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Morphological relaxation of glass surfaces

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A model for calculating the morphological relaxation of two-dimensional glass profiles for arbitrary temperature–time schedules is described. The model is based on a Fourier expansion of the surface profile for which the decay with time can easily be calculated for each of the separate terms. The effect of the variable temperature with time was accounted for by discretization of the temperature–time profile. Necessary input data are the viscosity and surface tension of the glass. The sensitivity to various geometrical details is limited, but heating/cooling effects appeared to be important. The predictions of the model are verified by measurements on glass samples with various profiles and relaxed according to a certain temperature–time schedule. Using a surface tension value of 0.19 N m^{-1}, as determined with recent fibre-on-plate experiments, excellent agreement between theory and experiment was obtained. Possible options for extension to three-dimensional profiles are indicated.

1. Introduction

At present, the morphology of glass surfaces is frequently produced in the pressing stage. During the pressing process a portion of glass is pressed in a mould by a die. This die has a certain surface morphology which is supposed to be transferred, wholly or partially, to the glass surface. During pressing, the surface temperature of the glass decreases considerably. After retreat of the die, due to the large volume of glass pressed, the surface temperature of the glass generally increases again. The final morphology is thus determined by, first, the amount of transfer from the die to the glass and, second, the subsequent relaxation of the glass surface.

The present work deals with the second aspect, the relaxation. For the time being, the modelling is two-dimensional.

2. Theory

The basic idea was to use an expansion of the surface profile in orthogonal functions. If the deformation behaviour can be modelled for such a function, the whole surface morphology can also be modelled. In fact, a similar idea was used by Frenkel [1] for the viscous deformation of a near-spherical shape towards a sphere. In his case, the near-spherical shape was expanded in spherical harmonics. For a single term in the series, he was able to formulate a solution based on his considerations for viscous flow, presented earlier in his paper. Adding the various terms yielded the deformation behaviour for the near spherical shape.

In our case, the surface morphology is expanded in a Fourier series. Thanks to previous work on the relaxation of viscously deforming shapes, the solution for a single Fourier term rapidly became clear. If we take the cosine for a single term, the relaxation of the cosine $f(x, 0) = \cos\omega x$ is given by [2]

$$f(x, \tau) = e^{-\omega\tau/2}\cos\omega x \tag{1}$$

where

$$\tau = t/t_c, \tag{2}$$

with $t_c = \eta D_c/\gamma$, and

$$\omega = 2\pi/\lambda, \tag{3}$$

with $\lambda = \lambda_0/D_c$. The parameters t, γ, η, D_c and λ_0 denote the time, surface tension, viscosity, characteristic size and wavelength of the cosine, respectively. Substitution gives

$$f(x, t) = e^{-\pi\gamma t/\eta\lambda_0}\cos\omega x \tag{4}$$

An identical result was also given by Hopper [3, 4]. It should be noted that, apart from the assumption that curvature gradients are small, which always applies in the present cases, no approximations are made

The surface morphology is usually measured with a stylus instrument which measures the height of a surface along a line as a function of position. Normally profiles measured in this way are characterized by one or more roughness parameters, such as $R_a = N^{-1}\sum|y_i|$, $R_q = N^{-1}\sum y_i^2$, etc., where the set of y_i values represents the height of the profile as measured with respect to the centre-line average. Here we make use of the complete profile. For the discrete set of height data, the Fourier transform is calculated using the Fast Fourier Transform (FFT) algorithm [5] and cyclic boundary conditions. Each term relaxes with the exponential expression given above for a certain time. After that, the relaxed Fourier terms are synthesized to the relaxed profile. This profile represents the deformed surface after the given temperature–time treatment.

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The procedure is thus as follows.

(i) Fourier analysis. The profile at time $t = 0$, $f(x, 0)$, is analysed in Fourier terms which results in

$$f(x, 0) = \sum_i A_i\,(\cos\omega_i x + j\sin\omega_i x)\ \ (j = -1^{1/2}) \tag{5}$$

(ii) Relaxation. This is done for each coefficient

$$A_i \rightarrow A_i' = A_i \exp(-\omega_i \tau_i/2) \tag{6}$$

(iii) Fourier synthesis. The profile at time $t = t, f(x, t)$, is synthesized according to

$$f(x, t) = \sum_i A_i'(\cos\omega_i x + j\sin\omega_i x) \tag{7}$$

The considerations given above pertains to an isothermal situation only. Because both the viscosity, η, and surface tension, γ, are temperature-dependent, a numerical discretization scheme for the temperature–time profile was introduced using Romberg integration [5]. Instead of calculating the relaxation for each term for the whole time interval, the complete temperature dependence of the physical parameters is taken into account. The time steps are optimized within this integration procedure. This makes it possible to deal with varying temperature as a function of time in a numerically accurate and efficient way.

