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Electron-microscopic study of grain-size distribution function in splat-cooled aluminium

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The one-dimensional grain-size distribution function in splat-cooled aluminium samples and its dependence on sample storage conditions (temperature and time) were determined by electron microscopy. In contrast to previously published results [1], the theoretical logarithmic normal distribution function gave a very good representation of the experimental data obtained in this work. In addition, some aspects of quenching efficiency and reproducibility of the results for the two-piston splat-cooling device are discussed.

1. Introduction

Numerous papers published to date have dealt with the splat-cooling technique, by which some extensions of the solid solubility limit, and many metastable crystalline and even amorphous phases for various alloy systems have been realized [2]. In this way it has been demonstrated that the quenching rate (which is several orders of magnitude higher during splat-cooling or liquid-quenching than in the course of the solid-quenching) does influence the structure and many related properties of quenched materials.

Thus, the splat-cooling technique is important not only in the technical application of liquid-quenched materials but also in experiments where up to now some fundamental relationships have not been established because of the limited ranges of variables investigated, of course, including the cooling rate itself. A good example was reported in a paper published several years ago in which an excellent correlation between the grain size and the quenching-rate was revealed only after employing the splat-cooling technique [3].

Although the distribution (frequency) function or the probability density (pd) function for variation of grain sizes in different metals and alloys (in one, two and three dimensions) have been examined extensively [1], most experiments were performed on metal samples which have been annealed long enough for grain growth to occur. To the authors' knowledge, no-one has so far examined the influence of rapid quenching on the grain size distribution function.

Hence, the objective of this paper is to report the results of our study on the grain-size distribution function determined in one dimension in splat-cooled aluminium samples. The investigation was performed by means of transmission electron microscopy (TEM). Pure aluminium was chosen since the other properties of this system have been systematically studied earlier [4–7]. The average cooling rate of splat-cooled samples was estimated using the determined frequency function. In addition, the influence of sample storage conditions, i.e. temperature and time, with respect to grain-size stability and grain growth was examined. Furthermore, on the basis of the experimental data obtained, some aspects of the reproducibility and efficiency of the two-piston splat-cooling device will be discussed.

2. Experimental details

The splat-cooling of high purity aluminium (99.997% Al) was performed by using the modified two-piston splat-cooling device [8]. The resulting splats were in the form of approximately circular flakes about 1 to 5 mm diameter and 10 to 20 μm thick. Electron microscope observations, using Philips EM 300 type equipment, were made either on margins of the quenched flakes where areas suitable for investigation (less than 1 μm thick and transparent for 100 keV electrons) were mostly located, or on replicas (consisting of a very thin aluminium oxide layer) which were prepared in the usual way from thicker samples which did not contain regions transparent to electrons. In order

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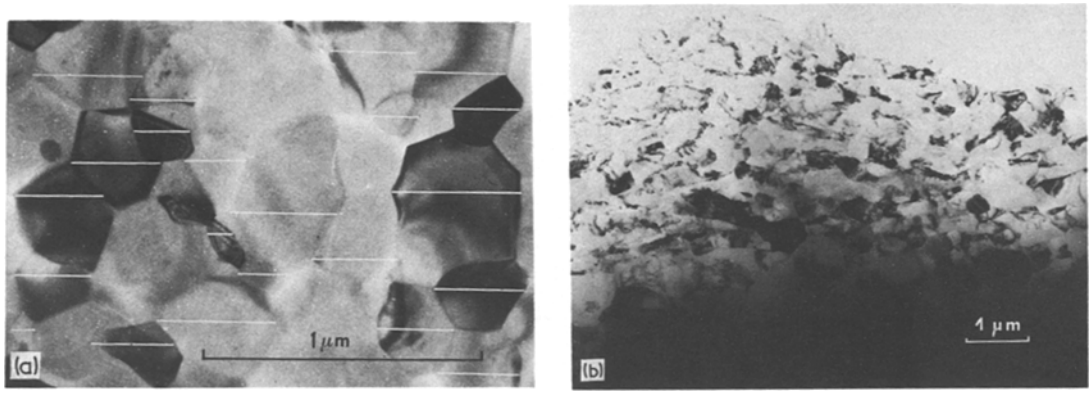

