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Pulling of 3 mm diameter AlSb rods by micro-pulling down method

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Summary

Reminder :

Fibercyrst proposed a program to investigate the crystal growth of Aluminum Antimonide (AlSb) by micro pulling down method (µPD). The definition of the most effective synthesis procedures was our aim. We proposed initial growth attempts utilizing basic 6-9's pure components (Al and Sb) and AlSb crystal provided by LBNL. Alumina and stabilized zirconia were expected as crucibles,
The goal was to pull small single crystals at least 1 cm long, and at least 3 mm in diameter.

Introduction :

We designed and supplied special crucibles for AlSb material. Thermal insulation and limitation of Sb losses were our first work. The protection of the growth environment was also one of our priority to avoid any pollution of the Fibercryst µPD facility.

When this work was achieved, the next step was the calibration of the heating power for these new crucibles. Then, it was the definition of single crystal growth conditions that oriented our research.

Following our proposal, many growths attemps were performed. We started from Al & Sb pure powder or from LBNL AlSb crystal as expected. We used different crucibles and different seeds.

1 Crucibles supplying and calibration

First crucibles available were alumina ones. Due to the high AlSb wetting on this material we decided to work with Vitreous Carbon crucibles (Fig.1). We have to notice alumina crucibles supplying was very difficult and manufacturers refused to machine this crucible shape with zirconia.

Fig 1 : vitreous carbon crucibles

Growth setup and crucibles curve calibration were presented in our previous report, Fig 2 & 3 remind it.

Fig 2 : setup

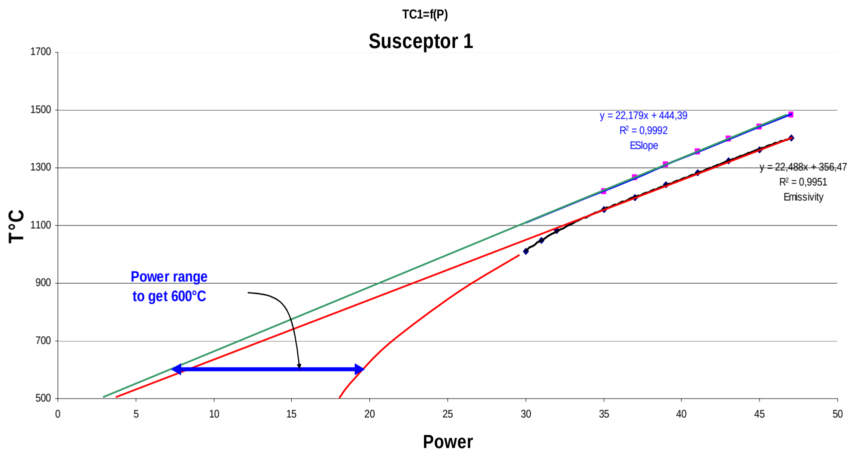


Fig 3 : Crucible calibration curve

To heat alum ina crucibles we used Carbon su sceptor . The vitreous carbon crucibles were heated directly by RF coupling.

2 Experiments

A/ Alumina crucibles

We tried several growths and melting cycle in alumina crucibles (cf table 1). Melting condition and Sb losses limitation were obtained (low residual material in the setup) with our setup. Unfortunately, no samples were pulled, seed “connections” were suitable but we didn’t success in pulling down raw material.

AlSb wetting behaviours is not compatible with alumina crucible. Wetting is too high to pull down across a capillary hole. Fig 4 shows AlSb affinity for Alumina.

Fig 4 : AlSb molten in alumina crucible

B/ Vitreous carbon crucibles

We decided to work with these crucibles due to the low wetting with usual material.

At the beginning we calibrated the AlSb melting point with these crucibles. We checked that AlSb had a good behaviour in vitreous carbon but also that crucibles became quickly warped (Fig 5 & 6).

Fig 5 & 6: Warped crucibles after AlSb melting

In a second time, we tried to pull with AlSb seed or alumina seed; with raw material powder or raw material crystal. All these experiments are resumed in the table 1.