The above-mentioned procedure was programmed in Pascal for use on a PC. The program contains various options, apart from the relaxation calculation. The software developed can be used:

(1) to process roughness data. A polynomial base line correction of the raw data can be applied. The profile can be characterized by means of the conventionally used roughness parameters. These include R_a, R_q, R_z, R_p, R_m, R_y and R_{max} [6]. The height, the slope and the curvature distributions, the (auto-) correlation function and the spectral density (power spectrum) can also be calculated. A maximum number of 4096 sample points can be used at present;

(2) to calculate relaxed profiles using any temperature–time schedule. The viscosity and surface tension can be entered as temperature-dependent data via the VFT parameters for the viscosity (see Section 5) and a linear dependency for the surface tension, respectively;

(3) to show an animation of the relaxation process, and

(4) to calculate and plot the roughness parameters as a function of the relaxation time.

3. Roughness assessment

With respect to the roughness parameters, a few remarks should be made. First, the stylus apparatus itself and the associated software normally apply a filtering, often with an RC-filter. Moreover, the zero level is determined by least-squares fitting all data to a linear curve before filtering. Roughness parameters can be reduced by as much as 25% by this filtering. An example of such roughness data is given in Table I. In fact, the roughness profile as shown in Fig. 11 (see later) was used here. Second, apart from this effect, this filtering should be avoided in our case, because it "deforms" the original profile. In particular, the long-wavelength components are modified. We only apply a base line correction for taking into account the global geometrical shape by subtracting a polynomial baseline determined with the least-squares technique on the whole profile. A parabola as base line suffices in most cases.

TABLE I Changes in roughness parameters upon filtering

Parameter	2-RC[a]	P-1[b]	P-2[c]
R_q	0.18	0.21	0.22
R_{max}	0.99	1.13	1.22

[a] NEN 3635 ISO 3274 phase corrected filter, cut-off 800 μm, step 2 μm, 6400 μm scan length, 4000 μm analysis length (6400 − 2 × 1.5 × 800 μm).

[b] Parabola baseline correction using the same analysis length (4000 μm)

[c] Parabola baseline correction using the full scan length (6400 μm).

4. Experimental procedure

In order to validate the relaxation scheme experimentally, a glass sample with various two-dimensional profiles was produced. Two-dimensional in this connection indicates, within an x–y–z axis system, a profile given by $y = y(x)$. Hence any cross-section parallel to the x–y plane should yield the same profile. A modified Na-K-Ba-Sr-silica glass, as described before [7], was used.

The glass was profiled by wet chemical etching. The aim of the etching procedure was to form two-dimensional profiles that can be described as ridges and valleys of varying width and a height (or depth) of about 0.5 μm. Originally, the etching procedure was as follows [8]:

(i) chemo-mechanical polishing using Syton® (Monsanto Technical Centre, Louvain-la-Neuve, Belgium) and cleaning;

(ii) sputtering a chromium layer with a thickness of about 0.5 μm;

(iii) patterning the sample with a positive photoresist lacquer [9] (HPR 204);

(iv) etching the uncovered chromium layer with an aqueous solution of $(NH_4)_2$ Ce $(NO_3)_6$ at 45 °C;

(v) etching of the glass with a 2% HF solution for 5 min;

(vi) removal of the photoresist lacquer with acetone;

(vii) removal of the remainder of the chromium layer with a solution of $CeNH_4(NO_3)_4$.

This procedure, however, yielded ridges with accompanying cracks at both sides of the ridge, especially in the case of wider ridges. These cracks are probably related to the stresses at the edge of the chromium mask. The procedure was therefore modified. After cleaning the glass, an annealing treatment was given as described in Table II ($x = 0$). The coating of the glass with chromium and all associated steps were omitted. This procedure would normally result in delamination of the lacquer, but because the etching time of the glass could be as low as 5 min, and an

TABLE II Temperature–time schedule for relaxation experiments

Ramp (°C h^{-1})	Level (°C)	Dwell (min)	Remarks
350	650	x[a]	Relaxation
1000	510	480	Annealing
12	475	0	Annealing
350	20	End	Annealing

[a] The value of x for the various experiments is indicated in the main text.

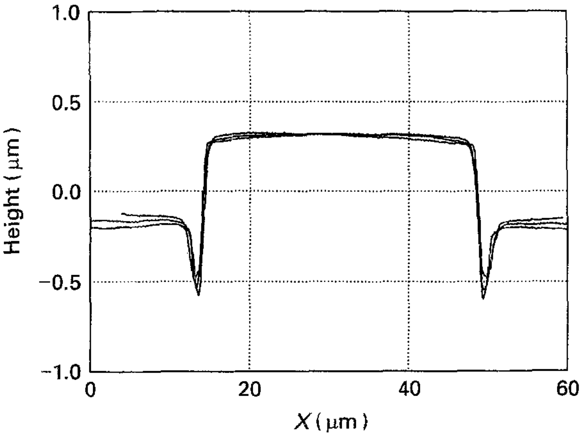

Figure 1 Profile as scanned in the forward and reverse direction at the same position. The profile shown is an early as-etched one still showing the cracks besides the ridge. Nevertheless, almost identical profiles are obtained.