Figure 1 TEM patterns of grain sizes existing in splat-cooled aluminium samples showing: (a) homogeneous grain-size distribution as well as the method of measuring, and (b) the increase in grain-size with thickness of the sample. In (b) lighter parts of the micrograph correspond to the thinner regions near the edge of the sample (small absorption of electrons), while the darker parts correspond to the thicker regions away from the edges (large absorption of electrons).

to obtain reliable data on grain sizes present in the samples, observations were carried out on at least four transparent areas of each sample and from each area about four randomly observed grain structures were photographed. The random sampling of the observed pictures was ensured both by using the specimen rotating holder and the goniometer stage, supplied with the equipment. During observations, the magnification ($\sim \times 80\,000$) was kept constant and allowed the error in the determination of the grain diameters to be less than 0.02 μm. Moreover, in order to reveal the influence of temperature and time on the stability of grain sizes and grain growth in splat-cooled samples, some of them were stored for periods of time either at room temperature or in liquid nitrogen. The experimental grain-size distribution function was constructed for each sample from the grain structure randomly observed and recorded by micrographs. The method consisted of drawing lines across each crystallite observed on a photomicrograph, keeping the rule that lines have to start always at the point of the crystallite situated closer to the left edge of the micrograph, go through each crystallite parallel to the bottom edge of the micrograph, to the next grain boundary (see Fig. 1a). Then the length of lines was measured and data were classified into about ten equal class intervals, covering the whole range of grain sizes. Thus, the grain-size distribution function was formed and in order to ensure the reliability of gathered data, several hundred values for grain sizes were collected.

3. Results and discussion

Although, from the fundamental point of view, the grain-size distribution function in three-dimensions is of the greatest importance, because there is a direct link between this function and various physical properties, unfortunately a direct measurement of that function in three dimensions is not feasible in practice [1], particularly in the case of the splat-cooled samples. Thus, instead, we determined the grain-size frequency function in one dimension for a number of splat-cooled aluminium samples. The results obtained are presented in Tables I to III, and in Figs. 2 and 3. The tables contain data for five representative samples. Since all the samples showed similar behaviour, only samples D and E are shown in Figs. 2 and 3. Each of these samples was produced in different quenching experiments, and the samples did not undergo the same storage conditions. In particular, sample A was examined after being kept for 15 days in liquid nitrogen, sample B was examined immediately after quenching, sample C after being stored 10 days in liquid nitrogen, sample D after 2 months storage at room temperature, and from sample E a replica was made immediately after being quenched and this replica was examined.

Before the analysis of the photomicrographs obtained, it was verified experimentally that neither the grain-size frequency function (derived from about 120 different micrographs), nor statistical parameters computed using them depended significantly on the slope of lines drawn on the

TABLE I The grain-size distribution functions for samples A, B, C and D as determined directly by TEM

Class intervals (μm)	Class midpoints (μm)	Number of observed grains			
		A	B	C	D
0.0–0.1	0.05	5	4	2	8
0.1–0.2	0.15	50	55	36	105
0.2–0.3	0.25	71	72	47	137
0.3–0.4	0.35	55	32	32	99
0.4–0.5	0.45	34	28	27	42
0.5–0.6	0.55	26	13	15	26
0.6–0.7	0.65	20	14	17	2
0.7–0.8	0.75	12	6	8	6
0.8–0.9	0.85	8	2	3	1
0.9–1.0	0.95	4	1	1	2
1.0–1.1	1.05	3	1	3	2
1.1–1.2	1.15	4	0	4	0
Calculated values for:					
the arithmetic mean grain size (μm)		0.39	0.33	0.40	0.30
the coefficient of asymmetry		1.13	1.21	1.21	1.73
the coefficient of skewness		4.02	4.15	4.34	7.09

photographs. Hence, we confirmed that not only was the sampling performed randomly in reality, but also that preferred orientation of crystallite shape did not exist in the sample. Furthermore, it was evident from the data obtained that all the determined grain-size distribution functions were asymmetric and cut off on the small size side, while on the larger size side their variation was considerably slower, vanishing only above about 1.0 μm (see Tables I and III).

Although no-one to date has put forward a model to explain experimentally determined data on grain sizes present in different metals and alloys, several authors have proposed theoretical pd functions, normal or bell-shaped [9], Poisson [5] and logarithmic (log-) normal [1, 10], which might be used as approximate bases for experimental data. In addition, it was stated that experimentally determined one-dimensional grain-size distribution functions deviated from the theoretical log-normal one, and that the latter function can only give a good description of those experimental data which refer to the three-dimensional measurement [1].

