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Splat-quenching of lead in vacuum

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A "gun" assembly for splat-quenching of materials in vacuum or controlled ambients has been set up. A metastable h c p structure (a = 3.48 Å, c = 5.59 Å, c/a = 1.60) has been observed in splat quenched pure lead. The h c p phase is stable up to 270° C and transforms to the equilibrium f c c structure on heating in the electron microscope. The transformation has also been confirmed by DTA. The observed h c p structure appears to be stabilized by traces of oxygen as well as a high rate ($\sim 10^8$ K sec^{-1}) of cooling. No such structure has been observed in vapour-quenched films under similar conditions.

1. Introduction

The technique of splat-quenching of materials has aroused considerable interest because it offers an excellent method of retaining the short-range order of a liquid in the solid state. New metastable crystalline and amorphous phases have been obtained and the solid solubility range increased in a large number of alloy systems after rapid quenching from the liquid state [1]. It has, however, not been possible to obtain metastable crystalline structures in pure metals by this technique. Some attempts on pure metals have yielded controversial results [2, 3].

Lead has an equilibrium f c c structure. No metastable phase has been observed in either splat-quenched or vapour-deposited lead (even at liquid He temperature) [4]. The existence of a hexagonal closed-packed structure of lead at high pressures ($\sim$ 161 kbar) has been predicted on the basis of energy considerations by Klement [5]. A discontinuous rise in resistance for lead at 161 kbar detected by Balchan and Drickamer [6] has been interpreted as a polymorphic transition. Rastogi *et al.* [7] have reported a discontinuity of 0.54×10^{-3} mole fraction of quenched-in vacancies at the melting point by electrical resistivity measurements, on lead samples quenched from temperatures above, as well as below, the melting point at cooling rates $\sim 10^4$ k sec^{-1}.

If the h c p phase of lead exists, it should, in principle, be possible to stabilize it by quenching the melt at very high rates of cooling under controlled ambients. Although a number of devices have been developed for rapid quenching from the melt, the "gun" technique of Duwez and Willens [8] is known to yield the highest rates of cooling. Cooling rates have been considerably increased by splat-quenching in vacuum/an inert atmosphere [9]. We have fabricated a "gun" assembly for splat-quenching metals and alloys in vacuum ($\sim 10^{-5}$ Torr) as well as in controlled ambients. High cooling rates ($\sim 10^8$ K sec^{-1}) have been obtained in pure lead on splat-quenching in vacuum. The high-pressure h c p phase of lead has been stabilized at room temperature. The technique employed and the effect of vacuum conditions on stabilization of the metastable h c p phase are the subject of this paper. For comparison, the structure of films obtained by quenching of lead vapours under similar vacuum conditions is also presented here.

2. Apparatus

A schematic diagram of the "gun" assembly is shown in Fig. 1. The propelling device is similar to that of Duwez and Willens [8]. The whole assembly is contained within a cylindrical steel chamber of 30 cm i.d., vacuum-sealed to the base plate with a neoprene gasket. A high-pressure gas container is connected to the high-pressure chamber of the "gun" with a thick-walled steel tube passing through the base plate via O-ring seals and through a coupling. The detachable high- and low-pressure chambers are separated by a diaphragm consisting of an aluminium foil $\sim$ 0.1 mm thick, sealed with O-rings and held together with a