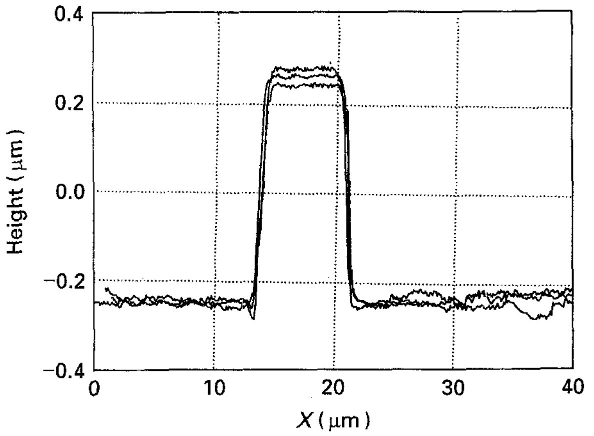

Figure 2 Profile as scanned at various positions. The profile shown is taken directly after the proper etching procedure.

adherence layer of A174 (2% trimethoxy-silyl-propyl-methacrylate in a 1:1 alcohol/water mixture) was spun on before patterning, the lacquer did not delaminate during this etching procedure. In this way, well-defined ridges and valleys could be made.

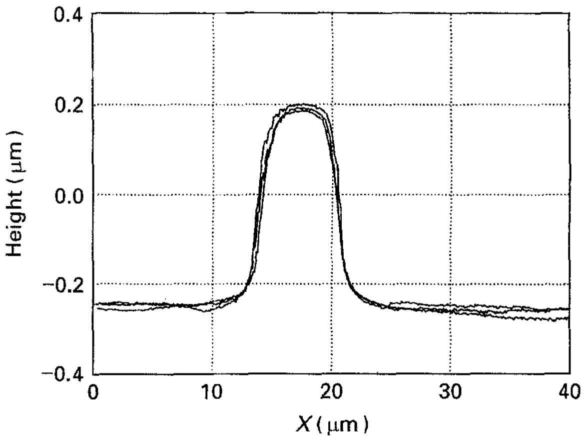

Figure 3 Profile as scanned at various positions. The profile shown is after a preliminary temperature treatment as given in Table II with $x = 0$ min.

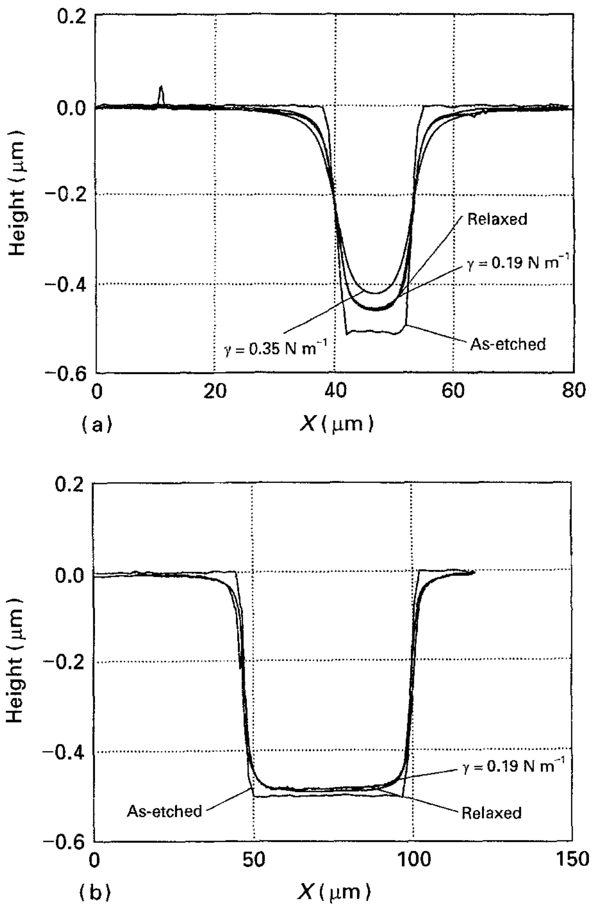

Figure 4 As-etched and relaxed (calculated and experimental) profile for (a) a 10 μm wide and (b) 50 μm wide valley. The temperature–time schedule is indicated in Table II with $x = 0$ min. The calculated profiles using $\gamma = 0.19$ and 0.35 N m^{-1} are indicated in the upper graph.

