Thermochimica Acta 631 (2016) 28–35

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

How nucleation-growth kinetics is influenced by initial degree of material crystallinity

Roman Svoboda*, Jiří Málek

Department of Physical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic

ARTICLE INFO

Article history:
Received 28 December 2015
Received in revised form 9 March 2016
Accepted 11 March 2016
Available online 15 March 2016

Keywords:
Crystallization kinetics
JMA model
DSC
Partial crystallinity

ABSTRACT

Differential scanning calorimetry was used to investigate the effect of initial partial crystallinity on the non-isothermal nucleation-growth Johnson-Mehl-Avrami kinetics – selected Se-Te chalcogenide glasses were used as model systems. Different reproducible degrees of initial crystallinity were achieved by non-isothermal heating to a selected temperature. In case of the materials that primarily crystallize from mechanically induced defects, no change of the activation energy or kinetic mechanism was observed with increasing degree of initial crystallinity. On the other hand, material that showed complex crystallization behavior consisting from two competing overlapping crystal growth processes originating from volume-located nuclei and mechanical defects, respectively, exhibited marked shift in the dominance between the two kinetic mechanisms. In particular, with the increasing degree of initial crystallinity the defects-based crystallization mechanism started to dominate over the classical classic-nucleation-theory-based nucleation-growth crystallization mechanism. Increased amount of defects-based crystallization centers formed during the primary pre-crystallization appears to be the key factor for this change of the kinetic mechanism, rather than decreased activation energy (associated with the already existing crystal/glass interface) accelerating the actual crystal growth micro-mechanism.

1. Introduction

The nucleation-growth Johnson-Mehl-Avrami (JMA) model [1–4] belongs to the most popular equations applied in order to describe kinetics of chemical reactions and phase transformation kinetics (crystallization kinetics in particular) [5–8]. Nowadays, usage of this equation increases even more as the state-of-art softwares and methodological tools [9,10] allow to reliably deconvolute complex kinetic processes and apply the JMA equation to describe the individual sub-processes. At the same time, these softwares also enable the application of the JMA description in case of complicated multi-stage temperature programs. However, in such case an assumption of the kinetic mechanism not changing with the degree of conversion α needs to be adopted. In the present article we will investigate justness of this assumption for the case of multi-stage (repeated/continued) crystallization process – Se-Te chalcogenide glasses will be used as model systems.

In a recent series of papers [11–15] we have shown that the $Se_{(100-y)}Te_y$ chalcogenide glasses from the compositional range of $y = 0 - 30$ at.% represent an ideal model system for studying the JMA crystallization kinetics. These studies have shown that with both, increasing particle size and Te content, the values of the JMA kinetic parameter n change from ~1.5 (determined for fine powders and low Te contents) to ~3 (found for bulk samples and higher Te contents). This reflects the complex character of crystallization in the Se-Te glassy materials, where two competing crystallization mechanisms occur: crystal growth originating from volume-located nuclei following classic nucleation theory (CNT) and crystal growth originating from mechanical or stress-induced defects [13,14]. Regarding the latter, note, that certain types of surface crystallization may proceed via similar crystal growth mechanisms. The ratio between the intensity of manifestation of the two mechanisms naturally depends on the initial particle size and amounts of the respective crystallization centers (defects vs. quenched-in nuclei). The lower n values in the case of fine Se-Te powders correspond to one- to two-dimensional sterically restricted growth originating from mechanically induced defects, whereas the higher n values found for coarse powders and bulk samples correspond to a combination of two- and three-dimensional growth of surface- and

---

* Corresponding author.
E-mail address: roman.svoboda@upce.cz (R. Svoboda).

http://dx.doi.org/10.1016/j.tca.2016.03.017

Table 1
Pre-crystallization temperatures used for the studied particle size fractions of the three prepared Se-Te glasses and the correspondingly reached degrees of partial crystallinity. See text for details.

	20–50 μm		125–180 μm		300–500 μm	
	$T_i/^\circ$C	α_{cry}	$T_i/^\circ$C	α_{cry}	$T_i/^\circ$C	α_{cry}
$Se_{90}Te_{10}$	–	0	–	0	–	0
	108.7	0.269 ± 0.046	119.6	0.210 ± 0.055	131.6	0.233 ± 0.043
	114.6	0.524 ± 0.028	129.1	0.477 ± 0.026	145.7	0.502 ± 0.036
	118.9	0.743 ± 0.015	135.5	0.700 ± 0.018	155.0	0.777 ± 0.034
	122.9	0.904 ± 0.012	141.3	0.868 ± 0.021	162.3	0.910 ± 0.024
$Se_{80}Te_{20}$	–	0	–	0	–	0
	106.8	0.199 ± 0.052	116.6	0.178 ± 0.066	125.9	0.158 ± 0.056
	112.1	0.444 ± 0.035	124.3	0.406 ± 0.036	135.5	0.353 ± 0.017
	115.7	0.645 ± 0.010	129.4	0.622 ± 0.031	141.7	0.580 ± 0.039
	119.1	0.828 ± 0.015	133.9	0.812 ± 0.021	147.2	0.784 ± 0.025
$Se_{70}Te_{30}$	–	0	–	0	–	0
	104.4	0.187 ± 0.035	114.7	0.227 ± 0.031	123.2	0.228 ± 0.040
	109.7	0.446 ± 0.027	121.8	0.463 ± 0.032	130.0	0.492 ± 0.035
	113.4	0.659 ± 0.025	126.2	0.672 ± 0.025	133.5	0.702 ± 0.028
	116.6	0.842 ± 0.018	130.0	0.855 ± 0.010	136.0	0.845 ± 0.010

volume-located crystallites. Considering the compositional trend along the Se-Te line, the Se-richer compositions were found to be more prone to the crystallization from mechanically induced defects, while the increased Te content led to dominating growth of volume-located crystallites [11–15].