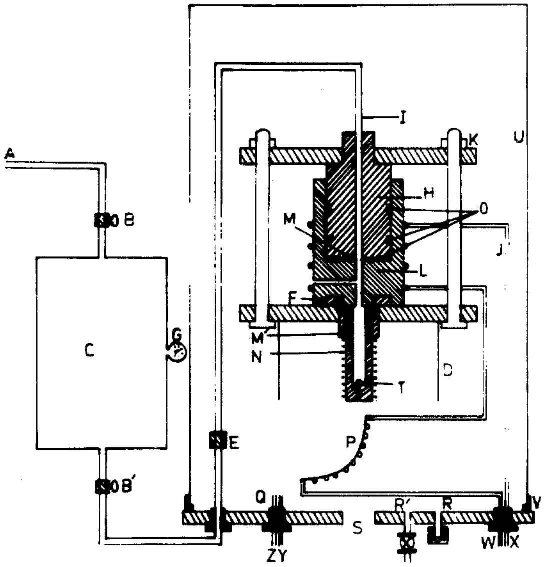


Figure 1 Diagram of the "gun" assembly used for splat-quenching in vacuum and controlled ambients. A, high pressure gas inlet; B and B′, high pressure valves; C, high pressure gas storage; D, reflector; E, coupling; F, hanging attachment; G, pressure gauge; H, high-pressure chamber; I, steel tube; J, cooling tubes; K, clamp; L, low-pressure chamber; M, diaphragm; M′, graphite crucible; N, heater; O, O-rings; P, copper substrate; Q, multiple feedthrough; R, pressure release valve; R′, gas admittance valve; S, port for diffusion pump; T, molten sample; U, steel chamber; V, neoprene gasket; W, water inlet with outlet X; Y, leads to the heater; Z, leads to the thermocouple.

clamping system. The substrate and the "gun" are water-cooled by copper tubes passing through the base plate. The curved copper substrate has provision for vertical, lateral and tilt adjustments by appropriate attachments. A graphite crucible having an orifice of ~0.9 mm diameter at its base is attached vertically below the "gun" through an adjacent hanging attachment. The crucible is heated by resistively heated Kanthal wire and its temperature is measured with a chromel–alumel thermocouple. An aluminium reflector is provided around the furnace to increase its efficiency as well as to minimize heating of the sealing chamber. The leads to the thermocouple and to the furnace are taken through a multiple feedthrough. An automatic pressure release valve and a gas admittance valve (for producing inert atmosphere) are also incorporated into the base plate. The chamber is connected to a conventional diffusion pump vacuum system through a port and can be evacuated down to $\sim 10^{-5}$ Torr.

To promote good adhesion of the quenched foil to the substrate and to ensure it to be free of oxide, the copper substrate is abraded with fine SiC paper and cleaned prior to each quench. Inert gas is stored in the high-pressure gas container at a pressure $\sim 8\,\mathrm{MN\,m^{-2}}$ (≈ 1160 psi) and released suddenly through the high-pressure valve. It is to be noted that the decrease in gas pressure through the connecting steel tube is very small because of very large container volume/tube volume ratio and is compensated by a slightly increased pressure in the gas container. The diaphragm ruptures at this pressure, thus producing a shock wave. This shock wave travels through the low-pressure chamber without any appreciable loss in intensity and ejects the molten metal onto the water-cooled copper substrate. The melt spreads on the conducting substrate and heat is removed at a high rate by conduction from the thin solidifying layers. The resulting foils are irregular and their thickness varies from a fraction of a micron to a few microns. These are easily stripped off the copper substrate. Near the edges the foils are transparent to the electron beam and hence can be directly examined in an electron microscope.

High-purity lead was surface-etched, cleaned properly and splat-quenched in air and in vacuum $\sim 10^{-2}$ and $\sim 10^{-5}$ Torr for determining the role of prevailing vacuum on as-quenched material. The foils were examined in an AEI EM 802 electron microscope operating at 80 kV without any further preparation. Differential thermal analysis (DTA) of the as-quenched lead foils was carried out using Stanton-Redcroft DTA 673-4 thermal analyser. Structure of lead films prepared by vapour deposition under varying conditions of thickness, substrate temperature and prevailing vacuum was also studied.

3. Results and discussion

Irregular foils of thickness ranging from 0.1 to 10 μm were produced by quenching approximately 100 mg pure lead from the melt. Quenching rates have been estimated on the basis of the theoretical values calculated by Sarjeant and Roy [10] for various splat thicknesses of pure lead. Accordingly, the quenching rate comes out to be $\sim 10^8\,\mathrm{K\,sec^{-1}}$ for a splat thickness of 0.1 μm which is obtained in our splat-quenched lead specimens.

