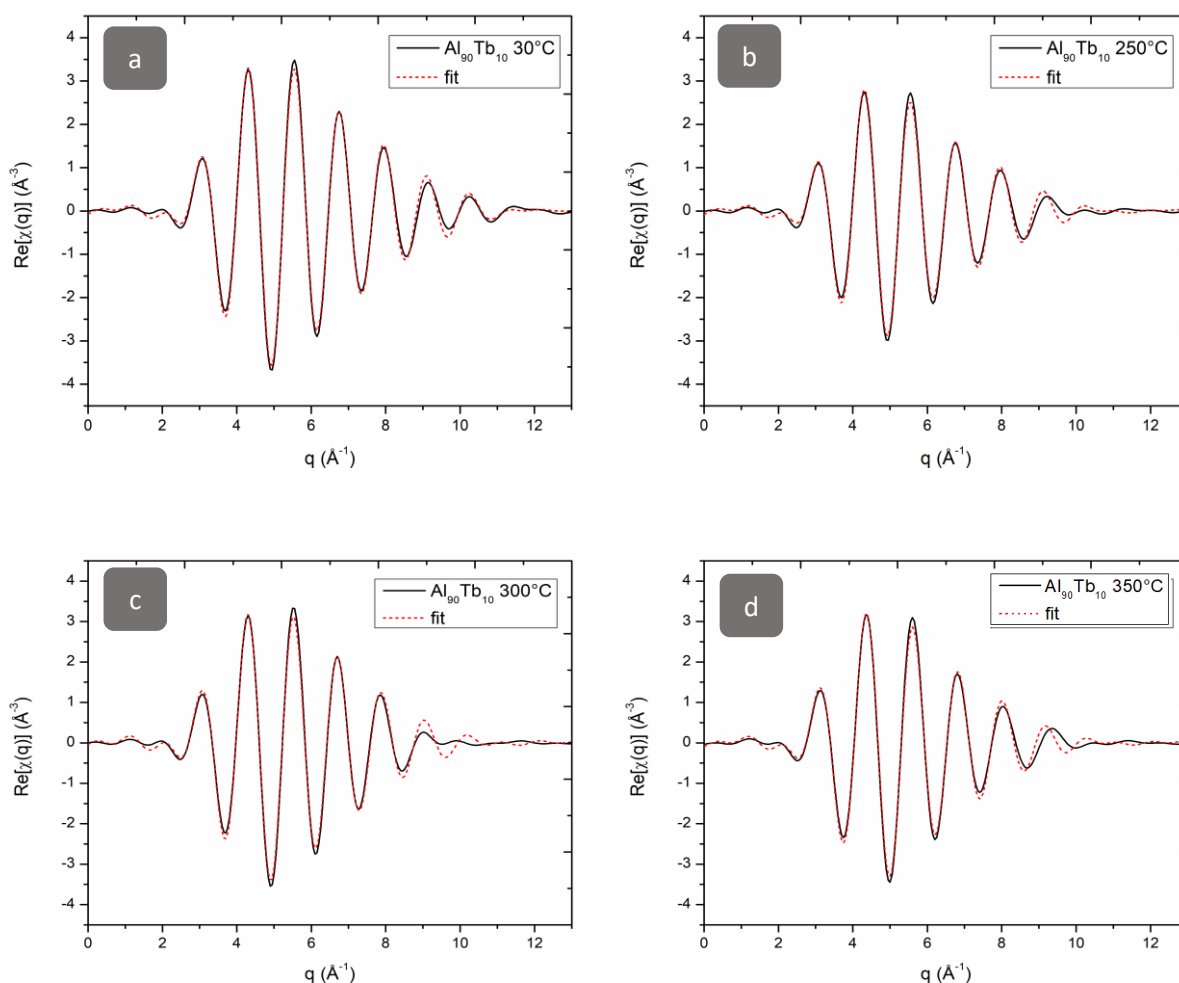
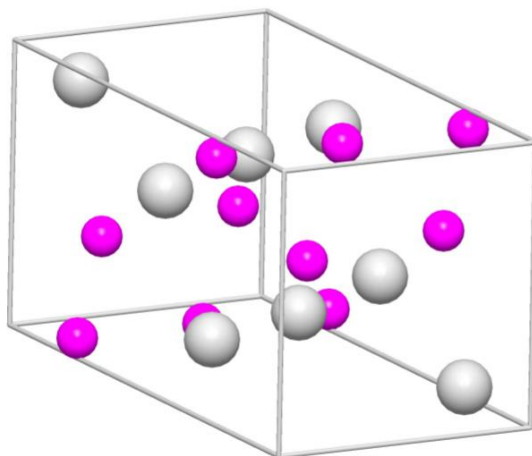


Figure 9. Q space data in real space of $\chi(q)$ of $\text{Al}_{90}\text{Tb}_{10}$ melt-spun alloys at 30°, 250°C, 300°C, and 350°C, respectively

XAFS analysis requires the photoelectron scattering amplitudes and phases of the material under investigation. In crystalline data, this process is relatively straightforward. Still, amorphous materials can pose problems since the structure is unknown, and the XAFS analysis is performed to reveal the structure in the first place. In this case, Al-Tb crystal data is taken from Pearson's Crystal Data; the 3D structure is given in Figure 10. Details of the structure are given in Table 1.

Table 1. Unit cell parameters of the Al-Tb system used in EXAFS fitting^{48,49}

<i>Cell length</i> <i>a</i>	<i>Cell length</i> <i>b</i>	<i>Cell length</i> <i>c</i>	<i>Cell angle</i> α, β, γ	<i>Cell</i> <i>Volume</i>	<i>Cell formula</i> <i>units Z</i>	<i>Space</i> <i>group</i>
5.831	11.368	5.624	90°, 90°, 90°	372.8	8	pbcn

**Figure 10.** 3D atomic rendering of the Al-Tb crystal data used in XAFS fitting. Al (pink) and Tb (gray) are color-coded with their respective atomic sizes.

The photoelectron scattering amplitudes are calculated by ATOM and FEFF implemented in ARTEMIS. All the possible scattering events are calculated, and the sum of their contributions forms the measured fine structure $\chi(\Gamma)_{\text{total}}$ signal. Contribution for any specific scattering event can be calculated as:

$$\chi_{\Gamma}(k) = \frac{N_{\Gamma} S_0^2 F_{\Gamma}(k)}{2kR_{\Gamma}^5} e^{-2k^2\sigma_{\Gamma}} e^{-2R_{\Gamma}/\lambda(k)} * \sin(-2kR_{\Gamma} + \phi_{\Gamma}(k) - 4k^3C_{3,\Gamma}/3) \quad [5]$$

S_0^2 (the passive electron reduction factor and N_{Γ} (number of atoms which are at the same distance from the absorbing atom) together represent the amplitude reduction factor given in equation 1.⁵⁰ S_0^2 was assumed to be 0.73 as is taken in the literature for all rare earth elements^{51–54}. Calculated coordination numbers, R factor, R distances, Enot (photoelectron energy shift), and σ^2 (mean square disorder) corresponding to this assumption are given in Table 2. All the parameters calculated by the ARTEMIS are in acceptable ranges for a physically good fit.

Table 2. Unit cell parameters of the Al-Tb system used in EXAFS fitting. R factor: Relative error of the fit and data, C.N.: Coordination number, Enot: Change in photoelectron energy, $R_{\text{Tb-Al}}$: Tb-Al distance, Delr: Change in interatomic distance relative to initial path length, σ^2 : Mean square relative displacement or Debye-Waller Factor.

$\text{Al}_{90}\text{Tb}_{10}$	R factor	CN	Enot (eV)	$R_{\text{Tb-Al}} \pm \text{Delr} (\text{\AA})$	$\sigma^2 (\text{\AA}^2)$
30°C	0.0052	15.23 ± 1.79	-2.15 ± 1.33	3.06625 ± 0.0081	0.016 ± 0.002
250°C	0.0084	15.53 ± 1.53	-1.73 ± 1.76	3.06774 ± 0.0125	0.018 ± 0.003
300°C	0.0085	15.58 ± 1.50	-1.09 ± 0.75	3.09392 ± 0.0116	0.018 ± 0.002
350°C	0.0075	15.62 ± 1.54	-1.82 ± 0.74	3.04615 ± 0.0115	0.020 ± 0.002

R vs. $\chi(R)$ graphs of the fits at different temperatures are given in Figure 11 in magnitude, and real part of the Fourier transforms. Fitting ranges in R space is indicated. All the fits include the first shell main peak since the second shell fits physically unrealistic results. Attempts to fit the second shell result in low R values and visually good fits but fitting parameters have strong correlations.

The large width of the main peak at all temperatures indicates disorder around center atom Tb, a characteristic behavior of amorphous materials that results in relatively high delr values. The magnitude and real part of the Fourier transform of the data are in excellent agreement with the fit given in Figure 11.

Magnetron sputtered $\text{Al}_{90}\text{Tb}_{10}$ metallic glasses were also investigated to reveal the effect of the production path. However, due to the samples' lower thickness, absorption quality was insufficient to create clean and meaningful data even in fluorescence mode. As seen in Figure 12, $\chi(k)$ data of the sputtered sample has a very high noise ratio. Data after the k space of $9 \text{ \AA}^{-1}$ at 30°C, $6 \text{ \AA}^{-1}$ at 250°C, $7 \text{ \AA}^{-1}$ at 300°C, and $8 \text{ \AA}^{-1}$ at 350°C are not purposeful and attempts to fit data to these data resulted in visually and physically unrealistic fits.