The profiles were characterized by stylus measurements (Taylor Hobson Talystep, stylus radius 1.0 μm, apex angle 90°, step size 0.1 or 1.0 μm, scan length 6400 steps) across the profiles. The influence of the scanning direction was assessed by reversing the direction. This yielded nearly identical profiles (Fig. 1). The variability of the width of a profile along the length was also examined. A scan was made at the middle and both ends of a narrow ridge after etching (Fig. 2) and after preliminary heat treatment (Fig. 3). This yielded almost identical profiles. For relaxation experiments the samples with ridges and valleys were relaxed several times. After each thermal treatment (the temperature–time schedule used is given in Table II) the samples were characterized by stylus measurements (Figs 4–7). The temperature of the sample during relaxation was recorded using

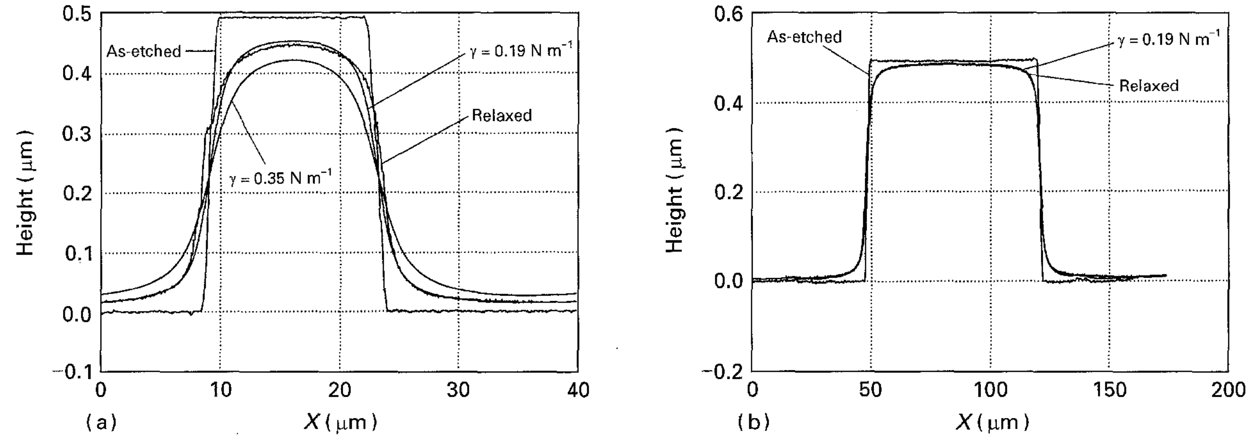

Figure 5 As-etched and relaxed (calculated and experimental) profile for (a) a 15 μm wide and (b) 75 μm wide ridge. The temperature–time schedule is indicated in Table II with $x = 0$ min. The calculated profiles using $\gamma = 0.19$ and $0.35\ \mathrm{N\,m^{-1}}$ are indicated in (a).

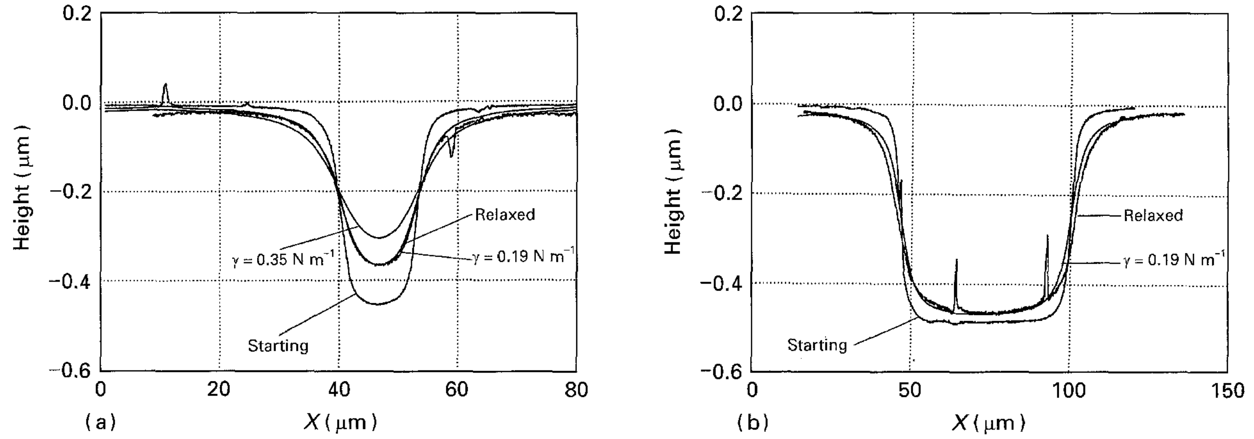

Figure 6 As-etched and relaxed (calculated and experimental) profile for (a) a 10 μm wide and (b) 50 μm wide valley. The temperature–time schedule is indicated in Table II with $x = 5$ min. In (a) the calculated profiles using $\gamma = 0.19$ and $0.35\ \mathrm{N\,m^{-1}}$ are indicated.

