DTU Library

Growing Beta-Brass Single Crystals

Als-Nielsen, Jens Aage; Kofoed, W.

Publication date:
1967

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
Als-Nielsen, J. A., & Kofoed, W. (1967). *Growing Beta-Brass Single Crystals*. Risø National Laboratory. Denmark. Forskningscenter Risoe. Risoe-R No. 149

Risö Report No. 149

Danish Atomic Energy Commission

Research Establishment Risö

Growing Beta-Brass Single Crystals

by J. Als-Nielsen and W. Kofoed

March, 1967

Sales distributors: Jul. Gjellerup, 87, Sölvgade, Copenhagen K, Denmark
Available on exchange from: Library, Danish Atomic Energy Commission, Risö, Roskilde, Denmark

March, 1967 Risö Report No. 149

GROWING BETA-BRASS SINGLE CRYSTALS

by

J. Als-Nielsen and W. Kofoed

The Danish Atomic Energy Commission
Research Establishment Risö
Physics Department

Abstract

The apparatus for growing large single crystals by the Bridgman method is described, and the growth of beta-brass crystals is discussed in particular. Evaporation of Zn is avoided by encapsuling the graphite crucible in a stainless steel container, and with an appropriate growth rate of 7 mm/hr through a temperature gradient of $14^{\circ}C/cm$ large perfect crystals (100 grams) were obtained from the melt.

CONTENTS

INTRODUCTION

The order-disorder transition in a pure beta-brass crystal has recently been studied by neutron diffraction techniques in this laboratory[1, 2]. The temperature dependence of the long-range-order, below the transition temperature T_c, and of the short-range-order, above T_c, were in excellent agreement with the theoretical predictions of the Ising model. This is a basic theoretical model in the treatment of phase transitions in general, and intense studies during the last decade have revealed detailed and accurate theoretical results[3, 4]. An additional comparison between theory and experiment could be obtained by using a Cu^{65} enriched crystal[5], since the signal intensity would be increased by a factor of seven compared to that from a crystal of normal abundant Cu.

One of the aims in setting up a crystal growing programme in this laboratory is, thus, to make possible the growth of an enriched beta-brass crystal, if a sufficient amount of Cu^{65} can be borrowed from one of the isotope store centres in the future.

The neutron diffraction study mentioned above also indicated that the short-range-order depends on the composition of the alloy. However, only two markedly different crystals had been examined, and it was felt that a systematic investigation of the effect could only be carried out, if the crystals were grown in the laboratory where the neutron diffraction study was to take place.

Finally the experience gained during this programme would provide the necessary experience for the growth of other large crystals as required in neutron diffraction studies of the solid state.

The growth of beta-brass crystals is encouragingly easy and has been reported on since the thirties[6, 7]. A technique was used here where the melt is placed in a crucible and solidifies while passing a temperature gradient by vertical translation - the so-called Bridgman method[8]. However, there are minor complications due to rapid Zn evaporation and segregation of the components in the alloy. To prevent Zn evaporation, the crucible must be tight or encapsuled. The segregation can be kept at a minimum by an appropriate rate of growth and can be further reduced by annealing the crystal just below the melting point after the growth.

A general description of the apparatus is given in the following section. The subsequent section describes the special procedure in growing beta-brass crystals and also gives the results of the composition distribution as determined by chemical methods.

DESCRIPTION OF APPARATUS

Fig. 1 shows a cross section of the vacuum furnace. The melt (1) is contained in a graphite crucible (2), which when growing beta-brass is encapsuled in the stainless steel container (3) to prevent Zn evaporation. The crucible or container is mounted on a stainless steel pedestal (4) designed for appropriate heat conducting. The pedestal is screwed on to the water-cooled shaft (5), which through the bearing (6) is led out of the vacuum and is constantly rotated (4 rpm) by the motor drive (7) during the vertical translation furnished by the spindle drive (8). The gear wheels (9) are easily interchangeable and 56 velocities from 0.24 mm/h to 45 mm/h are readily obtainable. A perspex rod (10) connected to the shaft (5) indicates the position of the crucible.

