Medium-Range Order of Metallic Glass Thin Films

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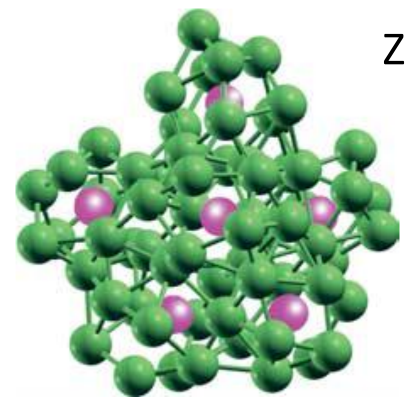
Findings of this work

- Medium range order in metallic glass thin films is lower than the bulk materials, for both the marginal glass $Al_{90}Tb_{10}$ and the bulk metallic glass $Zr_{53}Cu_{29}Al_{12}Ni_6$.
- In ZrCuAlNi glass, annealing induces short and medium range structural at temperatures much lower than Tg. Annealing over time also widens compositional segregation of Zr and Cu.

Introduction: formation of medium range order in metallic glass

- MROs result from connection of short-range-order clusters.

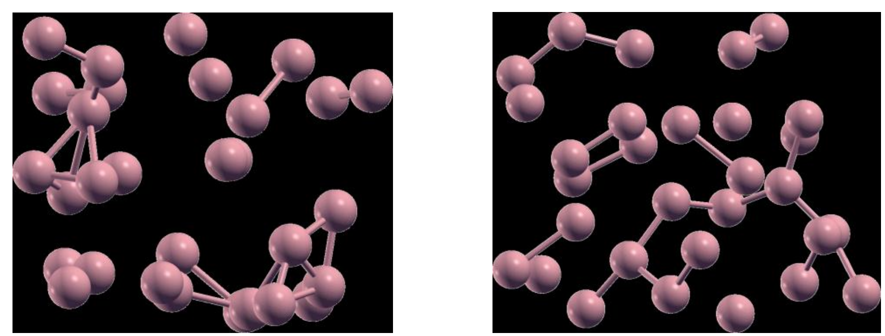


$Zr_{84}Pd_{16}$

H. W. Sheng et al, NATURE **439** 26, 2006

- To study how MROs change with MG cooling condition, our experiment compares MROs in liquid-quenched bulk MG with vapor deposited MG thin film.

$Zr_{70}Pd_{30}$

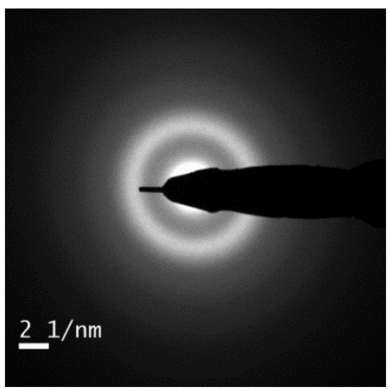


1800 K   300 K

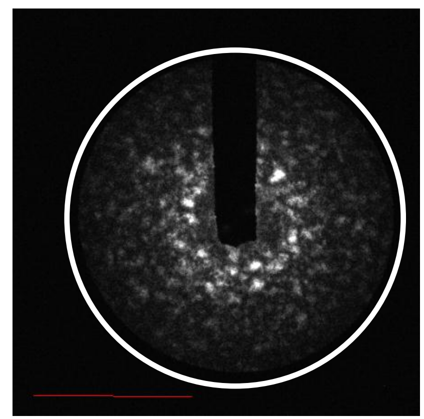
Experiment: fluctuation electron microscopy

- MRO: three or four body correlations in atomic structures depicted in <I^2>.

$$V(k) = \frac{< I(k,\boldsymbol{r})^2 >_{\boldsymbol{r}}}{< I(k,\boldsymbol{r}) >_{\boldsymbol{r}}{}^2} - 1$$