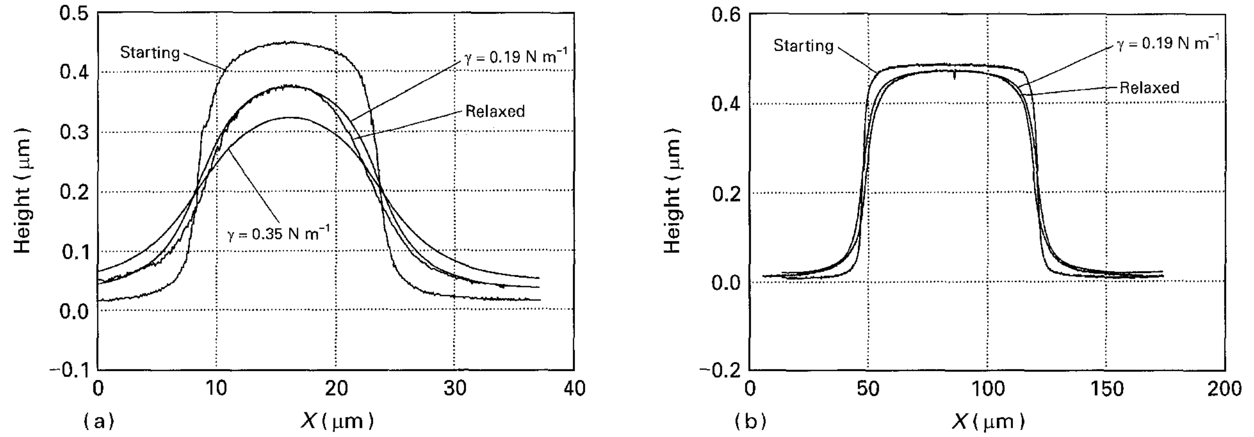

Figure 7 As-etched and relaxed (calculated and experimental) profile for (a) a 15 μm wide and (b) 75 μm wide ridge. The temperature–time schedule is indicated in Table II with $x = 5$ min. The calculated profiles using $\gamma = 0.19$ and $0.35\ \mathrm{N\,m^{-1}}$ are indicated in (a).

a Pt/Pt–10% Rh thermocouple, positioned just below the ridged surface, in the same way as described previously [7]. We would again like to stress the importance of reliable temperature measurement, as discussed before, for this type of experiment.

5. Results

Taking the measured as-etched profile as the input structure, the relaxed profile was calculated according to the scheme described in Section 2. The viscosity, η, of the glass used can be described over a wide temperature range by the Vogel–Fulcher–Tammann (VFT) equation [10]

$$\log \eta(T) = a + b/(T + c) \tag{8}$$

with the parameters $a = -1.582$, $b = 4548$ and $c = -197.3$ and η given in dPas and the temperature, T, in °C. More details on the viscosity behaviour can be found elsewhere [7]. The surface tension was taken constant at the value of 0.19 N m^{-1}, as determined by fibre-on-plate experiments [7]. The as-recorded temperature–time data were taken into account for calculations. The number of Fourier terms was 512, unless otherwise indicated. This number generally proved to be sufficient for an accurate representation.

Figs 4 and 5 show the as-etched profiles of two valleys and ridges, respectively, and the corresponding relaxed profiles (calculated and experimentally determined) obtained after preliminary thermal treatment (see Table II, $t = 0$ min). The relaxed as-measured profiles of the same valleys and ridges as in Figs 4 and 5, and the corresponding relaxed profiles (calculated and experimentally determined) obtained after main thermal treatment (see Table II, $t = 5$ min) are presented in Figs 6 and 7. It should be recalled that a value of 0.19 N m^{-1} for the surface tension was determined from fibre-on-plate experiments at 650 °C, while extrapolation from high-temperature sessile drop data [7] resulted in a value of 0.35 N m^{-1}. For convenience in assessing the agreement between experiment and model, the relaxed profiles using $\gamma = 0.35$ N m^{-1} are given in a number of cases.

From Figs 4–7 it can be concluded that a good agreement between theoretical and experimental profiles is obtained. Moreover, it is clear that the γ-value of 0.19 N m^{-1}, as obtained from the fibre-on-plate experiments, yields an accurate prediction, contrary to the value of 0.35 N m^{-1} extrapolated from high-temperature data.

6. Sensitivity analysis

In this section the influence of some aspects upon the relaxation of a profile is discussed. The viscosity and surface tension data, as given in Section 5, corresponding to the modified Na-K-Ba-Sr-silica glass, are used for all calculations in this section.

The first point studied was the influence of the heating and cooling period upon the relaxation. In Fig. 8a the profile calculated for constant heating at 650 °C for 300 s is shown as compared with the result calculated for the same level and time, but with a heating and cooling rate of 0.1 °C s^{-1} included. This figure clearly shows the importance of the incorporation of the heating and cooling period in the simulation.

