Up to 255° K the second moment is practically constant and this suggests the absence of any sort of torsional oscillations which often occur[14] in amino compounds. After this temperature, the second moment rapidly falls off from the rigid lattice value indicating the onset of some motion in the molecular space. The way the molecules link, the spatial location of amino protons and their strong binding with halo atom, may safely rule out the possibility of rotation of bound amino group. We thus consider the probability of molecular rotation. The reduced S_1 calculated by method of Gutowsky and Pake[11] comes nearly to be 3·01 G^2 and reduced S_2 was found to be 0·37 G^2 (Andrew and Eades[7]). The total second moment 3·38 G^2 thus remotely compares with the observed second moment value of (4·45 ± 1 G^2). The second moment afterwards decreases gradually up to the melting point. This fall perhaps may be due to tendency of the amino proton oscillation at the input of large thermal energy of this range. The approximate value of activation energy for the reorientation was found to be the order of 7·8 Kcal/mole (Waugh and Fedin[13]).

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PRODUCTION OF ZINC BICRYSTALS BY MODIFIED BRIDGMAN TECHNIQUE

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ABSTRACT

An account is given of a modified Bridgman technique for the production of bicrystals of zinc. The present technique, in addition to being simple and fast, allows the production of zinc bicrystals free from striations with better perfection. The use of the same technique could be extended to the production of bicrystals of other low melting temperature metals.

INTRODUCTION

THE bicrystals of metals have been produced by a variety of techniques involving either solid-solid or liquid-solid equilibria. Of the techniques involving liquid-solid equilibrium, the crystal pulling technique[1] and the horizontal boat technique[2] are the most important. The horizontal boat technique is simpler than the crystal pulling technique which requires rather complex equipment. However, the crystals produced by the crystal pulling technique have been found to be of fairly high perfection compared to those produced by horizontal boat technique.

One of the factors responsible for the lower perfection of the crystals, produced by the horizontal boat technique, is the non-uniform heat flow from the melt, as the melt in this case is covered by the mould on three sides only. Moreover, substantial thermal convection currents, present during horizontal growth[3], tend to produce variable growth conditions leading to the formation of striations in the crystal. If the convection is suppressed or eliminated by the application of a dc magnetic field to the melt during horizontal growth[4], structurally sound crystals could be obtained; but then the simplicity of the technique is lost.

In the present work an attempt has been made to grow striation free bicrystals of zinc using a modified Bridgman technique. A set of experiments involving different lowering rates and temperature gradients have been carried out.

Experimental Procedure

The principle on which the present work is based is a simple extension of the Bridgman technique used for growing single crystals. A specially designed pyrex mould providing two independent sources for nucleation as shown in Fig. 1 has been used in the present work for the production of bicrystals. The mould containing the metal, sealed under vacuum, is lowered into a vertical furnace at a controlled rate through a definite temperature gradient. Since solidification will start at the tips of the two arms, one can expect a single nucleus, to survive after competitive growth in each of the arms. On passing beyond the arms upwards, the frozen metal should consist of a bicrystal with crystal orientations as in the arms. The line diagram of the experimental set up used in the present work is shown in Fig. 2. The temperature gradients in the range of 16° C/cm to 25° C/cm and the lowering rates in the range of 3 cm/hr to 12 cm/hr have been tried.

