

(1) *Building the master curve.* These authors adopt the same procedure as we in building the master yield stress curve but, to justify the vertical shifts used to generate this master curve, they invoke the existence of a recovery stress borne at yield by an elastic element. Therefore, from their point of view, this recovery stress:

(a) must decrease linearly with T , the absolute temperature, throughout the whole range of temperatures explored;

(b) does not depend on the imposed strain-rate (although this quantity varies in the proportion of 1 to 2.5×10^4 for each isothermal yield stress curve). The behaviour of this elastic element has yet to be confirmed experimentally and its nature must be discussed.

(2) *Linear behaviour.* Our proposed approach leads to the following relation for the viscosity at small stresses:

$$\eta = \text{const. } T \cdot \exp \frac{Q}{RT} \quad (1)$$

where Q equals Q_α or Q_β according to the range of temperatures explored. Equation 1 is the expression of the viscosity related to the linear behaviour of high polymers.

As Fotheringham and Cherry consider that n segments take part in viscous flow, their expression of the viscosity at yield does not reduce to linear viscosity at small stresses.

(3) *Shape of the master curve.* Both conceptions imply that the master curve admits a slanting asymptote at high stresses and strain-rates. However, from our treatment it can be seen that the master curve exhibits another linear part at moderate stresses and strain-rates; this straight portion is related to the case where the observed yield stress reduces to:

$$\frac{\sigma}{T} = \frac{\sigma_\alpha}{T} = \text{const.} \left(\ln \dot{\epsilon} + \frac{Q_\alpha}{RT} + \text{const.} \right) \quad (2)$$

In the master curve obtained for PMMA and PVC, this straight portion is rather narrow and, therefore, these examples are of no help to settle the question, but the case of PC is more interesting. For this high polymer the data fit a set of parallel straight lines from 20 to 120°C [1]. Moreover, using tensile creep and impact tests it is possible to extend the study of the tensile yield stress to strain-rates which cannot be reached in tension tests, we have thus measured the yield stresses related to strain-rates varying from 10^{-8} to 10^2 sec^{-1} . From room temperature to 80°C, the data obtained on PC fit Equation 2 over ten decades of strain-rates [7]; this experimental fact cannot be explained by Fotheringham and Cherry's treatment. We are of the opinion that the master yield stress curve of PC exhibits such a wide straight part, simply because, for this polymer, the β transition is located far below the glass transition.

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Received and accepted 3 March 1976

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Thermal behaviour of silver amalgam

Long, needle-like, six-faced single crystals of silver amalgam, silver-grey in colour, grow on the surface of mercury placed in 0.02 N AgNO_3 solution. Some aspects of the growth features of these crystals have been reported by Sake Gowda and Madaiah [1]. The stoichiometry of the compound, the powder diffraction data, and the cell constants, have already been reported by Nirmala and Sake Gowda [2]. A

brief literature survey has been given in the above paper [2] with the intention of comparing the author's results with the earlier work.

Silver amalgam crystals obtained by the above method crystallize in the space group $P6_2$ or $P6_22$ or their enantimorphic complements. The lattice parameters obtained from Weissenberg patterns were used to index the powder pattern of silver amalgam crystals unambiguously [2]. The thermal behaviour of silver amalgam crystals grown from

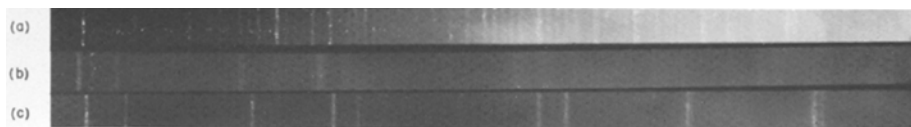


Figure 1 Powder photographs of silver amalgam at different temperatures. (a) β phase at 23°C ; (b) $\alpha + \beta$ phase at 85°C ; (c) α phase at 330°C .

0.02 N AgNO_3 and a globule of mercury is discussed in the present paper.

The crystals of silver amalgam used in the present study were kept in vacuum for 2 h at about 110°C to remove any excess of mercury adhered to the surface of the crystals. The crystals were then powdered. The specimen for the thermal expansion study was prepared by filling a quartz capillary (0.7 mm diameter) with the powder. This was sealed and mounted on the specimen holder using alumina cement. Using a Unicam 19 cm high temperature camera, powder patterns were obtained at different temperatures, ranging from room temperature up to 330°C . $\text{CuK}\alpha$ radiation was used. The exposure time was about 30 h and the vacuum in the chamber was of the order of 10^{-4} mm Hg. The diffraction lines corresponding to Bragg angles $(62.56)\alpha_1, \alpha_2$, $(67.89)\alpha_1, \alpha_2$, $(69.91)\alpha_1, \alpha_2$ and $(74.55)\alpha_1, \alpha_2$ were used to evaluate the lattice parameters of the β phase (hexagonal) at different temperatures. Reflections corresponding to Bragg angles $(54.46)\alpha_1, \alpha_2$, $(56.59)\alpha_1, \alpha_2$, $(65.75)\alpha_1, \alpha_2$ and $(75.53)\alpha_1, \alpha_2$ were used to evaluate the lattice parameters of the α phase (fcc) at different temperatures.

