Letters

Liquid-quenching of laser-melted oxides

The ultra-rapid solidification of molten materials by accelerating the liquid onto a high conductivity solid substrate has been applied extensively to metallic systems [1, 2]. This method, in which molten specimens are quenched at rates of the order of 10^6 °C sec^{-1}, is here referred to as liquid-quenching. The extension of solubility limits, retention of metastable crystalline phases, and the presence of amorphous phases are characteristic of liquid-quenched specimens. The high melting points of most oxides have, however, limited research involving the liquid-quenching of oxides.

Lasers offer attractive heat sources for liquid-quenching systems. Jones [3], Elliott *et al.* [4] and Laridjani *et al.* [5] used pulsed solid state lasers to produce local melting in Al–Fe, Ag–Cu and Ag–Ge alloys, respectively. Because of the high thermal conductivities of metals, the melted areas experienced a very rapid quench (of the order of 10^6 °C sec^{-1}) when the laser radiation was terminated. Unfortunately, the poor thermal conductivity of ceramics precludes the use of this technique. In an attempt to find new oxide glasses, Topol *et al.* [6] used a continuous output CO_2 laser to melt drops off rotating oxide rods. The drops were quenched in air, and the percentage of glass yield was determined.

This paper reports a new method that was developed in this laboratory for the liquid-quenching of oxides. The technique utilizes a high intensity continuous-wave laser, together with a hammer-and-anvil quenching device (Fig. 1). The hammer-and-anvil apparatus is similar to that first developed by Pietrokowsky [7]. A liquid drop is caught between the copper faces of a rapidly moving hammer and a stationary anvil. Quench rates of about 10^5 °C sec^{-1} have been reported for metals quenched in this manner [8]. Oxide quench rates are, however, expected to be considerably lower.

A continuous-wave CO_2 laser* with a maximum output of 400 W was employed. The beam was focused by means of a water-cooled gallium arsenide lens having a focal length of 12.5 cm. The radiation incident on the specimens had a power density of about 5×10^3 W cm^{-2}, with the beam defocused so that the incident spot diameter was approximately equal to that of the specimen rods (0.1 in.). It was found that droplets did not fall off the specimen rods because of high surface tension. A solenoid was, therefore, employed to knock molten drops off the specimens. A signal from this solenoid was used to activate the trigger solenoid, releasing the

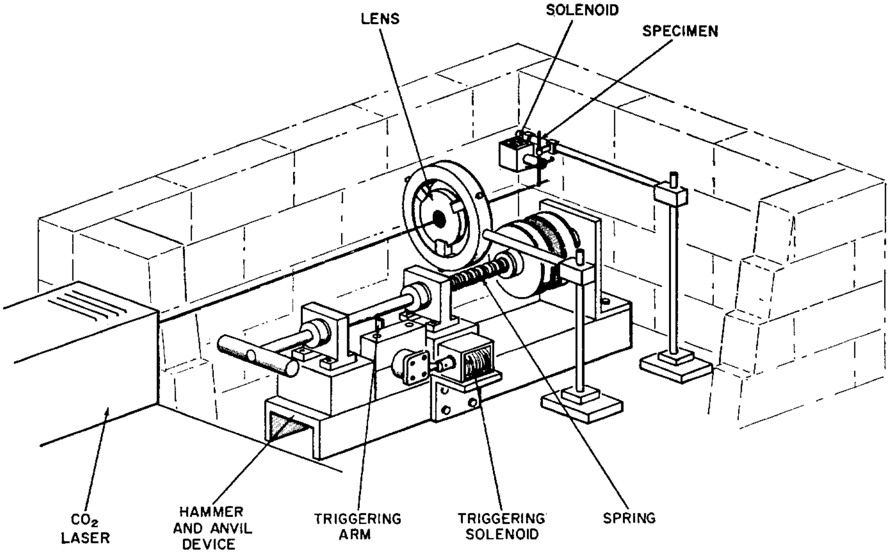

Figure 1 Liquid-quenching system.

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*American Optical Corp. Model 45A.

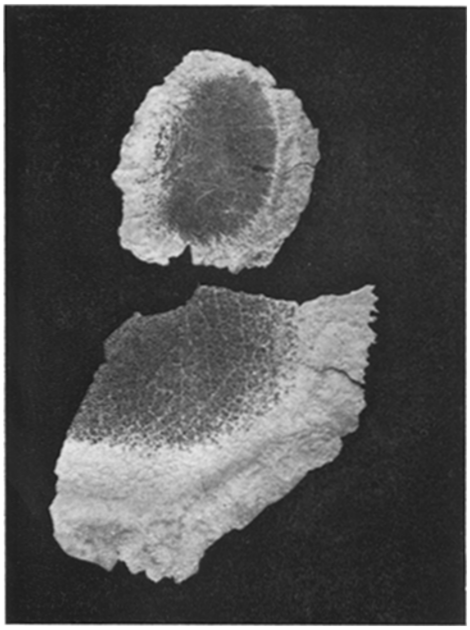

Figure 2 Liquid-quenched alumina × ~ 1.5.