Alumina seeds (Fig 7) didn't "melt down" compared to AlSb seed (Fig.8) so it is a little bit easier to control the connection. However, thermal conductivity of alumina is 12W/m.K vs 59W/m.K for AlSb at room T°. We are going to see (paragraph C), it not seems to be a good way to improve AlSb growth.

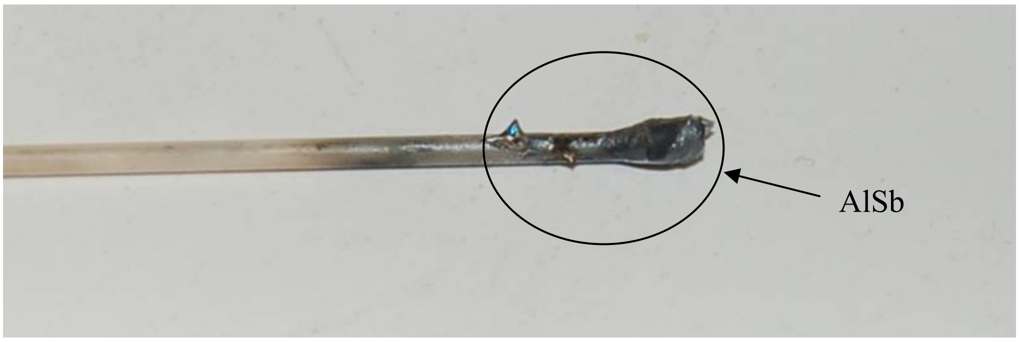
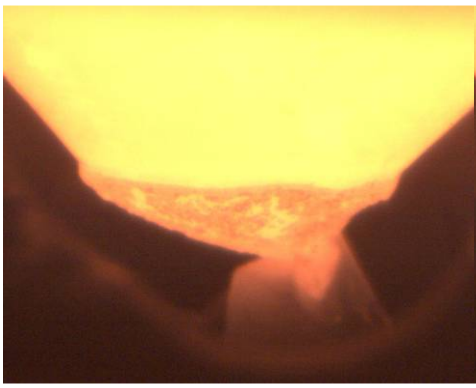


Fig 7: alumina seed with AlSb grown from a vitreous carbon crucible

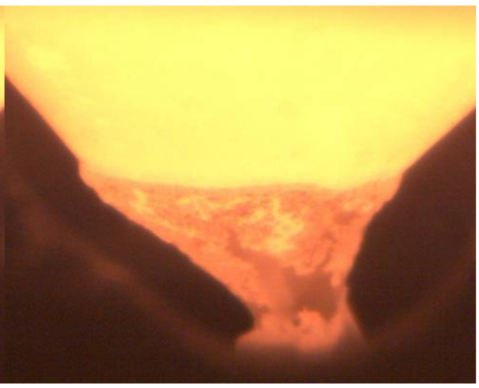
Fig 8: AlSb that melted on itself

C/ Crystals pulling

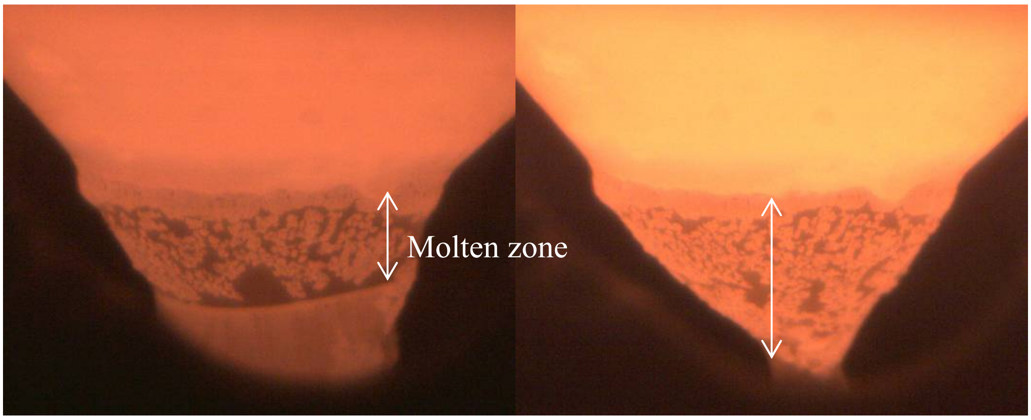
The following photographs show the different steps during the growth. As we can see, the Sb losses are very low because even in the "cold" area in front of the video aperture, we didn't notice any Sb deposit.



