

FIG. 12. Equilibrium temperature-pressure diagram for Fe-Mn showing the effect of manganese on the triple point: (a) Fe-7Mn and (b) Fe-14Mn.

observation. It is of interest to calculate the change in density which is produced only by shock-generated dislocations and point defects. The density change from dislocations¹³ is given by

$$\Delta D/D = \frac{3}{2}b^2\rho_D,\tag{2}$$

where ρ_D is the density of dislocations, D is the material density, and b is the Burgers vector. Using the dislocation density observed for iron at 300 kbar, a decrease in $\Delta D/D$ of 7.3×10^{-5} should result. This value is too small to be observed experimentally, and by itself it should have produced a decrease in density, while an increase was observed in the present case. The point-defect density based on the observations of Kressel and Brown¹⁴ is too small to be observed experimentally.

Saturation magnetization of annealed Fe-Mn alloys as measured previously¹⁵ is consistent with the results

of this investigation and showed a sudden change in the slope of the saturation magnetization vs manganese curve at 7 wt% Mn. Shock deformation produces a significant drop in the saturation moment when the wt% Mn concentration exceeds 4%, as shown in Fig. 10(b). This drop occurs at all shock pressures. It should be noted that after shock deformation, the approach to saturation is more gradual due to the dislocations and point defects produced by the shock. This factor increases the uncertainty in the location of the saturation field, and it is probable that saturation was not actually reached at fields of 1000 Oe. Thus the decrease in saturation magnetization after shock loading Fe-0.4Mn should be attributed to dislocations and point defects rather than to a retained close-packed phase.

Density, saturation magnetization, and susceptibility⁶ measurements indicate that the transformation occurs at pressures below 90 kbar. This agrees with the work of Keeler and Mitchell⁴ who found that a partial phase transition to the nonmagnetic hcp phase can occur at shock pressures as low as 50 kbar. It is obvious that the addition of manganese to iron lowers the transition pressure. This is consistent with the magnetization data of Fig. 10(b). It is noted in Fig. 10(b) that the changes in saturation magnetization for the Fe-14Mn alloy occurs well below 90 kbar, and for the lower manganese alloys the transformation seems to occur at about 90 kbar. The transformation pressures, according to the Hugoniot curves of Fig. 11,^{16,17} are generally higher for each corresponding manganese content.

Bowden and Kelly¹⁸ using electron microscopy have studied the pressure-induced phase transformation in Fe-C and Fe-Ni-C. In the case of Fe-Ni-C it was found that the high-pressure phase was fcc, which was retained after the passage of the shock wave. These authors, however, were not able to retain the high-pressure phase in the Fe-C alloys. In a separate study Leslie, Stevens, and Cohen¹⁹ were able to retain the high-pressure fcc phase of a shock-loaded α -martensite Fe-32% Ni alloy. Bowden and Kelly¹⁸ found that under shock-loading conditions, α' transforms to γ by an exact reversal of the original transformation which produced the α' martensite. This finding is consistent with our optical observations on the Fe-7Mn alloy. Koul and Breedis²⁰ likewise were able to retain high-pressure phases of shocked titanium alloys. It is also noted that a commercial method of producing diamonds is based on the retention of the high-pressure phase after shock loading. Table V summarizes previous work done on retained high-pressure phases in alloys.

B. Thermodynamic and Stability Considerations

The results of the present investigation have shown that the high-pressure phase has been retained after the passage of the shock wave. The addition of manganese to iron has modified the temperature-pres-

4168

sure diagram by increasing the field of stability of the fcc and hcp phase. Therefore, the shock loading of a bcc-martensite structure with an appropriate solute content results in an $\alpha' \rightarrow \gamma$ or $\alpha' \rightarrow \epsilon$ transformation. Figure 12 shows that the triple point has been lowered to about 90 kbar for Fe-7Mn and 70 kbar for Fe-14Mn, and hence the fcc and hcp fields have been greatly stabilized with respect to the bcc phase. The T_0 -P lines for the Fe-7Mn and Fe-14Mn alloys as a first approximation were drawn parallel to the phase lines for pure iron, and were also made to pass through the two experimentally known states $(T_0, P=0)$ and (T_c, P_c) . The presure P_c is the transformation pressure obtained from the Fe-Mn Hugoniot, and T_c is the temperature of the compressed solid at P_c calculated using the equations of McQueen et al.²¹ From the present observations the phase line between the fcc and hcp phase must deviate as shown in Fig. 12 so as to explain the roomtemperature stability of fcc for Fe-7Mn and hcp for Fe-14Mn.

The calculation of the initial $P-T_0$ slope ($P=0, T = T_0$) for Fe-7Mn and Fe-14Mn is based on the Calusius-Clapyron equation. The initial PT slope for the bcc \rightarrow fcc transformation has the following values:

$$\left(\frac{dT}{dP}\right)^{\alpha \cdot \gamma} = -10.5$$
 °K/kbar.