By means of a standard 1-inch diffusion pump together with a rotating pump, the pressure is kept below 20 microns during growth. (Of course, the furnace can be filled with any appropriate gas if required.)

The heater (11) is connected to the top of the water-cooled container (12) and these can be lifted as a unit, enabling easy access to the crucible. Between the heater and the container there are three irradiation shields of Mo foil.

The heater with its diaphragm is shown in more detail in Fig. 2. The heater (1) is composed of three coils above the diaphragm (2) and three coils below. The coils can be externally connected and shunted until a suitable temperature distribution is obtained. A 0.75 mm diameter Mo wire is used as a heating wire with 5 turns/cm on the three top coils and $3\frac{1}{2}$ turns/cm on the lower coils. The heater body is of stumatite and the diaphragm (2) also is composed of stumatite and of a Mo foil (3). The diaphragm can be heated separately. The temperature distribution shown in Fig. 3 was measured with a beta-brass crystal in the crucible and with Cromel-Alumel thermocouples placed at A, B and C (Fig. 2). The coil currents from a Vario transformer directly fed from the net, are given in the right part of Fig. 3. The radial gradient from A to C was less than 1^{o}, A being cooler than C. The temperature was continuously monitored by means of a thermocouple placed at D. It was not necessary to use any servo control system to keep the temperature constant. The crystals were grown during night where the net voltage was rather constant and kept the temperature constant within 2^{o}.

PROCEDURE IN GROWING BETA-BRASS CRYSTALS

The copper and zinc were delivered as rods of 99.9999% purity from ASARCO, South Plainfield, New Jersey, U.S.A. After removing the surface oxides and acid-washing with HNO_3, the weighted Cu and Zn rods were placed in the crucible, which was encapsuled to avoid Zn evaporation. A convenient and tight container for the crucible was made of stainless steel. After placing the crucible in the container, a cover was Argon-welded on it. Through a nozzle in the cover, pumping took place for 24 hours at 300°C. The outer and inner diameter of the nozzle were respectively 5 mm and 2 mm and, by heating locally to red heat, it was possible to squeeze the nozzle, giving a vacuum tight sealing.

The container was then mounted on the pedestal in the furnace and the temperature was increased to approximately 40° above the melting point of the alloy. After 8 hours at this temperature the crucible was lowered at a constant velocity of 7.2 mm/hour through the temperature gradient around the baffle. It was finally left for 24 hours at 50° below the melting temperature to release the segregation which normally takes place in the growth of any alloy, and in this case would give excessive Cu at the bottom, and excessive Zn at the top of the crystal. After growth and annealing the crystal was etched, first in concentrated HNO_3 and afterwards in cooled HNO_3, whereby possible grain boundaries are immediately visible. An estimate of the orientation and of the quality of the crystal can be seen directly by observing the reflection of light when the crystal is turned.

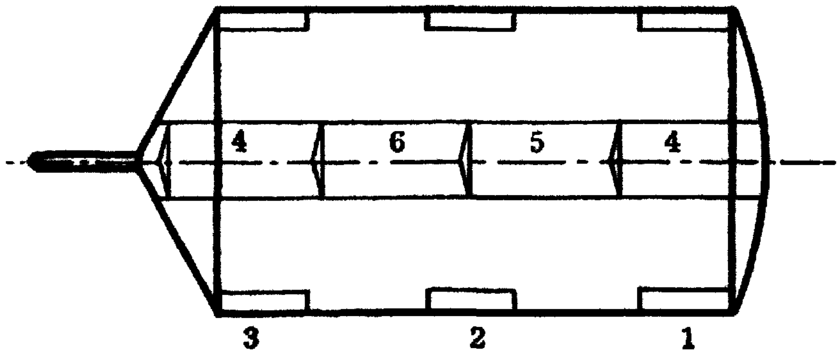
After a few unsuccessful attempts, a dozen crystals have been grown without any failures. Only the escape of Zn is not yet fully under control, but the Zn loss can be accurately measured by comparing weights before and after the growth. The final homogenity has been measured by chemical methods in an example given below, where a crystal with unusually high Zn loss was chosen to prove that the weight loss is entirely due to Zn.