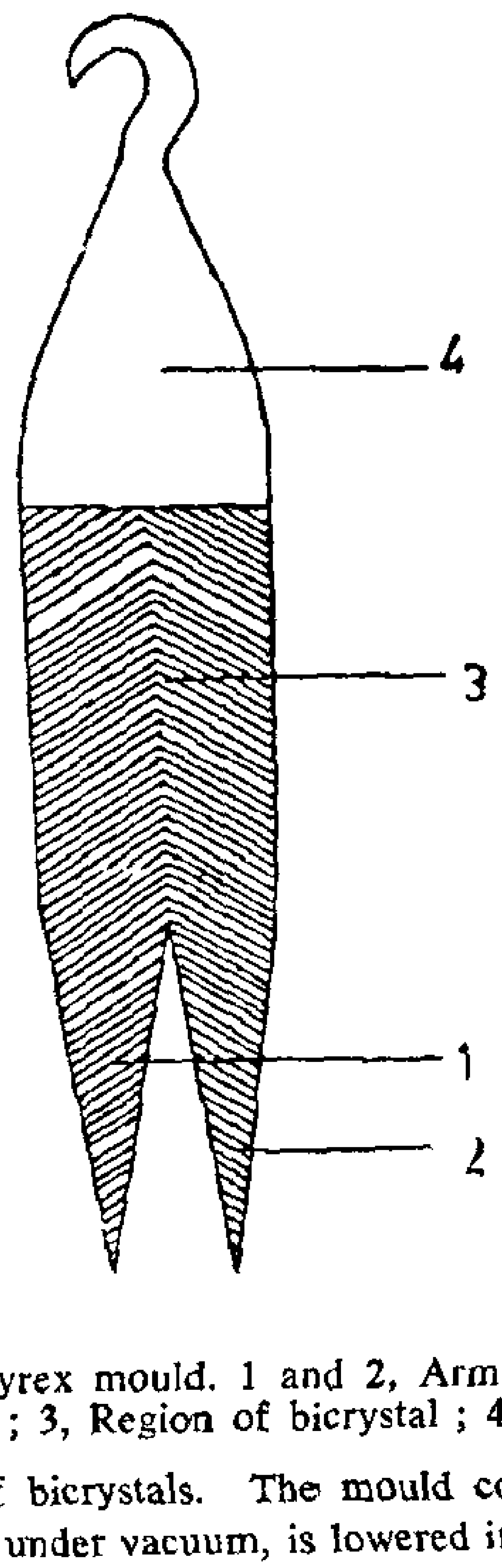

FIG. 1. Pyrex mould. 1 and 2, Arms containing single crystal; 3, Region of bicrystal; 4, Vacuum.

