CONTAINERLESS DROP TUBE SOLIDIFICATION AND GRAIN REFINEMENT OF $NiAl_3$

by

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INTRODUCTION

The present study was undertaken in order to investigate the possibility of undercooling Ni-Al alloys below the liquidus in order to produce a single phase peritectic structure by containerless drop tube solidification (Figure 1). Containerless processing is a technique for both high purity contamination free studies as well as for investigating the undercooling and rapid solidification of alloys by suppression of heterogeneous nucleation on container walls. In order to achieve large undercoolings one must avoid heterogeneous nucleation of crystallization. It has been shown that the Marshall Space Flight Center drop tubes are unique facilities for containerless solidification experiments and large undercoolings are possible with some alloys (Lacy et al., 1981; Robinson 1981).

Nickel alloys rich in Al are used as Raney catalyst materials. In general, Raney alloys consist of two metallic components, one of which is a catalytically active transition metal such as Ni. Upon reacting the Ni-Al alloy with caustic aqueous solution, the Al atoms preferentially leach out of the alloy leaving behind an ultra high surface area Ni sponge. The sponge is catalytically active and is used for a number of chemical reactions such as the methanation of hydrogen and carbon monoxide to methane and water (Baird and Steffgen 1977), the steam re-formation of hydrocarbons, and hydrogenation reactions (Fasman et al., 1972; Oden et al., 1977; O'Hare and Mauser 1977; Stiles 1971).

The objective of this work was to containerlessly solidify samples of an Ni-Al alloy with a composition close to that of the compound $NiAl_3$. It has been demonstrated that the $NiAl_3$ eta phase is catalytically the most active component of a Rainey type alloy (Petrov et al., 1969; Baird and Steffgen 1977) such that the overall activity of Raney Ni depends mainly on the $NiAl_3$ phase content of the alloy (Fasman et al., 1972). The desired result was the formation of a high percentage of the $NiAl_3$ compound with minimal amounts of the other surrounding compounds Ni_2Al_3 (delta phase) and Al solid solution.

EXPERIMENTAL PROCEDURE

The Marshall Space Flight Center 30-meter drop tube was used to process the samples for this study (Figure 2). The drop tube consists of a 6 in. diameter welded stainless steel tube with turbomolecular pumping ports on the top and bottom levels. At the top is a connection for a vacuum feedthrough ring and bell jar into which sample processing equipment is placed. At the bottom is a sample catcher that is used to remove samples that have solidified in freefall down the tube. The system is designed to operate either in a vacuum (i.e., 10^{-5} torr) or in an inert atmosphere. For these experiments we used an atmosphere of He with 6%H at slightly greater than one atmosphere pressure.

Premelted samples of the alloy were placed into an alumina crucible and inserted into the furnace shown in Figure 3. A pneumatic gas line was attached to the crucible to provide a back pressure used to eject molten sample drops from a small orifice in the bottom of the crucible. We found that a difference in pressure between the bell jar and the crucible of 20 mm Hg was sufficient to extrude a number of molten drops out of the crucible.

RESULTS

Figure 4 shows scanning electron micrographs of three different size drops solidified in containerless conditions. One could see dendrites on the surface of all of the samples. Also there is a noticable large difference in scale of the microstructural features with the different size samples.

Light micrographs of the samples also show that there is a strong influence of sample size on microstructural features (Figure 5). Also in Figure 5 one can see that the same types of phases are present in all three sizes of samples. Figure 6 identifies the phases present in the microstructure. The microstructure of all of the samples is similar to that of traditionally solidified alloy. The first phase to solidify is the Ni_2Al_3 phase. Normally it solidifies when the liquidus temperature is reached and continues to solidify until the peritectic temperature is reached. At the peritectic temperature the $NiAl_3$ phase begins to solidify and continues until the eutectic temperature is achieved. At the eutectic, the remaining liquid solidifies as a eutectic mixture of $NiAl_3$ and Al. Except for the size of the features, the microstructure for the crucible solidified sample in Figure 6 is very similar to the containerlessly solidified samples in Figure 5.