To study the effect of partial crystallinity on the change of JMA kinetics obtained for the repeated DSC measurement, a series of partially crystallized powders with different initial degrees of crystallinity was prepared for three selected Se-Te compositions. The present article will report the data obtained during the repeated DSC measurements of these partially crystalline materials; the corresponding changes in the crystallization kinetics will be discussed as well as it will be demonstrated how these changes depend on the initial crystal growth mechanism inherent with the given material.

2. Experimental

The selected Se-Te chalcogenide glasses ($Se_{90}Te_{10}$, $Se_{80}Te_{20}$, $Se_{70}Te_{30}$) were prepared by a melt-quenching procedure: proper amounts of pure elements (5N, Sigma Aldrich) were inserted into a fused silica ampoule, which was then evacuated, sealed, annealed at 450 °C for 24 h in a rocking furnace and finally quenched in cold water. The EDX and XRD techniques were used to verify the composition (accuracy better than 0.5 at.% for all glasses) and amorphous character of the prepared bulk glasses. The bulk glasses were then crushed in an agate mortar and, using a set of sieves with defined mesh size, three particle size fractions (20–50, 125–180 and 300–500 μm) were prepared for each prepared composition.

The DSC measurements were performed by using a Q2000 heat-flow DSC (TA Instruments) equipped with an autosampler, an RCS90 cooling accessory, and T-zero technology. The DSC was calibrated using In, Zn, and H_2O; dry N_2 was used as purge gas at a flow rate of 50 $cm^3\,min^{-1}$. The sample masses were approx. 8 mg. Cubic spline baselines were used to subtract the thermokinetic background from the obtained crystallization peaks in order to obtain the true signal corresponding to the crystallization process. Good repeatability of the measurements was confirmed.

The samples with different degrees of partial crystallinity were prepared directly in the DSC instrument by applying the following set of steps: equilibration at 50 °C, heating at 5 °C min^{-1} to a selected temperature T_i, immediate cooling at 60 °C min^{-1} to 50 °C. List of the temperatures T_i used for the three respective compositions as well as the resulting degrees of partial crystallinity α_{cry} is given in Table 1. Each partially crystalline powder was then subjected to a series of measurements performed at different heating rates q^+ (0.5, 1, 2, 5, 10 and 20 °C min^{-1}) applied from 50 to 200 °C, which were consequently used for evaluation of the crystallization kinetic behavior. In Fig. 1 an example of such combined measurement is shown. In addition, also the source, fully non-crystalline Se-Te materials were subject to the same measurement/evaluation procedure in order to serve as a control group. The raw crystallization behavior is visualized in Supplemental online material, where for each particle size fraction of each composition two graphs are shown, displaying crystallization peaks obtained for all tested α_{cry} values at 1 and 20 °C min^{-1}, respectively.

XRD data have shown that in all cases the hexagonal *P*3121 (152) crystals form and that the positions of their diffraction lines shift in accordance with previously published results [16], reporting the XRD patterns for the whole Se-Te compositional line. Note that since both Se and Te crystallize in the same hexagonal lattices differing only slightly in their parameters, the Se-Te glasses exhibit a gradual compositional transition between the two sets of lattice parameters. [16] In this regard, even though there are essentially almost no XRD standards for the Se-Te crystalline products in the JCPDS database, it is clear that the Se-Te crystallites of similar (or very close) composition, as is that of the starting amorphous materials, are formed.

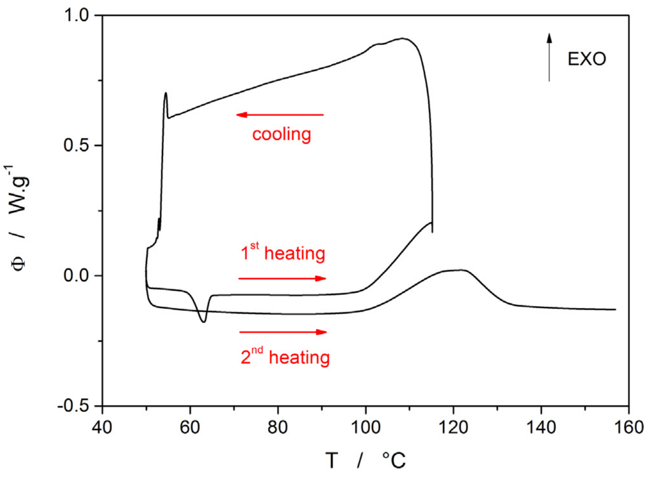

Fig. 1. Example of a typical double-stage DSC experiment, where certain degree of crystallinity was achieved during the first heating; the sample was cooled afterwards followed by a second heating scan during which the kinetic data (crystallization DSC peak) were collected.