Broad electron beam diffraction

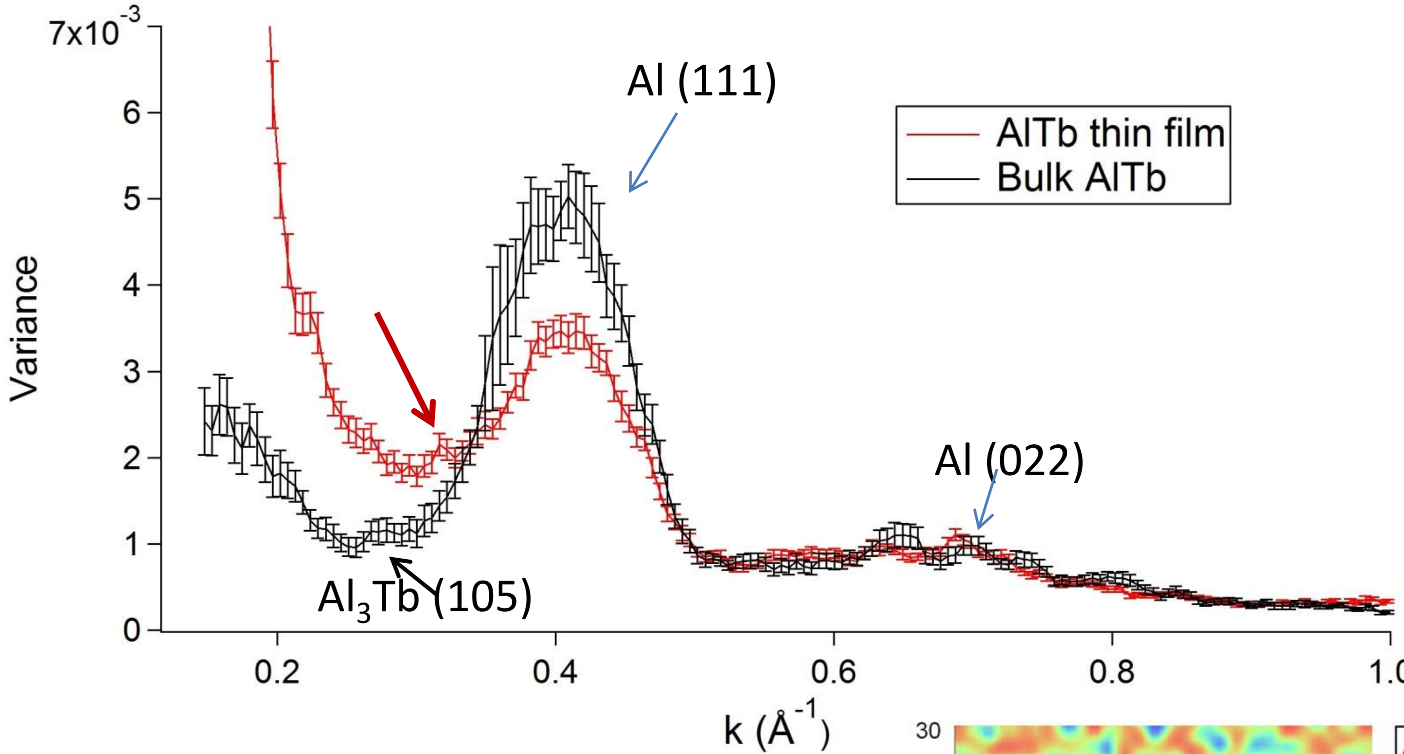


Nano beam diffraction

Average I and I^2 over the same k.

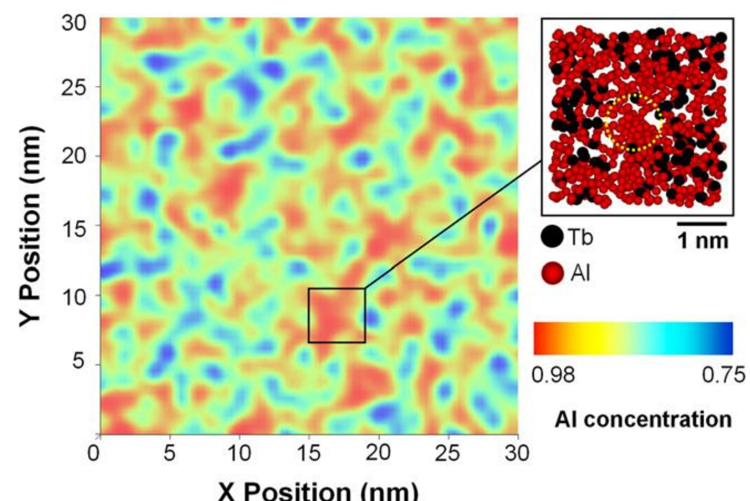
M M J Treacy et al., Rep. Prog. Phys. **68** (2005) 2899–2944
“Fluctuation Electron Microscopy” Jinwoo Hwang and P. M. Voyles, in *Characterization of Materials*, E. N. Kaufmann, ed., Wiley (2012).

Metallic glass I: AlTb



MG samples: bulk $Al_{90}Tb_{10}$, melt-spinning; $Al_{90}Tb_{10}$ film, sputtering. FEM conditions: 2 nm electron beam, 1000 sample positions.