Electron diffraction and microscopy studies of lead specimens splat-quenched under different ambients revealed the presence of two crystalline phases. The crystallographic structures of these were found to be (1) f c c, with $a = 4.94 \pm 0.01$ Å,

TABLE I Observed d-spacings and indices of reflection $(h k l)$ for the metastable h c p phase identified in splat-cooled lead (VS = very strong, S = strong, MS = medium strong, M = medium W = weak)

d(Å) (observed)	Intensity (visually observed)	$h k l$
3.02	VS	1 0 0
2.66	S	1 0 1
2.11	MS	1 0 2
1.75	MS	1 1 0
1.59	MS	1 0 3
1.45	MS	2 0 1
1.17	M	2 0 3
1.09	W	1 1 4
1.02	W	2 0 4

which is the known equilibrium phase, and (2) hcp with $a = 3.48 \pm 0.01$ Å, $c = 5.59 \pm 0.01$ Å and $c/a = 1.60$. The electron diffraction pattern of the hcp phase and its microstructure are shown in Fig. 2. The observed d-spacings, visually observed intensities and the corresponding $(h k l)$ values are listed in Table I.

The hcp phase is a new metastable phase of lead and corresponds to the high-pressure phase, suggested by the theoretical work of Klement [5]. It is stable up to ~270° C and transforms to the equilibrium fcc phase in the heating stage of the electron microscope. The electron diffraction pattern of the transformed fcc phase and its microstructure during transformation by the electron-beam heating are shown in Fig. 3. The structural transformation has also been confirmed by DTA, which shows an exothermic peak at 270° C. The quantity of the metastable hcp phase in as-quenched material being small and not precisely known (being a mixture of both the fcc and hcp phases), one can only roughly estimate the energy of transformation. This comes out to be $\sim 0.1\,\mathrm{kcal\,g \cdot atom^{-1}}$ if we assume the whole material to consist of the hcp phase. Note that the corresponding theoretical value of Klement [5] is $\sim 0.46\,\mathrm{kcal\,g \cdot atom^{-1}}$.

The metastable hcp and equilibrium fcc phases are randomly distributed throughout the electron-transparent regions of the foil. The relative proportions of these phases depend upon the growth conditions, in particular the amount of oxygen present during the quenching process. The metastable hcp phase was present in almost all regions of the foil when quenched in poor vacuum ($\sim 10^{-2}$ Torr). Regions of the metastable phase, however, were found to be fewer in foils quenched both in high vacuum ($\sim 10^{-5}$ Torr) as well as at atmospheric pressure. The higher proportions of the hcp phase in the specimens prepared under poor vacuum conditions suggest that the stabilization of the hcp phase is due to the presence of traces of oxygen. The lower proportions of the metastable hcp phase in lead foils quenched at atmospheric pressure may be attributed to the

