1

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POLYMER CRYSTALLIZATION IN A TEMPERATURE GRADIENT FIELD WITH CONTROLLED CRYSTAL GROWTH RATE

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15

In extrusion and molding of crystalline polymers a melt under stress cools and crystallizes under non-isothermal conditions. Both the stress and the temperature gradients influence the course of the crystallization and thus the morphology and properties of the product. It is difficult to devise experiments for studying crystallization which separate and control these effects. This paper is concerned with a method for studying the influence of a temperature gradient on the crystallization of a quiescent polymer melt.

When a polymer melt is injected into a cold mold the rapid transfer of heat to the mold can establish steep temperature gradients in the polymer. Clark and Garber (1, 2) have reported observations on injection molding of poly-oxymethylene which related the depth of oriented crystal growth from the surface to factors influencing the crystallization temperature and temperature gradients (mold temperature and pressure). Others have reported characterizations of transcrystalline polymer growths from metal surfaces (3-6). Attempts to control the gradient during polymer crystallization have been made using techniques derived from zone-melting (7-10). Highly oriented polyethylene and polypropylene specimens have been prepared by this technique. However, the zone-melting technique is not well suited to a systematic study of temperature gradient effects on polymer crystallization. The apparatus is complex and the temperature gradient is poorly defined.

APPARATUS

For this study a simple apparatus was conceived which is indicated schematically in Fig. 1. A layer of polymer is sandwiched between two metal plates (brass). Temperatures of the plates are controlled by embedded electrical resistance heaters and cooling coils through which air or water may be circulated. Temperatures of the plates are sensed by embedded thermocouples. The faces of the plates are four inches by six inches with a central area two inches by three inches occupied by the sample. An asbestos gasket covering the remainder of the face contained the molten sample and shielded against excessive heat transfer between the plates.

A crystallization experiment is conducted by placing a polymer specimen of the desired thickness between the plates and then programming the temperature of the plates as indicated in Fig. 2. First the plates are heated so that both are above the melting point of the polymer and a temperature difference is established between them. Both plates are then cooled at a constant rate so that the temperature difference between them remains constant. At the start sufficient time is allowed to establish the steady-state linear temperature profile in the polymer. Provided the sample is not too thick or the cooling rate too fast an essentially linear temperature profile is maintained in the polymer melt as it is cooled. Temperature control in our experiments was by manual adjustment of heaters and cooling fluid. The sensitivity was such that we stayed within ±1C of the desired temperatures except in the fastest cooling rate experiments where deviations of ±2C occurred. When the lower temperature plate reaches T_m, the equilibrium melting point of the polymer, crystallization may begin at that surface. However, as crystallization rates for a polymer are very slow at temperatures near the melting point, supercooling occurs. The crystallization rate increases rapidly with supercooling which tends to stabilize the crystallization rate with respect to the cooling. If we assume that crystallization has begun at the colder face and proceeded outward into the melt establishing a crystal-melt interface which is at a temperature T_i then two conditions are possible. If the crystallization rate at T_i is faster than the rate of progression of the temperature, the front will move out to a region of higher T_i and lower crystallization rate. If the crystallization rate is slower than the temperature progression, T_i will decrease and the crystallization rate will increase. The tendency then is for the interface to arrive at a temperature where the crystallization will keep pace with the temperature. Crystallization will then occur at a constant temperature, T_i, and at a rate consistent with the progression of T_i.

Taking time zero when the colder plate is at the equilibrium melting point then:

$$T_1 = T_m - b\theta$$

$$T_2 = T_1 + \Delta T = T_m - b\theta + \Delta T$$

$$T_x = T_m - b\theta + (\Delta T/L)x$$

where θ is time, b the cooling rate, T the temperature difference between plates and L the thickness of the polymer

then:

$$T_i = T_m - b\theta + (\Delta T/L)x_i$$

$$x_i = T_i - T_m + b\theta/\{(\Delta T/L)\}$$

or

$$dx_i/d\theta = b/\{(\Delta T/L)\} = b/g$$

where $(dX_i/d\theta)$ is the rate of progression of the front at T_i which is then also the rate of progression of the crystal growth front. g is the temperature gradient, $(\Delta T/L)$. Since b, T and L can be independently chosen it is possible to excercise separate control of the crystal growth rate (and thereby of the temperature at which crystallization occurs) and of the temperature gradient during crystallization