DISCUSSION

In spite of the large undercoolings and unique microstructures achieved in other studies utilizing the MSFC drop tube, we did not see this with the $NiAl_3$ alloy. In other micrographs the spacings of the dendrite arms indicate that the dendrites nucleated at the surface and grew through the sample. Since the vapor pressure of oxygen in the atmosphere was not zero, some surface oxidation in the form of Al_2O_3 would always be present. Other studies have postulated that Al_2O_3 is a strong surface nucleant for melts containing Al (Turnbull and Cech 1950). These results indicate that even in the absence of containers during solidification, surface heterogeneous nucleation may result from the reaction of some melts with gases in the surrounding atmosphere.

Another interesting observation, however, was made. The microstructural feature separation is a strong function of sample size. More accurately the microstructure is a function of cooling rate, since the sample size determines the cooling rate. In Figure 7 the relation between dendrite arm spacing (DAS) and cooling rate as published by Brooks et al. (1982) is shown. On this line we have superimposed data from the present study. This data illustrates that containerless solidification in free fall down the drop tube is another means of achieving rapid solidification and microstructural refinement.

CONCLUSIONS

Although we were successful with the original goal of undercooling the liquid metal well below the liquidus to the peritectic temperature during containerless free to form primarily $NiAl_3$, the microstructures were interesting from another point of view. The microstructure from small diameter samples is greatly refined. Small dendrite arm spacings such as these could greatly facilitate the annealing and solid state transformation of the alloy to nearly 100% $NiAl_3$ by reducing the distance over which diffusion needs to occur. This could minimize annealing time and might make it economically feasible to produce $NiAl_3$ alloy.

ACKNOWLEDGMENTS

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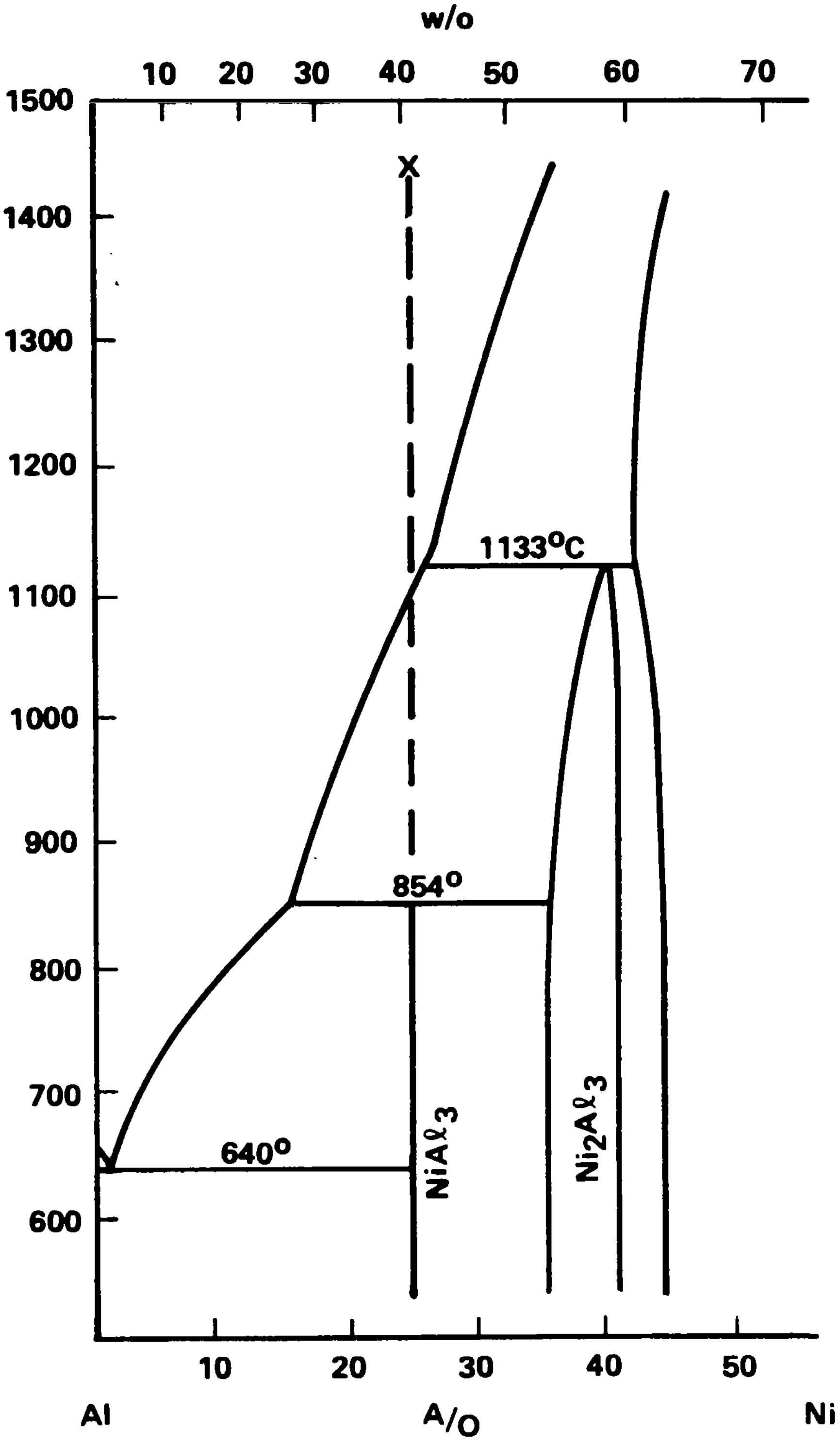