Thus, merely on the basis of computed values for statistical parameters such as the coefficient of asymmetry and coefficient of skewness [11] (see Table I and Fig. 2a and c) we were immediately able to reject the possibility that our experimental data belong to the normal pd function. However, in order to decide which of pdf, the Poisson or the log-normal, better describe our experimental data on grain sizes, a more stringent check on fitting data was needed. For that purpose the Chi-square (χ^2-) test has been proposed as a rather good criterion for deciding which hypothesis could be accepted. It is possible to calculate the χ^2- value and on the basis of that value to make statistical decision, at some significance level (say equal or higher than 0.05), about the goodness of fit of a chosen theoretical pdf to the experimental data [11]. Hence, only after applying χ^2-test were we

TABLE II Fitting the Poisson and log-normal pd functions to data belonging to sample E as determined by TEM via the replica method

Class intervals (μm)	Class midpoints (μm)	Number of grains		
		Observed experimentally	Estimated by	
			the Poisson pdf*	the log-normal pdf*†
0.5–1.5	1.0	15	34.0	14.3
1.5–2.5	2.0	97	68.1	88.3
2.5–3.5	3.0	110	91.0	119.3
3.5–4.5	4.0	98	91.2	97.4
4.5–5.5	5.0	47	73.1	62.6
5.5–6.5	6.0	47	48.9	37.1
6.5–7.5	7.0	26	28.0	20.5
7.5–8.5	8.0	17	14.0	11.7
8.5–9.5	9.0	5	6.2	6.5
9.5–10.5	10.0	1	2.5	3.4
10.5–11.5	11.0	0	0.9	2.1
11.5–12.5	12.0	1	0.3	1.2
12.5–13.5	13.0	3	0.1	0.7

Significance level P calculated for:
the log normal pdf $0.10 > P(\chi^2 \geqslant 13.12) > 0.05$.
the Poisson pdf $P(\chi^2 \geqslant 37.53) < 0.001$.

* Using the average grain-size value $\bar{x} = 4.01$ μm and †also the standard deviation $D = 1.99$ μm.

TABLE III Fitting the Poisson and log-normal pd functions to data belonging to sample D as determined directly by TEM

Class intervals (0.1 μm)	Class midpoints (0.1 μm)	Number of grains		
		Observed experimentally	Estimated by	
			the Poisson pdf*	the log-normal pdf*†
0.5–1.5	1	39	62.5	37.4
1.5–2.5	2	140	95.1	140.2
2.5–3.5	3	115	96.3	125.8
3.5–4.5	4	80	73.2	68.4
4.5–5.5	5	32	44.5	32.3
5.5–6.5	6	12	22.5	14.4
6.5–7.5	7	7	9.8	6.5
7.5–8.5	8	3	3.7	2.8
8.5–9.5	9	2	1.3	1.3

Significance level P calculated for:
the log-normal pdf $0.50 > P(\chi^2 \geqslant 3.99) > 0.30$.
the Poisson pdf $P(\chi^2 \geqslant 43.5) < 0.001$.
* Using the average grain-size value $\bar{x} = 3.04 \times 10^{-7}$ m, and †also the standard deviation $D = 1.42 \times 10^{-7}$ m.

able to make an unexpected conclusion, at higher than 0.05 significance level (see Tables II and III for samples E and D, respectively), namely that the log-normal pd function fitted all our experimental data well, while the Poisson pd function fitted only part of the data, i.e. for only two of the five samples. Such a good fit to the log-normal pdf was probably a consequence of the method of preparation of our samples, i.e. the application of the splat-cooling technique. Figs. 2 and 3 also indicate that the log-normal distribution fits the observed data better than the normal or the Poisson distributions.