This analysis is an oversimplification. At fast cooling rates or with thick specimens there will be deviation from a linear temperature profile. This, however, is not serious and the distortion is predictable. The crystalline polymer and the melt have different thermal conductivities which also produces a distortion which is predictable if one knows the relative conductivities of the phases. There is also a volume change on crystallization. This can also cause a minor distortion if L and thus the gradient change. More seriously the contraction can lead to poor contact between polymer and the plates. This was avoided in our experiments by applying sufficient pressure on the plates to maintain contact and absorbing the polymer contraction by letting L decrease. In some experiments L was maintained constant by feeding molten polymer under pressure through a hole in the hotter plate to compensate for the volume shrinkage on crystallization. More important than these abberations however are the effects of nucleation and crystallization ahead of the growth front.

EXPERIMENTS:

Experiments were done using three different polymers; linear polyethylene (Marlex 6050) isotactic polypropylene (origin unknown) and another high density polyethylene of unknown origin. In all experiments the apparatus was initially heated to a point where the lowest temperature was 50C above the nominal melting point of the polymer and these conditions were maintained for one hour before cooling began.

The appearance of the Marlex 6050 after crystallization with a gradient was typically as shown in Fig. 3, a micrograph of a section viewed between crossed polarizers. Wide angle Xray diffraction of the specimens also reflected the oriented crystallization which was characterized by measuring the width of the peaks on a densitometer trace of the (200) ring. As may be seen from the listing of the half widths in Table 1, orientation is favored by a steep gradient coupled with a slow cooling rate. With fast cooling no orientation may result even if a steep gradient is maintained.

Qualitatively similar results were obtained with polypropylene. Micrographs of the structures of polypropylene samples are shown in Fig. 4. Sample 1 shows spherulites elongated in the growth direction, similar to what was observed for the Marlex 6050 polyethylene. These are also evident in samples 2 and 3 while in samples 4, 5 and 6 the spherulites are more severely elongated, sometimes traversing the thickness of the sample. Another type of growth is also evident in samples 2, 4 and 5. The progression rate, and hence the crystallization rate was quite slow in these experiments which were terminated (by quenching) when the hot face reached 135C. Continuing to a hot face temperature of 100C for specimens 1 and 6 apparently permitted sufficient time to avoid this growth while for sample three the progression rate was much faster. Thus we conclude that this growth proceeded from nuclei within the melt primarily after the experiment was terminated by quenching.

We conclude from this that the role of a temperature gradient in producing oriented crystallization is in producing conditions which lead the spherulitic growth pattern to proceed primarily in one direction. Since there is supercooled melt ahead of the growth front the potential for nucleation and three dimensional growth exists. The faster the cooling rate or progression of the oriented growth front, the less time will be available for nucleation and unoriented growth. On the other hand, the faster progression is associated with greater supercoolings which may promote the rate of nucleation and unoriented growth. The net effect of cooling rate on orientation will be the balance of competing effects and will depend on the relative sensitivity of nucleation and growth rates to temperature. The gradient effect is direct. Steep gradients diminish the penetration of supercooling and thus favor oriented growth.

The last series of experiments, on another high density polyethylene produced no apparent orientation. Light microscopy revealed a morphology of minute, barely discernible spherulites. This material apparently nucleated more readily and more densely than the Marlex 6050 so that under comparable conditions of gradient and cooling rate oriented growth was prevented by more rapid random nucleation and growth.

The simplicity of design and operation of this apparatus recommends it for use in studying polymer crystallization or preparing oriented polymer crystal growths for other studies. Also it may be useful for preparation of "isothermally" crystallized polymers. Polymer melts can be isothermally crystallized only as thin sheets or at very small supercoolings because in larger sizes the poor heat conductivity prevents maintaining a uniform temperature while cooling the melt and a significant supercooling cannot be achieved without prior crystallization. In this apparatus the oriented crystallization progresses with the cooling and the crystallization occurs at an essentially constant temperature moving front.