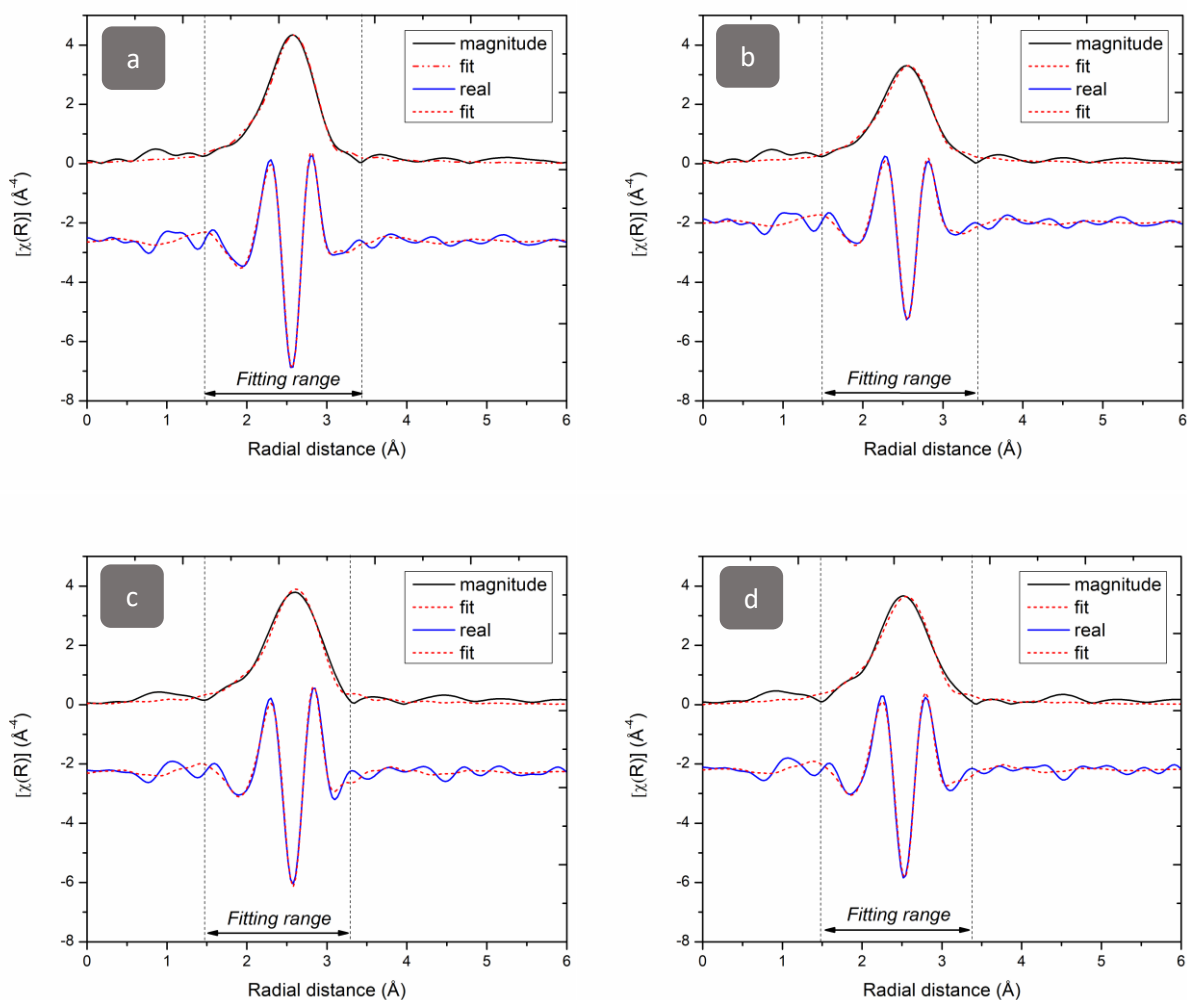


Figure 11. Experimental EXAFS data (Tb L3 edge) and fit results for $\text{Al}_{90}\text{Tb}_{10}$ melt-spun ribbons at 30°C (a), 250°C (b), 300°C (c), and 350°C (d). The comparison shows the magnitude and the real part of the Fourier-transform. The fitting range is indicated.

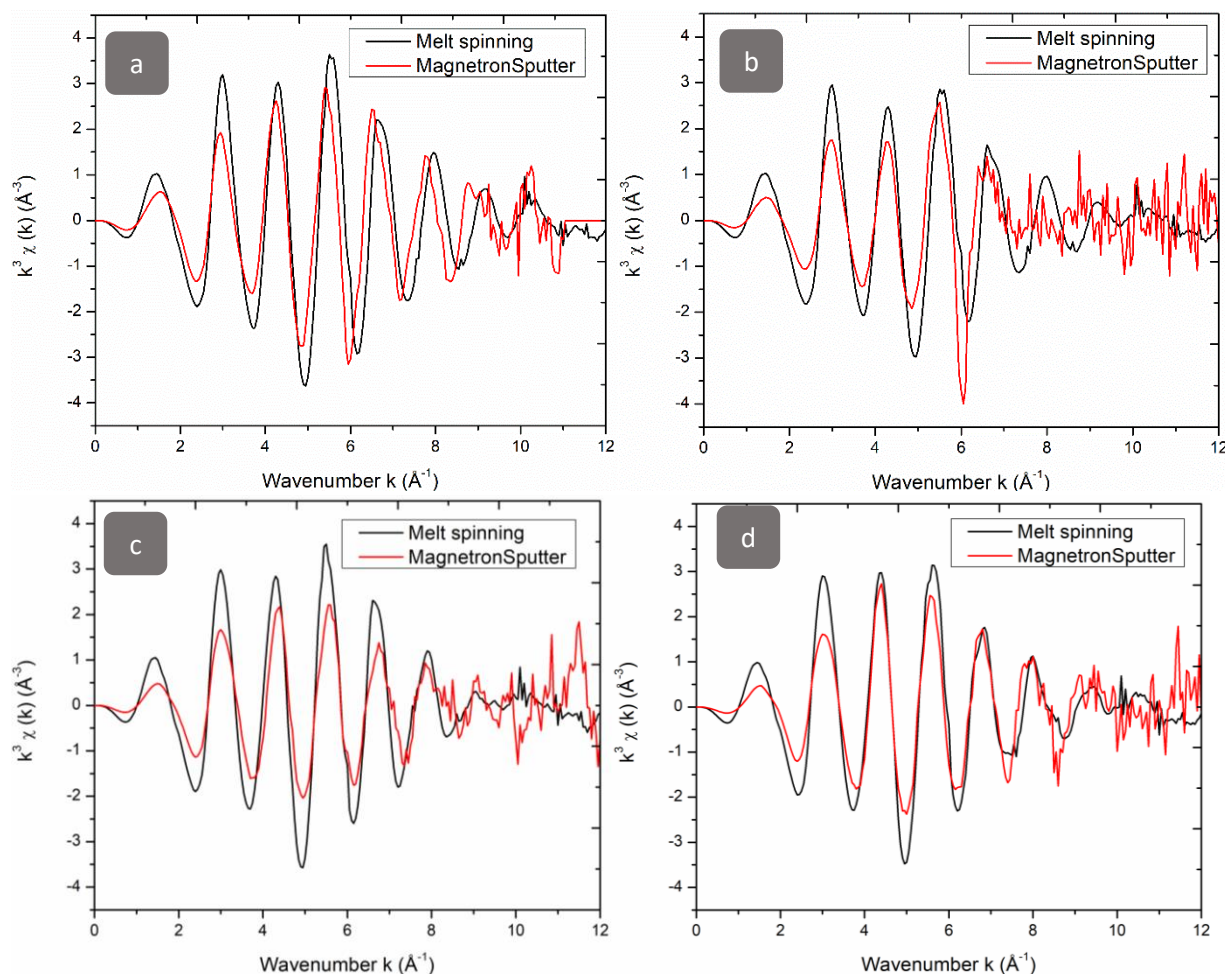


Figure 12. K3-weighted $\chi(k)$ graphs of Al₉₀Tb₁₀ melt-spun (transmission mode) and magnetron sputtered (fluorescence mode) alloys at 30°, 250°C, 300°C, and 350°C, respectively.

3.3. Short Range Order Analysis

Synchrotron-based XRD experiments were conducted to confirm the amorphous nature of the Al₉₀Tb₁₀ melt-spun ribbons and magnetron sputtered thin-films. Figure 13 shows the S(Q)-Q data with amorphous humps and accompanied pre and side peaks that are characteristics of Al-RE marginal metallic glasses. The pre and side peak formations were previously studied for Al-RE marginal metallic glasses^{3,55}. The existence of pre-peak and side-peak reflections located at approximately 1.3 and 3.4 Å⁻¹ indicates a pseudo-order in amorphous structure^{33,56}.

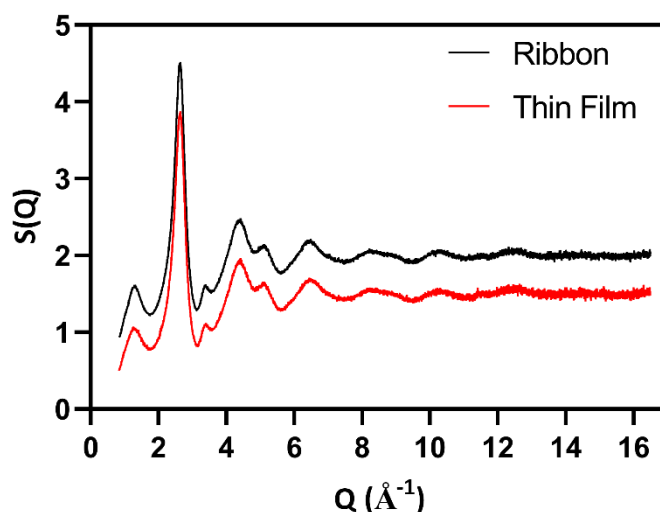


Figure 13. Total X-ray structure factors of melt-spun ribbon and magnetron sputtered thin-film.

RMC simulation is widely used for the structural analysis of the amorphous materials due to its practical ability to derive three-dimensional atoms directly from experimental data without assuming any prior candidate models⁵⁷. However, using RMC with only $S(Q)$ - Q can be misleading since $S(Q)$ - Q is one-dimensional data without an absolute ability to discriminate among models that can result in the same XRD pattern. Using other experimental constraints sensitive to chemistry and local atomic structure, such as EXAFS, is crucial to creating models closest to the exact atomic structure. In that sense, we have coupled our $S(Q)$ - Q data with Tb L3 edge EXAFS spectra and cut-off distances to obtain the most representative 3D atomic configuration of amorphous structure using RMC. Figure 14 shows the experimental HEXRD and EXAFS data with corresponding RMC fits. For the ribbon, XRD data are almost in perfect agreement with the RMC fit. EXAFS data, on the other hand, have a reasonably good fit since EXAFS has restricted data points when compared to $S(Q)$ due to its derivation. A similar situation is also valid for thin-film data. $\sigma(Q)$ and $\sigma(k)$ parameters for XRD and EXAFS data were $5 \cdot 10^{-4}$ and $5 \cdot 10^{-7}$, respectively. After approximately 10^8 iterations, a cubic simulation box with 30000 atoms and an edge length of ~ 8.30 nm was obtained, as shown in Figure 15 (a). The simulation box was then analyzed by breaking it into distinct Voronoi cells. For example, Figure 15 (b) and Figure 15 (c) show the $\langle 0,3,6,4 \rangle$ type structure atoms and their Voronoi cells.