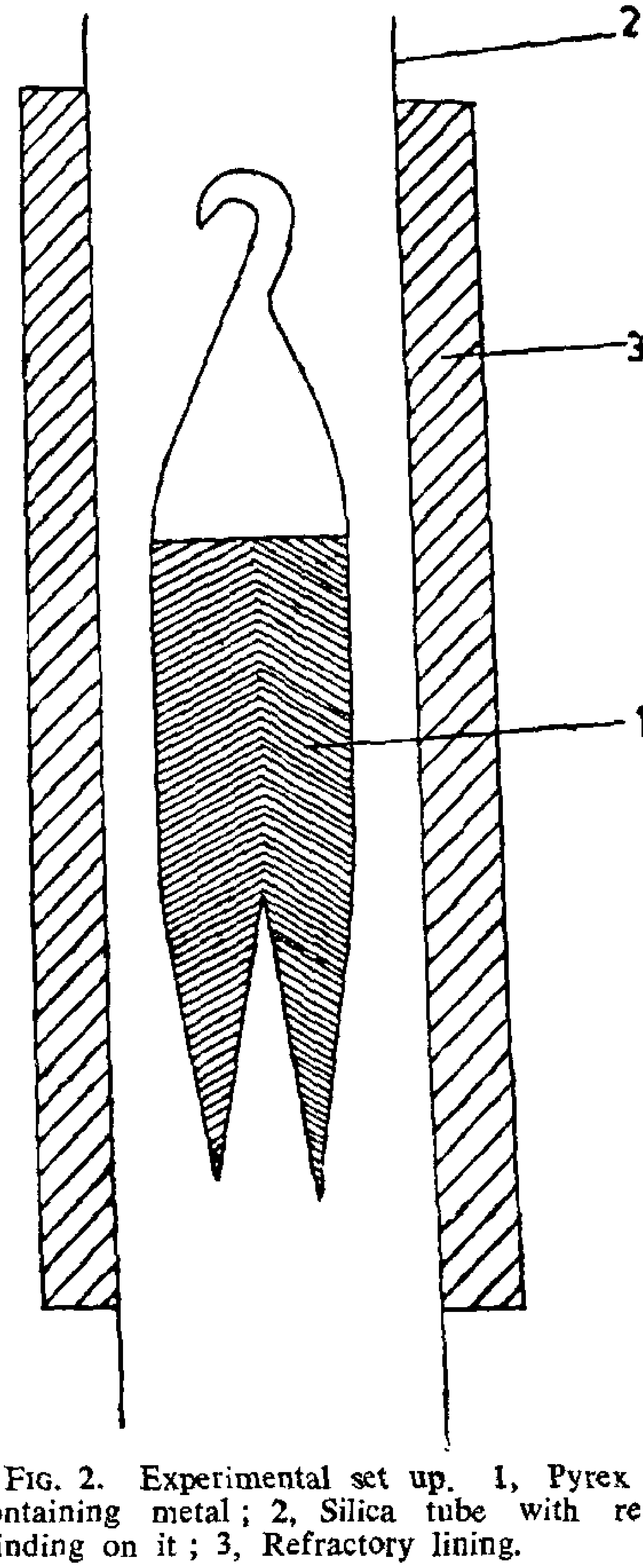

FIG. 2. Experimental set up. 1, Pyrex mould containing metal; 2, Silica tube with resistance winding on it; 3, Refractory lining.

The experimental procedure was as follows:

The pyrex mould was filled under vacuum with zinc of 99·95% purity. After sealing, a hook was made out of pyrex at the top of the mould to facilitate lowering of the mould. The mould was immediately kept in a preheated oven and allowed to cool in it to avoid cracking which would otherwise take place after sealing due to differential cooling. The mould was then lowered through the vertical gradient furnace at a selected rate in the range of 3 cm/hr to 12 cm/hr.

After the crystallisation was completed, the mould was carefully broken open and the crystal extracted. On being subjected to a sharp tap at low temperature the two arms showed perfect cleavage along the basal plane thus proving the single crystallinity of the arms. Once it was confirmed that both the arms were single crystals, the sample was cut in the bicrystal region and was polished using standard metallographic techniques for microscopic examination. A chemical polishing reagent[5] consisting of a freshly made solution containing equal parts of concentrated nitric acid, hydrogen peroxide and ethyl alcohol was used. The specimen was then etched with concentrated hydrochloric acid and examined under a metallograph. Microscopic and the X-ray diffraction examination of the product confirmed its bicrystallinity.

Results and Discussion

Four sets of growth conditions have been tried out and the summary of the experimental results is presented in Table I. It can be seen from the results tabulated in Table I, that the growth of bicrystals is favoured under the conditions of lowering rates in the range of 3 cm/hr to 12 cm/hr and temperature gradients in the range of 16° C/cm to 25° C/cm. The technique reported in this paper has two important advantages over the horizontal boat technique as evident from the following discussion.

In the horizontal boat technique the crystals grown in a graphite boat are covered from three sides only and therefore the rate of heat transfer from the melt is non-uniform. In the present technique the melt is covered completely by the mould and therefore the rate of heat transfer is more uniform. Secondly, the strong convection occurring in the horizontal boat technique, above a critical value of the horizontal temperature gradient, is absent in the present technique because the temperature gradient is parallel to the gravitational axis. Therefore the striations occurring due to the substantial thermal convection currents in the horizontal boat technique do not exist in the bicrystals grown by modified Bridgman technique.

In conclusion it may be pointed out that:

(i) The modified Bridgman technique allows the use of a fairly wide range of growth parameters and is a relatively simple and fast technique and

(ii) The perfection of the bicrystals obtained by modified Bridgman technique is fairly high as the formation of striations during growth is suppressed.

It is suggested that the modified Bridgman technique could be applied to produce bicrystals of several other low melting temperature metals.

Table I

Summary of the experimental results

Experiment No.	Lowering rate cm/hr.	Temperature gradient ° C/cm.	Arm 1	Arm 2	Volume beyond the two arms
1	3 cm/hr	16° C/cm	Single crystal	Single crystal	Bicrystal
2	3 cm/hr	25° C/cm	Single crystal	Single crystal	Bicrystal
3	12 cm/hr	16° C/cm	Single crystal	Single crystal	Bicrystal
4	12 cm/hr	25° C/cm	Single crystal	Single crystal	Bicrystal

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