Bulk $Al_{90}Tb_{10}$ atom probe data

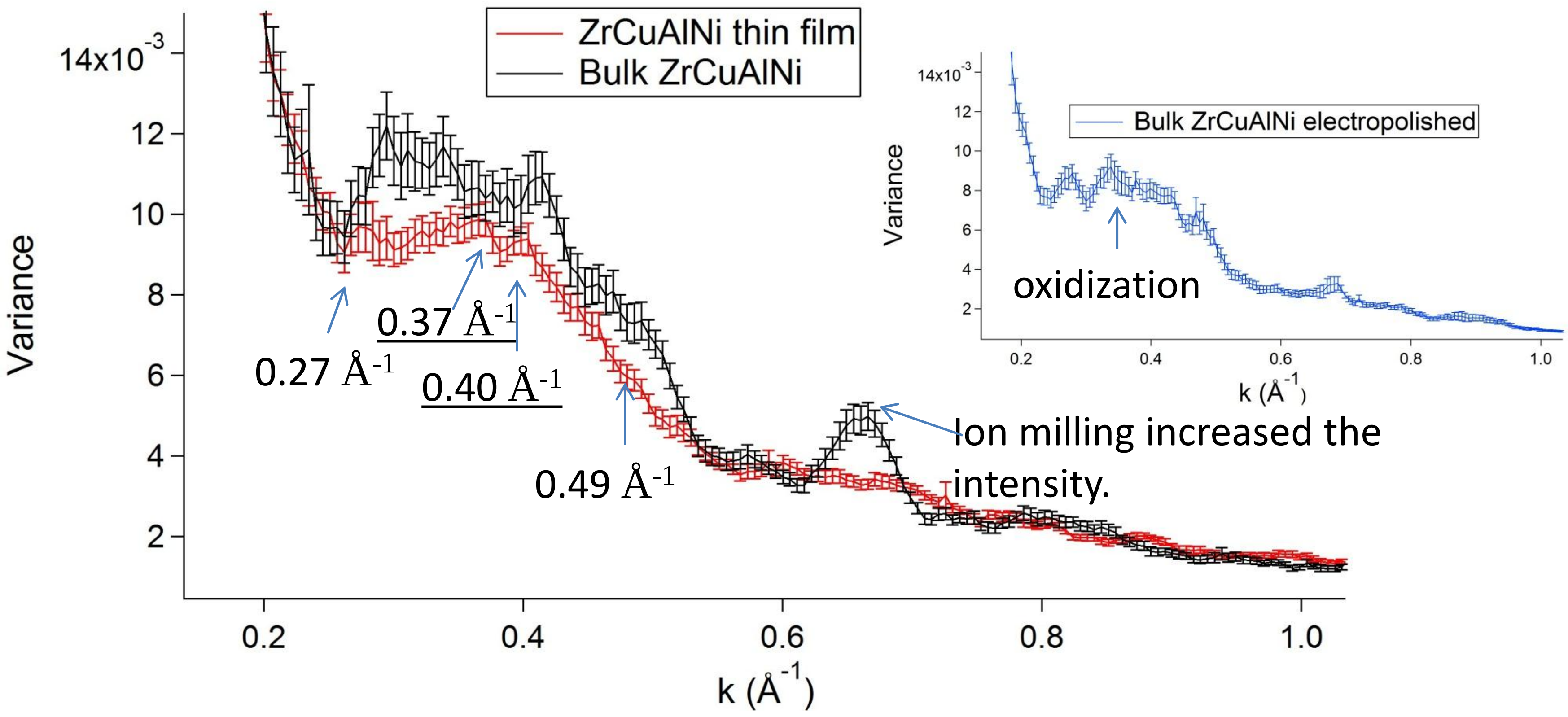


Y.E. Kalay et al. / Acta Materialia **60** (2012) 994–1003

MRO in AlTb

- Lower variance intensity at the major peak suggests lower level of Al-like MROs or more homogeneous glass are present in the thin film.
- The pre-peak (indicated by arrows) shifts to higher k.
- Variance peaks at high k (0.6-0.8 $Å^{-1}$, k=1/d) is lower in the thin film. As smaller d is more sensitive to disorder, this reflects a more disordered structure.
- **Increasing cooling rate appears to reduce MROs and increase intermixing of Al and Tb.**

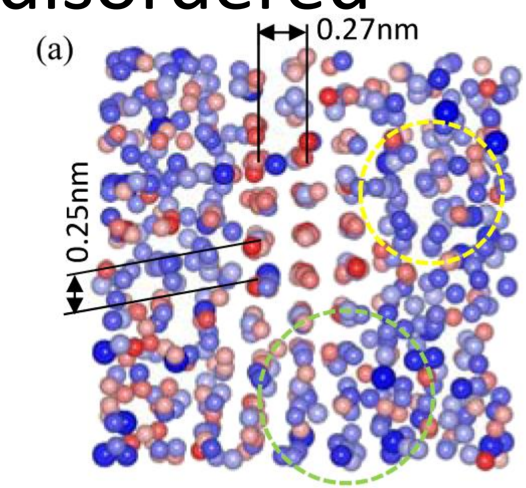
Metallic glass II: ZrCuAlNi



$Zr_{53}Cu_{29}Al_{12}Ni_6$, 20 nm thin film was sputtered on 5 nm thick amorphous Si. Bulk ingot was produced by arc melting. Ion milling: 4 kV Ar^+.