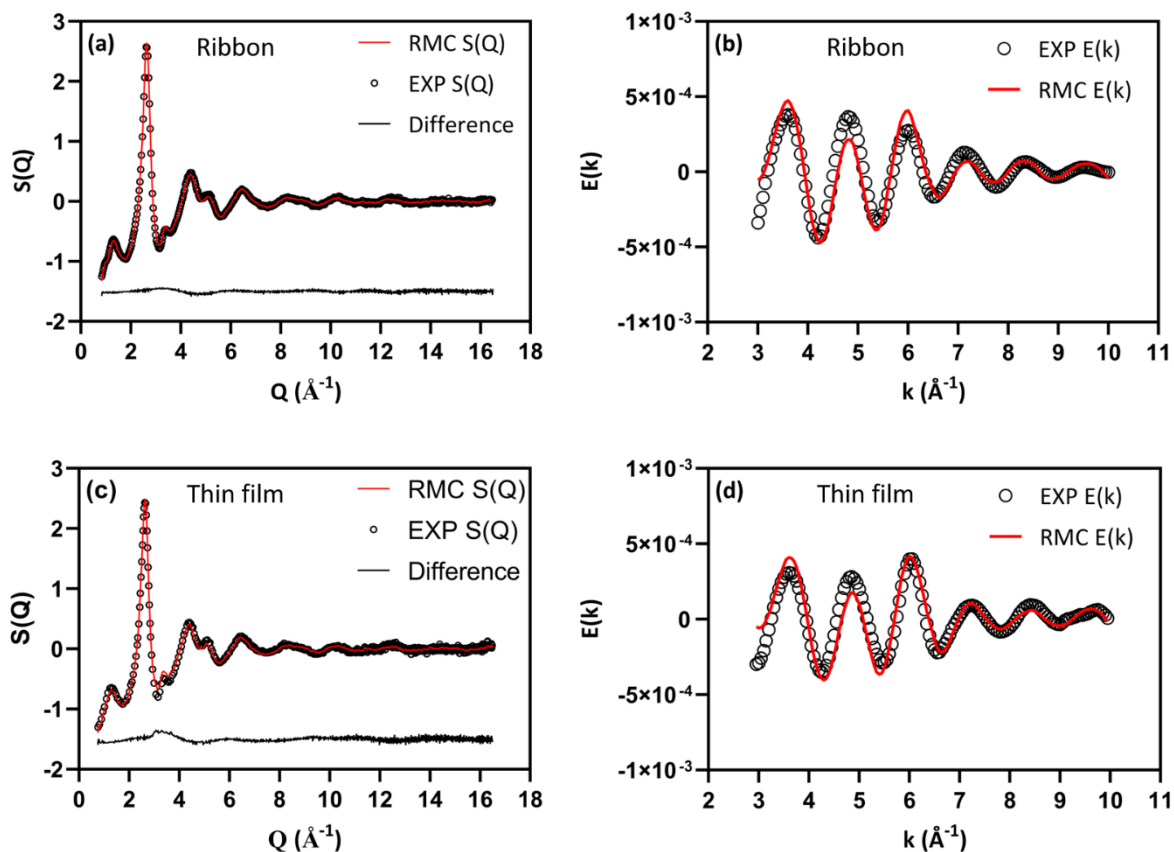


Figure 14. a) Total X-ray structure factor experimental and RMC fit for ribbon, b) EXAFS data and RMC fit for ribbon, c) Total X-ray structure factor experimental and RMC fit for thin-film, and d) EXAFS data and RMC fit for thin film.

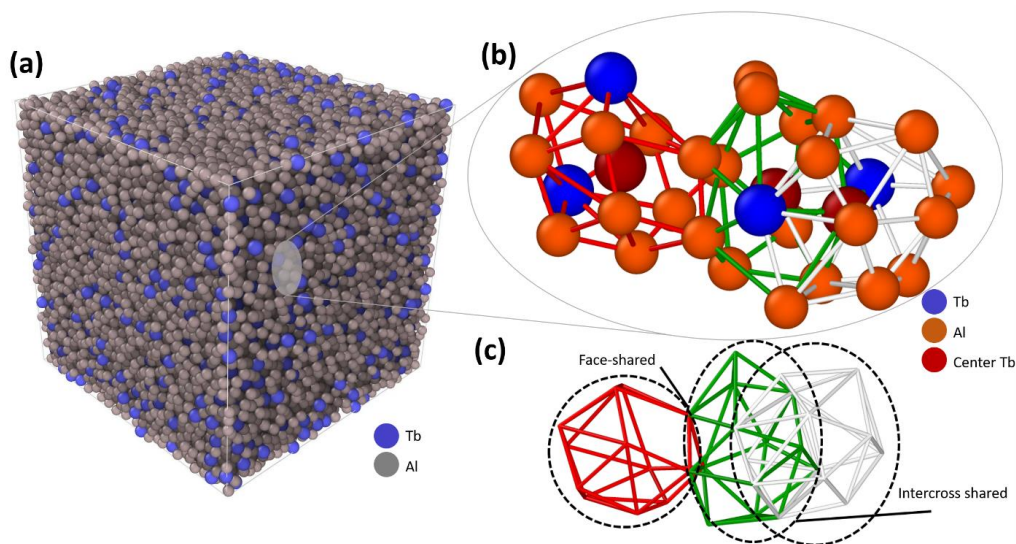


Figure 15. (a) RMC simulation box after fitting, (b) close up view of triple $\langle 0,3,6,4 \rangle$ Voronoi cell interacting with each other, and (c) same clusters with face and intercross sharing.

The Voronoi tessellation method ^{44,45} reveals the local atomic environment in RMC simulated configurations. Voronoi polyhedra (V.P.) are analyzed under Al Centered, and Tb centered subclasses. Fifteen most populated V.P.s for melt-spun ribbons and magnetron sputtered samples are given in Figures 16a and 16b. Most populated Al centered clusters are <0,3,6,4> and <0,2,8,4> types for both ribbon and sputtered samples. For Tb centered clusters, VPs with higher coordination number (CN) i.e. <0,2,8,5>, <0,2,8,6>, <0,1,10,4> and <0,1,10,5> are found to dominate the configuration. Another interesting point is that for Al centered cluster, most of the V.P.s in the ribbon has a higher population than the ones in sputtered samples. Although the difference seems small, it is always present in most of the Voronoi cells and all other consecutive simulations. So, it is safe to say that short-range structural order is more pronounced in melt-spun ribbons since a higher percentage of certain V.P.s indicate higher repetition in the structure. This difference is considered to be originated due to different processing histories of amorphous precursors. Melt-spun ribbons solidify from the liquid state, and thin-films form from the gaseous phase. Ribbon and sputtered samples have similar C.N. values, as seen in Figure 16c and 16d. On average Tb centered clusters has 16 neighboring atoms, and Al centered clusters have 14.

To fully understand short-range order throughout the simulation cell, VPs are categorized under the main structures they resemble, as seen in Figure 16e and 16f. Al centered VPs are categorized as fcc-like: <0,3,6,4>, <0,3,6,5>, <0,4,4,6>, <0,4,4,7>, icosahedral like (ICO): <0,2,8,X>, <0,1,10,X>, <0,0,12,0>, where X= 1,2,3,4 and 5 ³; Tb centered VPs are analyzed under same categories with the addition of high coordination number Frank-Kasper Z15: <0,0,12,3> (with increasing disclination density <0,1,10,4>, <0,2,8,5>, <0,3,6,6>) and Z16: <0,0,12,4> (with increasing disclination density <0,1,10,5>, <0,2,8,6>, <0,3,6,7>) type cells ³. Al-centered VPs were mostly dominated by ICO-like and fcc-like clusters where ribbons are having higher amounts indicating a more ordered structure than sputter. Tb centered VPs have a more dominating structure than Al centered VPs as Frank-Kasper Z15, Z16 types. Again, in these clusters, ribbons have a higher percentage than sputtered samples in all three categories. They support the idea that the amorphous precursor type in the samples has the same composition, resulting in order-wise different structures.

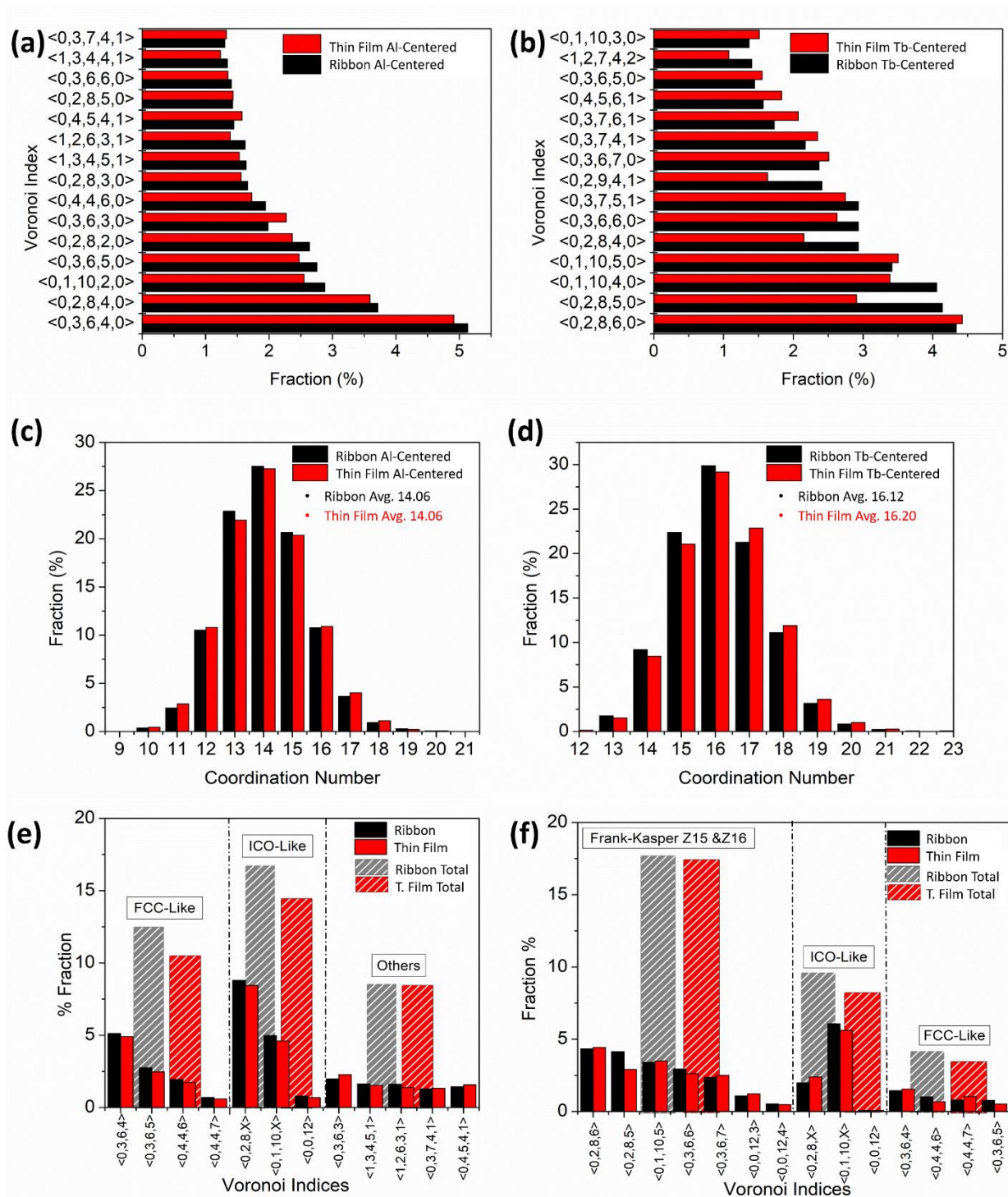


Figure 16. Fifteen most populated Voronoi cells of melt-spun ribbon and magnetron sputtered film for (a) Al centered cells, and (b) Terbium centered cells, Coordination number distribution of melt-spun ribbons and magnetron sputtered films around (c) Al atoms and (d) Tb atoms, most populated Voronoi cells categorized under the structures that they resemble of for (e) Al centered and (f) Tb centered atoms.