ACKNOWLEDGMENT

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TABLE 1

Sample No.	Sample Thickness mm	ΔT C	Cooling Rate, b C/min.	Gradient, g T/L C/mm	Progression Rate b/g, mm/min.	(200) arc Half Width Degrees	Density gm/cc
POLYETHYLENE (MARLEX 6050)							
1	1.60	0	0.56	0	----	---	0.971
2	1.60	50	0.58	31.3	.0184	78.2	0.969
3	1.60	55	0.37	34.4	.0108	70.5	0.970
4	1.25	100	1.22	80.0	.0153	56.5	0.968
5	1.25	80	0.98	64.0	.0153	63.5	0.967
6	1.25	50	9.4	40.0	.2350	--	0.965
POLYPROPYLENE (UNIDENTIFIED)							
1	1.59	50	1.85	31.4	0.059		
2	1.59	100	1.55	62.8	0.025		
3	1.59	100	7.50	62.8	0.119		
4	0.508	100	1.50	196.	0.0077		
5	0.508	50	1.55	98.	0.0158		
6	0.254	95	0.31	374.	0.00083		
POLYETHYLENE (UNIDENTIFIED, HIGH DENSITY)							
1	1.59	43	0.45	27.0	0.0167		
2	1.59	68	0.93	42.8	0.0217		
3	1.59	46	1.02	28.9	0.0353		
4	1.59	66	0.54	41.5	0.0130		

FIGURE CAPTIONS

1. APPARATUS DIAGRAM
2. TEMPERATURE - TIME PROGRAMMING
3. POLYETHYLENE (MARLEX 6050) AFTER CRYSTALLIZATION IN A TEMPERATURE GRADIENT. 20 MICRON SECTION VIEWED BETWEEN CROSSED POLARIZERS
4. POLYPROPYLENE AFTER CRYSTALLIZATION IN A TEMPERATURE GRADIENT. 20 MICRON SECTIONS VIEWED BETWEEN CROSSED POLARIZERS