Figure 1. Phase diagram for the Al rich side of the Ni-Al alloy system, after Wiley (1967).

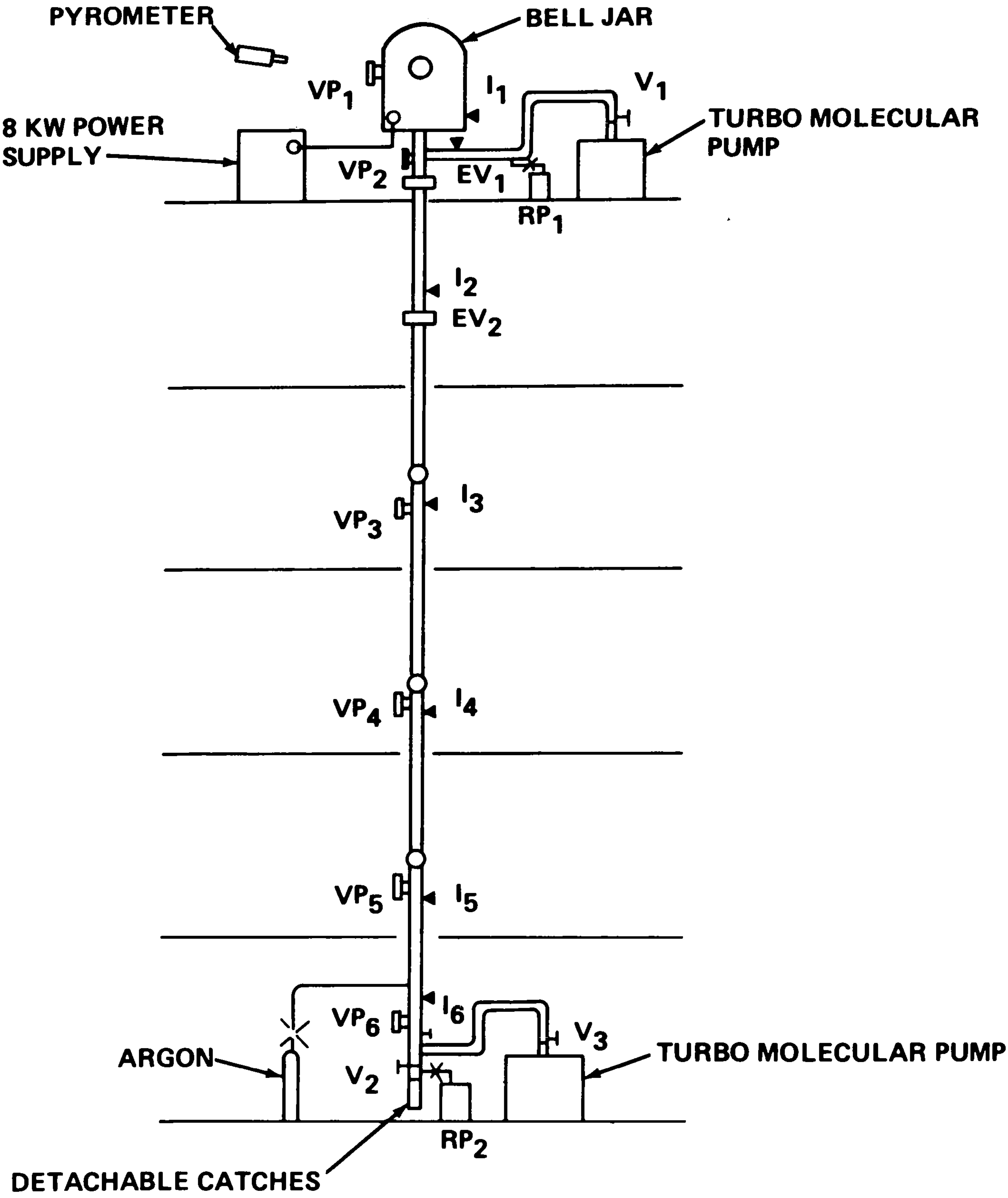

Figure 2. Schematic diagram of the 30-meter drop tube at the Marshall Space Flight Center.