3.4. Cluster Analysis

Longer range correlations are structurally revealed by analyzing how certain types of clusters interact with each other. Interactions of the ten most populated Voronoi cells within themselves revealed two types of clusters in the structure. These are network clusters of much higher size extending beyond the simulation cell regardless of the simulation cell position and separate clusters in between the branches of the network clusters that can fit in a single simulation cell depending on the cell's position due to periodic boundary conditions. Network clusters are a single network of Voronoi cells which are interacting with each other, as given in Figures 15b and Figure 15c. These cells are present as a whole in the structure when the periodic boundary conditions are considered. Network clusters were extracted from the whole simulation cell in three steps. First central atoms of certain Voronoi cell atoms are left in the simulation box. Their first neighbor atoms included, and finally, upon the formed clusters, the ones that don't extend beyond the simulation cell and stand as a separate cell without contact from other clusters, considering the periodic boundary conditions, were removed. These two cluster types are not a direct result of a scattering experiment rather a combined result of XRD and EXAFS data used in RMC. Figure 17 a and b show $\langle 0,2,8,5 \rangle$ clusters, c and d the network clusters, e and f the separate clusters for the ribbon and sputtered samples, respectively.

Ten most populated V.P.s dominating the structure are analyzed, and the results are categorized under the three most pronounced structures in Tables 3 and 4 for ribbon and sputtered samples. Regardless of the Voronoi cell type, atoms in ribbon form a more extensive network cluster and a smaller number of separate clusters than atoms in thin-film. Thin-film samples have a smaller number of atoms overall. However, they form a bigger number of clusters, which indicates a more disordered structure on a larger scale for three types of structures indicated in Table 3 and Table 4.

Table 3. Cluster analysis of the atoms for the three most pronounced structures of ribbon sample.

Structure	Total # of Clusters	Total Atoms	Network cluster atoms	Separate cluster atoms
Ico-like	97	35356	32310 92.80%	2506 7.20%
Fcc-like	24	31144	30515 97.98%	629 2.02%
Frank Kasper Type Z15 & Z16	74	19847	17460 87.97%	2387 12.03%

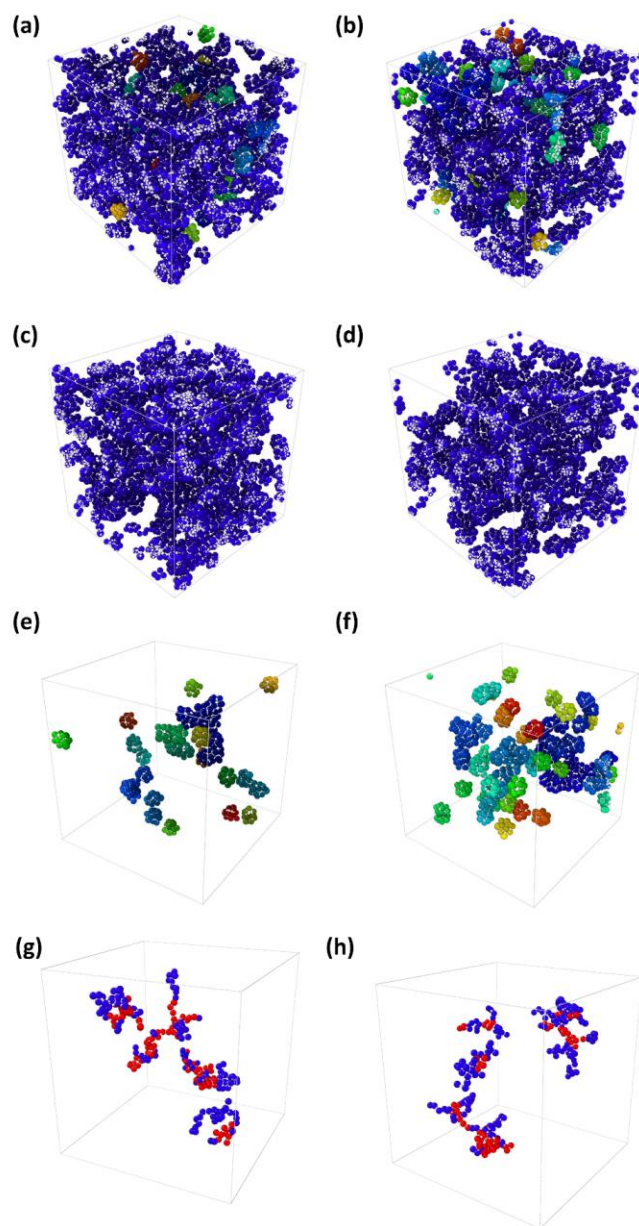


Figure 17. (a) and (b) cluster analysis of $\langle 0,2,8,5 \rangle$ Voronoi cells, (c) and (d) network clusters, (e) and (f) separate clusters for melt-spun ribbon and magnetron sputtered film respectively (Clusters were color-coded). Pure Al clusters in the structure for (g) melt-spun ribbon and (h) magnetron sputtered films, fcc-like cluster atoms (red) others (blue).

Table 4. Cluster analysis of the atoms for the three most pronounced structures of the thin-film sample.

Structure	Total # of Clusters	Total Atoms	Network Cluster atoms	Separate cluster atoms
Ico-like	104	32733	29528	3205
			90.21%	9.79%
Fcc-like	37	30139	29984	852
			97.24%	2.76%
Frank Kasper Type Z15 & Z16	89	19990	17239	2751
			86.24%	13.76%

Another point of interest is the pure Al clusters. These clusters were derived from the whole simulation box by removing all the terbium atoms with their first shell neighbors. This guarantees that Al atoms that were only in contact with other Al atoms were left in the simulation box. These atoms also form clusters of various sizes. The five biggest clusters of ribbon and sputtered samples are given in Figure 17g and 17h. There are 33 atoms at the center of fcc-like V.P.s; with the addition of the first shell neighbor, this number goes up to 120 (45%) atoms in a total of 263 atom systems for the ribbon. For sputtered samples, there are 23 atoms at the center of fcc-like V.P.s, added with the first neighbor shell going up to 87 (%34) atoms in a 253 atoms system. Just as in the previous cluster analyses, the pure Al cluster also has a more ordered ribbons structure. The percentage of fcc-like clusters is higher in the ribbon, as well.

Figure 18 shows the TEM images of melt-spun and sputtered thin-films in as-quenched and partially devitrified conditions. In as-quenched states, ribbon and thin-film specimens are fully amorphous, as shown in Figure 18a and 18. The initial crystallization product of both specimens is fcc-Al during continuous heating, as it was also detected in XRD studies. However, a significant difference between ribbon and thin-film is the morphology, size, and distribution of fcc-Al nanocrystals. In melt-spun ribbons, fcc-Al nanocrystals are highly dendritic and gathered together, as shown in Figure 18c.

On the other hand, sputtered thin-films devitrifies to spherical fcc-Al nanocrystal, which is well separated even at lower magnifications, as shown in Figure 18d. This statement is also confirmed by SAD patterns collected at similar magnification (Figure 18e and f). The fcc-Al reflections in melt-spun ribbons are in the form of discrete spots; however, in sputtered thin-films, they are continuous rings. This indicates that fcc-Al grains are much more refined in sputtered thin-film as compared to a melt-spun ribbon.

We consider that the difference in fcc-Al nanocrystallization behavior is directly related to the as-quenched structures. As previously indicated, independent of Voronoi cell type, atoms in ribbon form a bigger network cluster and a smaller number of separate clusters than the atoms in thin-film. Moreover, when the pure Al regions are investigated, ribbons have a higher percentage of fcc-like clusters. This shows that topological and chemical ordering in melt-spun ribbons is higher as compared to thin-films. Thin-films quenched from the vapor phase with a much higher cooling rate displays a relatively random distribution of Al-rich clusters.

On the other hand, in melt-spun ribbons, the sizes of the Al-rich clusters are larger with higher ordering. Upon heating, well separated fcc-Al nuclei are formed in thin-films. This was also previously confirmed by calculating the number of nucleation density of fcc-Al nanocrystals. In thin-films, the population of fcc-Al nanocrystal reaches up to 10^{24} m^{-3} . However, in the melt-spun ribbon, this value is measured as 10^{21} m^{-3} ³³. Three orders of magnitude difference in the number of nucleation density also affect the grown crystals' morphology. The rejection of Tb atoms from highly scattered Al-rich domains during crystallization causes a severe impingement in sputter thin-films, which results in restricted growth of nanocrystals.

The very same effect also causes the morphology of nanocrystals to stay as spheres in thin-films. On the other hand, the impingement is less significant as Al-rich domains are larger and far apart. In this case, fcc-Al grains grow into larger dendrites. The size and distribution of Al-rich domains also affect the crystallization temperature, as shown in Figure 19a. Peak temperatures of the first exothermic reaction indicating fcc-Al crystallization in sputtered thin-films and melt-spun ribbons were measured as 480 and 530 K, respectively. Ribbon samples show a relatively sharper and narrower peak at higher temperatures, whereas the thin-films peak is much broader at lower temperatures. By calculating the activation energies for the fcc-Al phase transformation by Kissinger and Ozawa approaches as given in Figure 19b and c, ribbons were found to have higher activation energy by a difference of 84 kJ/Mol as shown in Table 5. These measurements are in good agreement with the atomic configurations of amorphous ribbon and thin-films. The higher population of Al-rich domains with relatively smaller domain sizes in sputtered thin-films drives fcc-Al crystallization threshold to lower temperature with much lower activation energy. By analogy, this resembles supercooling observed in the melting of colloidal nanocrystals. The shape and size of nanocrystals affect several thermodynamic properties, including melting point⁵⁸. In that sense, fcc-Al's activation energy and crystallization temperature in sputtered thin-films are considerably different from those in melt-spun ribbon specimens. The difference in local topological and chemical orders in amorphous structure drives the system into an altered crystallization behavior during devitrification.