1 gram probes were taken from seven regions of the crystal as indicated in Fig. 4. The composition was examined by titration of Cu as well as of Zn, and by a polarographic method, where the deviation from a standard (here probe 6) is determined.

Table 1

Composition of a β-brass crystal

Region	Titration Cu %	Titration Zn %	Titration Sum %	Polarography Cu %	Weights
1	53.32	46.00	99.32	54.44	Cu 52.000 g Before
2	53.30	46.32	99.62	53.43	Zn 48.351 g Growth
3	53.42	46.10	99.52	53.44	Total 100.351 g
4	53.49	46.00	99.49	53.22	Total 96.661 g After
5	54.20	45.88	100.08	54.54	Growth
6	53.63	46.11	99.74	Standard	
7	53.96	46.10	100.06	53.88	
Average	53.62	46.07	99.69	53.80	53.80 % Cu



It is concluded from these data that fluctuations in the composition in the crystal were less than about ± .5% the estimated uncertainty of the chemical methods.

A preliminary neutron diffraction study of some of the crystals shows that they are monocrystals with a satisfactory mosaic spread.

CONCLUSION

Large beta-brass crystals (100 gram) have been grown by the Bridgman method in an apparatus shown in Fig. 1. Evaporation of Zn is avoided by encapsuling the crucible in a tight stainless steel container. With a growth rate of 7.2 mm/h over a circular cross section of 8 cm^2 and a temperature gradient of $14^{o}C/cm$ and a final annealing (homogenization) for 24 hours 50^{o} below the melting point, perfect, homogeneous crystals were obtained. The apparatus has also been used successfully for growing Pb and Zn crystals.

ACKNOWLEDGEMENTS

We are indebted to Dr. Keating, Brookhaven National Laboratories, who generously provided us with information about his detailed experience in growing beta-brass crystals. A. Thorboe kindly made a chemical examination of the composition of a crystal while A. Thuesen gave useful assistance during the investigation.

REFERENCES

1) O. W. Dietrich and J. Als-Nielsen, NBS MICS. PUB. 273, p. 144 (1966).

2) J. Als-Nielsen and O. W. Dietrich, Phys. Rev. 153, 706 (1967).

3) C. Domb, Advances in Physics 9, 245 (1960).

4) M. Fisher, "Lectures in Theoretical Physics" Vol. VII C (University of Colorado Press 1965).

5) C. B. Walker and D. T. Keating, Phys. Rev. 130, 1726 (1963).

6) Gilman "The Art and Science of Growing Crystals" J. Wiley (1963).

7) H. L. Burghoff, Yale University, M S Thesis (1930).

8) P. W. Bridgman, Proc. Am. Acad. Arts Sci. 60, 305 (1929).