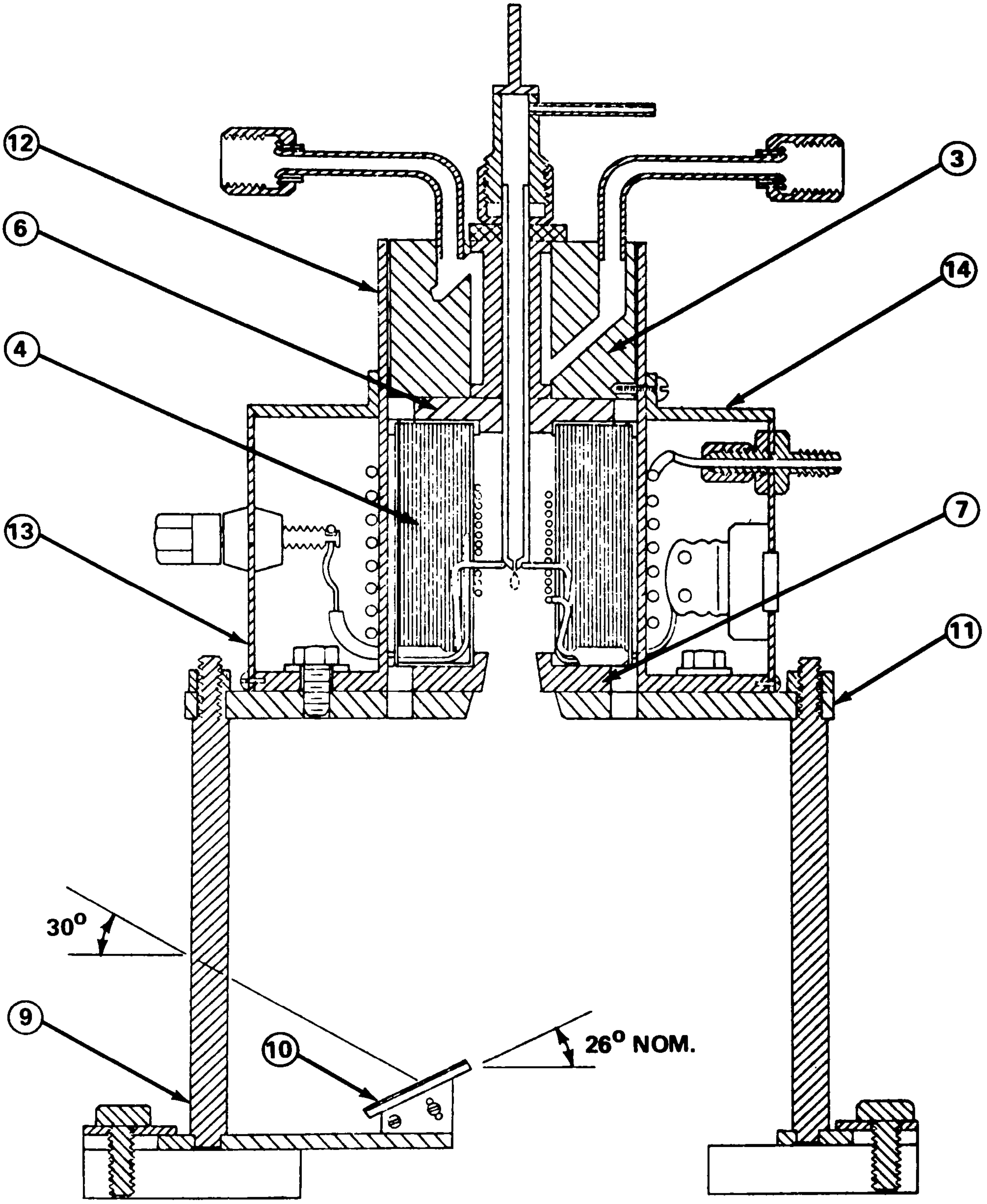

Figure 3. Schematic diagram of the furnace used to melt and process the alloy samples for the drop tube experiments.

