1982

NASA/ASEE SUMMER FACULTY RESEARCH FELLOWSHIP PROGRAM

MARSHALL SPACE FLIGHT CENTER
THE UNIVERSITY OF ALABAMA

CONTAINERLESS PROCESSING OF Nb-Ge ALLOYS IN A LONG DROP TUBE

Prepared by:	Robert J. Bayuzick, Ph.D.
Academic Rank:	Professor
University and Department:	Vanderbilt University Department of Mechanical and Materials Engineering
NASA/MSFC:	
(Laboratory)	Space Sciences
(Division)	Space Processing
(Branch)	Solid State
MSFC Counterpart:	M. B. Robinson
Date:	August 12, 1982
Contract No.:	NGT-01-002-099 (University of Alabama)

CONTAINERLESS PROCESSING OF Nb-Ge ALLOYS IN A LONG DROP TUBE

By

Robert J. Bayuzick, Ph.D.
Professor of Materials Science
Vanderbilt University
Nashville, Tennessee

ABSTRACT

The thirty-two meter drop tube at the Marshall Space Flight Center is being used to study the effect of zero gravity containerless processing on the structure and properties of materials. The concept involves the suppression of heterogeneous nucleation of solid in liquid and, therefore, solidification accompanied by large degrees of undercooling. Under these conditions metastable phases can be formed or, at the very least, unique nonequilibrium microstructures (containing equilibrium phases) with unique properties can be produced.

The drop tube solidification is being applied to niobium base alloys with emphasis on the Nb-Ge binary system in an effort to produce metastable phases with high superconducting transition temperatures in bulk specimens. In the past, only lower Ge alloys (Nb-13 a/o, Nb-18 a/o, and Nb-22 a/o) could be undercooled. However, techniques have now been worked out so that higher Ge alloys (e.g., Nb-25 a/o Ge and Nb-27 a/o Ge) can now be undercooled on a routine basis. Measurement of superconducting transition temperatures and determination of microstructure of the undercooled alloys will now follow.

INTRODUCTION

A potentially useful characteristic of processing materials in space is the capability of containerless solidification. One of the most important aspects of such a process is the elimination of heterogeneous nucleation at container walls thereby resulting in large degrees of undercooling. These large departures from equilibrium can in turn result in the production of unique microstructures and/or metastable phases with unique properties.

Containerless solidification is being studied at the Marshall Space Flight Center through use of drop tubes. A 100 m long tube will soon be available but up until now all the work has been done in a 32 m drop tube (11 cm in diameter). Simply stated, the alloys are electron-beam-melted in vacuum. The molten drops fall off the end of a support wire into the evacuated drop tube and cool by radiation in free fall.

The emphasis of the work has been on Nb-Ge alloys where the motivation is the possible production of metastable phases to give bulk superconductors with high superconducting transition temperatures (Tc). The expectation lies in the fact that the highest Tc measured in any metal or alloy has been in Nb-25 a/o Ge obtained in a thin film by sputtering.(1) The Tc was about 23°K as compared to a Tc of about 7°K in an as-cast alloy of a similar composition. The constituent responsible for the high Tc is the Nb_3Ge compound (A 15 crystal structure) which is unstable with respect to the two phase mixture, β phase plus Nb_5Ge_3. The β phase is an intermediate solid solution whose Ge-rich limit is about 20 a/o.(2) Nb-Ge alloys prepared by other techniques have also exhibited rather high transition temperatures; chemical vapor deposition has resulted in a Tc of 22°K(3) and quenching rapidly from the melt has given a Tc of about 17°K.(4) However, by their very nature these techniques are unable to produce bulk forms. On the other hand it has recently been recognized by Lacy, Rathz and Robinson that high Tc Nb_3Ge in bulk form might be obtainable by drop tube solidification.(5)

Relatively large amounts of undercooling in the drop tube have already been achieved for Nb-18 a/o Ge, Nb-Ge 22 a/o Ge, and in one specimen for Nb-25 a/o Ge. The microstructures developed by the undercooling are unlike arc-melted structures and depend on the rate of quenching at the bottom of the drop tube.(6) For Nb-18 a/o Ge, dendrites of α (solid solution of Ge in Nb) in a β matrix are seen at a quenching rate of 700°K/sec; when the alloy is splat-cooled at the bottom (for which the quenching rate is orders of magnitude higher), a single phase but highly segregated β is observed. Similarly, for

Nb-22 a/o Ge, a quenching rate of 700°K/sec produces β dendrites with an interdendritic Nb_5Ge_3, but the higher quenching rate of 1700°K/sec gives a segregated single phase β. The Nb-25 a/o Ge alloy also exhibited the segregated single phase β structure when it was splat-cooled at the bottom of the drop tube with large undercooling. It is interesting to note that in each case solidification occured by impact at the bottom. That is to say, larger degrees of supercooling could be attained in a longer drop tube.