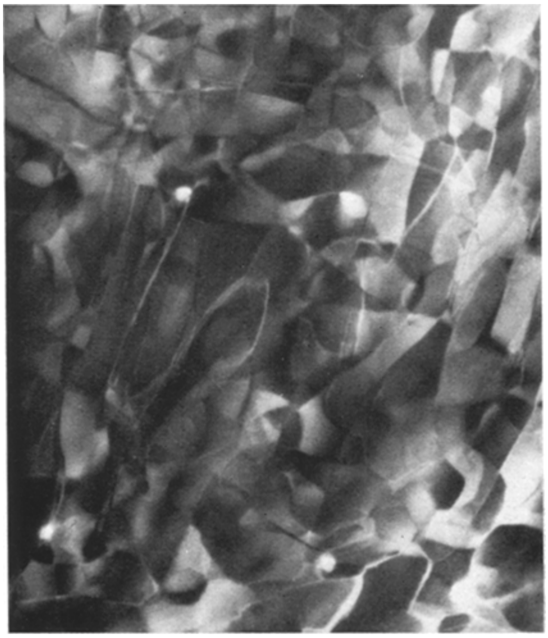

Figure 3 Electron micrograph of liquid-quenched alumina (ion-thinned) × ~ 125 000.

spring-loaded hammer.

The first material investigated was α-Al_2O_3 (99.5% purity). The melting point of this material (2050°C) is low enough to allow easy melting, but sufficiently high to test the feasibility of the technique. Several phases of alumina are obtainable under various conditions. The phases present in liquid-quenched specimens might be expected to reflect the quench rate.

Typical liquid-quenched alumina specimens are shown in Fig. 2. Specimens generally weighed about 100 mg, with diameters ranging from 0.5 to 1.5 in. and maximum thicknesses of approximately 0.002 in. (50 μm). Edge regions, however, were much thinner. The central regions of some specimens were almost transparent. Debye-Scherrer analysis revealed that these transparent central areas were composed largely of metastable δ-alumina. Using the flame-spraying technique, Ault [9] obtained metastable γ-alumina when α-alumina was sprayed on stainless steel. The outer edges of the specimens were predominantly α-alumina, which is the usual phase obtained when Al_2O_3 is solidified normally from the melt. The quench rate for the centre of a specimen should indeed be higher than that for the outer edges, since the centre makes contact with the hammer-and-anvil faces first.

Specimens suitable for transmission electron microscopy (TEM) were prepared by means of ion-thinning. Fig. 3 is an electron micrograph of a central specimen region and illustrates the typical microstructure obtained. Selected-area diffraction indicated that this is probably δ-alumina. There was no evidence of any amorphous phase. Topol *et al.* [6] reported that no alumina glass was obtained using their system. Further TEM work is currently underway, and the study of oxide alloy systems has commenced.

Acknowledgement

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Attenuated total reflectance infra-red spectra of Portland cement

The advantages of attenuated total reflectance (ATR) technique of infra-red spectrometry of cement materials have been emphasized in an earlier publication [1]. In order to establish the previous finding, six Portland cements of significantly variable composition have been studied by the ATR technique. The results of this analysis are presented in this short communication, to

(1) substantiate the characteristic band pattern of normal Portland cements in 1050 to 450 cm^{-1} region, where the fundamental modes are known to appear,

(2) establish the reproducibility of ATR spectra of Portland cements, and

(3) qualitatively assess the formation of relative proportions of tricalcium and dicalcium silicates in cements.

The ATR spectra of six Portland cement samples (NBS/SRM nos 633, 635, 636, 637, 638 and 1016) were taken on a KRS-5 crystal in an ATR attachment using a Perkin–Elmer 621 spectrometer. The critical angle of incidence of the radiation was maintained approximately at 40°. An ordinate scale expansion of × 5 was used in each case. The cements were used without any special treatment. Each sample was subjected to a repeated number of runs and one of the representative spectra of each sample has been reproduced in Fig. 1. The important bands have been listed in Table I. The accuracy of the

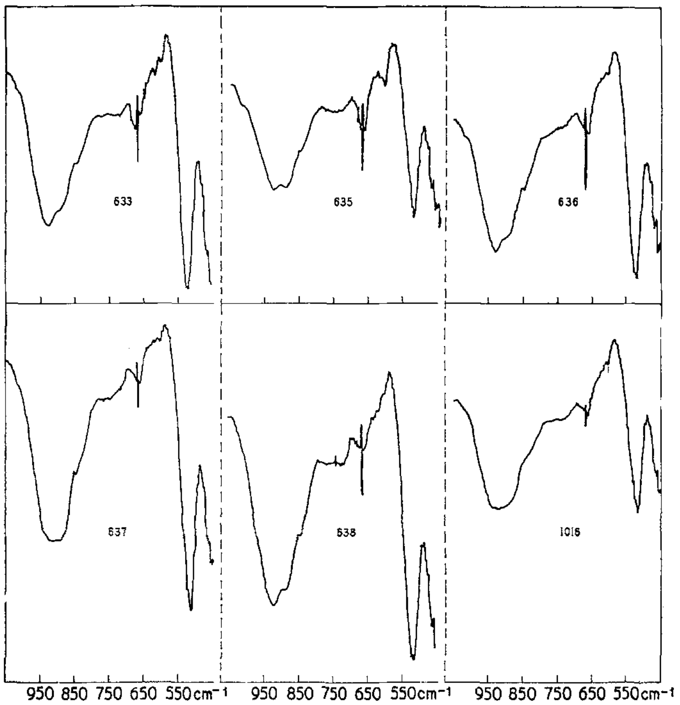

Figure 1 ATR infra-red spectra of Portland cements.