The enthalpy change $\Delta H_{\alpha \rightarrow \gamma}$ and the entropy change $\Delta S_{\alpha \rightarrow \gamma}$ are functions of temperature and solute concentration.²² Therefore the slope of the $P-T_0$ curve will deviate from the initial dT/dP slope and from the slope of the pure-iron phase lines.

In addition to the thermodynamic considerations, dislocations generated by (a) the quench and (b) shock deformation and their interactions may stabilize the high-pressure phases. The first set of dislocations produced during quenching will have an internal stress field which is related to the shear mechanism during the martensitic transformation via quenching; an entirely different set of dislocations is produced by the martensitic transformation under shock, these two sets of dislocations interacting to form an extremely high dislocation density. When the shock pressure is removed, an entirely new set of dislocations must be produced in order for the high-pressure phase to revert to bcc. The shear process necessary for this reversion is prevented by the interaction of the existing dislocations. It is surprising that reversion of the high-pressure phase does not even occur when the specimens are cooled to liquid-nitrogen temperatures. Experiments will be performed to see if reversion occurs when specimens are cooled to 4.2 °K.

V. CONCLUSIONS

Based on the experimental findings of this work, shock deformation of quenched Fe-4Mn, Fe-7Mn, and Fe-14Mn results in a shock-induced phase transformation with the high-pressure phase retained upon relief. Furnace-cooled alloys up to 14 wt% Mn do not show retained close-packed phases after shocking. These results are explained by the conclusion that bcc iron with at least 4% Mn in solid solution will retain the close-packed phase produced by shock loading. The addition of manganese to iron also decreases the transition pressure from 133 kbar to less than 90 kbar for Fe-14Mn.

ACKNOWLEDGMENTS

This work was supported by the Defense Department through Advanced Research Project Association of the Department of Defense. A. Christou wishes to acknowledge the support of N.W.L. Independent Research funds. Shock loading was accomplished with the assistance of Dr. F.I. Grace and D. Altman. The authors also wish to acknowledge the assistance of Dr. S. Hooker for his helpful comments and assistance on the electron probe analysis, L. Flaer for his assistance in the density measurements, and D. Malyevac, head of the Materials Science Division, for his interest in the problem.

- val Weapons Laboratory, Dahlgren, Va. 22448.
- ¹R. S. Davies, *Iron and Its Dilute Solid Solution* (Interscience, New York, 1963), p. 61.
- ²P. G. Johnson, B. A. Stein, and R. S. Davies, J. Appl. Phys. 33, 557 (1962).
- ³D. Bancroft, E. L. Peterson, and S. Minshall, J. Appl. Phys. 27, 291 (1956).
- ⁴R. N. Keeler and A. C. Mitchell, Solid State Commun. 7, 271 (1969).
- ⁵Troiano and S. F. McGuire, Trans. Am. Soc. Metals 31, 340 (1943).

⁶A. Christou, Phil. Mag. 21, 203 (1970).

⁷G. E. Duval and G. R. Fowles, High Pressure Physics

and Chemistry (Academic, New York, 1963), p. 69.

⁸F. Rose, M. P. Villere, and T. L. Berger, Phil. Mag. 19, 39 (1969).

⁹R. Castaing, Advan. Electron. Phys. 13, 317 (1960).

¹⁰D. B. Wittry. University of Sourthern California Engineering Center Report No. 84-204, 1963 (unpublished).

¹¹D.C. Brillhart, R.G. DeAngelis, A.G. Preban, J.B. Cohen, and P. Gordon, Trans. AIME, 239, 836 (1967).

¹²D.C. Brillhart, A.G. Preban, and P. Gordon, Trans. Am. Soc. Metals 1, 969 (1970).

- ¹³W. M. Lomer, Phil. Mag. 2, 1053 (1957).
- ¹⁴H. Kressel and N. Brown, J. Appl. Phys. 38, 1618 (1967).
- ¹⁵C. Sadron, Ann. Phys. (Paris) 17, 371 (1950).
- ¹⁶A. Christou, U.S. Naval Weapons Laboratory Technical Note No. TN-F-24/69, 1969 (unpublished).
- ¹⁷T. R. Loree, R. H. Warnes, E. G. Zukas, and C. M. Fowler, Science 153, 1277 (1966).
- ¹⁸H. G. Bowden and P. M. Kelly, Acta Met. 15, 1489 (1967).
- ¹⁹W. C. Leslie, D. W. Stevens, and M. Cohen, Second International Symposium on Materials, San Francisco, 1964 (unpublished).
- ²⁰M. K. Koul and T. F. Breedis, *The Science*, *Technology*, and Application of Titanium (Pergamon, New York, 1969), p. 790.
- ²¹R. G. McQueen, E. Zukas, and S. Marsh, Response of

^{*}Paper based on material submitted by Aristos Christou in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Pennsylvania. *Present address: Materials Science Division, U. S. Na-