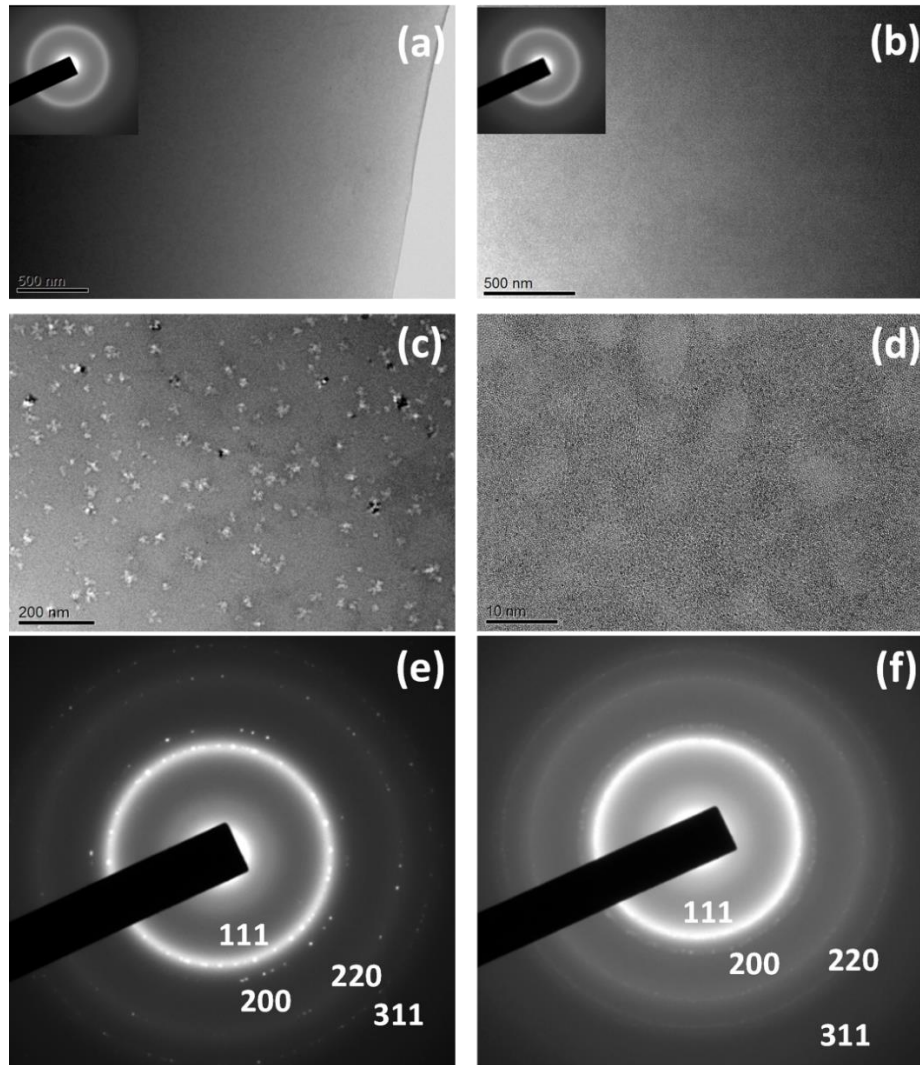


Figure 18. (a, b) Bright-field images and corresponding SAD patterns (in-sets), (c, d) bright-field images, and (e, f) SAD after initial crystallization of as-quenched ribbon and thin-film Al₉₀Tb₁₀, respectively. SAD indexing represents fcc-Al reflections.

Table 5. Activation energies for the crystallization of fcc-Al phase by Kissinger and Ozawa analysis in

$\text{Al}_{90}\text{Tb}_{10}$ metallic glasses

$\text{Al}_{90}\text{Tb}_{10}$	Kissinger E_c (kJ/Mol)	Ozawa E_c (kJ/Mol)
Ribbon	298 ± 1	291 ± 2
Thin-film	210 ± 1	207 ± 2

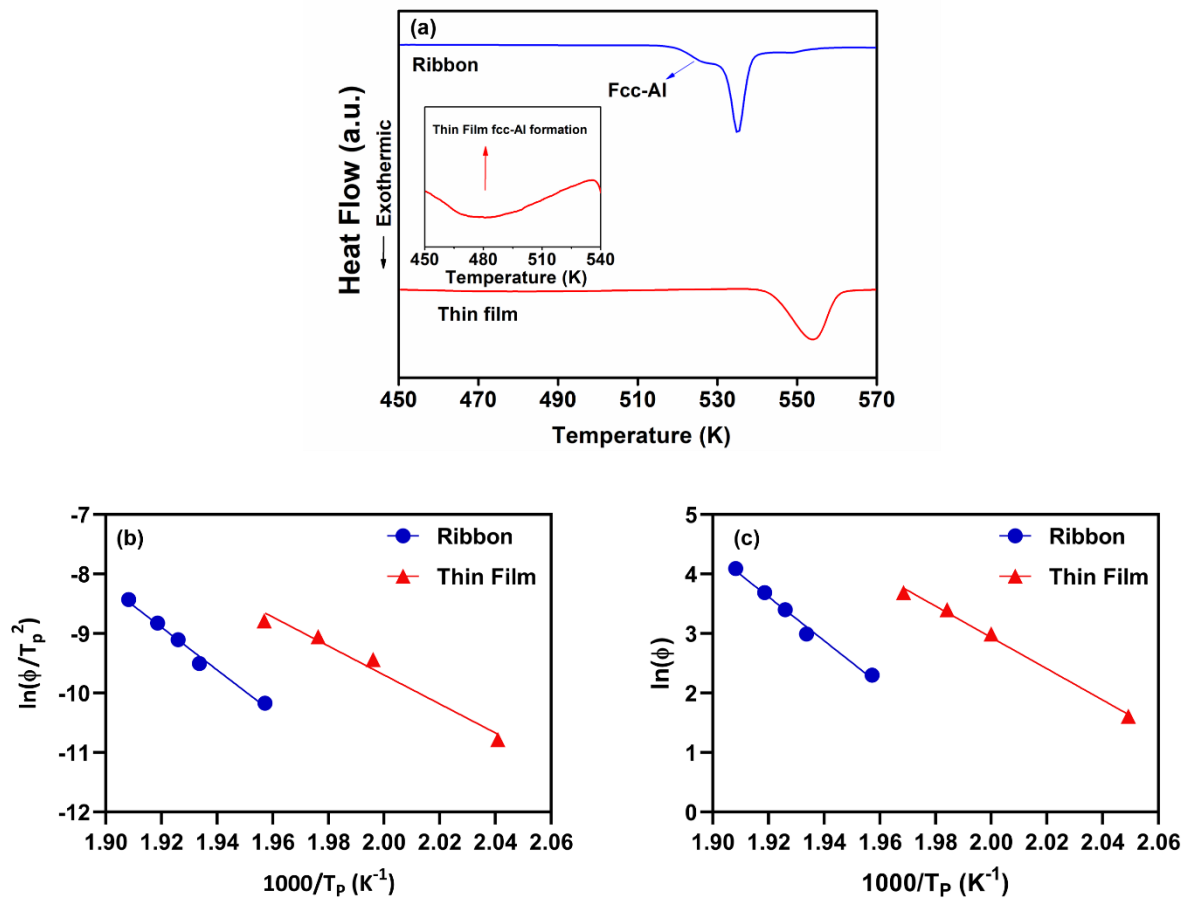


Figure 19. (a) Continuous DSC traces for melt-spun ribbons and sputtered thin-films collected at 40 K/min heating rate (b) Kissinger and (c) Ozawa plots.

3.5. Mechanical Testing

DSC traces of the $\text{Al}_{90}\text{Tb}_{10}$ sample given in Figure 20 shows the structural changes accompanied by heating from room temperature up to 500 °C. The first exothermic peak labeled as transformation region from around 230 °C is the fcc-Al nanocrystal formation region. Four heat-treated samples are chosen as 241 °C as the start of the fcc-Al crystallization, 251 °C deeper into the fcc-Al region, 259 °C the end of fcc-Al and the start of intermetallic region, and finally 263 °C deeper into the intermetallic region.

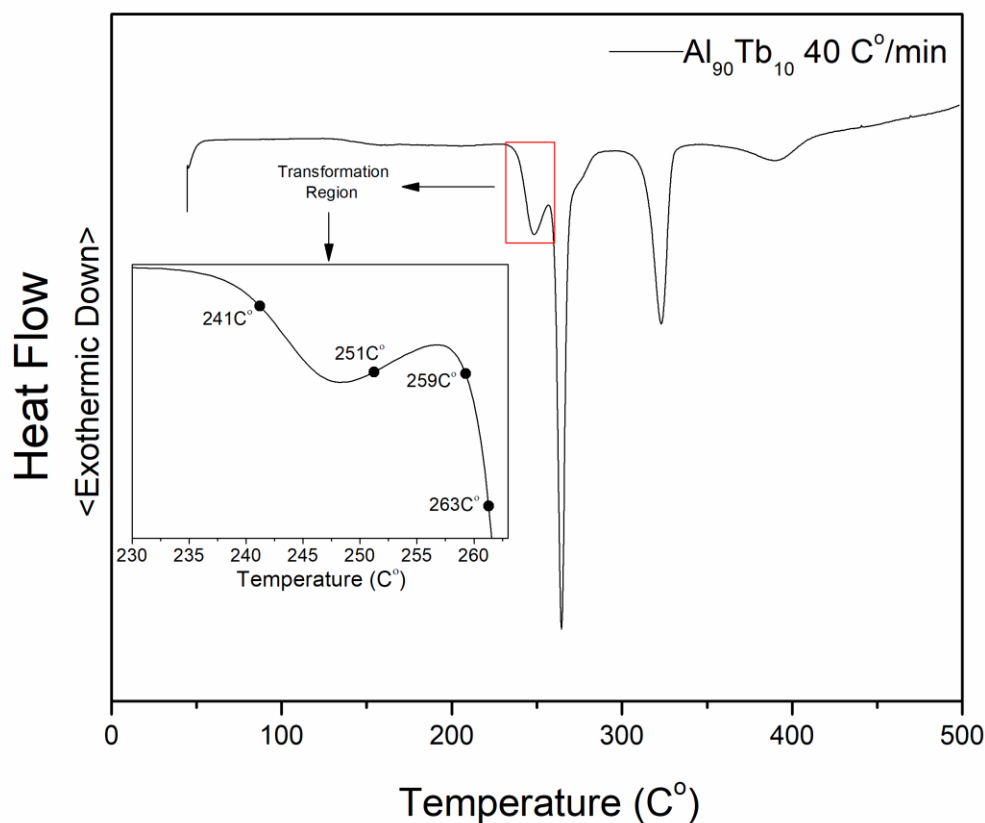


Figure 20. Differential scanning calorimetry traces of $\text{Al}_{90}\text{Tb}_{10}$ samples. Inset showing the annealing temperatures in the first fcc-Al crystallization and second the intermetallic compound formation.

A fully amorphous non-heat treated sample as a reference is given in Figure 21. Micropillars showed that the samples were broken in a brittle manner with serrated flow starting from lower stress values with smaller strain bursts. As stress increase, strain bursts become broader and more extended. Fracture stress for these samples is about 0.9 GPa. The brittle nature of the samples can also be observed from the SEM images of deformed micropillars. Multiple shear bands formed are at around 45°, and almost all shear bands start and extend through the sample.