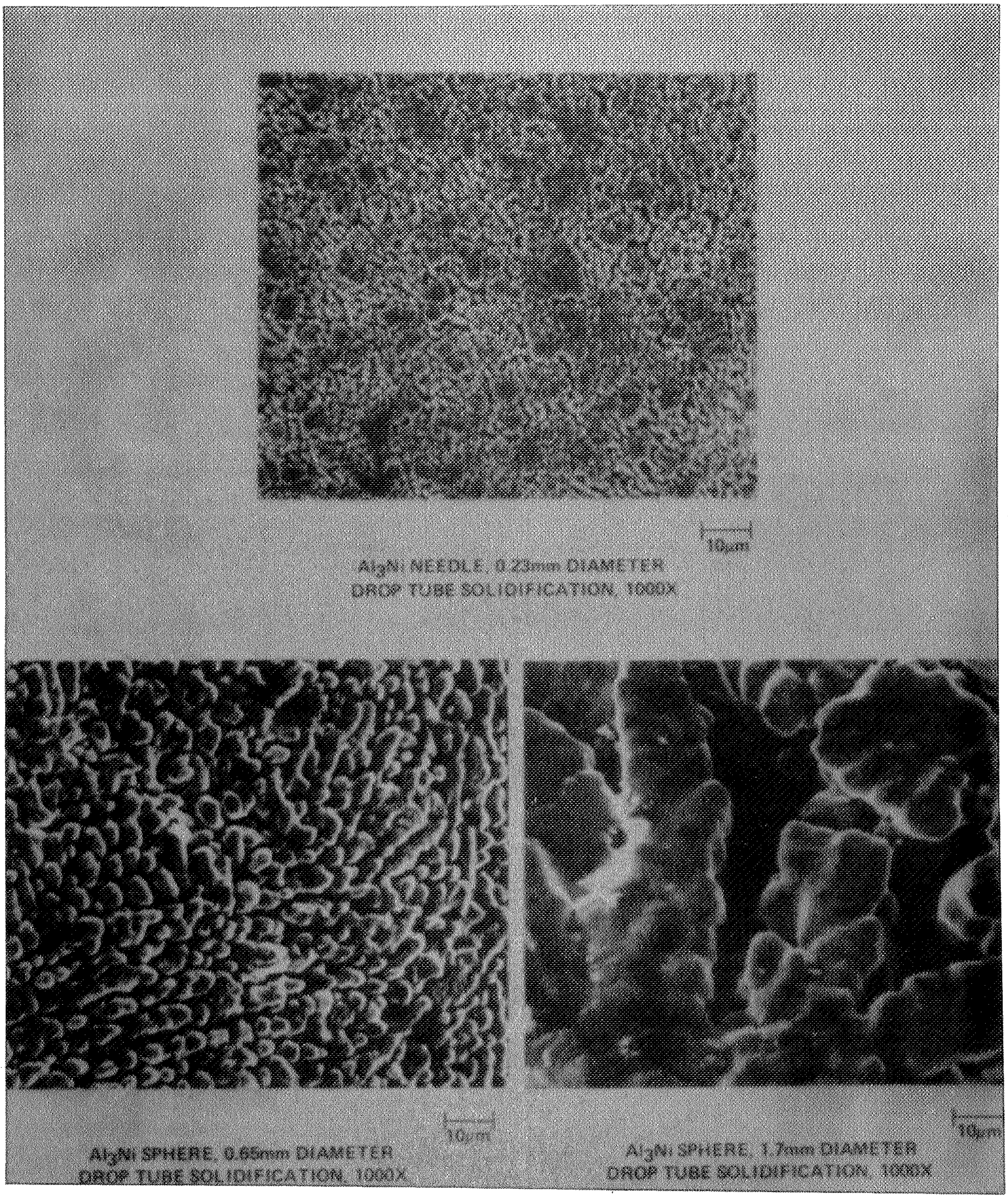

Figure 4. Scanning electron micrographs of containerlessly solidified spherical samples.