The fact that the experimentally determined

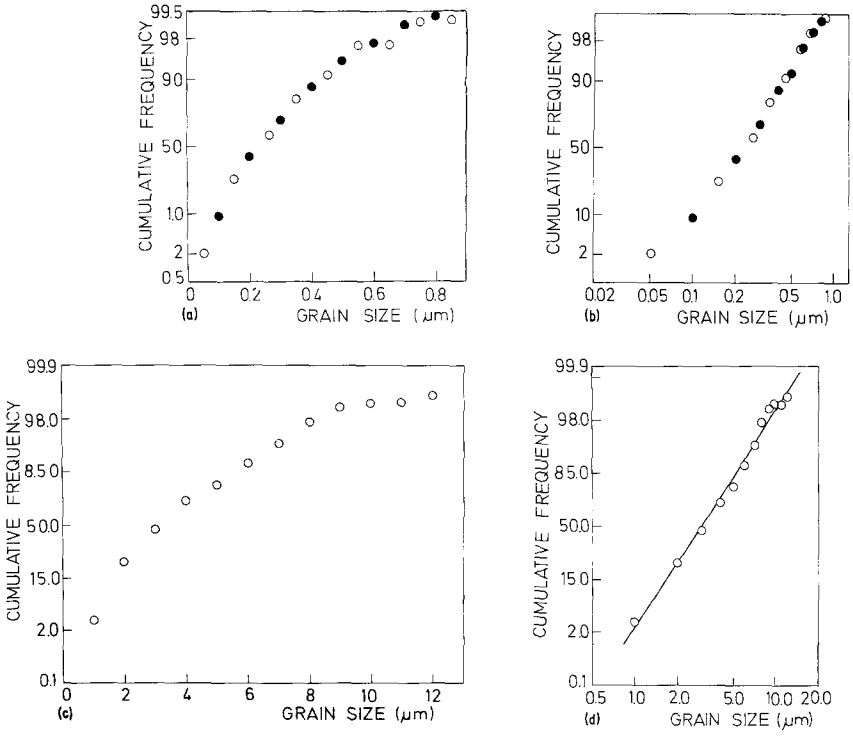

Figure 2 Experimental variation of cumulative grain-size frequency for: (a) and (b) sample D, and (c) and (d) sample E. Data are shown on arithmetic normal (a) and (c) and log-normal (b) and (d) scales. Two sets of data for sample D are shown: from Table I, ○ and Table III, ●. The latter is grouped in such a way as to fulfil the requirement of the grain-size Poisson variable. The line in (d) is drawn using the linear least-squares method.

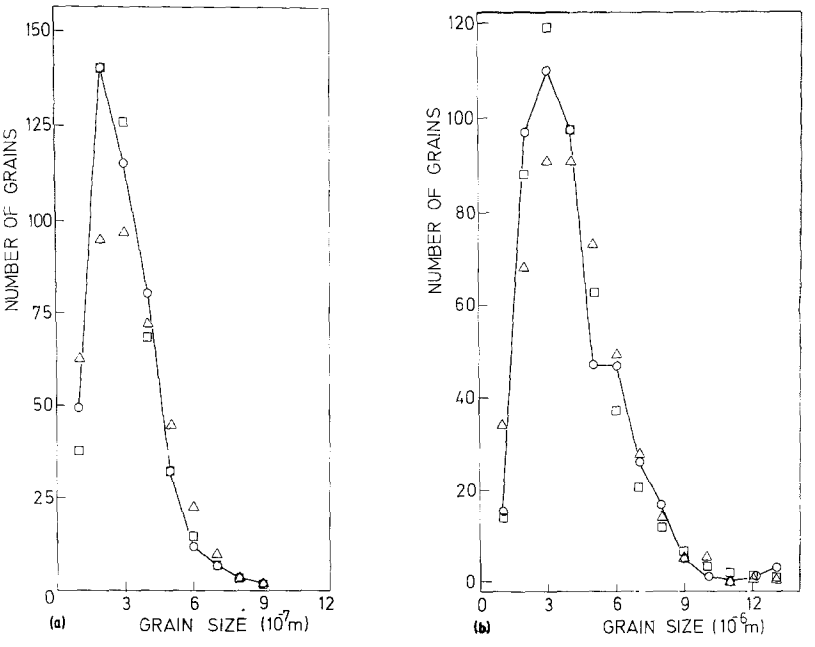

Figure 3 Variation of observed and estimated number of grains for: (a) sample D, and (b) sample E. Experimental points ○, and estimates according to the Poisson (△) and log-normal (□) pd functions.