In order to assess the influence of scan length versus ridge width, the relaxation of various types of profiles was simulated. Indicating the relative length of the flat part before the ridge, the width of the ridge itself and the length of the flat part after the ridge by (a–b–c), the following profiles were taken: (1–10–1), (1–1–1), (10–1–10), (100–1–100) and (1–1–2). The relaxation of each profile was calculated for constant heating at 650 °C for 300 s. The results for the simulations are indicated in Fig. 8b, from which it becomes clear that as soon as the sequence (1–1–1) is reached the differences in the relaxed profile become insignificant. The effect of an asymmetric position of the ridge is also negligible. This indicates that the results are practically independent of the scanned length in spite of the assumption of cyclic boundary conditions.

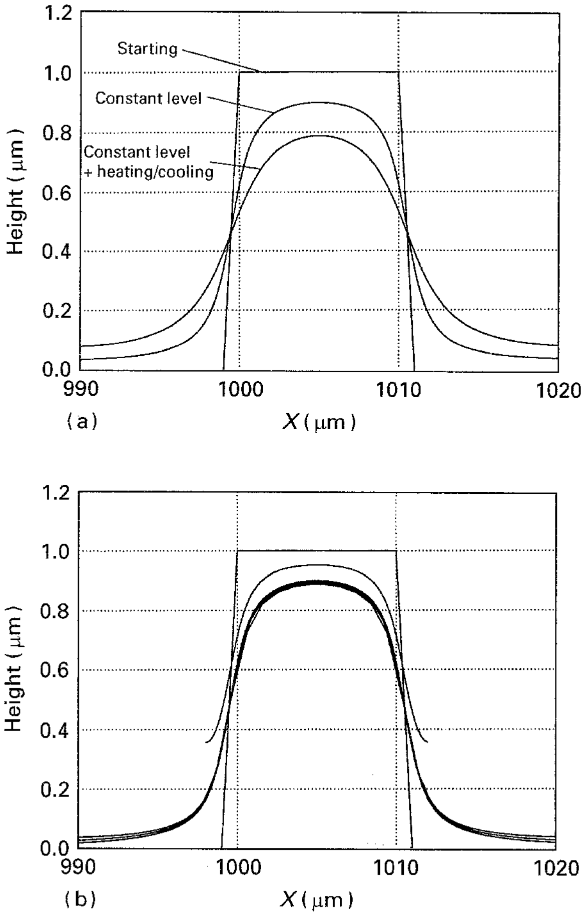

Figure 8(a) Simulation showing the effect of heating and cooling at a rate of 0.1 °C s^{-1} for constant heating at 650 °C for 300 s (upper curve). The importance of incorporating the heating and cooling part of the temperature–time schedule (lower curve) is clearly shown. (b) Relaxation of profiles with characteristics (1–10–1), (1–1–1), (10–1–10) and (100–1–100) for 300 s at 650 °C. For the latter, 2048 Fourier terms were taken. For an explanation of the code, see the main text. Also shown is a profile with characteristic (1–1–2). Only the ridge itself and its direct surroundings are shown. Apart from the profile (1–10–1), all other profiles are almost identical.

A third effect that could be worrying is the height of the baseline as a function of geometry and time/temperature. This height is important for the positioning of the calculated and experimental relaxed profiles. In Fig. 9 the increase in height of the baseline level is indicated for a typical profile. From this figure it is clear that taking a "flat" part length of about twice the ridge width results in a sufficiently well-defined baseline level.

In order to show the sensitivity of the relaxation factor $\alpha = \exp(-\pi\gamma t/\eta\lambda_0)$ (see section 2) for various time and temperature regimes, a relaxation–temperature–time (RTt) map for a sine profile with $\lambda_0 = 10$ µm was plotted (Fig. 10). This map shows the behaviour of the parameter α as a function of time and temperature for the viscosity and surface tension data as given in Section 5. Similar maps can be produced for other wavelengths, viscosity and surface tension data. Equivalent time–temperature points can be easily spotted in this map, giving a first impression of the effect of time–temperature during relaxation which can be useful in a factory environment.

