Experimental report

15/02/2021

Proposal: 6-05-1011 **Council:** 4/2019

Title: Impact of Sulfur on the structure and dynamics of glass-forming metallic melts

Research area: Materials

This proposal is a continuation of 6-03-439

Main proposer: Johanna WILDEN

Experimental team: Maria Dolores RUIZ MARTIN
Fan YANG
Jinliang HU
Johanna WILDEN
Dirk HOLLAND MORITZ
Bastian ADAM
Maximilian FREY
Sandro SZABO
Tobias AUMUELLER
Nico NEUBER
Elke SONDERMANN
Toni SCHILLER
Till SCHULZENDORFF

Local contacts: Thomas HANSEN

Samples: Ti-Ni, Ti-Ni-S, Nb-Ni-S

Instrument	Requested days	Allocated days	From	To
D20	5	4	21/02/2020	26/02/2020

Abstract:

Bulk metallic glasses (BMGs) combine a spectrum of interesting physical properties. However their commercialization is difficult as most of them consist of harmful/expensive elements. Recently, a new family of S-based BMGs was discovered. Due to its accessibility, S has the potential to commercialize this material class. Simultaneously, it increases the glass forming ability (GFA) of various BMGs. In order to understand the complex mechanisms of GFA enhancement, the structure of these melts needs to be studied. In fact, molten S has a complex coordination behavior and might increase the complexity of the melt. Such a situation is prone to vitrification due to geometrical frustration.
We performed synchrotron X-ray diffraction experiments on levitated Ti-Ni-S droplets. Nevertheless, with this technique no partial structure factors of the individual elements can be extracted. Therefore, we propose neutron diffraction experiments on Ti-Ni, Ti-Ni-S, as well as on Nb-Ni-S at D20, with isotope substituted samples (natural Ni, 58Ni and 60Ni). The structural studies are supplemented by quasi-elastic neutron scattering experiments at NEAT (Helmholtz-Zentrum Berlin), scheduled in July 2019.

Impact of Sulfur on the structure and dynamics of glass-forming metallic melts

1. Objectives

The current experiment was intended to study the liquid structure of the binary Ti-Ni and ternary Ti-Ni-S alloys, with the goal to better understand the origin of the improved glass forming ability with sulfur addition. Ti-Ni-S metallic glass is a promising candidate for commercialization since it contains neither harmful nor expensive elements (e.g. beryllium and zirconium). At the meantime it is suitable for biological and lightweight applications [1]. The primary focus of the experiment lies on resolving partial structure factors employing neutron diffraction with isotope substitution, combined with containerless processing techniques (in this case electrostatic levitation).

2. Results

Neutron diffraction measurements with Ni-isotope substitution (^{nat}Ni, ^{58}Ni, ^{60}Ni) were performed at the powder diffraction instrument D20 using an incoming wavelength of 0.94 Å. This gives an accessible momentum transfer of more than q = 12 Å^{-1}. Since titanium-based metallic melts are highly reactive, we applied electrostatic levitation on liquid droplets of 5 - 6 mm diameter. This avoids contamination as well as heterogeneous nucleation due to the absence of crucible walls. For the binary $Ti_{75}Ni_{25}$ (T_L = 1215 K), together with the results from synchrotron X-ray diffraction, a full set of partial structure factors can be derived at four different temperatures (1150 K (undercooled), 1285 K, 1410 K, 1590 K). For ternary sulfur containing alloys, total structure factors at 1450 K and 1590 K were measured with ^{nat}Ni and ^{60}Ni.