MRO in ZrCuAlNi

- A variety of MROs exist in both thin film and bulk ZrCuAlNi. The difference in MROs could be rotational symmetry or others[1].
- Thin film is more homogeneous than bulk material. The missing of MRO peak in thin film at ~0.68 $Å^{-1}$ also reflects a more disordered structure.

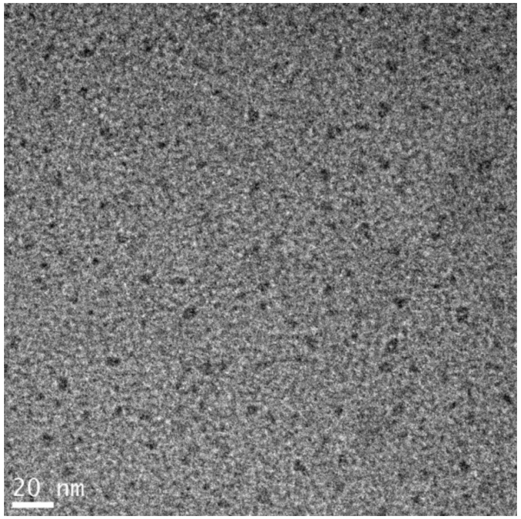


1. Jinwoo Hwang et al, PRL **108**, 195505 (2012)

This paper reports 0. 37 $Å^{-1}$ and 0.40 $Å^{-1}$ MROs in $Zr_{50}Cu_{45}Al_5$ are icosahedral-like or crystal-like MROs, respectively.