OBJECTIVES

This work is part of a broader cooperative effort that has been underway for about one year and is anticipated to continue. The goals of this effort are:

1. To explore the application of solidifying materials from a deeply undercooled state in order to produce unique microstructures, metastable phases, and amorphous materials.
2. To explore the limitations on undercooling melts in the absence of wall-induced nucleation.

In the narrower context of the work on Nb-Ge in general and of the work connected with the NASA/ASEE program in particular, interest was directed toward developing techniques for undercooling Nb-25 a/o Ge, Nb-27 a/o Ge, and Nb-35 a/o Ge on a routine basis. With respect to the emphasis on producing high Tc alloys, these specific compositions are important. However, with the exception of a single Nb-25 a/o specimen, it has not been possible to undercool these alloys in the past.

NATURE OF EXPERIMENTS

Twenty six different Nb-Ge specimens were dropped during the course of the project. These are tabulated in Table 1 where it can be seen that the breakdown is twelve Nb-25 a/o Ge specimens, eleven Nb-27 a/o Ge specimens, and three Nb-35 a/o Ge specimens.

Slices were hung on a support-wire in an electron beam furnace at the top of the 32 m drop tube. Based on previous experience, a starting mass of 70 mg was chosen. The primary requirement for the choice is the ability to radiate enough heat from the molten drop so as to achieve about 300°C or more undercooling upon arrival at the bottom of the tube. Having chosen the sample size, a support-wire diameter of 5 mils was selected. The basic criteria for this selection is the balance of forces due to surface tension (between the molten alloy drop and the wire) with the forces due to gravity; again the particular choice was based largely on experience. Nb was selected initially as the support-wire material to minimize contamination by a third element and because its melting point was much higher than the alloy liquidus lines (for example about 600°C higher in the case of Nb-27 a/o Ge).

No undercooling was obtained with the initial configuration. The reason for the failure was clear on microscopic examination. First, it was seen that the Nb support-wire had been partially dissolved. Second, the final drop contained Nb_5Ge_3 in the same morphology as the beginning slice. These observations in conjunction with the realizations that the microstructure of the beginning slice is β plus Nb_5Ge_3, that dissolution of Nb_5Ge_3 in liquid is rather slow, and that Nb_5Ge_3 melts about 280°C higher than β (2180°C versus 1900°C) explains the result. Namely, the Nb_5Ge_3 remains solid while the β melts into a liquid matrix and the Nb support-wire dissolves in the liquid matrix down to a diameter such that gravity forces exceed surface tension forces. The "mushy" drop with solid Nb_5Ge_3 then falls down the tube and the Nb_5Ge_3 causes solidification by heterogeneous nucleation without large undercooling. As shown in Table 1, four more drops with the Nb support-wire were attempted. In these cases the drop mass was reduced to lessen the effect of gravity. The idea was simply to accept some Nb dissolution but to enhance overheating with the smaller mass such that the Nb_5Ge_3 phase would melt. None of these attempts succeeded and the concept was abandoned.

The support-wire was then changed to 5 mil diameter W and, as shown in Table 1, large degrees of undercooling occurred frequently in alloys of the 25 a/o Ge and 27 a/o Ge compositions. Note however that undercooling could not be obtained in the three 35 a/o Ge specimens. In the successful drops dissolution of the support-wire was still evident under microscopic examination but the rate was slow enough to allow sufficient overheating to melt the Nb_5Ge_3. The Nb-35 a/o Ge alloy simply contains a much larger fraction (about 80%) of the high melting Nb_5Ge_3 constituent.