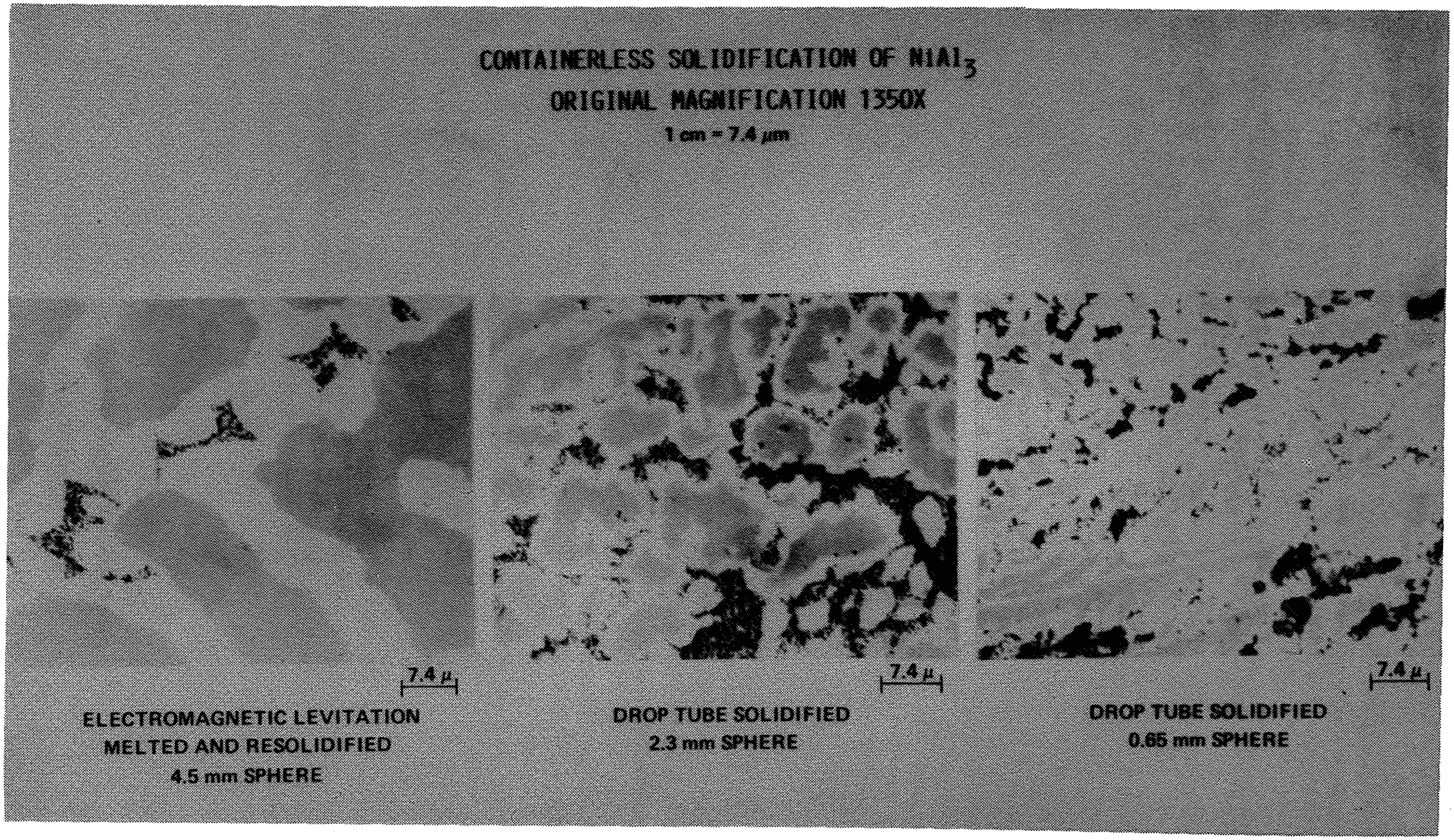

Figure 5. Light micrographs of samples of various diameters.

