Journal of ELECTRONIC MATERIALS, Vol. 42, No. 7, 2013
DOI: 10.1007/s11664-012-2358-1

Melt Spinning of Clathrates: Electron Microscopy Study and Effect of Composition on Grain Size

A. PROKOFIEV,[1,2] M. IKEDA,[1] E. MAKALKINA,[1] R. SVAGERA,[1] M. WAAS,[1] and S. PASCHEN[1]

1.—Institute of Solid State Physics, Vienna University of Technology, Wiedner Hauptstr. 8–10, 1040 Vienna, Austria. 2.—e-mail: andrey.prokofiev@ifp.tuwien.ac.at

The perspective of melt spinning–rapid quenching of a melt to produce nanocrystalline intermetallic clathrates is discussed, using main-group and transition-metal clathrates as examples. While melt spinning was originally developed for production of amorphous materials, our first experiments on melt spinning of clathrates revealed a surprisingly large grain growth rate, resulting in grain sizes of at least 1 μm. However, using the "confusion effect," i.e., complicating the chemical composition of the material by increasing the number of constituent elements, we have succeeded in reducing the grain size to 200 nm. We present our scanning electron microscopy, transmission electron microscopy, and transport property investigations and discuss the effect of composition on grain size, as well as thermodynamic and kinetic aspects of clathrate crystallization.

Key words: Melt spinning, clathrates, nanostructured materials

INTRODUCTION

One of the most promising strategies to enhance the efficiency of thermoelectric materials is to use the numerous interfaces in nanocrystalline materials to scatter phonons more efficiently than electrons. A number of nanostructuring approaches have been proposed. Recently the melt-spinning technique was used to prepare Bi_2Te_3 with nanolayered microstructure with layer thickness of 10 nm to 40 nm.[1]

Melt spinning comprises injecting a metal melt onto the surface of a rapidly rotating copper wheel, which results in very high cooling rates of the order 10^5 K/s to 10^6 K/s. This process was originally developed for preparation of amorphous materials and has been the main technique for metallic glass production. Metal alloys with low glass-forming ability (GFA) usually form nanometer-size polycrystalline materials. The advantage of the technique for preparation of nanocrystalline materials is its simplicity and short process duration resulting in a lower probability of oxidation. However, our first experiments on melt spinning of clathrates yielded samples with grain sizes of at least 1 μm.[2–5] The formation of foreign phases appeared to be kinetically suppressed. This points to a very high crystallite growth rate of the clathrate phase. On the one hand this is a great advantage for producing bulk clathrates, since the long-term annealing typically needed to remove foreign phases can be omitted. On the other hand this restricts the applicability of melt spinning for production of nanostructured clathrates.

The ability of a material to be quenched in nanocrystalline form is determined by the relationship between the crystal nucleation rate and the bulk crystal growth rate. Upon cooling, nucleation is delayed relative to the melting point T_m while bulk crystal growth begins immediately below T_m. The crystal growth rate increases at first with supercooling but then falls because of slowdown of diffusion. If nucleation starts when the crystal growth rate is still high, a small number of nuclei grow rapidly and large-grain material is formed. If, on the other hand, nucleation is delayed until the melt has cooled down to very low crystal growth rates, a glass phase is formed. The formation of nanocrystalline materials corresponds to an intermediate case.

(Received July 6, 2012; accepted November 8, 2012; published online December 11, 2012)