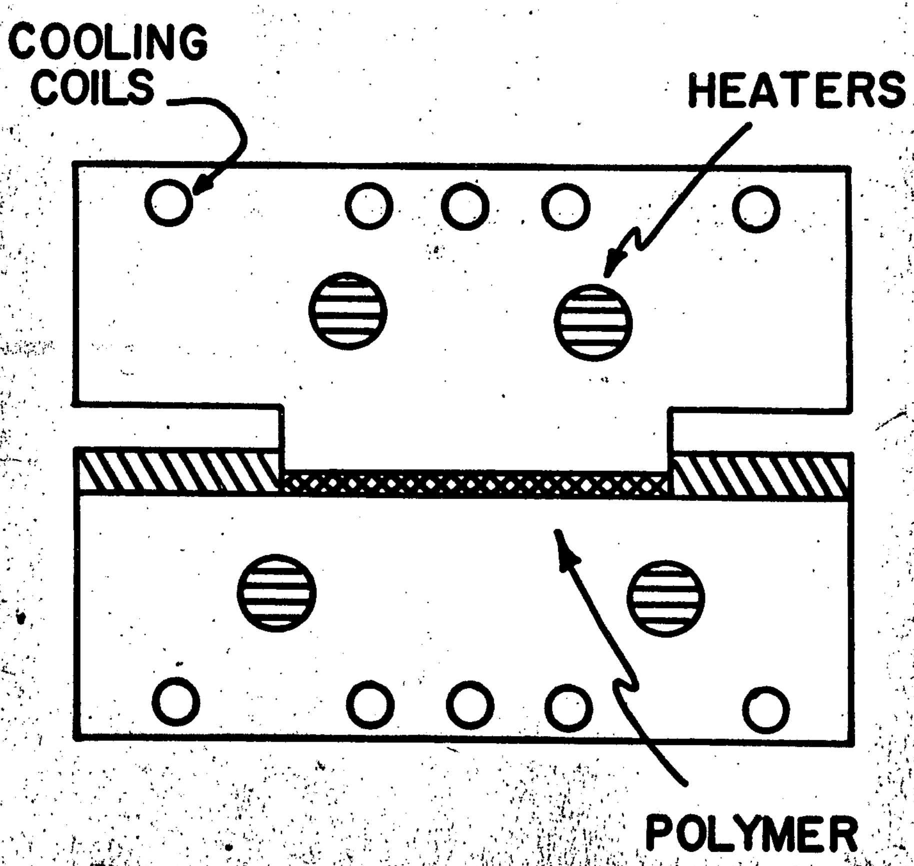

Figure 1

