G. E. Duvall and R. A. Graham: Phase transitions under shock wave loading



FIG. 19. Transition stress versus input stress for iron of different thickness, as reported by Barker *et al*. (1974). The solid lines fit to the data are characterized by a relaxation time of $0.18 \ \mu s$ for the $\alpha - \epsilon$ phase transition.

observed irregularities below the transition appear to be well within the reproducibility of the measurements and do not provide convincing evidence of the postulated low stress partial transformation. Based on eddy current decay times, Royce (1968) and Keeler and Mitchell (1969) showed smooth change in resistance with stress below 8.0 GPa and an increase of resistance at 17.5 GPa. The importance of shock-induced defects in changing the resistance of shock-loaded iron is evident in the large discrepancy between static data of Balchan and Drickamer (1961) and shock loading data below 13 GPa. The strong influence of deformation details on resistance of shock-loaded metals is apparent in the extensive work on Manganin under shock loading (Graham and Asay, 1977) and in shock measurements on silver (Dick and Styris, 1975).

Although resistance measurements under shock loading clearly show a large increase in resistance associated with the 13 GPa transition, they have not been performed at sufficiently small stress increments to accurately determine a value for transformation pressure. Projectile impact experiments appear to be well suited for such a determination should further work of this kind be undertaken.

Shock-induced magnetization changes are less sensitive to details of plastic deformation than are changes in resistance and are subject to more direct interpretation. Royce (1968) has made shock demagnetization measurements at 17, 22, and 32 GPa and at higher pressures. They indicate that iron is nonferromagnetic above 32 GPa and show substantial decreases in magnetization at 18 and 22 GPa. These observations are in agreement with the nonferromagnetic character of ϵ iron deduced from Mössbauer effect measurements of Pipkorn et al. (1964). The shock demagnetization measurements were made using explosive loading techniques with large input pressure increments, and measurements of the pressure to complete the transition were not made. A similar measurement by Graham (1968) on 3% SiFe with projectile impact loading provides detail on critical pressures. A more detailed review of electronic property measurements with impact loading techniques is given by Graham (1967).

Wong (1969), from results of a double shock loading

experiment, inferred that magnetization change in iron is complete at 16 GPa. This result disagrees with measurements of the R-H curve and with demagnetization measurements of Royce (1968). Keeler and Mitchell (1969) also showed substantial demagnetization at 17.5 GPa. They reported apparent demagnetization signals at 8 GPa which they interpreted as due to a partial transformation, having failed to recognize that such effects can easily result from stress-induced magnetic anisotropy and do not require the proposed transformation at low stress. Recently, Novikov and Mineev (1974) have reported shock demagnetization measurements in an iron-bakelite mixture that minimizes eddy currents, and they found no evidence for a lower-pressure transition.

Even though several authors have proposed partial transformation below 13 GPa based on electronic property measurements, the data are fragmentary and incompletely analyzed and give no compelling evidence for transformation at low pressure.

Other works on the iron transition that are of less direct interest include the prediction of a rarefaction shock (Drummond, 1957), observation of smooth spalls in iron as a result of the rarefaction (Erkman, 1961; Lethaby and Skidmore, 1959; Ivanov et al., 1962), and observation of the rarefaction shock by flash radiography (Balchan, 1963). Low-pressure R-H curve measurements have been performed by Taylor and Rice (1963) and Barker (1975). Pressure-volume measurements to 170 GPa were obtained by McQueen and Marsh (1960), to 900 GPa by Al'tshuler et al. (1962) and Krupnikov et al. (1963), and to 3.4 TPa by Al'tshuler et al. (1968a). Curran (1971) has reported a small effect of magnetic field on transition stress in disagreement with theory and with later observations of Barker and Hollenbach (1974). Al'tshuler (1965) has reviewed other shock compression measurements on iron in the Soviet Union.

C. bcc iron base alloys

As previously mentioned, early attempts to identify the low-temperature, high-pressure phase of iron were directed toward the hypothesis that the high-pressure phase was fcc. Accordingly, shock loading investigations of the effect of alloying on the transition stress were initiated in hope that trends established might help in the identification. Although the alloy studies did not accomplish that goal, the investigations were extensive and established well-defined trends that are largely uninterpreted to date. Quantitative interpretation of the effect of alloying on the 13 GPa transition remains one of the significant unsolved problems in high-pressure metallurgy.