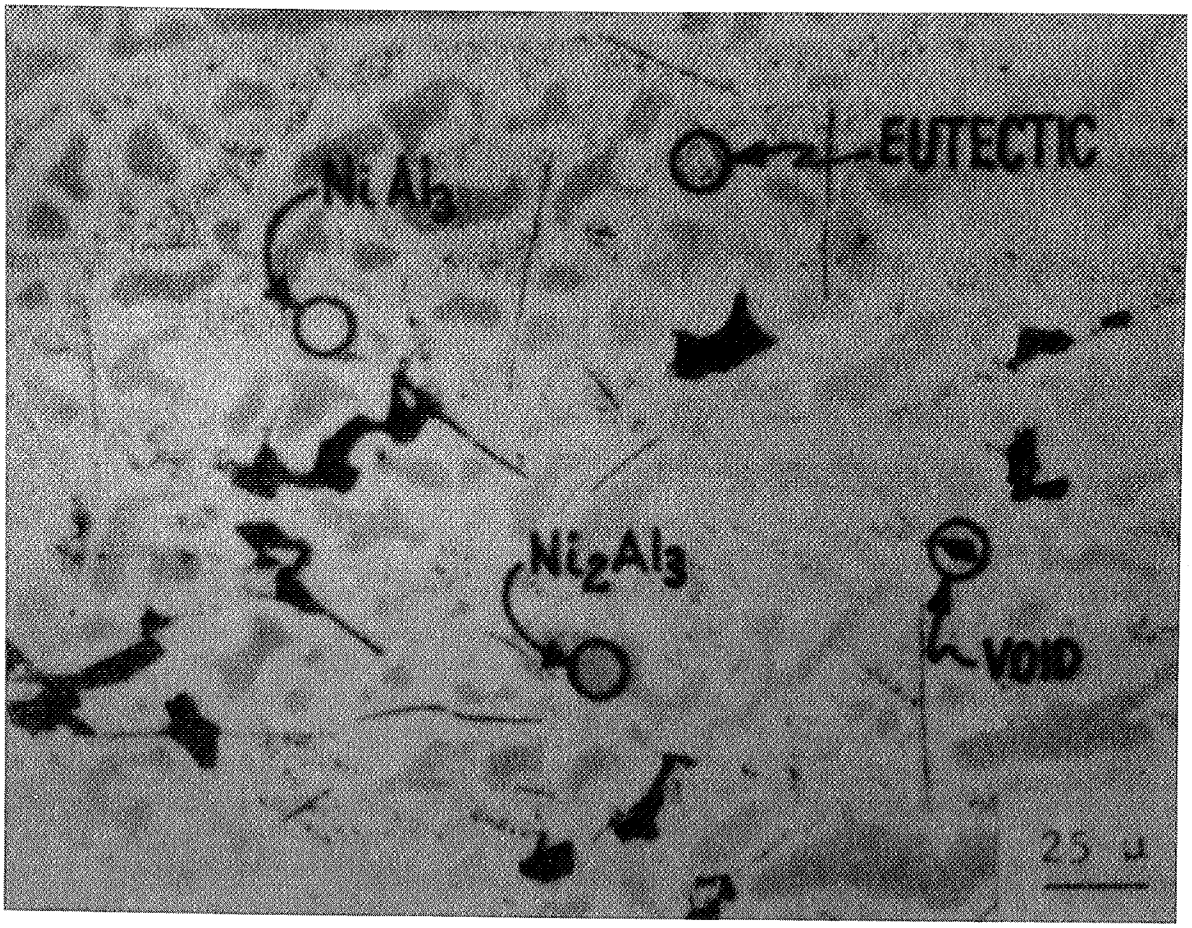

Figure 6. Light micrograph of a traditionally solidified sample illustrating the phases present.

