Undercooling, Rapid Solidification, and Relations to Processing in Low Earth Orbit
(A Review of the Works of Bingbo Wei)

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January 1999
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Introduction

This is a survey of the published works of Prof. Bingbo Wei of the Department of Applied Physics at Northwestern Polytechnical University, Xian P.R. China.

Transformations among solid – liquid – and vapor are fundamental to the foundations of life and culture on Earth. The development and understanding of materials has lead the evolution and advancement of the human race since antiquity. Materials and fluids research is continuing today, with us standing on the shoulders of those that have gone before us. Technological and scientific breakthroughs continue due to studies of greater and greater complexity, that include for example, research done at high pressures, in high magnetic fields, at temperatures near absolute zero, and in the low gravity environment of low Earth orbit. Of particular technological importance is the liquid to solid transformation of metals and alloys. Solidification processing is generally the most important factor in the final properties of objects made of metal; and undercooling is the fundamental driving force for all solidification. The interest and resources dedicated to the study of solidification and undercooling are great and World wide. For many years B. Wei and his coworkers have been studying undercooling and rapid solidification and have amassed a significant body of published research in this important field, contributing to the leading edge of the state-of-the-art. It is the goal of this memorandum to provide a review of the research of B. Wei et al.; publications in Chinese are included in the reference list but are not discussed.

The bulk of Wei’s work has been in the area of undercooling and rapid solidification [1-11, 13-16, 24-36] with papers dating back to 1989, the same year he earned his Ph.D. Below, discussions of Wei’s undercooling and rapid solidification research have been grouped together mostly on the basis of alloy type, such as eutectic, intermetallic, or monotectic.
Eutectic solidification from a bulk undercooled melt

The objectives of this work include: development of the glass flux technique to achieve high undercoolings in bulk sized metal samples; measure crystal growth velocities; examine heterogeneous and homogeneous nucleation phenomena; study of growth morphology among dendritic – lamellar eutectic and anomalous eutectic modes; compare experimental results such that metallurgical solidification models and theories are tested and improved; and measure physical properties such as specific heat.

Using a glass fluxing technique to achieve a variety of undercoolings, the eutectic and dendritic growth of CoSb alloys were examined. The glass flux technique surrounds the metal sample being undercooled with glass; the glass dissolves, entraps, or otherwise renders ineffective, nucleation sites and impurities. Early work [1,2] showed critical undercooling thresholds, one applicable to lamellar growth, and a second (at a higher undercooling) indicating the onset of anomalous eutectic growth. It was pointed out that the onset of anomalous growth is in principle in agreement with established eutectic growth models, however, since the kinetic growth assumptions of the models are not consistent with anomalous growth, their applicability is limited to lamellar growth. These findings highlight well a need for improved analytical modeling and provide some valuable data for comparison to new solutions. This work continued to include CoSb hyper and hypo eutectic compositions near the eutectic point [2] and at the extremes of the eutectic horizontal [3] yielding dendrite growth velocity measurements, and determination of the “dendritic-equiaxed” transition, which was also discussed in reference to solute trapping and a dendrite fragmentation model. The “dendritic-equiaxed” transition is the transition of the microstructure from dendritic to small spherical particles of about the same size as the previous dendrite arm spacing. It is believed that recalescence causes the dendritic structure to fragment, and with further coarsening, creating the spherical, equiaxed particles.

Wei’s eutectic solidification publications include work in Ni-Sn [4,5,6], Ni-Si [6,7,8], Co-Mo [9], Ag-Ge [10], Co-Sb and Fe-Sn [6] alloys. In all these studies [4-10] the glass flux denucleation technique was used and developed – with more than 45 different glasses being examined. Denucleation is the process of removing and/or making ineffective nucleation sites; thereby enabling high undercoolings to be achieved. Wei’s efforts to optimize this fluxing has resulted in very high bulk undercoolings; for example, in [4] Wei achieved 397 K undercooling in Ni-32.5%Sn, were Piccone et al. [11] achieved about 220 K in the same alloy. Evidence of nonreciprocal nucleation was found in Ni-Sn; this phenomenon was observed by de Groh [12] in the Pb-Sn system and is explained by both Wei and de Groh on the basis of interfacial surface energy.

I disagree with points regarding the scientific and technological motivations for undercooling research in low Earth orbit as proposed in [6]. Although the data and conclusions in this work are of excellent quality – the motivation and justification for its progression to low-gravity processing as stated are not strong and warrant discussion here. Wei states in the introduction [6] that rapid solidification (undercooling research) in space is worthwhile because: gravity is low, and containerless processing, ultrahigh vacuum, and higher undercoolings can be achieved in space. I have been intimately involved with NASA’s containerless processing program and various undercooling studies in space and to the best of my knowledge, none of these benefits are valid. It is
true gravity is very much reduced in low Earth orbit (to about $10^6 \, g_o$ where $g_o$ is Earth’s normal gravity) however, there is no theoretical basis for undercooling to increase with reductions in gravity; there is also no reliable body of experimental evidence implying a link between gravity and undercooling. In general, the benefit of low-g processing is the reduction in natural convective flows. Wei’s work shows that very high undercoolings can be achieved without any regard for convective flow – in fact – convection is generally very high in his work due to electromagnetic heating. Fundamentally there is presently no established link between convection and undercooling. The influence of convection on the structure of undercooled liquids is an area of new and exciting research that has yet to be developed. Containerless processing, ultrahigh vacuum, and higher undercoolings can at present all be achieved more effectively on Earth and are not valid justifications for processing in low gravity.