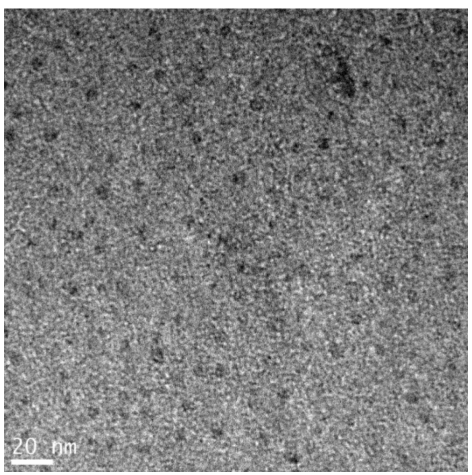
In-situ annealing of ZrCuAlNi thin film

20 nm

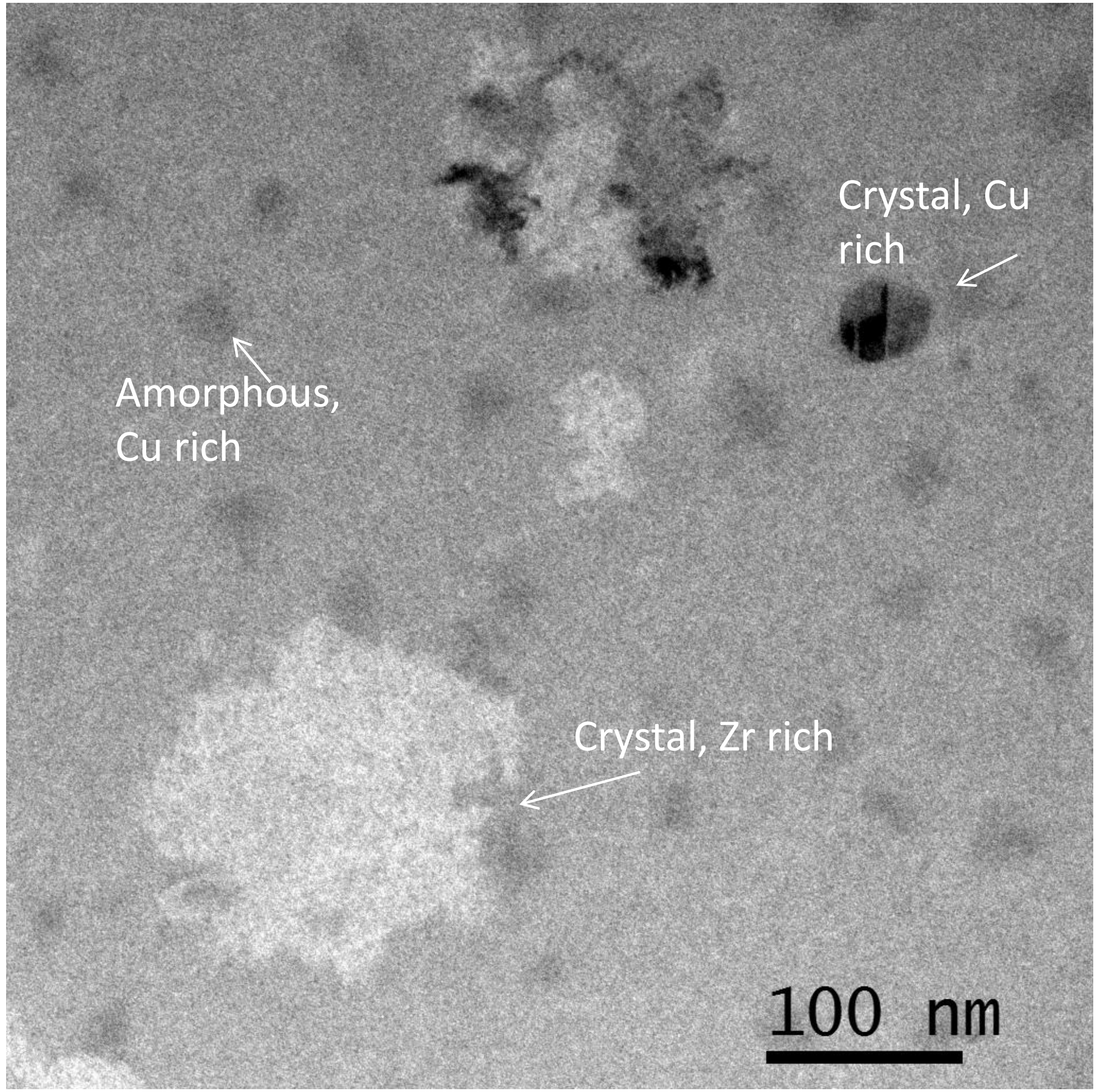


TEM bright field image, R.T. **as deposited**.

20 nm

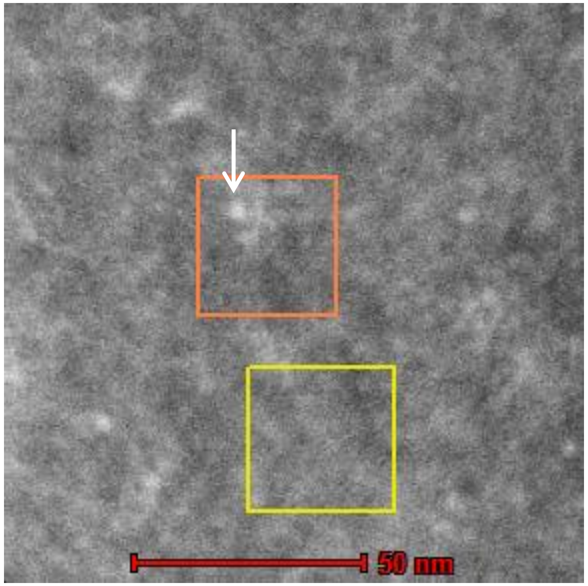


R.T. after heating up to **405 °C** (2 hours 10 minutes at 405 °C)