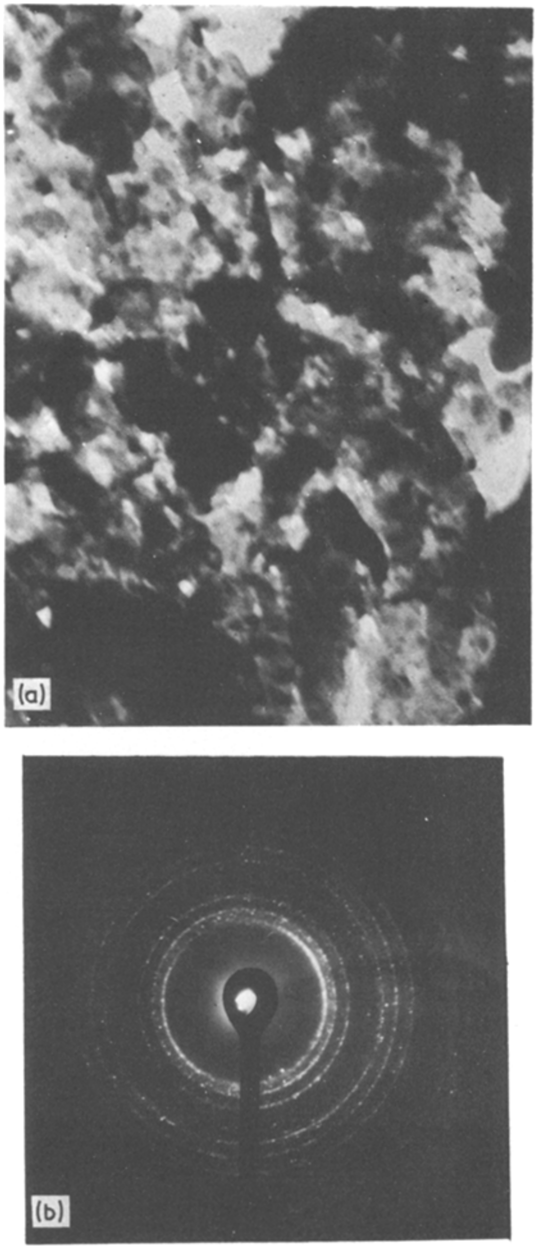
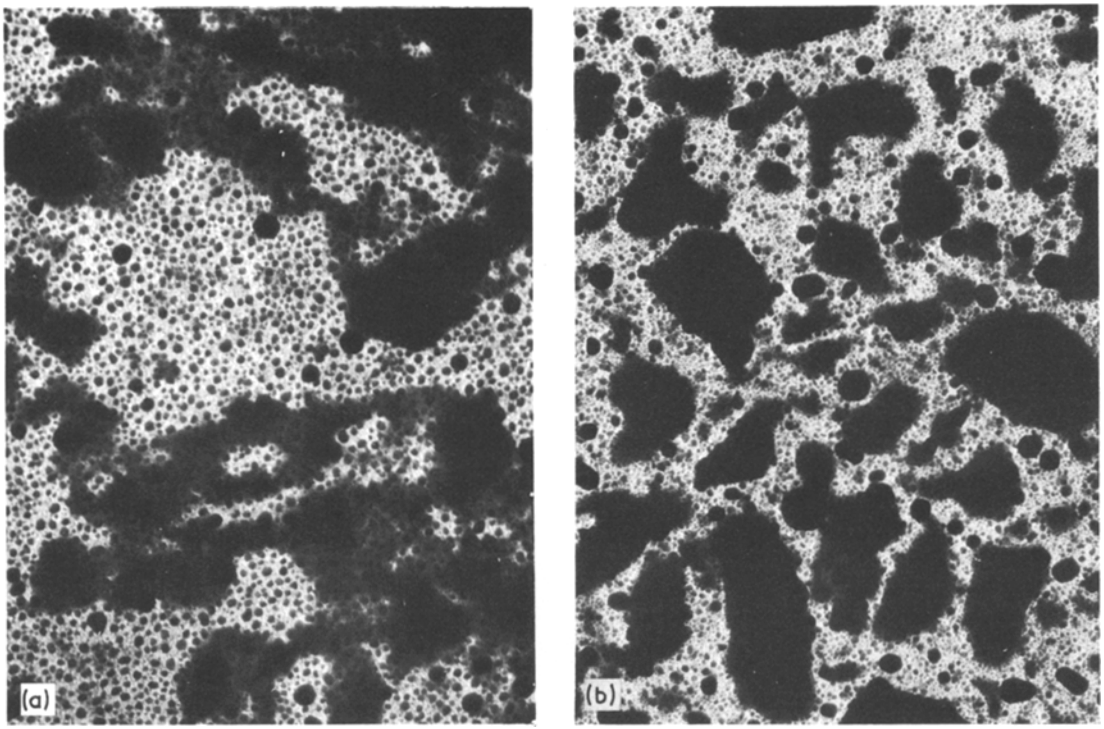


Figure 2 (a) Electron micrograph of the hcp phase in splat-quenched lead (× 60 000). (b) Electron diffraction pattern of the same area.



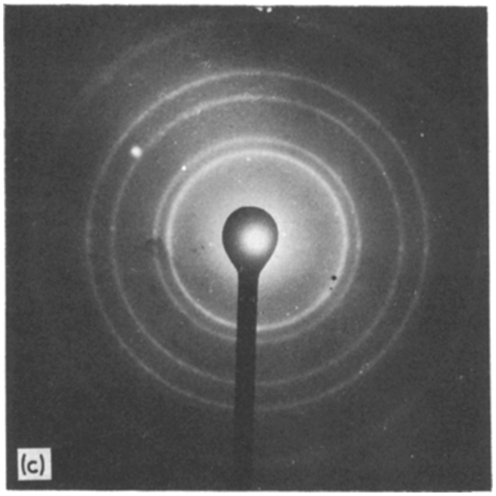


Figure 3 hcp to fcc transformation in splat-quenched lead. (a) Electron micrographs after slight heating of the hcp phase, showing mixed hcp and fcc phases (X 32 000). (b) Pure fcc phase obtained on further heating (X 32 000). (c) Electron diffraction pattern of (b).

lower cooling rates due to the presence of an oxide layer on the surface of the molten droplets.