In an effort to minimize W contamination of the 25 a/o and 27 a/o Ge alloys and to increase the undercooling by reducing overheating, 3 mil diameter W wire was tested. This size wire proved to be unfeasible. Lighter drops tended to travel up the wire under the influence of surface tension forces. Slightly heavier drops tended to drop before the Nb_5Ge melted completely.

Table 1 shows another significant characteristic of the experiments. As determined by weight change measurements of the drops and the support-wires, the compositions of the alloys are modified by the process. There is considerable Ge loss by evaporation during melting and, as previously mentioned, addition of support-wire material by dissolution. The Ge content can be decreased by as much as 6 a/o and as much as 1 a/o W can be added.

CONCLUSIONS AND RECOMMENDATIONS

Undercooling of high Ge alloys can be obtained in the 32 m drop tube by electron beam melting. The successful technique involves the use of a 5 mil diameter W support-wire. However, the alloy compositions are modified by the loss of Ge by evaporation and the addition of W by dissolution. Furthermore, solidification is ultimately caused by impact of the drop at the bottom of the drop tube. While not previously mentioned, solidification by impact results in disintegration of the specimen and therefore follow-up analytical work is extremely difficult if not impossible.

The limit of processing of Nb-Ge alloys by electron beam melting in the 32 m drop tube appears to have been reached. Further improvements will necessitate the incorporation of levitation melting. Under these conditions, contamination by the support-wire will be eliminated. In addition, as opposed to the vacuum of electron beam melting, an inert gas atmosphere can be used in the drop tube to accentuate heat removal from the drop. Also, some of the overheating necessary to melt all constituents can be eliminated by simply turning down the power slightly in the melter while continuing levitation of the drop. Both conditions will increase the degree of undercooling in the drop tube and therefore enhance solidification before impact.

Still further improvements in the research will result by application of the 100 m drop tube that is now in the final stages of completion. The longer drop tube with the slightly longer free fall time offers promise even under electron beam melting. However, as is already planned, the ultimate combination would involve the 100 m drop tube with levitation melting. Once this arrangement is in place, experiments will quickly follow.

REFERENCES

1. L. R. Testardi, J. H. Wernick and W. A. Rayer, Solid State Commun. 15, 1, 1974.

2. J. L. Jorda, R. Flukiger and J. Muller, J. of Less-Common Metals, 62, 25, 1978.

3. J. R. Gavaler, M. A. Janocko, A. I. Braginski and G. W. Roland, IEEE Trans. on Magnetics, Mag 13, 192, 1975.

4. B. T. Matthias, T. H. Geballe, R. H. Willens, E. Corenzwit and G. W. Hull, Jr., Phys. Rev. 139 A 1501, 1965.

5. L. L. Lacy, T. J. Rathz and M. B. Robinson, Space Sciences Laboratory Preprint Series No. 81-107, 1981; to be published in J. Appl. Phys.

6. L. L. Lacy, M. B. Robinson, T. J. Rathz, N. D. Evans and R. J. Bayuzick, Proceedings of Symposium on Materials Processing Research in The Reduced Gravity Environment of Space, Elsevier Publishing Co., New York, N.Y., 1982.

TABLE 1. Drop Tube Data for Nb-Ge Alloys

Drop Tube No.	Initial Composition, a/o Ge	Support Wire	Overheating, °C	Undercooling, °C	Change in Composition, a/o
253	25	5 mil Nb	--	None	-2 a/o Ge
254	27	"	153	"	-1.3 a/o Ge
255	25	"	125	"	-0.8 a/o Ge
256	27	"	163	"	-2.4 a/o Ge
257	25	"	118	"	-2.5 a/o Ge
258	27	5 mil W	229	301	
259	25	"	252	288	
260	27	"	240	280	
261	25	"	259	271	
262	27	"	191	279	
263	27	"	198	None	
264	25	"	191	289	
265	25	"	276	264	
266	27	"	--	None	
267	27	"	--	"	
270	25	3 mil W	149	"	
271	25	"	--	"	-3.7 a/o Ge; + 1 a/o
272	27	"	--	"	-6.3 a/o Ge; + 0.4 a/o
273	27	"	--	"	
274	25	"	--	"	
275	25	5 mil W	--	"	
276	27	"	--	280	
277	25	"	--	None	
278	35	"	--	"	
279	35	"	--	"	
281	35	"	--	"	