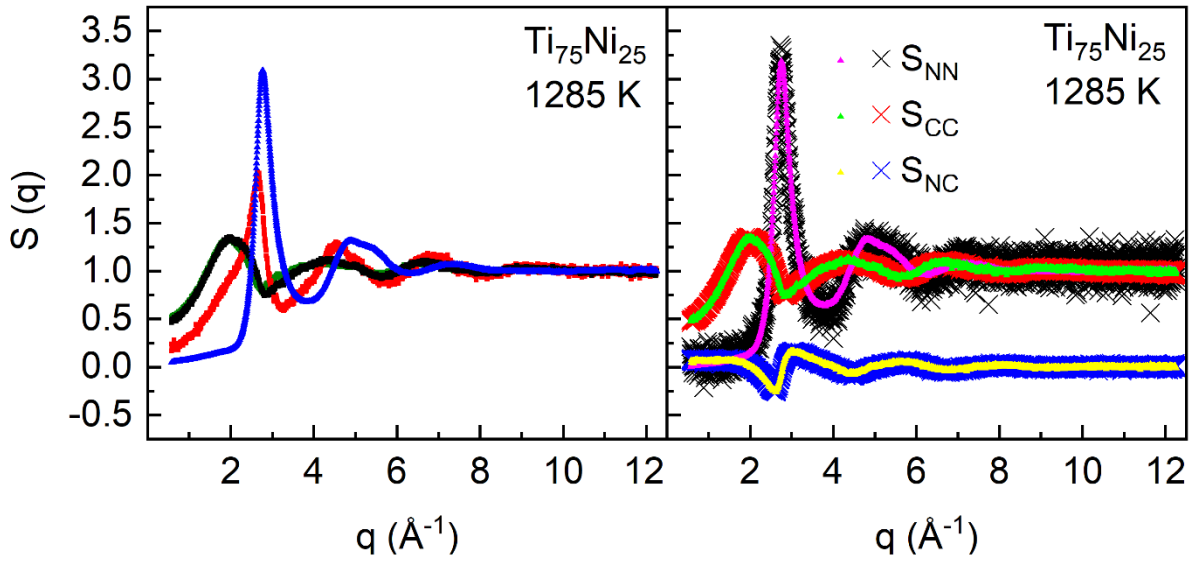

Figure 1. Left panel: Total structure factors of $Ti_{75}{}^{nat}Ni_{25}$ (black curve), $Ti_{75}{}^{58}Ni_{25}$ (green curve), and $Ti_{75}{}^{60}Ni_{25}$ (red curve) at 1285 K determined with neutron diffraction, compared with the total structure factor determined with synchrotron X-ray diffraction (blue curve) (same composition, same temperature). Right panel: Bathia-Thornton (S_{NN}, S_{CC}, S_{NC}) partial structure factors of $Ti_{75}Ni_{25}$ at 1285 K calculated with different scattering contrasts. S_{NN} (black cross), S_{CC} (red cross), S_{NC} (blue cross): $Ti_{75}{}^{nat}Ni_{25}$, $Ti_{75}{}^{58}Ni_{25}$, $Ti_{75}{}^{60}Ni_{25}$ determined with neutron diffraction. S_{NN} (pink triangle), S_{CC} (green triangle), S_{NC} (yellow triangle): $Ti_{75}{}^{58}Ni_{25}$, $Ti_{75}{}^{60}Ni_{25}$ determined with neutron diffraction and $Ti_{75}{}^{nat}Ni_{25}$ determined with synchrotron X-ray diffraction.

Figure 1 (left panel) shows the obtained total structure factors of $Ti_{75}{}^{nat}Ni_{25}$, $Ti_{75}{}^{58}Ni_{25}$, $Ti_{75}{}^{60}Ni_{25}$ at 1285 K, compared to the total structure factor of $Ti_{75}{}^{nat}Ni_{25}$ determined with X-ray diffraction

(same composition, same temperature). From these four different scattering contrasts, the Faber-Ziman (S_{TiTi}, S_{NiNi}, S_{TiNi}) and Bathia-Thornton (S_{NN}, S_{CC}, S_{NC}) partial structure factors were calculated. Here we considered both, the neutron diffraction results only and a combination of $Ti_{75}{}^{58}Ni_{25}$, $Ti_{75}{}^{60}Ni_{25}$ and X-ray diffraction results, as shown in Figure 1 (right panel). It can be seen that the obtained partial structure factors agree with each other within the measurement uncertainties. In the case of the partial structure factors determined with X-ray diffraction, the scattering of the data points is much smaller since the variation of the scattering contrast is larger. On the other hand, the good agreement between the neutron and synchrotron X-ray diffraction results, in particular at structure factor maxima, demonstrates the good quality and reproducibility of the measurements employing electrostatic levitation.