Seed connection



Beginning of the growth



Growth in acceptable condition *Disconnection*

It is very difficult to manage the molten zone, if we are not "enough hot" there is a risk of frozen and then the seeding is broken (Fig.9). If we over heat, the molten zone become very long and it is not possible to control it and a disconnection occurs.

Fig 9 : AlSb « frozen » on the crucible

Conclusion:

Our goal was to define the good parameters to control the growth that was equivalent to control the molten zone. We tried many possible solutions (growth speed after heater and crucible temperature) to increase the thermal gradient above the crucible but it was unsuccessful. To come back to the seed material, a higher thermal conductivity would be better so it would be a good way to work with a metal which have a high melting point (platinium, iridium…). Thermal conductivity of AlSb is > alumina one but the problem was AlSb seed melted.

3 Table of growths attempts

Growth	Raw Material	Crucible	Power/T°	Speed (mm/min)	Seed	Results
510	Crucible Calibration					
511						
540 Powder		Alumina	Melting Calibration			
541 Powder		Alumina				
545 Powder		Alumina	30%		AlSb	Not connected
546 Crystal		Alumina	35%		AlSb	Not connected
559 Crystal		Carbon	70%		AlSb	Overheated
560	Crystal	Carbon	58,8% min 63,7 max	0,7	AlSb	6mm and seed broken
561 Crystal		Carbon	61% min 63,5% max	0,2 0,82	AlSb Seed	melted
565 Crystal		Carbon + glue	59% min 65 % max	0,4 0,5 1	AlSb Not	connected
566 Crystal		Carbon + glue	57% min 63% max	Alum	ina	Not connected
567	Crystal	Carbon + glue	63%	0,2 0,5	Alumina	3mm
568 Crystal		Alumina	35%	0,5	AlSb	No
582 Crystal		Alumina	31% min 46% max	0,3 0,5	AlSb No	

Tab 1 : growths attempts

This table shows that AlSb is difficult to growth but that we obtained 2 samples with 2 different seeds.
In growth 650 we “froze” the molten zone because we wanted to keep it as thin as possible.
In growth 567, it was the contrary, molten zone was too long and was not controllable.
Our feeling is that it is more difficult to connect with AlSb seed than with alumina one’s but when we succeeded on it, then the molten zone was easier to control. We can think it is due to the higher thermal conductivity that increases the vertical thermal gradient. Continue to increase this gradient was tried, increasing growth speed or removing the after heater. Speed increase showed that molten zone became totally incontrollable. With a pedestal that didn’t heat (because pedestal is in alumina), we didn’t notice any improvement.

General conclusion

We developed a specific setup to growth AlSb single crystal with the micro pulling down method. Thermal insulation, Sb volatility protections and special crucibles were used.

Growth of two small AlSb samples was performed. This is a poor "material" result but this fisrt work results ingrowing experience and knowledge on AlSb that allows us to better understand the ways to growth AlSb by µPD. Actually, this know-how includes interesting information to improve the process.

First, vertical thermal gradient has to be increased to improve the control of the molten zone. We also could work on crucible and seed material to increase this gradient and to improve their compatibility with the AlSb melt.
However, we have to be careful because increasing thermal gradient is antagonist with crystal quality. Following this way required to find the exact ratio between all parameters to conserve a single crystal quality.

Recommendations for further work :

Working with a metallic seed:

- Iridium
- Tantalum

Working with a new crucible material:

- Tantalium
- Al/Ti

Trying to cool the molten zone (risk of polycrystalline phase)

- Machine modifications (water coil…)
- Oriented gas flux

Making a flux cap

- LiF, B2O3…

Working on thermal simulation would lead to a better understanding of the AlSb melt behaviour and how to manage it. We think this preliminary study would be indispensable for this material, and in general, to solve a lot of problem connected to the µPD growth.

Considering the difficulties we faced, the large number of parameters under investigation and an necessary important work on thermal simulation, we think that only a medium-long term work (such as a PhD thesis) could lead to successful AlSb rod growth by micro-pulling down.

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