These are the characteristics of faster shear band propagation and hence more catastrophic, brittle failure, as shown in Figure 21.

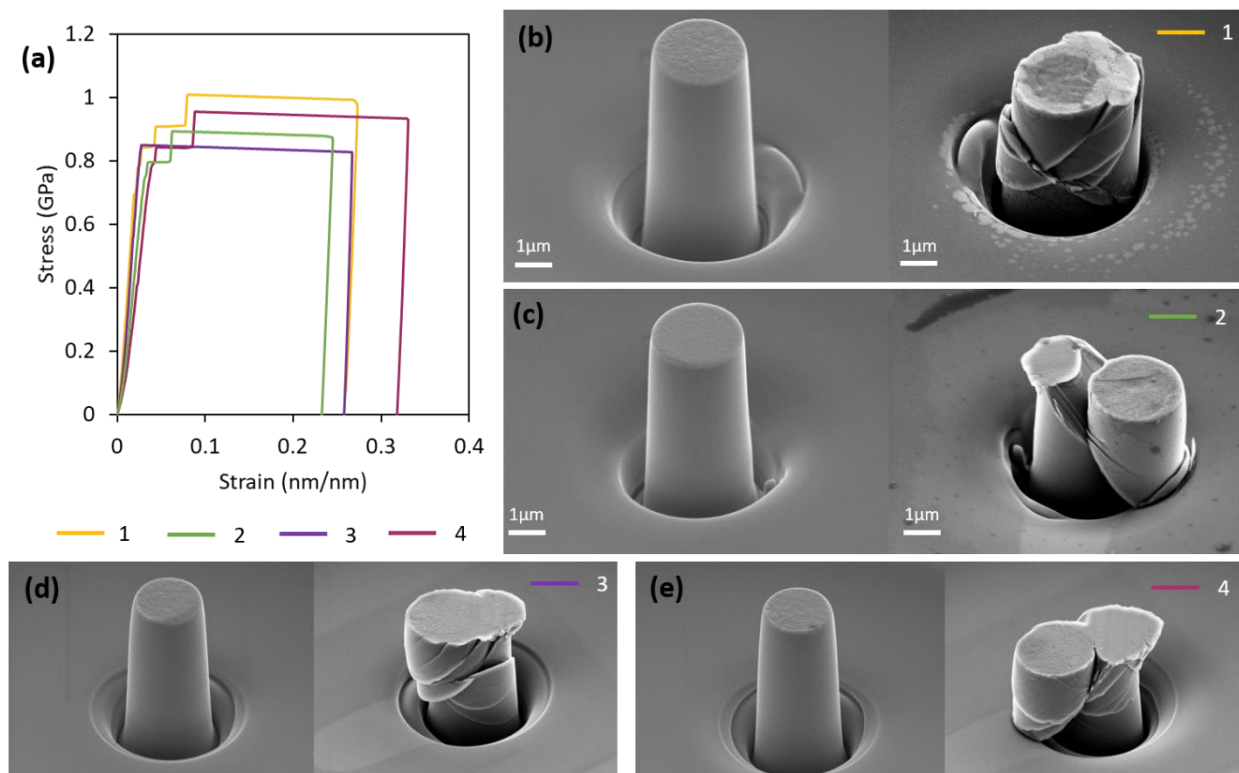


Figure 21. Al₉₀Tb₁₀ fully amorphous (a) Stress-strain diagram of 4 samples, (b), (c), (d), and (e) SEM images of micropillars and fracture surfaces.

Samples heat-treated at 241 °C show an increase in fracture stress. Following the introduction of nanocrystals, fracture stress goes beyond 1 GPa. Also, there is an increase in smaller shear bursts in the low-stress region and a decrease in big shear bursts. This behavior is considered a result of shear bands not finding an area to grow before they get intercepted by crystals. Similar results can be seen by SEM images of fracture surfaces as well. There is a noticeable decrease in the amount of big shear band cracks that extend through the sample, as shown in Figure 22.

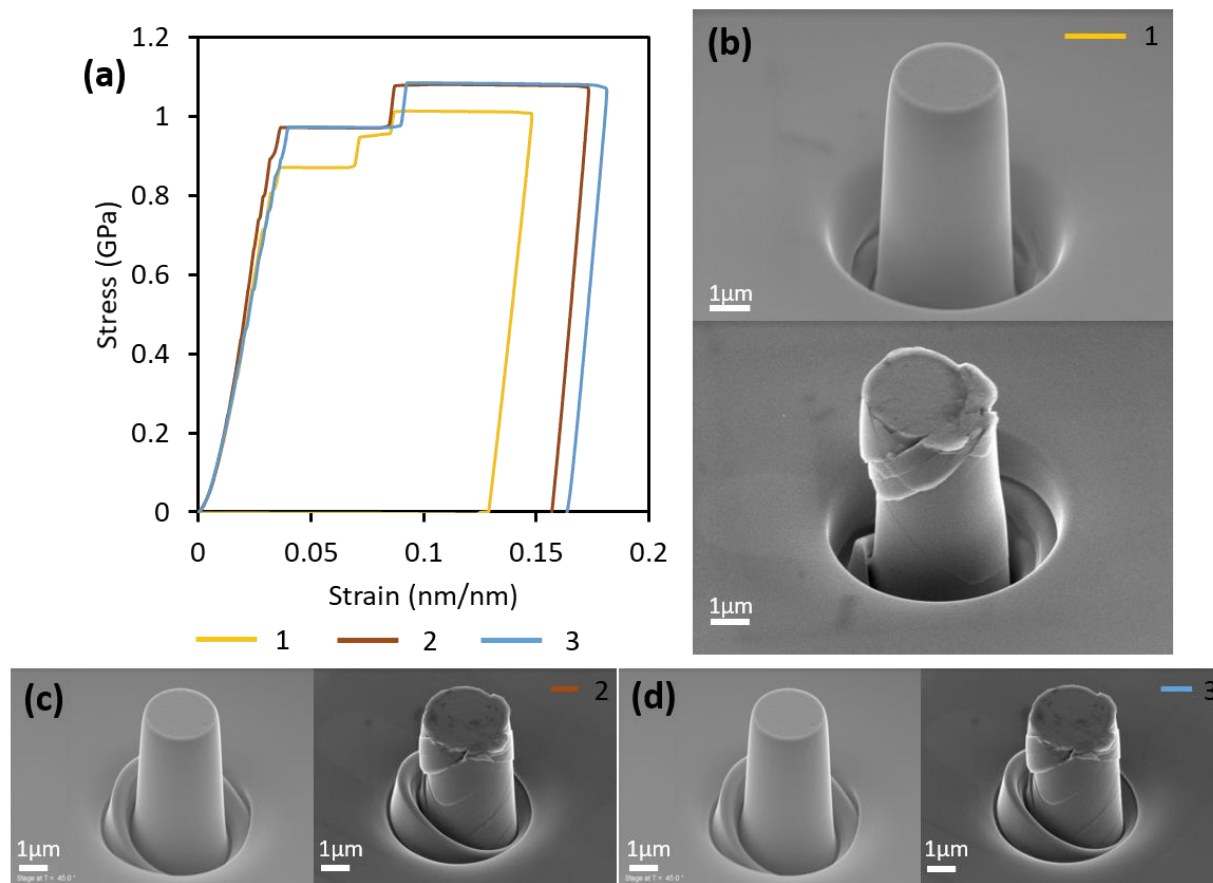


Figure 22. $\text{Al}_{90}\text{Tb}_{10}$ 241 °C heat-treated (a) Stress-strain diagram of 3 samples, (b), (c) and (d) SEM images of micropillars and fracture surfaces.

Samples heat-treated at 251 °C show similar behavior as fracture stress continues to rise to 1.2 GPa. Accompanied by the increased amount of nanocrystals introduced in the amorphous matrix, small shear burst regions in low-stress values become more ductile. In the 241 °C heat-treated samples, only one or two big shear bursts before failure at high-stress values. SEM images of the fracture surfaces show the one big shear burst that extends through the samples, causing the failure to accompany smaller shear bursts, as shown in Figure 23.

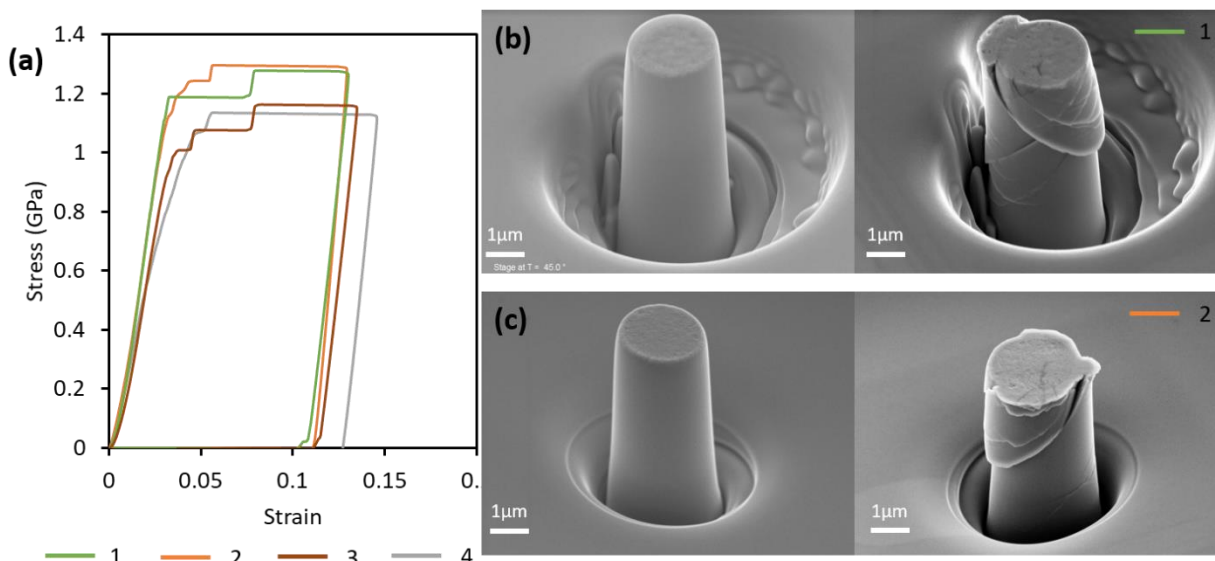


Figure 23. $\text{Al}_{90}\text{Tb}_{10}$ 251 °C heat-treated (a) Stress-strain diagram of 4 samples, (b) and (c) SEM images of micropillars and fracture surfaces.

As heat treatment temperature increases to 259 °C intermetallic compound formation starts, fracture stress increase comes to an end. Smaller shear bursts in the low-stress regions cease to exist, as shown in Figure 24.