From the present study it is found, silver amalgam crystals exists in the β phase up to 85°C . Between 85 and 125°C both β and α phases are present together. Above 125°C only the α phase is

present. The diffraction pattern of the silver amalgam crystals, showing the β phase, the β phase and the α phase together, and the α phase are given in Fig. 1. The lattice parameters of the β phase and the α phase at various temperatures are given in Table I and Fig. 2.

The lattice parameters a and c of the β phase increase with the increasing temperature and the variation is linear. The expansion of the β phase is reversible. Between 85 and 125°C , both the phases are present. The lattice parameters of the β phase in this range could not be determined as the lines were so diffuse to make any measurement. Hence, the extrapolated values of a and c at 85°C are given. The coefficients of linear expansion of silver amalgam crystals have been calculated using the formula,

$$\frac{1}{a_{23}} \left(\frac{a_t - a_{23}}{t - 23} \right)$$

for the a parameter and

$$\frac{1}{c_{23}} \left(\frac{c_t - c_{23}}{t - 23} \right)$$

for the c parameter. The mean coefficients of expansion of the β phase in the temperature range, 23 to 85°C are $16.1 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for a and $17.4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for c .

At about 125°C complete change to α phase takes place. The lattice parameter of the α phase decreases with increase of temperature till about 180°C . This is, probably due to evaporation of mercury present in silver amalgam. It is also observed that the expansion of the α phase over this range is irreversible. Beyond 180°C , the lattice parameter increases with the increase of temperature and this increase in lattice parameter with temperature compares well with that of the lattice parameter of the pure silver crystal (Fig. 2). The lattice parameters of pure silver crystal at various temperatures [3] are given in Table II and also shown graphically in Fig. 2 for comparison.

The silver amalgam crystal at 330°C was cooled

TABLE I The lattice parameters of silver amalgam at various temperatures.

Temperature ($^\circ\text{C}$)	a (\AA)	c (\AA)	Phase
23	8.147	8.842	β
45	8.149	8.845	
60	8.152	8.848	
85	8.155 4.197	8.852 —	$\alpha + \beta$
100	* 4.171	* —	
125	4.136	—	α
180	4.109	—	
330	4.115	—	

* a and c of β phase not determined at 100°C .

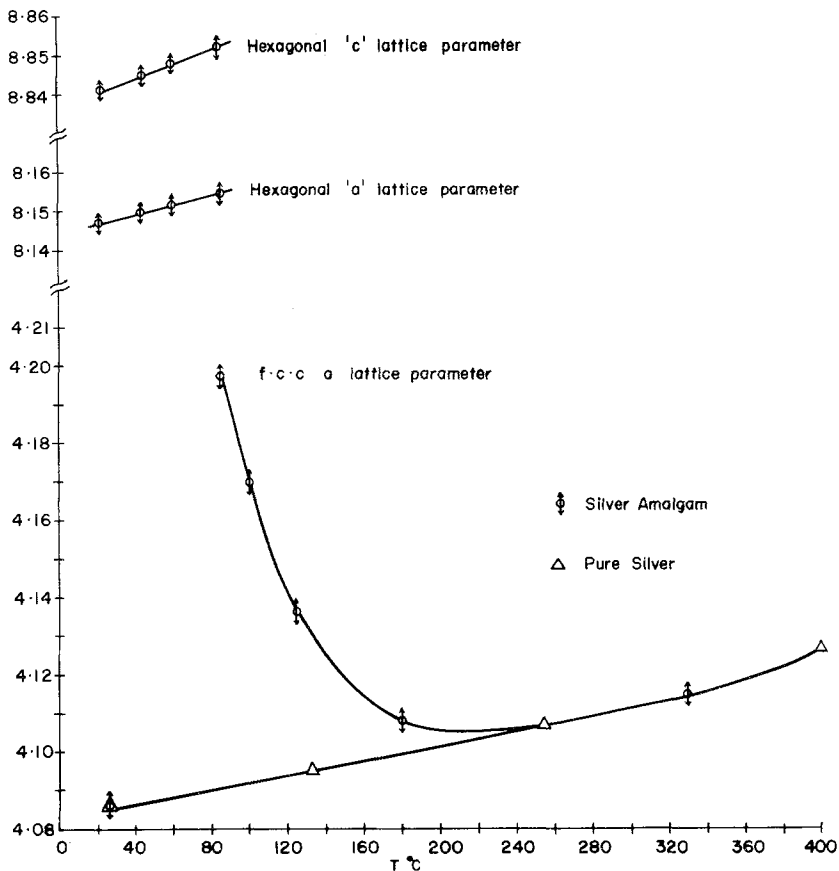


Figure 2 Lattice parameters of silver amalgam at different temperatures.

TABLE II Lattice parameters of pure silver at various temperatures.

Temp.(° C)	a(Å)	Temp.(° C)	a(Å)
16	4.0855	399	4.1185
22	4.0859	552	4.1313
134	4.0962	717	4.1479
257	4.1067	846	4.1625

to room temperature and its lattice parameter was determined. This lattice parameter was found to be 4.085 Å which corresponds to that of pure silver. At this temperature (330° C) only silver is present and mercury has evaporated completely. The expansion of α phase after 180° C is reversible indicating there by that this part of expansion is similar to characteristic expansion of pure silver crystals.

Acknowledgement

The authors wish to thank Professor R.M. Mallya, Indian Institute of Science, Bangalore for his use-

ful comments and suggestions. One of the authors (K.A.N.) thanks Bangalore University for granting her a Research Assistantship.

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Received 28 January
and accepted 1 March 1976

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