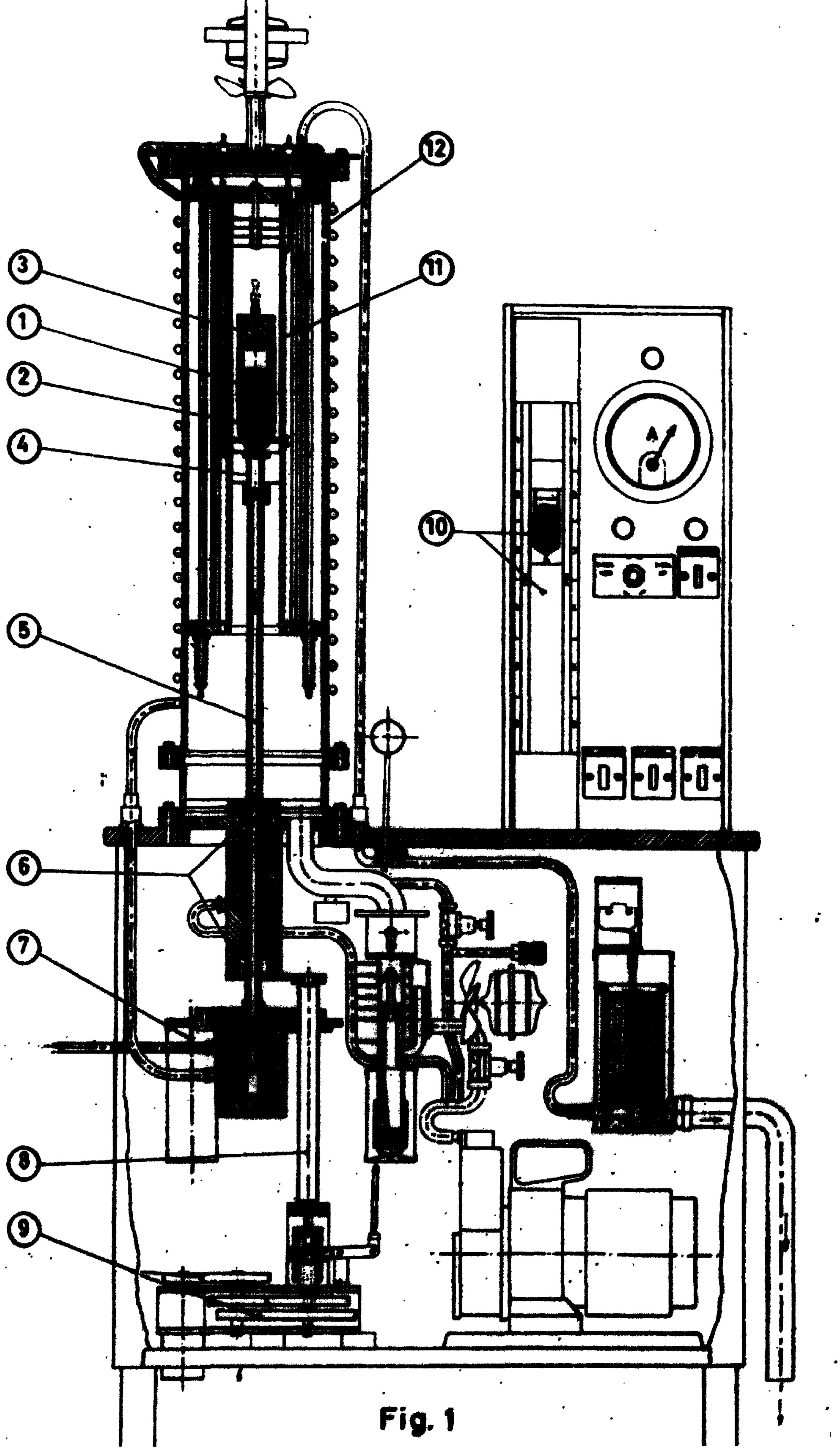