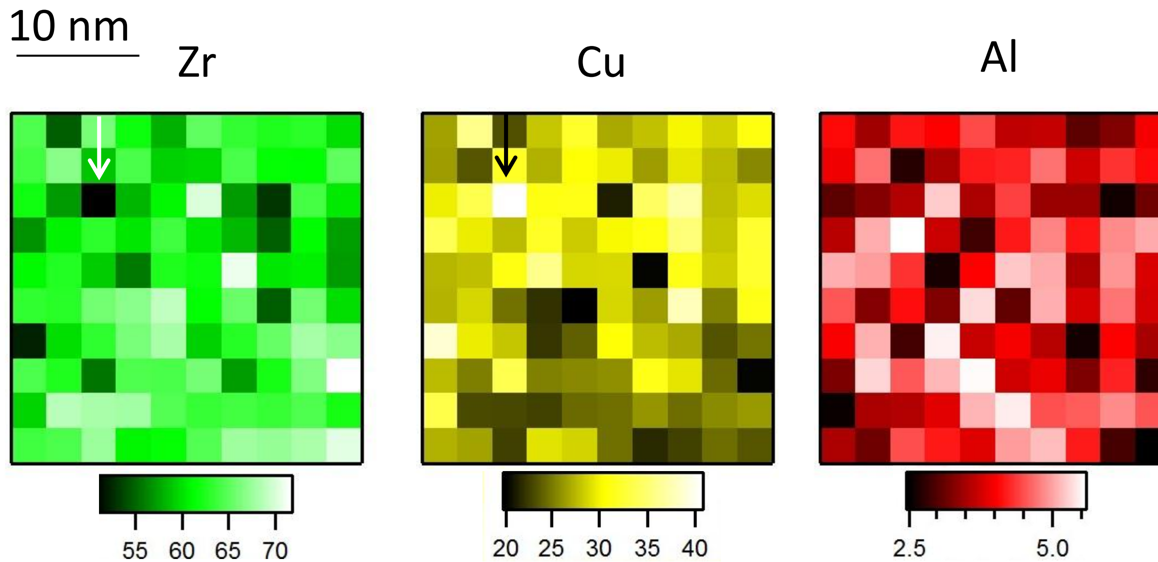


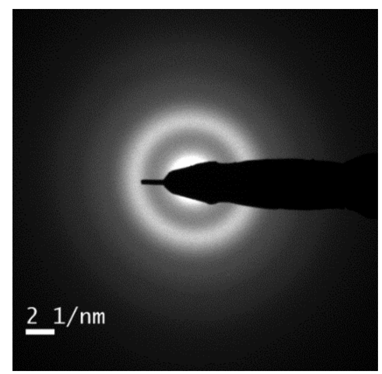
R.T. after heating up to **493 °C** (1 hours 29 minutes at 493 °C)

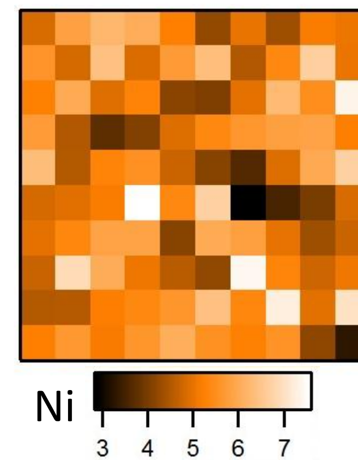
Chemical analysis of 150 °C annealed sample



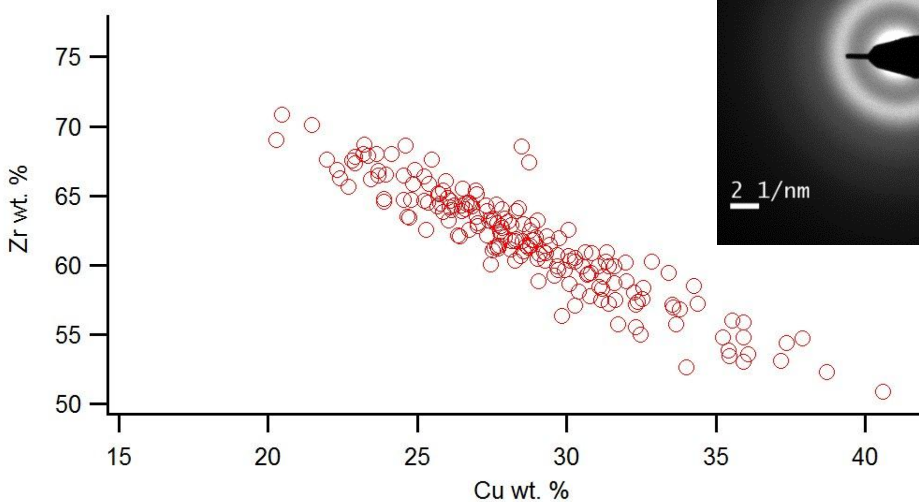
HAADF image, R.T. after heating at 150 °C for 11 min.