frequency function exhibited a cut off on the left side, i.e. that grains with diameters smaller than 0.05 μm (for samples appearing in Table I) were not found, was probably caused by the limited maximum quenching rate, while the tail of the curves came from the larger grains existing in the thicker parts of the samples. Grant [3], demonstrated that rapid quenching from the melt is an ideal way of achieving fine grain size, and gave an approximate curve relating the average dendrite and grain size to the cooling rate of aluminium and copper–zirconium alloys. In order to estimate the highest quenching rate which corresponded to the thinnest parts of samples, we used Grant's curve, and the highest rate turned out to be about 10^9 K sec^{-1}. On the basis of the weighted average grain size value $\sim 0.34\,\mu$m, which was computed from Table I, we derived the average quenching rate to be $\sim 10^7$ K sec^{-1}, again using Grant's curve.

Approximate laws for the average quenching rate during splat-cooling were established by Blétry [14], who found that the cooling rate varies as the square of splat thickness. Calculations and experimental observations made by other authors [12, 13, 15–17] confirmed this statement. To substantiate the average quenching rate derived above, we used approximations similar to those proposed by Ruhl [13], and also obtained a value of about 10^7 K sec^{-1}, in good agreement with the previous value.

It is worthwhile to note here that the average grain size in the sample can be determined less accurately by X-ray method [18]. In particular, for splat-cooled aluminium, a similar average grain size of more than 2500 Å has been reported [5]. Any difference might be explained by the different thicknesses of samples examined (10 to 25 μm versus 1 μm).

It is evident from Table I that not only are the grain-size distribution functions, regardless of whether they were obtained on samples investigated immediately after quenching or after prolonged storage at liquid nitrogen or room temperature, similar to each other, but also that the average grain size diameters centre around the same value of about 0.34 μm. Thus, it appears that the quenching conditions for samples investigated here were approximately the same. Furthermore, as far as the grain sizes are concerned, the samples were stable both at liquid nitrogen or room temperature for prolonged periods of time (at least up to 2 months), or in other words observable grain growth was not detected in this work.

The determined grain-size frequency function obtained from investigation by the replica method also exhibited the log-normal behaviour. However, the observed grain sizes were about one order of

magnitude larger than in those samples observed directly through the microscope. Possible explanations for this effect may be either that the larger thickness of the samples reduced the cooling rate and caused larger grain sizes, or the preparation procedure used for the replica production affected the observed grain sizes, or both effects were present.

Finally, accepting that the higher cooling rate belongs to the thinner parts of sample, we also claim that the thickness of the sample has a dominant role on the quenching rate regardless of the fact that the heat transfer is in that case in one direction only [13]. This stems from the observed fact that the grain sizes show a tendency to increase starting from the sample edges (thinner parts) to its middle (thicker parts) as seen in a number of micrographs obtained in this work (see Fig. 1b).

4. Conclusions

In the scope of the results described so far, the following conclusions may be drawn:

(1) despite the fact that in the splat-cooled aluminium samples inhomogeneous grain structure existed essentially over the whole sample, as was seen by electron microscopy, it was possible to find regions having homogeneous grain structure which were located mainly on the margins of samples and was suitable for electron microscope observations;

(2) the inhomogeneous grain structure in splat-cooled aluminium samples is governed mainly by the non-uniform cooling rate caused by the variation of thickness of different parts of samples;

(3) investigation of the grain-size distribution function in one dimension which existed in transparent parts (less than 1 μm in thickness for 100 keV electrons) of splat-cooled samples did not show a texture, but did reveal the log-normal behaviour, and that behaviour might be ascribed to the method of sample preparation, i.e. to the application of the splat-cooling technique;

(4) on the basis of experimentally derived grain-size frequency functions it was possible to compute the average grain size value and to reach, with the help of the Grant's curve, the average cooling rate, estimated to be about 10^7 K sec^{-1}, in agreement with those derived from the thickness of samples and the time of cooling [13];

(5) a one order of magnitude higher value obtained from grain sizes observed by the replica method in comparison to those investigated directly through the microscope might be caused either by different thicknesses of samples investigated or the method of replica preparation, or both;

(6) since the similar shape of the determined grain-size distribution curves were observed and roughly the same mean value for grain sizes existing in different samples was computed, one may conclude that the splat-cooled aluminium samples are stable in respect to grain structure at room temperature for prolonged periods of time. For the same reasons the two-piston splat-cooling device has rather good reproducibility and efficiency.

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