Fig. 1

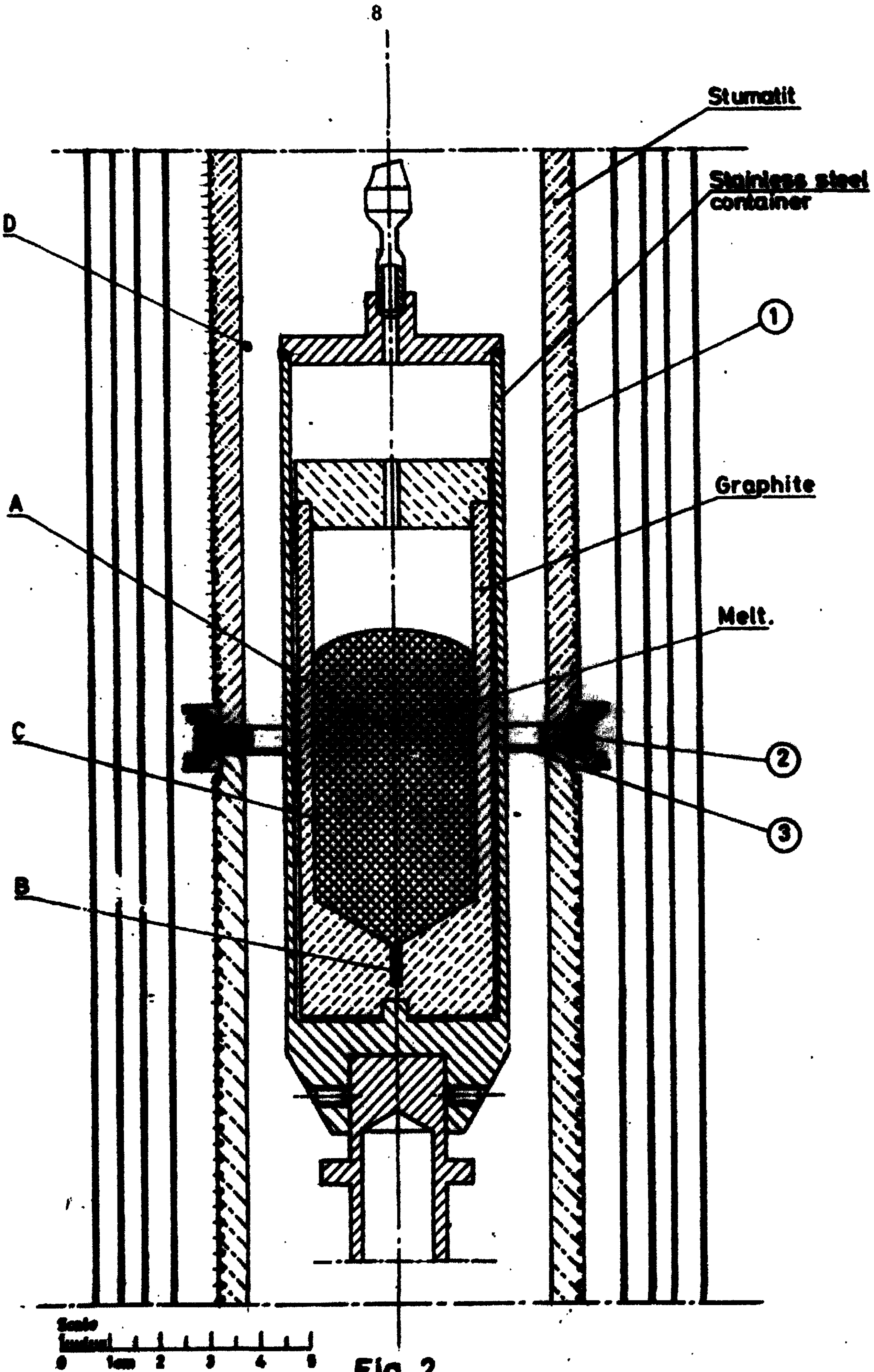