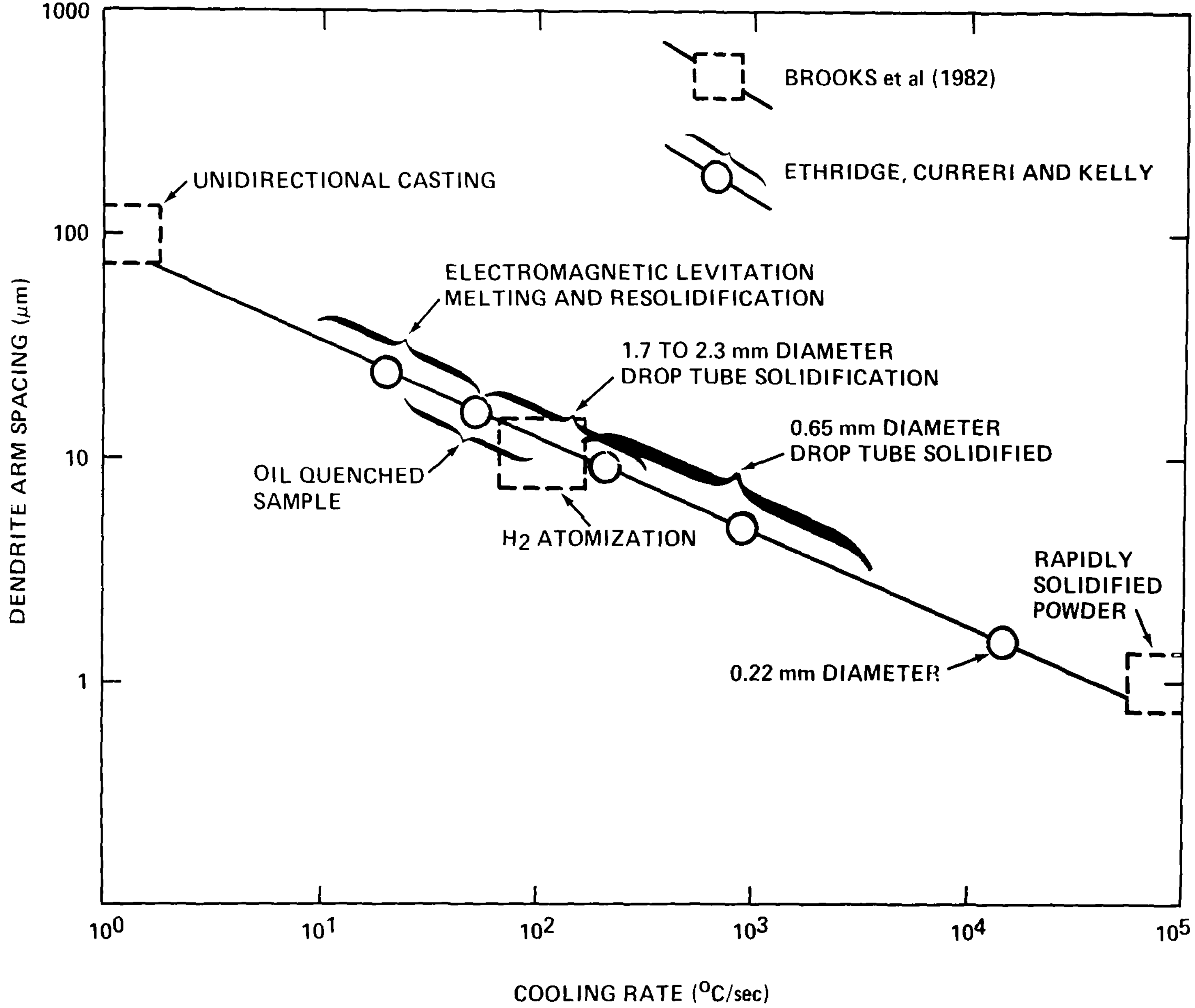

Figure 7. A plot of the Dendrite Arm Spacing (DAS) of $NiAl_3$ samples as a function of sample cooling rate.