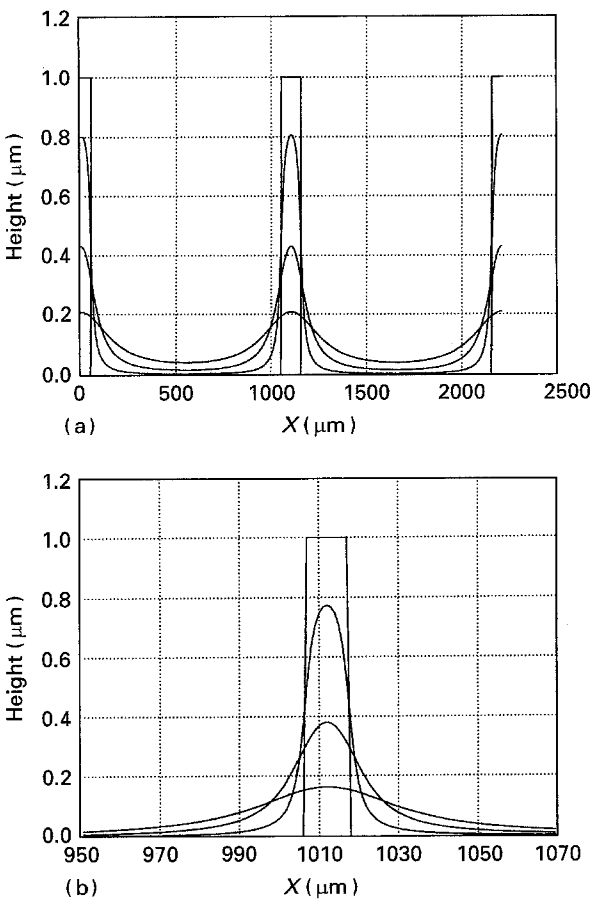

Figure 9 Effect of baseline level. (a) Simulation of profile with characteristic (1000–100–1000) for 5×10^3, 10^4 and 5×10^4 s at 650 °C. (b) Simulation of profile with characteristic (1000–10–1000) for 635, 2500 and 6500 s at 650 °C. Only the ridge itself and its direct surroundings are shown. For both simulations, 2048 Fourier terms were taken.

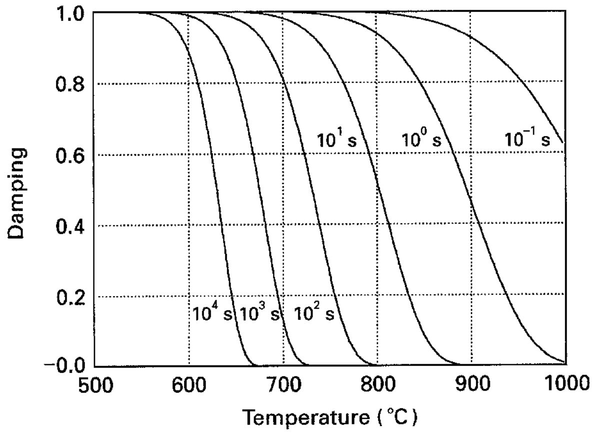

Figure 10 *RTt* map for a sine profile with $\lambda_0 = 10$ μm. The iso-time lines for $t = 10^{-1}$, 10^0, 10^1, 10^2, 10^3 and 10^4 s are indicated in the map.

The results of this section clearly show the insensitivity of the calculated profile to scan length versus ridge width details, as long as the size of the flat part before and after the ridge is at least about the same as that of the ridge itself. On the other hand, the effect of heating and cooling is significant and cannot be neglected in simulations for realistic time–temperature schedules.

7. Discussion

The calculation of the relaxation of a statistical profile is performed in the same way as for ridges and valleys. The profile presented in Fig. 11, the roughness of a die, was taken as an example for a statistical profile. It was assumed that this profile was fully transferred to the glass. The same data for glass as used before were taken for calculating the relaxation. Fig. 11 shows the relaxation of the roughness profile at 700 °C for 3000 s. The time dependence of some roughness parameters for the given temperature–time schedule are also presented (Fig. 12). This relaxation clearly shows the rapid decay of sharp features and the slower decay of long-wavelength features. It should be recalled that this relaxation is not the real relaxation of a three-dimensional glass profile because the profile is assumed to be two-dimensional. In reality, features will disappear faster than shown here for the same temperature–time schedule.

The extension of the relaxation procedure of two- to three-dimensional surfaces is possible along two, basically different, lines. The first line requires two actions: a calculation of the three-dimensional analogy of the cosine wave (normalization factors, etc.) and the modification of the Fourier analysis and synthesis to three dimensions. This can be done without any fundamental complications, but involves some effort. An experimental check is then made by mapping a rough surface and comparing the results of the calculation with those obtained for the relaxed, experimental surface. Two practical problems exist, however. A surface can easily be mapped in a research environment, but this may prove difficult elsewhere. A more important point is that exactly the same location has to be measured after relaxation. This requires labelling. Finally, it should be mentioned that, in general, we are not interested in the development of a certain profile but in the development of certain of its characteristics.

The second line therefore, considers only some statistical characteristics of the profile. Because, in the case of an isotropic surface, a roughness track contains an unbiased estimate of all the height alterations, it is possible to calculate the correlation function and the spectral density. As the decay of all wavelengths is known, the evolution of the spectral density with time can be calculated in principle.

8. Conclusions

The calculation of the relaxation of two-dimensional profiles can be done reliably with the software developed, once data on surface tension and viscosity are available. The sensitivity to various geometrical details is limited, but heating/cooling effects have to be taken into account. This opens up the possibility of assessing the influence of relaxation accompanying a certain temperature–time schedule without relaxation experiments. This is important for all kinds of morphology relaxation of surfaces, e.g. in flame polishing as well as pressed glass surfaces.