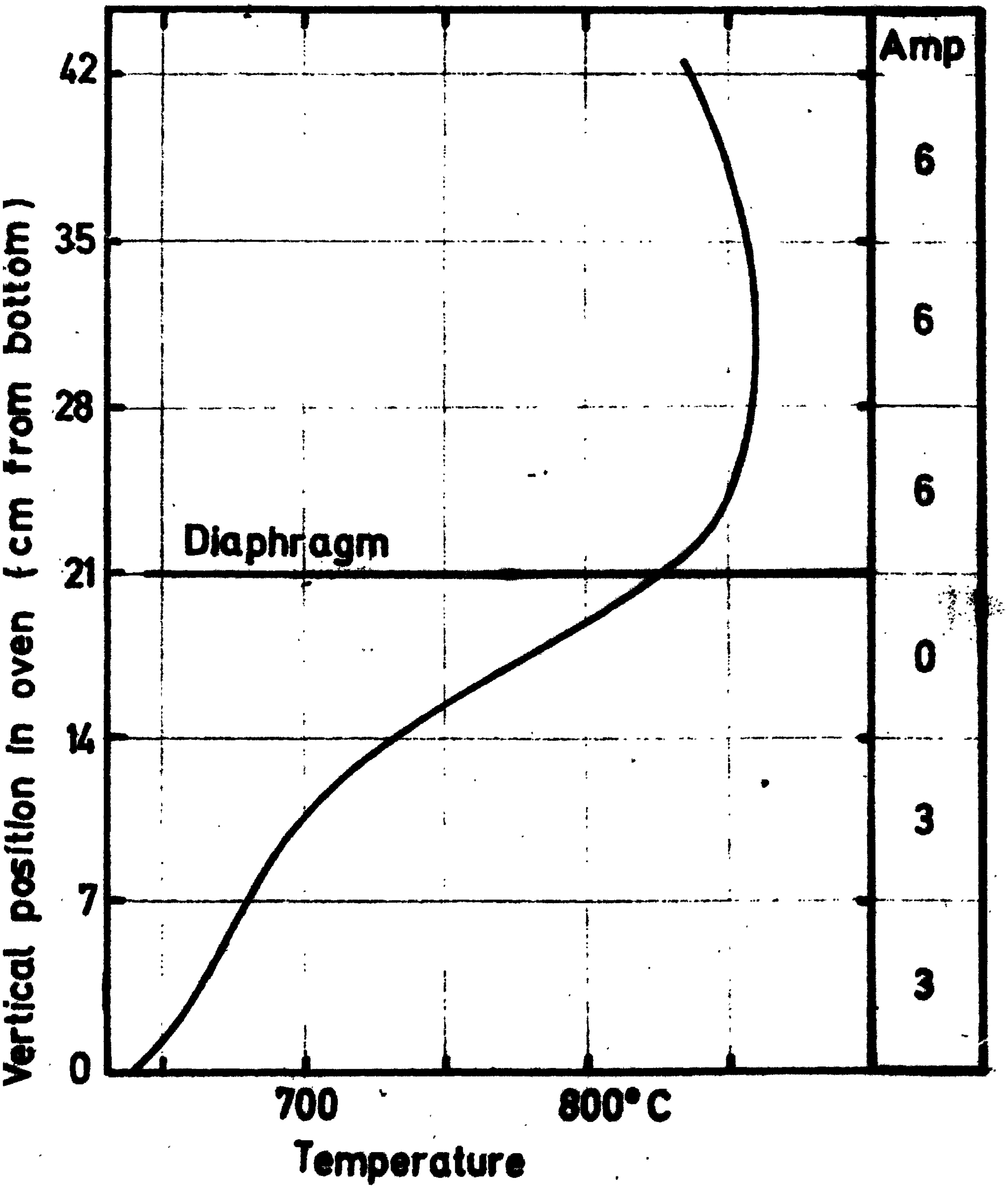