Films of lead, vacuum-deposited at temperatures down to 77 K exhibit only the equilibrium fcc phase at all thicknesses. Evaporation in the presence of different pressures of oxygen also yields only fcc films with slightly changed lattice parameters. The grain size increases with increasing film thickness. The microstructure of vapour-deposited lead films at two different thicknesses is shown in Fig. 4. The appearance of well-defined grains in vapour-deposited films shows a rapid recrystallization of the deposit to the equilibrium fcc structure. The fact that the metastable hcp structure is obtained only from the melt on rapid quenching must imply that this structure is present in the liquid at some stage of the splat-quenching operation and is frozen in by traces of oxygen.

It is noteworthy that the observed lattice parameters of the hcp structure of lead can be obtained from that of the fcc structure by assuming the same atomic volume for both the fcc and hcp structures. The presence of only equilibrium fcc phase in vacuum-deposited lead suggests that the metastable hcp phase can be stabilized only from the liquid state under optimum ambient conditions.

4. Conclusions

(1) A metastable hcp phase (a = 3.48 Å, c = 5.59 Å, c/a = 1.60) has been observed in pure lead on splat-quenching under controlled ambients, and corresponds to the high pressure phase predicted on theoretical grounds by Klement [5].

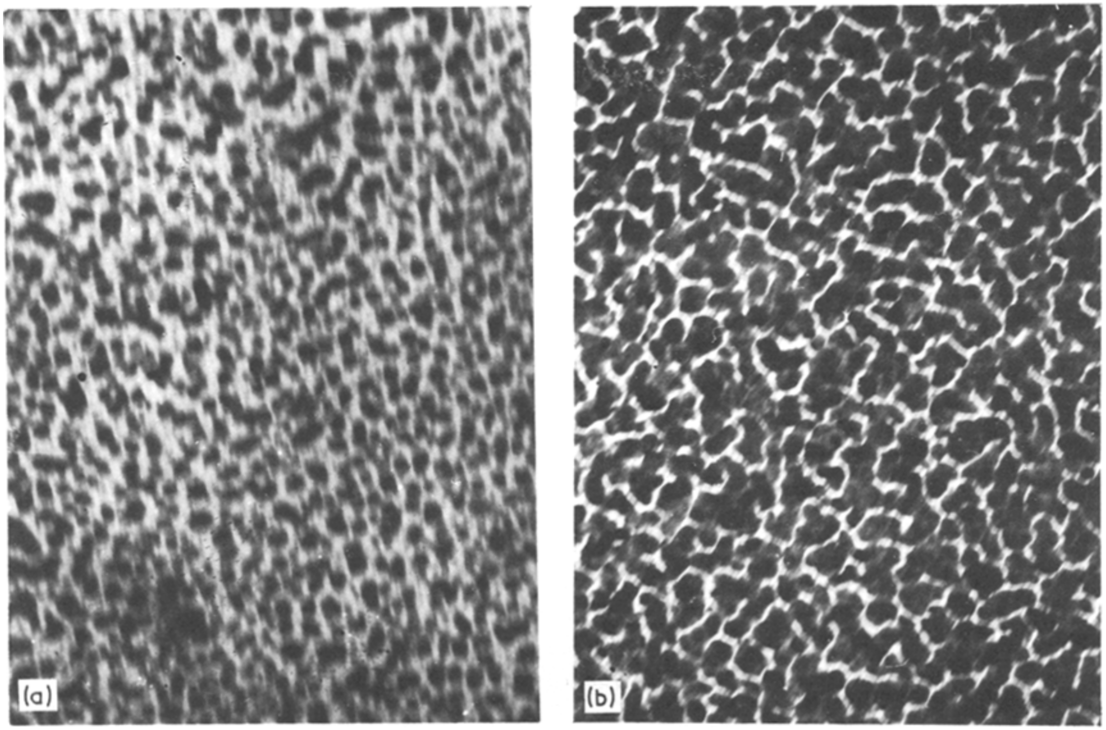


Figure 4 Electron micrographs of (a) thin and (b) thick region of vapour-quenched lead (X 50 000).

(2) The h c p phase is stable at room temperature and transforms to the equilibrium f c c structure at temperatures above 270° C.

(3) Both the rate of quenching and the prevailing vacuum affect the stabilization of the observed metastable h c p phase.

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