The low value of the surface tension for this glass as presented before yields an accurate prediction of the

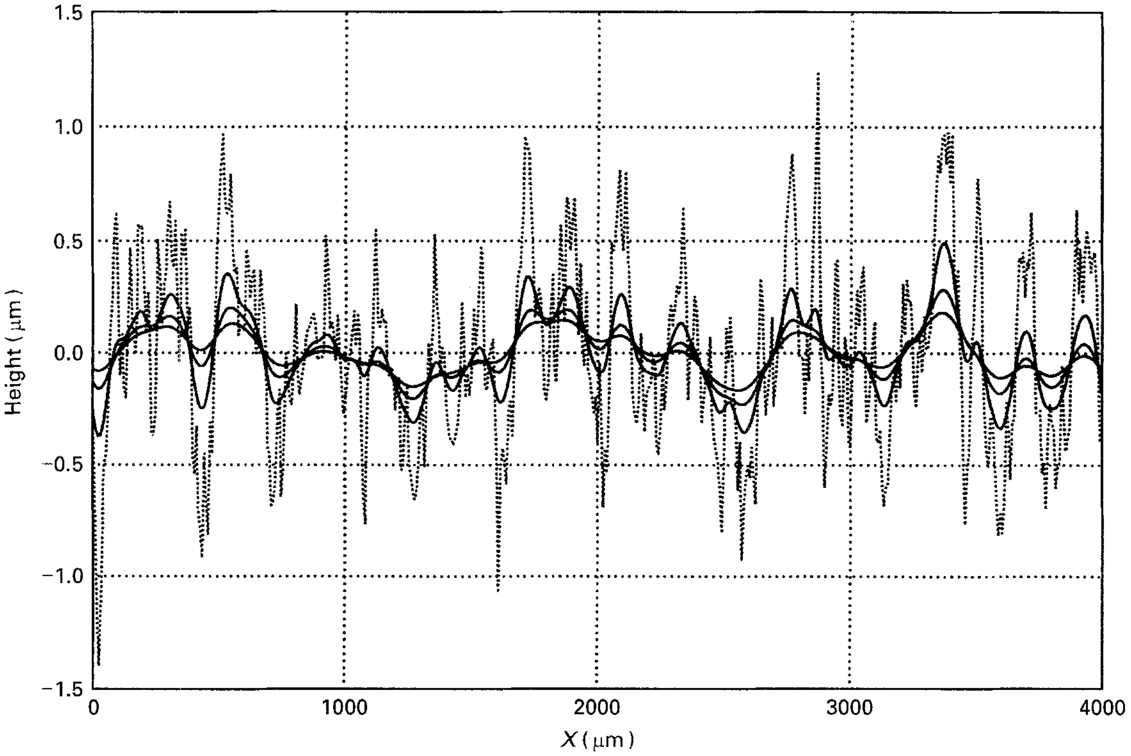

Figure 11 The development of a statistical profile, treated as two-dimensional. The figure shows the original profile (upper curve) and various profiles after relaxation at a constant temperature of 700 °C for 1000, 2000 and 3000 s (lower curves).

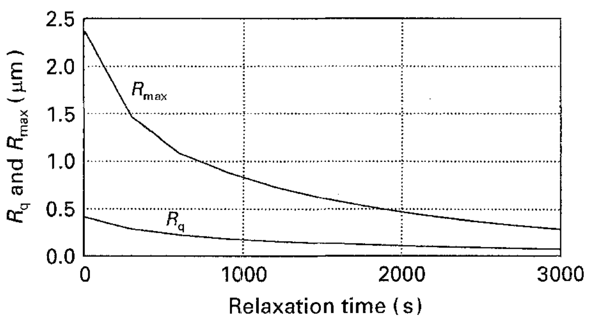

Figure 12 The development of R_q and R_{max} as a function of time for the situation as shown in Fig. 11. Real three-dimensional relaxation would be faster than shown here.

relaxed profiles. Extrapolation from high-temperature sessile drop data is thus not warranted.

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References

1. J. FRENKEL, *J. Phys. (Moscow) USSR* **9** (1945) 385.
2. H. K. KUIKEN, *J. Fluid Mech.* **214** (1990) 503.
3. R. W. HOPPER, *ibid.* **213** (1990) 349.
4. *idem, ibid.* **230** (1991) 355.
5. W. H. PRESS, B. P. FLANNERY, S. A. TEUKOLSKY and W. A. VETTERLING, "Numerical recipes in Pascal" (Cambridge University Press, Cambridge, 1990).
6. T. R. THOMAS (ed.), "Rough surfaces" (Longman, London, 1982).
7. G. de WITH and A. J. CORBIJN, *J. Mater. Sci.*, in press.
8. G. A. C. M. SPIERINGS and J. VAN DIJK, *ibid.* **22** (1987) 1869.
9. M. T. GOOSEY (ed.). "Plastics for electronics" (Elsevier, London, 1985).
10. H. SCHOLZE, "Glas: Natur, Struktur und Eigenschaften", 2nd Edn (Springer, Berlin, 1977).

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