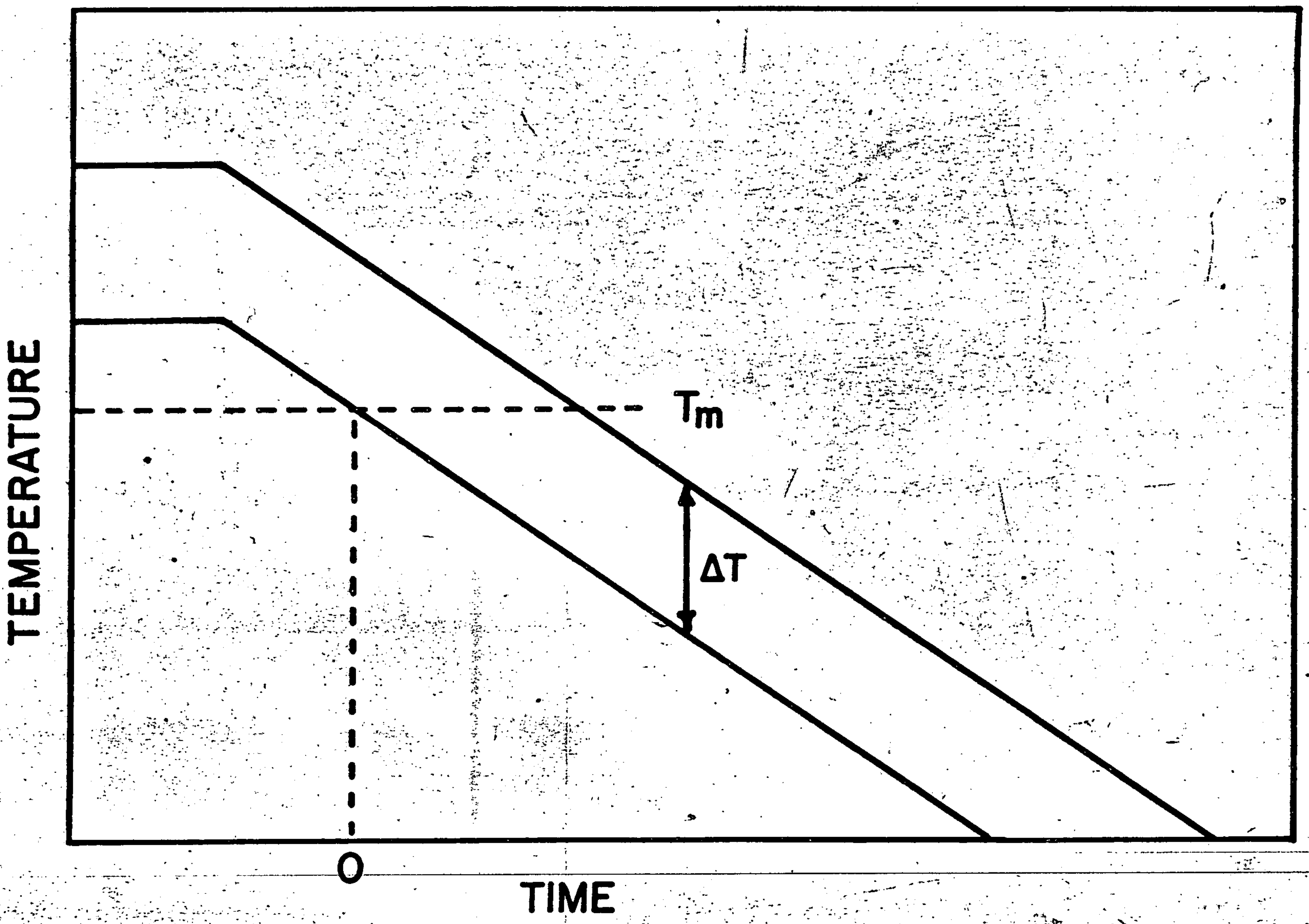

Figure 2

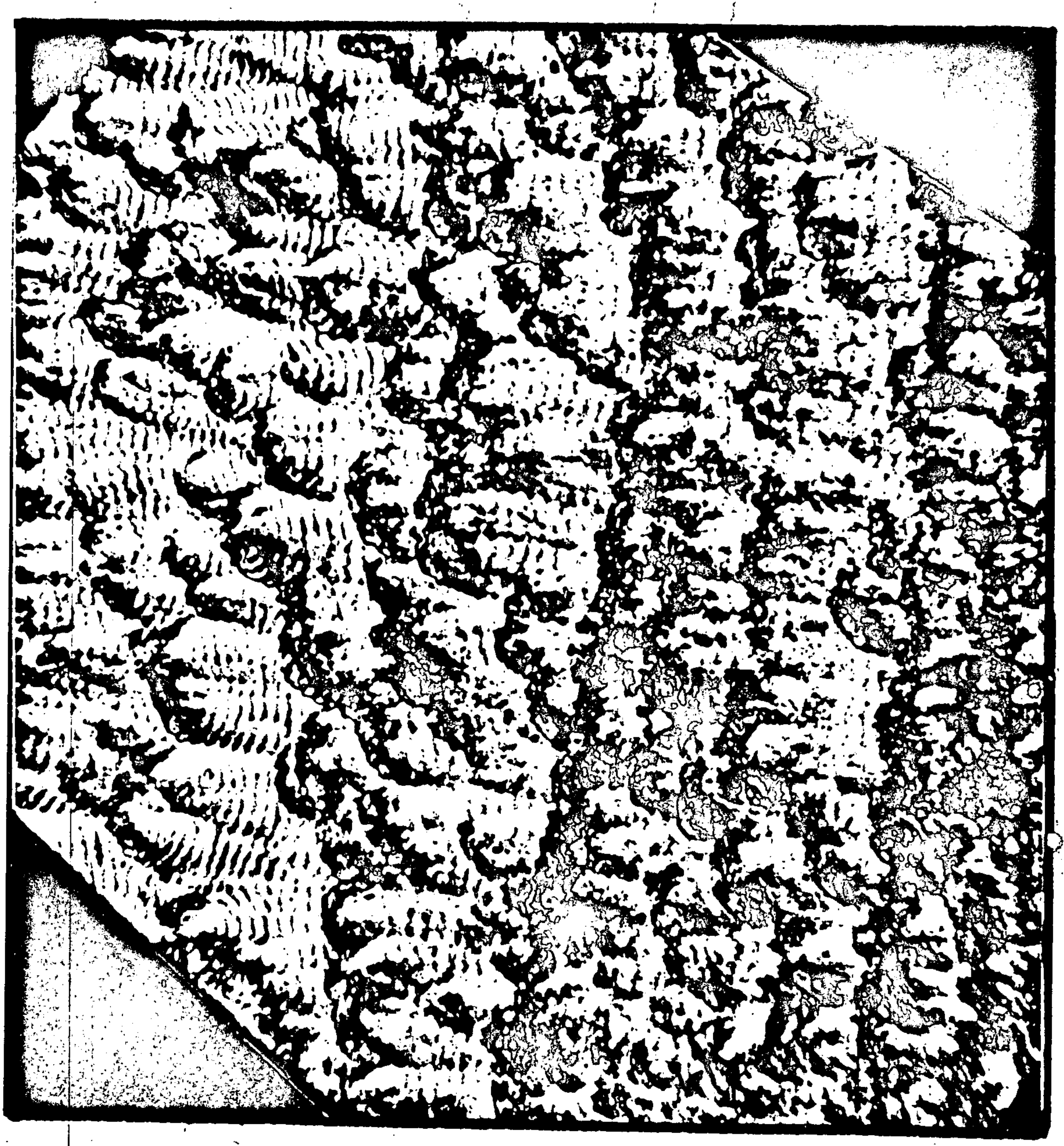