For the ternary alloys we were only able to determine the total structure factors for $Ti_{75}{}^{nat}Ni_{17}S_8$ and $Ti_{75}{}^{60}Ni_{17}S_8$. It turned out to be rather difficult to measure structure factors of the binary and the ternary alloys at the same temperature. A high temperature phase occurs for the sulfur bearing alloys, which limits the undercooling ability of the melt for the time scale of the neutron diffraction measurements. For measuring the partial structure factors of the binary alloy at temperatures above the liquidus temperature of the sulfur bearing alloys (T_L = 1430 K) evaporation in the high-vacuum environment became an issue. Nevertheless, we achieved this for 1590 K. Thus, a comparison between the binary and ternary alloys can be drawn.

Using the obtained binary $Ti_{75}Ni_{25}$ partial structure factors, we can show that the difference between the total structure factor between the binary and the ternary melt cannot be explained by the assumption of an isomorphous substitution of nickel by sulfur and the corresponding change of the scattering contrast. As shown in Figure 2, the calculated $Ti_{75}Ni_{17}S_8$ total structure factor differs from that measured one. Rather, the shift of the position of the first structure factor maximum towards lower q is in line with the reduction of the average packing fraction of the melt upon sulfur addition [2] and indicates more fundamental changes of the short-range order.

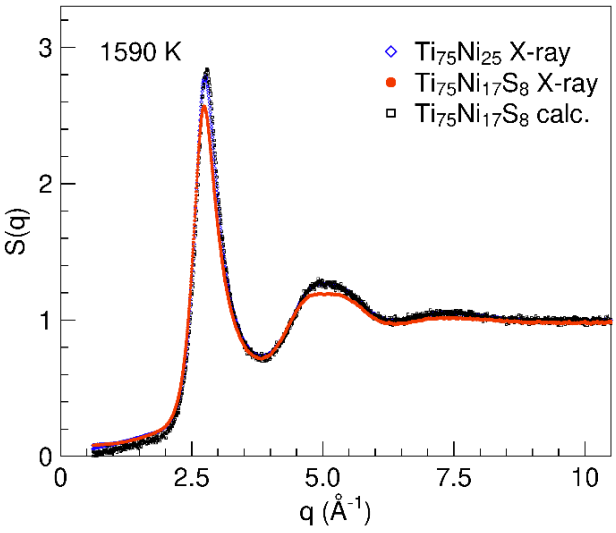

Figure 2. Total structure factors of $Ti_{75}Ni_{25}$ and $Ti_{75}Ni_{17}S_8$ measured with synchrotron X-ray diffraction at 1590 K, compared with calculated total structure factor of $Ti_{75}Ni_{17}S_8$ assuming an isomorphous substitution of nickel by sulfur. The shift of the first structure factor maximum towards lower q and a different shape of the second oscillation cannot be explained by the scattering contrast change upon sulfur addition alone.

References

[1] Kuball, A., Gross, O., Bochtler, B., & Busch, R. (2018). Sulfur-bearing metallic glasses: A new family of bulk glass-forming alloys. Scripta Materialia, 146, 73-76.

[2] Wilden, J., Yang, F., Holland-Moritz, D., Szabó, S., Lohstroh, W., Bochtler, B., Busch, R. & Meyer, A. (2020). Impact of Sulfur on the melt dynamics of glass forming Ti75Ni25−xSx. Applied Physics Letters, 117(1), 013702.