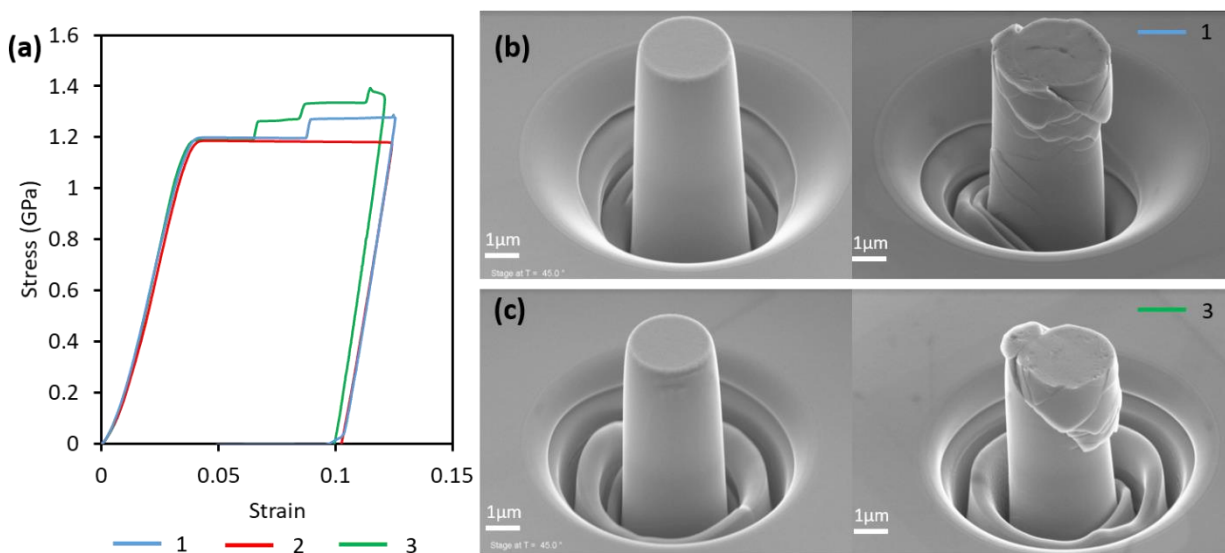


Figure 24. $\text{Al}_{90}\text{Tb}_{10}$ 259 °C heat-treated (a) Stress-strain diagram of 3 samples, (b) and (c) SEM images of micropillars and fracture surfaces.

Heat treatment up to intermetallic formation temperature results in an increase in fracture stress; however, small strain bursts are almost entirely gone. There is a slight increase in prominent strains, indicating an increase in brittleness as expected since Al and Tb's intermetallic compounds are extremely brittle in Figure 25.

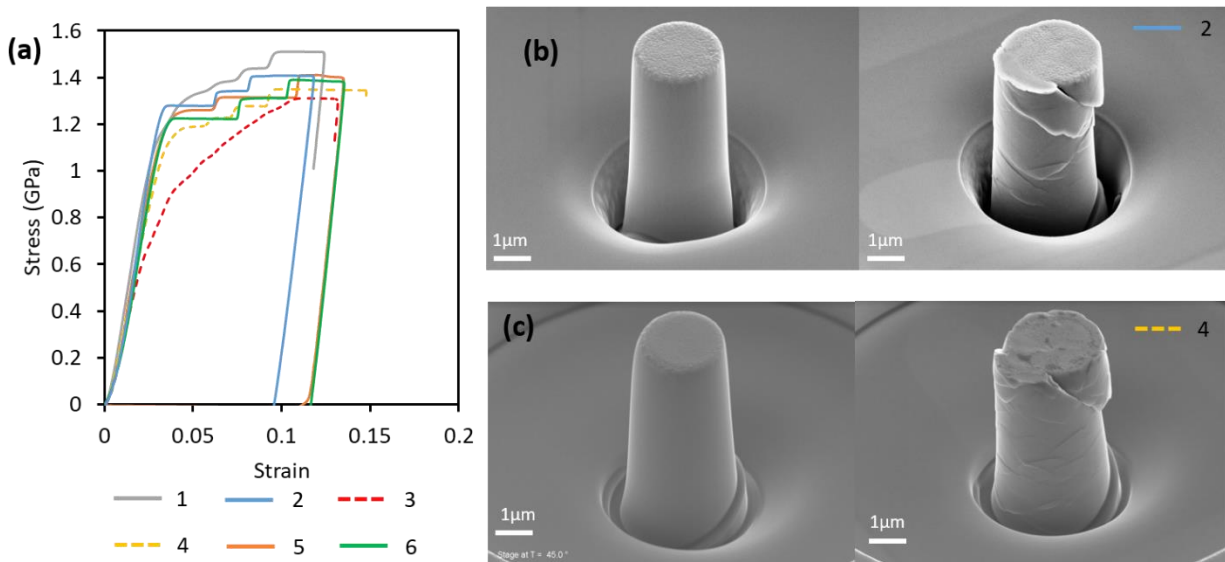


Figure 25. $\text{Al}_{90}\text{Tb}_{10}$ 263 °C heat-treated (a) Stress-strain diagram of 6 samples, (b) and (c) SEM images of micropillars and fracture surfaces.

4. Conclusion

In this project, the structural analysis, abnormal crystallization behavior, and mechanical properties of fully amorphous, partially crystallized $\text{Al}_{90}\text{Tb}_{10}$ marginal glass former alloys produced via melt spinning and magnetron sputtering were studied in detail.

The effects of amorphous structure in melt-spun ribbon and sputtered thin-film on nucleation and growth behavior of fcc-Al nanocrystals were comprehensively investigated by a combination of electron and X-ray oriented characterization techniques in $\text{Al}_{90}\text{Tb}_{10}$ metallic glasses. EXAFS, HEXRD, and ab-initio constrained RMC results showed that melt-spun alloys have a higher degree of order than sputtered thin-films. Ribbons having a higher % of 15 most populated Voronoi cells, which dominate the structure, show that amount of repetition is higher, and therefore, SRO is more pronounced than film samples. Clusters of pure Al identified by Voronoi analyses were smaller and spatially scattered in thin-film specimens than melt-spun ribbons. Analyzing the five most massive clusters for both conditions revealed that ribbon samples have a significantly higher percentage of fcc-like structures than the thin-film specimens. These pure Al clusters embedded in the structure were considered nucleation domains for fcc Al crystals upon heating. TEM investigations are in good agreement with RMC simulations. The fcc-Al nanocrystals nucleated and grown in thin-film specimens have a limited size with almost perfect spherical morphology. The population of these nanocrystals is three orders of magnitude higher as compared to ribbon specimens. The thermal analyses revealed that the energy barrier for nucleation of the first fcc crystals was significantly lower for thin-film specimens. The spatially

well-separated domains cause the energy barrier for nucleation of the first fcc crystals to be significantly lower for thin-film specimens. As the fcc-Al nanocrystals grow further, the rejected Tb atoms cause an aggressive soft impingement in thin-films, restricting individual fcc-Al nanocrystals' size to stay less than 50 nm.

Mechanical properties of the $\text{Al}_{90}\text{Tb}_{10}$ system were studied using micropillar analyses and nanoindentation. It has been seen that introduction of fcc- Al nanocrystals have made considerable improvements in both fracture stress and ductility, overcoming the ductility vs. strength trade-off. This is considered to be achieved by restricting the movement of shear bands at nanocrystals embedded in the amorphous matrix. Increasing the heat treatment temperature up to the end of fcc-Al transformation temperature promotes nanocrystals' formation and further improves ductility and fracture stress. However, increasing heat treatment temperature beyond this point causes intermetallic phase formation, which decreases ductility.

Acknowledgment

The PIs would like to acknowledge the funding and support from the Air Force Office Of Scientific Research, which made this research possible.

5. References

1. Lobzenko, I., Shiihara, Y., Iwashita, T. & Egami, T. Shear Softening in a Metallic Glass: First-Principles Local-Stress Analysis. *Phys. Rev. Lett.* **124**, 085503 (2020).
2. Guo, H. *et al.* Tensile ductility and necking of metallic glass. *Nat. Mater.* **6**, 735–739 (2007).
3. Cheng, Y. Q. & Ma, E. Atomic-level structure and structure–property relationship in metallic glasses. *Prog. Mater. Sci.* **56**, 379–473 (2011).
4. Hofmann, D. C. *et al.* Designing metallic glass matrix composites with high toughness and tensile ductility. *Nature* **451**, 1085–1089 (2008).
5. Inoue, A. & Takeuchi, A. Recent development and application products of bulk glassy alloys. *Acta Mater.* **59**, 2243–2267 (2011).
6. Wang, W. H. The elastic properties, elastic models and elastic perspectives of metallic glasses. *Progress in Materials Science* **57**, 487–656 (2012).
7. Ding, J. & Ma, E. Computational modeling sheds light on structural evolution in metallic glasses and supercooled liquids. *npj Computational Materials* **3**, 1–12 (2017).
8. Cheng, Y. Q., Ma, E. & Sheng, H. W. Atomic level structure in multicomponent bulk metallic glass. *Phys. Rev. Lett.* **102**, 245501 (2009).
9. He, Y., Poon, S. J. & Shiflet, G. J. Synthesis and properties of metallic glasses that contain aluminum. *Science (80-.).* **241**, 1640–1642 (1988).
10. Wagner, H. *et al.* Local elastic properties of a metallic glass. *Nat. Mater.* **10**, 439–442 (2011).
11. Schuh, C. A. & Lund, A. C. Atomistic basis for the plastic yield criterion of metallic glass. *Nature Materials* **2**, 449–452 (2003).
12. Nagahama, D., Ohkubo, T., Mukai, T. & Hono, K. Characterization of nanocrystal dispersed Cu₆₀Zr₃₀Ti₁₀ metallic glass. *Mater. Trans.* **46**, 1264–1270 (2005).
13. Dandliker, R. B., Conner, R. D. & Johnson, W. L. Melt infiltration casting of bulk metallic-glass matrix composites. *J. Mater. Res.* **13**, 2896–2901 (1998).
14. He, Y., Shiflet, G. J. & Poon, S. J. Ball milling-induced nanocrystal formation in aluminum-based metallic glasses. *Acta Metall. Mater.* **43**, 83–91 (1995).
15. Fan, C. & Inoue, A. Ductility of bulk nanocrystalline composites and metallic glasses at room temperature. *Appl. Phys. Lett.* **77**, 46–48 (2000).
16. Kalay, Y. E., Kalay, I., Hwang, J., Voyles, P. M. & Kramer, M. J. Local chemical and topological order in Al-Tb and its role in controlling nanocrystal formation. *Acta Mater.* (2012).