8
Stumatit
Stainless steel container
D
1
Graphite
A
Melt.
C
2
3
B
Scale
0
1cm
2
3
4
5

Fig. 2



Amp
42
35
28
21
14
7
0
6
6
6
0
3
3
Diaphragm
Vertical position in oven (cm from bottom)
700
800° C
Temperature

Fig. 3

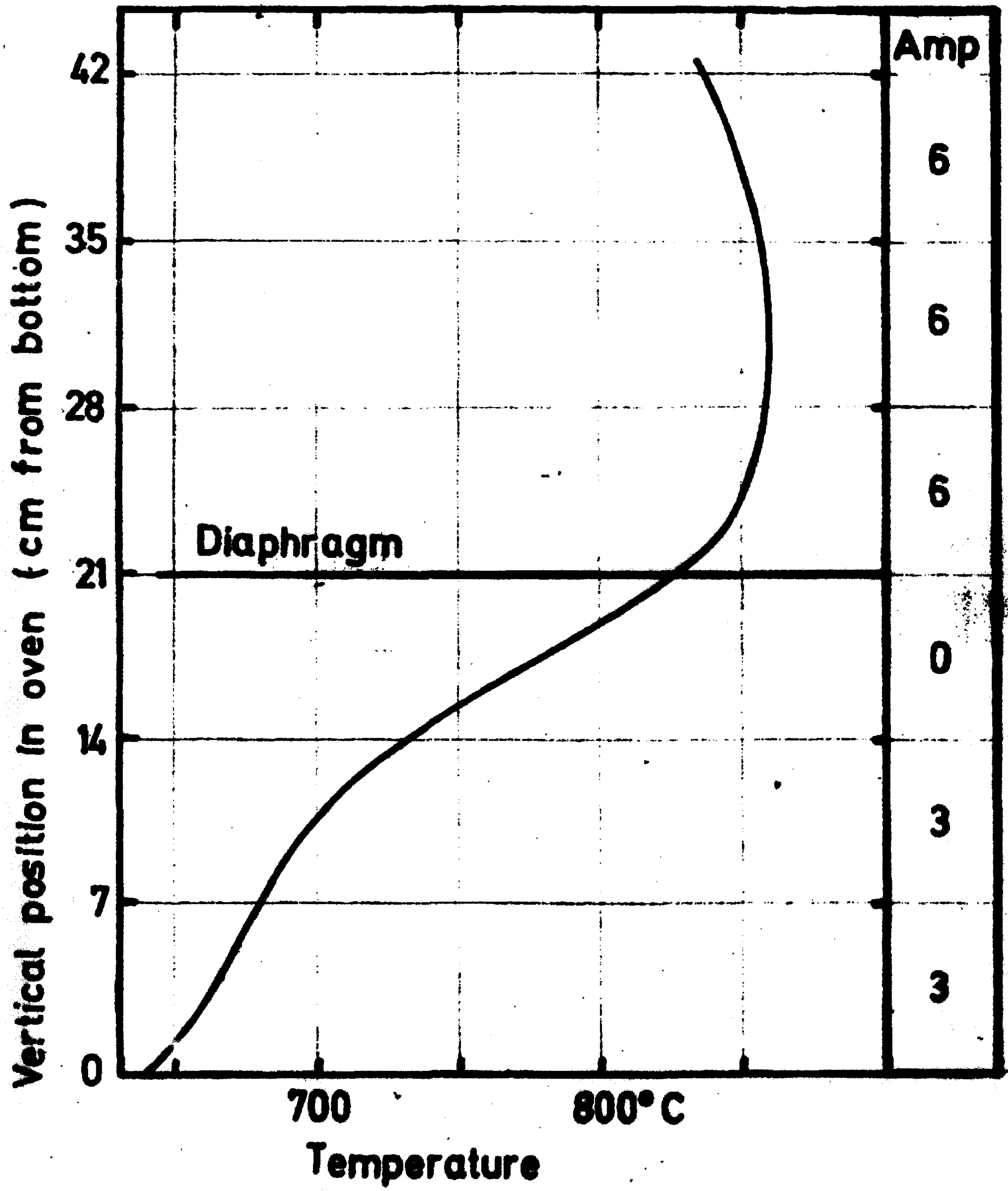

Amp
42
35
28
21
14
7
0
6
6
6
0
3
3
Diaphragm
Vertical position in oven (cm from bottom)
700
800° C
Temperature

Fig. 3