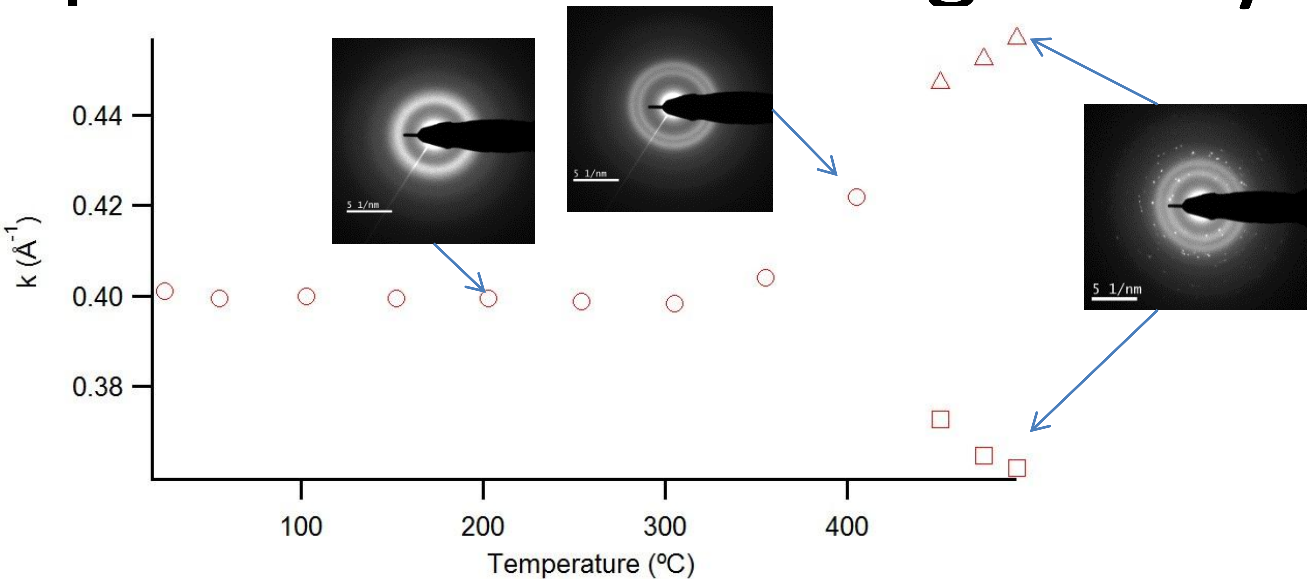


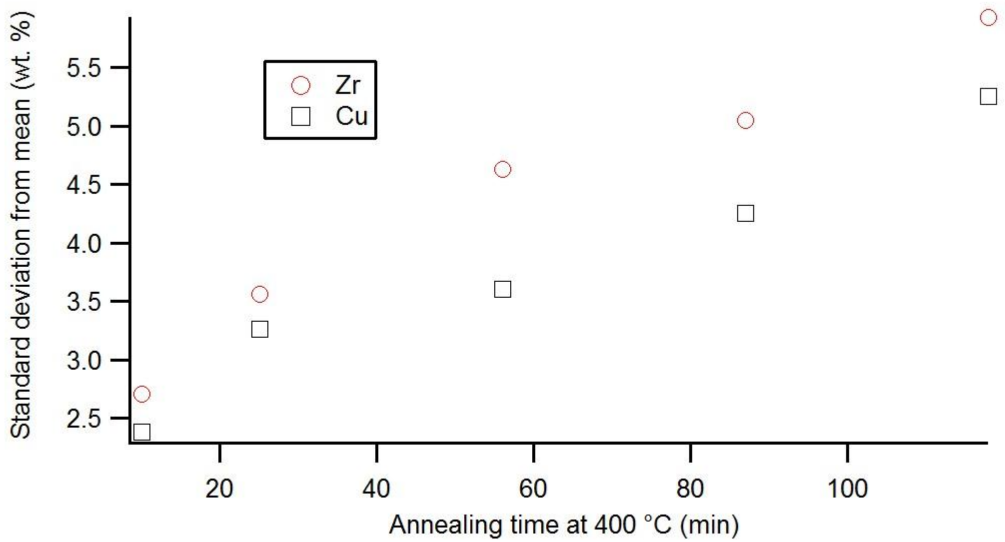


Nominal composition (wt. %): Zr 66, Cu 25, Al 4, Ni 5.