Alloys investigated included Fe-Si, Fe-Ni, Fe-Co, Fe-V, Fe-Cr, Fe-Mo, Fe-Mn, Fe-C, and various ternary Fe-Ni-Cr combinations. All alloys were in the bcc phase at 1 atm and 300 K. It is noteworthy that there has never been a pressure-induced polymorphic transition detected for an fcc iron alloy. However, certain of the fcc iron alloys undergo pressure-induced, secondorder phase transitions due to strongly pressure-dependent magnetic properties, as will be described in Sec. V.

One particular alloy, a low carbon 28.4 at.% (atomic percent) NiFe alloy, which is metastable in the martensitic, bcc phase, has been carefully investigated in static and shock loading experiments and is worthy of special note. The Fe-Mn alloy system has also been investigated under static and shock loading and gives an interesting test of Kaufman's method (Kaufman, 1969; Kaufman and Bernstein, 1970) of calculating effects of alloying on transition pressure.

Experimental determination of p_x^{TL} values for iron alloys were first reported by Fowler et al. (1961) for Fe-Ni, Fe-Cr, and Fe-Ni-Cr alloys. Zukas et al. (1963) studied transitions in Fe-Si alloys up to 6.8 wt% (weight percent) Si and in single crystals of 2.9 wt% Si along two different crystallographic directions. Loree et al. (1966a, 1966b) extended the alloy studies to Fe-V, Fe-Mo, Fe-Co, Fe-C, Fe-Ni, and Fe-Mn. All of these authors used direct contact high explosive loading and detected transition stresses with the pin technique. Fowler et al. (1961) used metallurgical examination of recovered samples to determine Hugoniot curves at pressures above the transitions. These data give some limited information on the effect of alloying on volume change at the transition. Zukas et al. (1963) used similar techniques and concluded that volume change at transition decreased as silicon content was increased; they found no difference between transition stresses observed in single crystals of two orientations and a polycrystalline sample of the same composition. At input pressures in the single shock region Loree et al. (1966a) found that R-H curves for the Fe-V alloys were the same, even though transition stresses increased significantly with vanadium concentration. Similar results were noted for the Fe-Co alloys.

A summary of effects of various solutes on transition pressure is shown in Fig. 20: addition of nickel and manganese substantially lowers it; addition of vanadium and cobalt substantially increases it. Transition pressures for vanadium concentrations greater than 11 wt% were not accurately determined, but p_x^{TL} values as high as about 58 GPa were observed at 40 wt% V. Work by Loree *et al.* (1966a) for iron-carbon is not shown in Fig. 20 since the observed strong effects of heat treatment



SOLUTION IN Fe, ATOMIC %

FIG. 20. Transition stresses observed for iron alloys under shock loading. The data on vanadium and cobalt alloys are from Loree *et al.* (1966a). The data on silicon alloys are from Zukas *et al.* (1963). The data on chromium alloys are from Fowler *et al.* (1961). Data from Gust and Royce (1970) on chromium alloys are similar to those of Fowler *et al.* (1961). The data on manganese alloys are from Loree *et al.* (1966b). The data on nickel alloys are from Fowler *et al.* (1966b). The data on nickel alloys are from Fowler *et al.* (1961) and Loree *et al.* (1966b). Loree *et al.* (1966a) report estimates of transition stresses as high as 58 GPa for 28 at. % vanadium alloys. Data on molybdenum alloys from Loree *et al.* (1966a) are not shown.

indicate that shear strength effects were significant. Data they obtained for Mo concentrations greater than 14 wt% are not shown because the samples were initially in a mixed phase condition.

Bundy (1967) observed transitions in Fe-V and Fe-Co alloys with static high-pressure resistance measurements. He found substantially higher transition pressures than those observed in shock experiments. This discrepancy is apparently resolved in later work by Bundy (1975), whose new measurements show excellent agreement between static and shock loading work in two Fe-Co alloys.

Trends in transition stress with alloy content are well defined. None of the alloy systems show discontinuous behavior as solute content is changed. Except for a few special cases, the effects of alloy composition on transition pressure have not been studied to determine their implications for phase stability at high pressure. The continuous changes in p_x^{TL} with solute indicate that high-pressure phases are hcp.

Giles and Marder (1971) studied transitions in Fe-Mn alloys under static pressure with their high-pressure x-ray diffraction apparatus. X-ray patterns on loading and unloading indicate a large hysteresis similar to that