**Solidification of intermetallics from undercooled melts**

Undercooling and solidification studies using either electromagnetic levitation or glass fluxing techniques of intermetallic alloys have included Ni-Al [13], Fe-Si and Co-Si [14], Ni-Ti-Al, Ni-Sn, and Fe-Al [15], and Co-Sn and Ni-Fe [16]. In these studies growth mode and measured velocities were examined, in conjunction with sample microstructures, in the framework of various dendritic and eutectic growth models. Crystal growth velocities were determined as a function of undercooling using a high speed photosensing device which enabled the heat wave associated with recalescence to be characterized. It was found that when growth was of the single phase solid solution type – growth kinetics were collision-limited, and that growth of the intermetallic compounds was diffusion-controlled. Analyses and comparisons to models were done and included the dendrite and eutectic growth models due to Lipton, Kurz, Trivedi, Boettinger, Coriell, Jackson, Hunt, and Magnin [17-21]. Wei’s work 1) shows that large interfacial undercoolings result during intermetallic growth, which are coupled to the short-range diffusion limited attachment kinetics at the solidification front which are necessary to sort the atoms onto the various sublattices; and 2) used theories of disorder trapping to deduce the dependence of the order parameter on the solidification velocity.

**Undercooling of monotectic systems**

Research using immiscible alloys and the low Earth orbital environment has been done for decades. However, many of these efforts failed due to massive segregation driven by preferential wetting, and/or Marangoni flow. Both of these failure modes and how to avoid them have been discussed by de Groh et al. [22, 23]. These failures have created a hostile environment towards immiscible alloy research within some organizations. Even though the methods many have used to examine immiscible alloys have been flawed – many of the fundamental motivations for the research are still valid. Wei has examined in detail high undercooling and solidification of monotectic, hypomonotectic, and hypermonotectic alloys, including Cu-Pb [24,25,26], Co-Sn and Ni-Ag [27], and Ni-Pb and Fe-Sn [28,29] alloys. Wei found the hypomonotectic Cu-20%Pb alloy to behave much like a normal binary with the microstructures comprised of mainly Cu dendrites; with solute trapping causing extended solubilities of Pb in Cu. In the monotectic Cu-37.4%Pb alloy undercooling was more difficult because nucleation
barriers associated with the liquid L_2(Pb) phase are small compared to the solid Cu phase. Thus the L_2(Pb) phase nucleates at a relatively small undercooling and once the L_2(Pb) phase forms, local composition gradients favor nucleation of the solid Cu phase. Still, high undercoolings of 209 K were achieved in the Cu-37.4%Pb alloy. Barriers to nucleation were estimated on the basis of interfacial surface energy, with the interfacial energy between the monotectic liquid and L_2 being about 10 times less than the energy between the monotectic liquid and the solid Cu phase. In these studies macrosegregation of Pb persists from the sedimentation and coalescence of L_2(Pb). It is shown that macrosegregation is made worse by the undercooling process (Ref. 26, 28 and 29). Apparently at low undercoolings the course dendritic structures impede the settling of L_2 phase. As undercooling increases and the dendrites get finer, L_2 droplets are pushed around more, rather than entrapped by the dendrite – resulting in larger L_2 droplets, more Stokes settling of the L_2 phase, and increases in macrosegregation. Said another way, at low undercoolings, the L_2 droplets are trapped among the secondary arms of the dendritic network; at higher undercoolings the L_2 droplets are pushed in front of the advancing secondary arm front and then settling down between the fine dendrites.

Other Research

In this final section several other works will be mentioned, including research on physical property measurement, directional solidification, and papers published in Chinese. In the development and examination of theories and models of the structure of liquids, in particular, undercooled liquids, and nucleation – reliable physical property data is needed. The areas of liquid structure and the process of nucleation, and how they relate or are influenced by convection, are of interest to myself and NASA due to the possible benefit and value of processing in low gravity. Wei et al. have measured enthalpy and specific heat in undercooled Ni-Sn eutectic alloys [5] and pure Fe and Ni [30]. A study was done in which samples were directionally solidified with varying amounts of longitudinal vibration [31]. Modifications to the dendritic structure and mechanical properties of the resulting samples were determined, and the mechanisms of convection, and dendrite fragmentation discussed. Noteworthy publications in Chinese include undercooling of bulk industrial Al-Si alloy [32], physical problems in materials science in space [33], papers on metallic glasses [34,35], and the thermodynamic properties of liquid Sn [36].
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**13. ABSTRACT (Maximum 200 words)**

This is a survey of the published works of Prof. Bingbo Wei of the Department of Applied Physics at Northwestern Polytechnical University, Xian P.R. China. Transformations among solid – liquid – and vapor are fundamental to the foundations of life and culture on Earth. The development and understanding of materials has lead the evolution and advancement of the human race since antiquity. Materials and fluids research is continuing today, with us standing on the shoulders of those that have gone before us. Technological and scientific breakthroughs continue due to studies of greater and greater complexity, that include for example, research done at high pressures, in high magnetic fields, at temperatures near absolute zero, and in the low gravity environment of low Earth orbit. Of particular technological importance is the liquid to solid transformation of metals and alloys. Solidification processing is generally the most important factor in the final properties of objects made of metal; and undercooling is the fundamental driving force for all solidification. The interest and resources dedicated to the study of solidification and undercooling are great and World wide. For many years B. Wei and his coworkers have been studying undercooling and rapid solidification and have amassed a significant body of published research in this important field, contributing to the leading edge of the state-of-the-art. It is the goal of this memorandum to provide a review of the research of B. Wei et al.; publications in Chinese are included in the reference list but are not discussed. The bulk of Wei’s work has been in the area of undercooling and rapid solidification [11, 11, 13-16, 24-36] with papers dating back to 1989, the same year he earned his Ph.D. Below, discussions of Wei’s undercooling and rapid solidification research have been grouped together mostly on the basis of alloy type, such as eutectic, intermetallic, or monotectic.

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