17. Demirtaş, T. & Kalay, Y. E. Kinetics of fcc-Al nanocrystallization in Al₉₀Tb₁₀ metallic glass. *J. Non. Cryst. Solids* (2013).
18. Perepezko, J. H., Hebert, R. J., Wu, R. I. & Wilde, G. Primary crystallization in amorphous Al-based alloys. in *Journal of Non-Crystalline Solids* (2003).
19. Allen, D. R., Foley, J. C. & Perepezko, J. H. Nanocrystal development during primary crystallization of amorphous alloys. *Acta Mater.* (1998).
20. Inoue, A. Amorphous, nanoquasicrystalline and nanocrystalline alloys in Al-based systems. *Progress in Materials Science* **43**, 365–520 (1998).
21. Stratton, W. G. *et al.* Aluminum nanoscale order in amorphous Al₉₂Sm₈ measured by fluctuation electron microscopy. *Appl. Phys. Lett.* (2005).
22. Wilde, G., Sieber, H. & Perepezko, J. H. Glass formation versus nanocrystallization in an Al₉₂Sm₈ alloy. *Scr. Mater.* (1999).
23. Gangopadhyay, A. K., Croat, T. K. & Kelton, K. F. Effect of phase separation on subsequent crystallization in Al₈₈Gd₆La₂Ni₄. *Acta Mater.* (2000).
24. Croat, T. K., Gangopadhyay, A. K. & Kelton, K. F. Crystallization in Al₈₈Re₈Ni₄ glass-forming alloys. *Philos. Mag. A Phys. Condens. Matter, Struct. Defects Mech. Prop.* (2002).
25. Sahu, K. K. *et al.* Phase separation mediated devitrification of Al₈₈Y₇Fe₅ glasses. *Acta Mater.* (2010).
26. Hono, K., Ping, D. H., Ohnuma, M. & Onodera, H. Cu clustering and Si partitioning in the early crystallization stage of an Fe_{73.5}Si_{13.5}B₉Nb₃Cu₁ amorphous alloy. *Acta Mater.* **47**, 997–1006 (1999).
27. Kajiwar, K., Ohnuma, M., Ohkubo, T., Ping, D. H. & Hono, K. APFIM/TEM/SAXS studies of early stage crystallization of a Zr_{52.5}Cu_{17.9}Ni_{14.6}Al₁₀Ti₅ metallic glass. *Mater. Sci. Eng. A* **375–377**, 738–743 (2004).
28. Kramer, M. J. & Li, M. Changes in short- And medium-range order in metallic liquids during undercooling. *MRS Bulletin* **45**, 943–950 (2020).
29. Meng, F. Q., Zhou, S. H., Ott, R. T., Kramer, M. J. & Napolitano, R. E. Competitive devitrification and metastable phase selection in amorphous Al–Sm. *Materialia* **9**, 100595 (2020).
30. Zhou, S. H. *et al.* Metastable intermetallic phases in the Al–Sm system. *Mater. Today Commun.* **21**, 100673 (2019).
31. Sun, Y. *et al.* Crystal Genes' in Metallic Liquids and Glasses. *Sci. Rep.* **6**, 1–8 (2016).
32. Ovun, M., Kramer, M. J. & Kalay, Y. E. Structural modeling of liquid and amorphous Al₉₁Tb₉ by Monte Carlo simulations. *J. Non. Cryst. Solids* (2014).
33. Yildirim, C. *et al.* The role of amorphous precursor in phase selection hierarchy in

- marginal metallic glasses. *Mater. Des.* **112**, 479–484 (2016).
34. An, Q., Johnson, W. L., Samwer, K., Corona, S. L. & Goddard, W. A. First-Order Phase Transition in Liquid Ag to the Heterogeneous G-Phase. *J. Phys. Chem. Lett.* **11**, 632–645 (2020).
 35. An, Q., Johnson, W. L., Samwer, K., Corona, S. L. & Goddard, W. A. Formation of two glass phases in binary Cu-Ag liquid. *Acta Mater.* **195**, 274–281 (2020).
 36. Zhang, H., Geng, J., Ott, R. T., Besser, M. F. & Kramer, M. J. Effect of Temperature on the Nano/Microstructure and Mechanical Behavior of Nanotwinned Ag Films. *Metall. Mater. Trans. A Phys. Metall. Mater. Sci.* **46**, 4078–4085 (2015).
 37. Juhás, P., Davis, T., Farrow, C. L. & Billinge, S. J. L. PDFgetX3: A rapid and highly automatable program for processing powder diffraction data into total scattering pair distribution functions. *J. Appl. Crystallogr.* (2013).
 38. Coati, A. *et al.* Status of the crystallography beamlines at synchrotron SOLEIL*. *Eur. Phys. J. Plus* **132**, 1–9 (2017).
 39. Ravel, B. & Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: Data analysis for X-ray absorption spectroscopy using IFEFFIT. in *Journal of Synchrotron Radiation* (2005).
 40. Savitzky, A. & Golay, M. J. E. Smoothing and Differentiation of Data by Simplified Least Squares Procedures. *Anal. Chem.* (1964).
 41. Calvin, S. *XAFS for Everyone. Igarss 2014* (2014).
 42. Gereben, O., Jóvári, P., Temleitner, L. & Pusztai, L. A new version of the RMC++ Reverse Monte Carlo programme, aimed at investigating the structure of covalent glasses. in *Journal of Optoelectronics and Advanced Materials* (2007).
 43. Gereben, O. & Pusztai, L. RMC-POT: A computer code for reverse monte carlo modeling the structure of disordered systems containing molecules of arbitrary complexity. *J. Comput. Chem.* (2012).
 44. Rycroft, C. H. VORO++: A three-dimensional Voronoi cell library in C++. *Chaos* (2009).
 45. Voronoi, G. Nouvelles applications des paramètres continus à la théorie des formes quadratiques. Deuxième mémoire. Recherches sur les paralléloèdres primitifs. *J. fur die Reine und Angew. Math.* (1908).
 46. Kissinger, H. E. Reaction Kinetics in Differential Thermal Analysis. *Anal. Chem.* (1957).
 47. Ozawa, T. A New Method of Analyzing Thermogravimetric Data. *Bull. Chem. Soc. Jpn.* **38**, 1881–1886 (1965).
 48. Pearson's crystal data: crystal structure database for inorganic compounds. *Choice Rev. Online* (2013).
 49. Gumeniuk, R. ., Stel'makhovych, B. . & Kuz'ma, Y. . The Tb–Ag–Al system. *J. Alloys Compd.*

- (2002).
50. Ravel, B. & Kelly, S. D. The difficult chore of measuring coordination by EXAFS. in *AIP Conference Proceedings* (2007).
 51. Bacewicz, R. & Antonowicz, J. XAFS study of amorphous Al-RE alloys. *Scr. Mater.* **54**, 1187–1191 (2006).
 52. Malet, P. *et al.* Methane Coupling Over Sm-Al Mixed Oxides. *Stud. Surf. Sci. Catal.* (1994).
 53. Bowron, D., Saunders, G., Newport, R., Rainford, B. & Senin, H. EXAFS studies of rare-earth metaphosphate glasses. *Phys. Rev. B - Condens. Matter Mater. Phys.* **53**, 5268–5275 (1996).
 54. Anderson, R. *et al.* An extended x-ray absorption fine structure study of rare-earth phosphate glasses near the metaphosphate composition. *J. Mater. Res.* **14**, 4706–4714 (1999).
 55. Hsieh, H. Y., Egami, T., He, Y., Poon, S. J. & Shiflet, G. J. Short range ordering in amorphous $\text{Al}_{90}\text{Fe}_x\text{Ce}_{10-x}$. *J. Non. Cryst. Solids* (1991).
 56. Kalay, Y. E., Chumbley, L. S., Kramer, M. J. & Anderson, I. E. Local structure in marginal glass forming Al-Sm alloy. *Intermetallics* **18**, 1676–1682 (2010).
 57. Luo, W. K. & Ma, E. EXAFS measurements and reverse Monte Carlo modeling of atomic structure in amorphous Ni₈₀P₂₀ alloys. *J. Non. Cryst. Solids* (2008).
 58. Liu, M. & Wang, R. Y. Size-dependent melting behavior of colloidal in, Sn, and Bi nanocrystals. *Sci. Rep.* **5**, 1–9 (2015).

6. List of Symbols, Abbreviations, and Acronyms

2D: 2 Dimensional

3D: 3 Dimensional

$\lambda(k)$: Mean Free Path of Photoelectrons

APT: Atom Probe Tomography BMG Bulk Metallic Glass CN Coordination number

DSC: Differential Scanning Calorimetry

EDS: Electron Dispersive Spectroscopy

ETM: Early Transition Metals

$f(k)$: Elastic Scattering Probability

$f_i(Q)$: Atomic Scattering Factor

FCC: Face Centered Cubic

EXAFS: Extended X-ray Absorption Fine Structure

FEM: Fluctuation Electron Microscopy

FCC: Face Centered Cubic

$g(r)$: Pair Distribution Function/Pair Correlation Function

GFA: Glass Forming Ability

GFR: Glass Formation Range

HEXRD: High Energy X-ray Diffraction

HRTEM: High Resolution Transmission Electron Microscopy

$I_c(Q)$: Coherently Scattered X-ray Intensity

K: Wavenumber

LRO: Long-Range Order

LTM: Late Transition Metals

MRO: Medium-Range Order

N: Degeneracy

PDF: Pair Distribution Function

SRO: Short Range Order

Q: Wavevector (nm^{-1})

R_i : Debye-Waller Factor

RE: Rare Earth Metal

RMC: Reverse Monte Carlo

SEM: Scanning Electron Microscopy

$S(Q)$: Total Structure Factor

S_0^2 : Amplitude Reduction Factor

SAED: Selected Area Electron Diffraction

SRO: Short-Range Order

TEM: Transmission Electron Microscopy

TM: Transition Metal

V.P.: Voronoi Polyhedra

XAFS: X-ray Absorption Fine Structure

XANES: X-ray absorption near edge structure

7. Project Outputs

Thesis:

T. H. Ulucan, MS Thesis: "Local Structure and Chemistry in Marginal Glass Forming Alloys", 2020.

Publications:

T. H. Ulucan, İ. Kalay, Y.E. Kalay " The Anomalous Nucleation in Al-Tb Metallic Glasses," Metallurgical and Materials Transactions A, accepted, in-press.

T.H. Ulucan, İ. Kalay, S. Özerinç, Y.E. Kalay, "Mechanical Properties of Amorphous and Partially crystallized Al₉₀Tb₁₀ Metallic Glasses.", to be submitted.

Presentations:

T. H. Ulucan, İ. Kalay, Y.E. Kalay, "The Intriguing Structure of Marginal Glass Forming Alloys", TMS, 2020.

İ. Kalay, T.H. Ulucan, S. Özerinç, Y.E. Kalay, "Micromechanical Properties of Marginal Glass Forming Alloys", TMS, 2020.

B. Yaşar, İ.Kalay, Y.E. Kalay, "The Influence of Liquid Structure on the Devitrification of Solid Amorphous Al-based Marginal Glass Forming Alloys", TMS, 2018.

Awards:

M. Kutsal, B. Yaşar, Y.E. Kalay, "The Effect of Transition Metal in Devitrification of Al-TM-RE Marginal Glass Forming Alloys", Best Poster Award-First Place, EPD Materials Characterization Awards, TMS 2018.