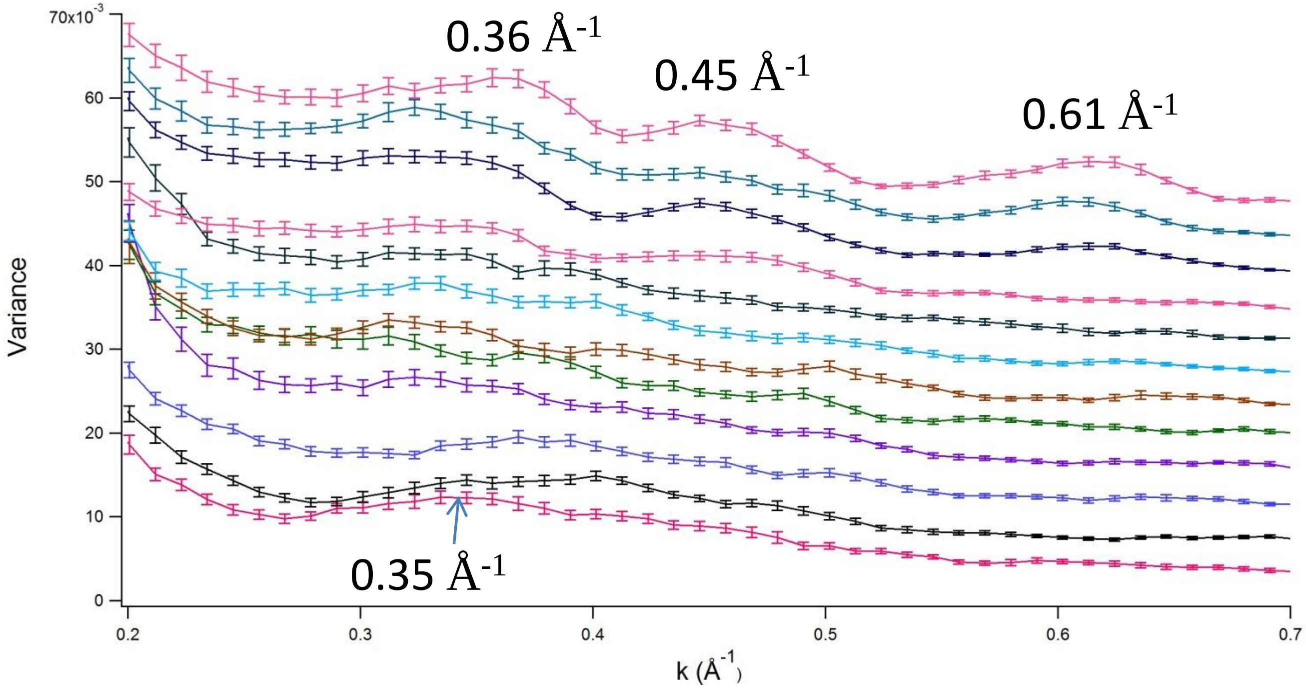


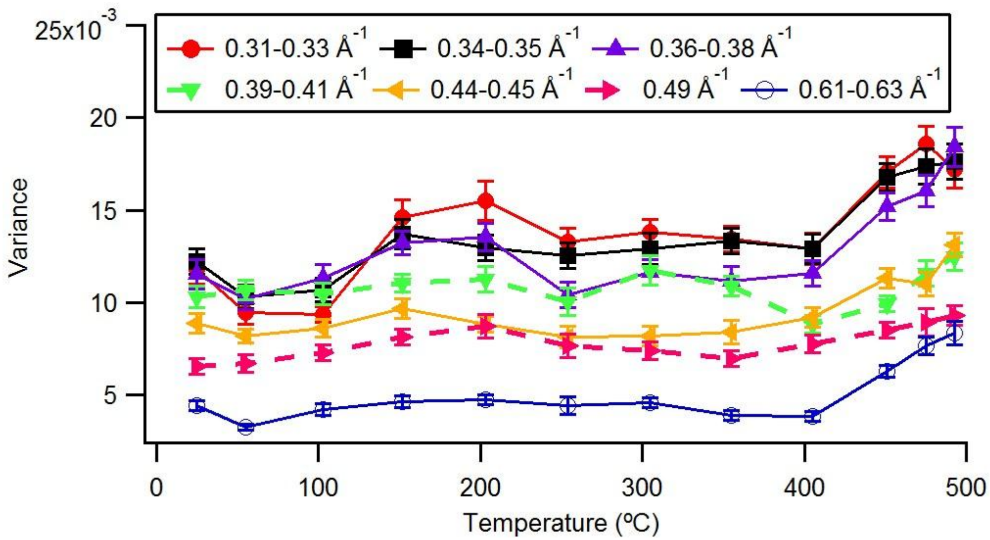
Short range order and compositional inhomogeneity





Annealing effect to ZrCuAlNi thin film MROs





Variance may increase (e.g., 0.36 Å^{-1}) or decrease (e.g., 0.40 Å^{-1}) at higher annealing temperature.

Conclusion

- Thin film $Al_{90}Tb_{10}$ and $Zr_{53}Cu_{29}Al_{12}Ni_6$ metallic glasses have less medium-range order than bulk materials.
- ZrCuAlNi thin film exhibits compositional inhomogeneity. Cu-rich and Zr-rich clusters are present. No phases (a certain compositions) are identified.
- Change of short range order/ atom spacing takes place at about 350 °C.
- Compositional inhomogeneity increases with annealing time at 400 °C.
- Medium range order increases as annealing temperature approaches above 400 °C.