Experimental Evidence of Crystal Fragmentation from Highly Undercooled Ni$_{99}$B$_1$ Melts Processed on an Electrostatic Levitator

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Employing an electrostatic levitator (ESL) equipped with a CO$_2$ laser heating setup, we solidified Ni$_{99}$B$_1$ bulk crystals through containerless processing at high undercoolings and observed grain-refined microstructures. The electron backscatter diffraction pattern (EBSP) and analysis of the twin directions were accomplished, from which the primary growth traces with a cellular-like structure were revealed on a macro-millimeter scale. In comparison with the strong mechanical electromagnetic stirring in a sample processed on an electromagnetic levitator, the ESL provides a quite quiescent state for the melt, which enables identification of the primary growth traces after solidification. The present observation supplied experimental evidence that the refined microstructure in the Ni$_{99}$B$_1$ alloys at the high undercooling regime was due to fragmentation of the primary growth crystal, rather than dynamic nucleation.

Walker[11] initially proposed that copious or volume nucleation in undercooled Ni melts may occur and thus yield refined microstructures, based on the assumption that the collapse of cavities ahead of a solid/liquid interface could produce high positive pressure differences and then result in copious nucleation.[2] However, solidified microstructures, in particular, in the medium undercooling range, are directional dendrites, starting from the nucleation site and then spreading throughout an entire specimen. Therefore, a copious nucleation mechanism was primarily excluded for refined microstructures from undercooled metallic melts.

After performing directional solidification of transparent model alloys of cyclohexanone with fluorescein added and carbon tetrabromide with salol added, Jackson et al.[3] found that partial remelting of the secondary and tertiary branches occurred, which they proposed was the origin of the refined microstructure at high undercoolings during recalescence. Note that Jackson et al.'s[3] discussions and conclusion were based on an organic model material, by which they mimicked the solidification behavior of metallic materials. However, the similarity between an organic model material, and a metallic material is still a concern. Following this pioneering work, Xiao et al.[4] proposed that remelting was responsible for the grain refinement in the Ni$_70$Cu$_{30}$ alloy from deep undercoolings after observing the microstructure of alloys, from which they made a qualitative discussion.

To have a quantitative description of the grain refinement mechanism, using an instability analysis of growing interfaces, Mullis and Cochrane[5,6] concluded that unstable dendrite growth may occur at both low and high undercoolings, which may be the origin of grain refinement. However, this analysis is somewhat abstract and hard to testify from an experimental view. Employing a phase-field model, Mullis and Cochrane[7] proposed that kinetically induced dendrite tip splitting results in spontaneous grain refinement at high undercoolings.

Dragnevski et al.[8] undercooled pure copper to $\Delta T = 280$ K and then revealed a seaweed morphology, which, they believed, was the experimental evidence of dendrite tip splitting in the high undercooling regime. To date, the most widely applied model for grain refinement at the high undercooling regime is the Karma’s fragmentation model, as Herlach and co-workers frequently cited.[9] With respect to this model, it should be emphasized that Karma[10] himself addressed in his original and complete development of the model, “a simple model to predict the occurrence of these transitions [from Coarse Grained (CG) to Grain Refined (GR) then CG and finally GR is presented.” Karma[10] goes on to state: “This model is based on the assumption that fine equiaxed grains are the product of the fragmentation of dendrites by remelting during the period following recalescence where the interdendritic melt solidifies.” Obviously, this model was developed to account for the critical undercoolings in microstructure transition (CG-GR-CG-GR) rather than the physical origin of grain refinement. Therefore, we propose that the term “microstructural transition—critical undercooling model” is more accurate than the “fragmentation model” to avoid misunderstanding. Experiments can be tailored from two aspects concerning this model. The first is to compare the experimentally observed critical undercoolings for the structure transitions with the theoretically calculated critical undercoolings for these transitions to verify the applicability of the model. Karma[10] himself compared undercooling data for microstructure

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transitions in Ni-Cu, Fe-Cr-Ni, Cu-O, Cu-Sn, and Co-Pd alloys and some pure metals, and Eckler et al.[11] examined the experimentally determined transitional undercoolings and theoretically calculated transitional undercoolings for grain refinement in Ni-C alloys. The second aspect is to provide direct experimental evidence to support the assumption that fragmentation occurs after recalescence. Wilde et al.[12] supplied indirect and necessary experimental facts in undercooled Co-Pd alloys by revealing a surface microstructure; fragmentation does not occur when the melt is undercooled beyond the hypercooling limit since there are no remaining liquids and not enough time for the primary dendrite to fragment after recalescence. Here we should once again emphasize that it is sensible to compare the experimentally observed critical undercooling with theoretically calculated critical undercooling so as to verify the applicability of the model. However, if the fragmentation model is simply employed to account for the physical origin of the refined microstructure, it uses the assumption in the model, i.e., fragmentation takes place, to interpret the experimentally observed refinement phenomenon, which is of less scientific merit although the assumption has physical fundamentals.

In this work, we supplied experimental evidence of fragmentation from highly undercooled Ni$_{99}$B$_{1}$ melts processed by an electrostatic levitator (ESL) when incorporating a laser beam heating system by employing the electron backscattered diffraction patterns (EBSP) technique equipped to an electron scanning microscope. To our knowledge, this is the first report with regard to refined microstructure from deeply undercooled metallic melts on an ESL.

The starting Ni grains with a purity of 99.97 pct (High Purity Chemicals Laboratory, Saitama, Japan) and B bulks with a purity of 99.8 pct (Nilaco Corp., Tokyo) were weighed on a high-accuracy balance with a resolution of 10 $\mu$g. The procedure for preparing an ingot in a water-cooled arc-melting furnace, similar to that for Ni-Sn eutectics, has been described elsewhere in detail.[13] The as-cast ingot was sectioned to get proper small bulks weighing about 35 mg for stable levitation.

The ESL chamber was evacuated to $5 \times 10^{-5}$ Pa and then maintained at approximately $8 \times 10^{-4}$ Pa throughout the entire experimental run. A CO$_2$ laser beam was used to preheat the sphere to achieve sufficient electron charging; this was essential for successful launching and stable levitation. After the sample was levitated, three laser beams were focused onto the sample from three directions at 120 deg so that the sample could be heated uniformly. A monochrome pyrometer was used to monitor the sample temperature. By controlling the overheating degree and heating-cooling circles, we could solidify the specimen at a desired undercooling. More details on the ESL setup and improvement of the stability of a levitated sphere have been described elsewhere.[14,15]

Figure 1(a) shows the EBSP of the alloy solidified at an undercooling of about $\Delta T = 200$ K, indicating that this