Figure 3

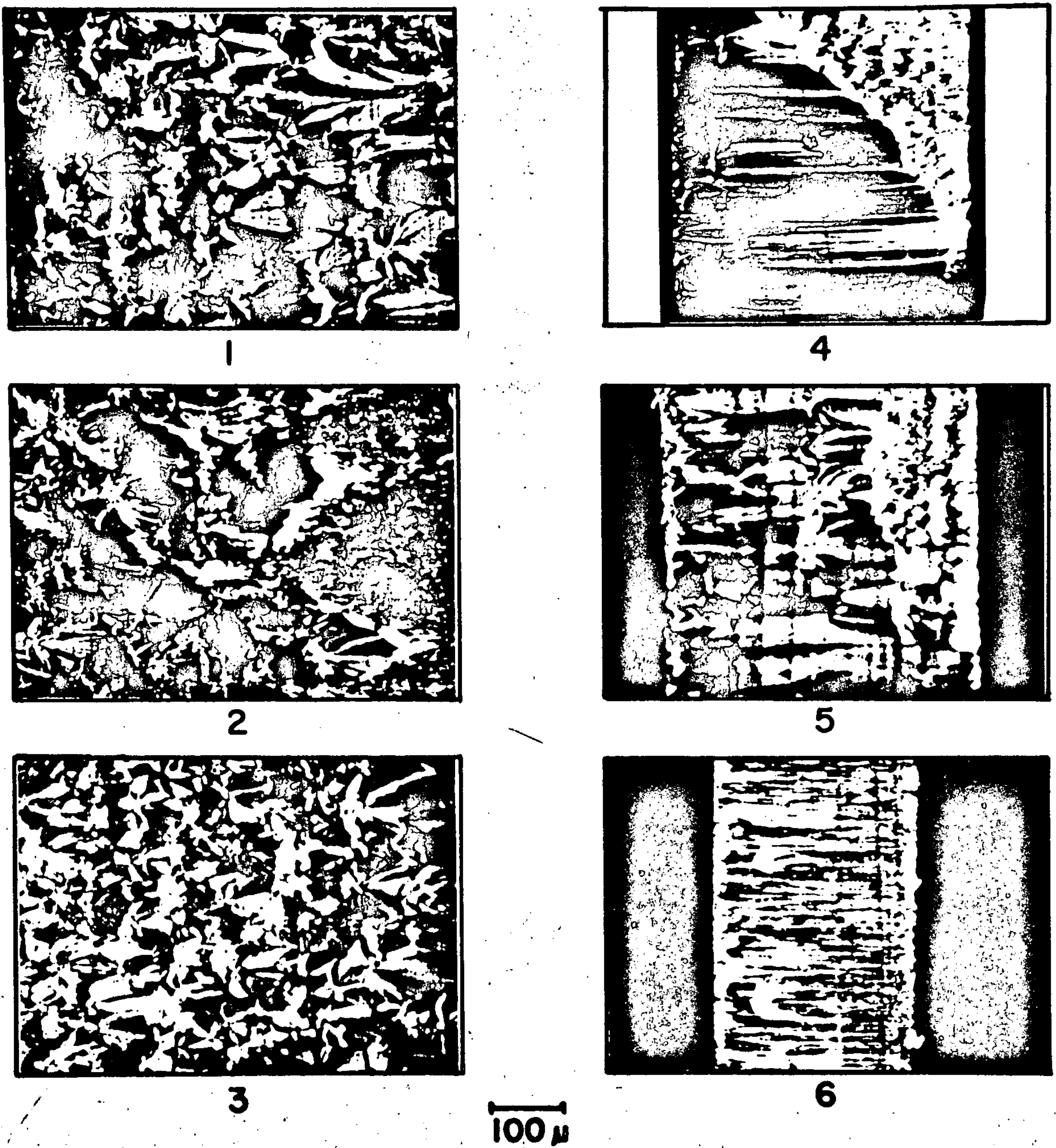

Figure 4