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Letters

Electron Microscopic Observations on the Phase Transformation in Sintered Iron Disilicide

Iron disilicide possesses a tetragonal metallic high-temperature modification (α-phase) and a semiconducting low-temperature phase (β-phase) with orthorhombic lattice structure [1-4]. According to the phase diagram [5] the β-phase can be formed by a solid state reaction, described in [5], during heat-treatment in its stability range. So far [5-8] the phase transformation has been investigated using the following methods: dilatometry, electrical conductivity, X-ray analysis and the change of the magnetic susceptibility. Using these integrating methods, however, different time characteristics for the phase transformation are obtained (fig. 1) due to the varying effect of additional phases [5], which participate in the transformation, on the physical properties investigated here. Since the grain-size in sintered material is small (some μm) it is difficult to detect details by optical observation. Therefore it was of interest to observe the phase change by electron-microscopic transmission. For this purpose the preparation of pure and differently doped $FeSi_2$ was carried out according to [9]. The doping concentrations were 2 at. % aluminium (p-type conduction) and 5 at. % cobalt (n-type conduction), respectively. These materials have practical importance for thermoelectric applications [10, 11].

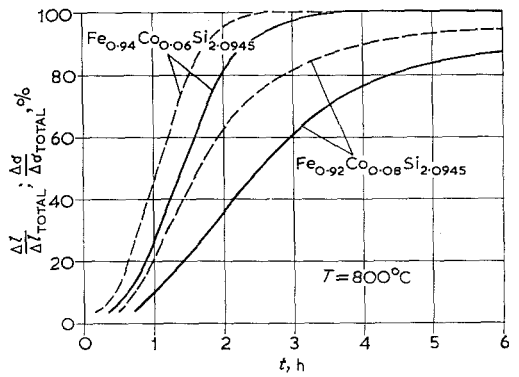

Figure 1 Length change $\Delta l/\Delta l_{total}$ (solid lines) and electrical conductivity change $\Delta\sigma/\Delta\sigma_{total}$ (dashed lines) during phase transition.

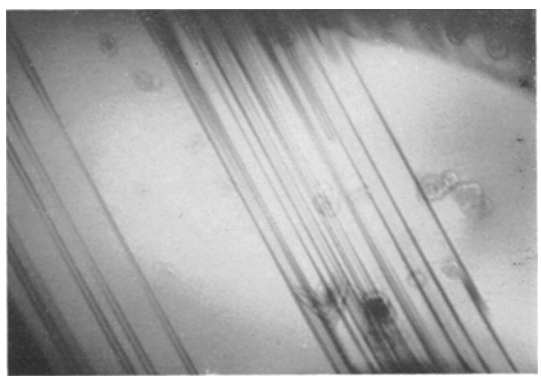

Figure 2 Lamellar structures in the low-temperature phase (× 73 300).

From large disc-shaped specimens of 500 μm thickness, smaller discs of 0.3 cm diameter were produced by means of an ultrasonic drill and were lapped to a thickness of about 200 μm. Then the specimens were thinned chemically in a solution of 30 vol % HNO_3, 10 vol % HF, 15 vol % HCl and 45 vol % H_2O. The electron-microscopic observations were carried out in a JEM electron microscope at 150 kV. An example of the observed transmission contrast of the low-temperature phase is shown in fig. 2, indicating a lamellar structure. The habit plane of these lamellae (which have a thickness of about 100 Å) was found to be {1 0 0}. No intersections could be detected. These properties were not affected by doping. Unfortunately, the evaluation of the selected area electron diffraction patterns shown in fig. 3 was complicated by splitting and displacement of the spots, owing to the fine lamellar structure of transmitted samples. However, using the known lattice parameters of α- and β-$FeSi_2$, it was possible to identify most of the spots.

The remaining spots cannot be due to the α- or the β-phase. This means that an additional phase must be present. Unfortunately, up to now the distorted lines and the splitting of the patterns have prevented the determination of the new phase, and further experiments are necessary. X-ray diffraction analysis gave no hint of an additional phase, presumably because of the smallness of the lamellae. It is of interest however to speculate on the observed lamella-shaped structures. Similar structures are known in copper - zinc - gallium [12] and copper - zinc - aluminium alloys [13] corresponding to a martensitic phase transformation. In $FeSi_2$ there is an influence of elastic stresses on the transformation: they lower the transformation temperature and the transformation velocity near scratches. Also the transformation hysteresis [6-8] supports the assumption that a diffusionless process participates in the phase change in iron disilicide. In order to detect a surface relief as evidence of a martensitic process we have investigated electron-microscopically carbon replicas from the surface of completely and incompletely transformed specimens. No relief effects could be found which could be attributed unambiguously to a diffusionless transformation. On the other hand, in the present work the transformation temperature was relatively high (750 to 900° C) and this makes the assumption of a diffusionless transformation in $FeSi_2$ difficult to check. Direct observation of this transformation by heating of a thin α-$FeSi_2$ foil up to 850° C in electron-microscopic transmission yields a linear growth velocity of the lamellae of the order of 10^{-5} cm sec^{-1}. Such a velocity is consistent with diffusion. Similarly the appearance of lamellae does not rule out a diffusion process. This means that more information on the structure of the unknown phase from distortion-free diffraction patterns is needed to decide whether the transformation occurs by diffusion or shear.

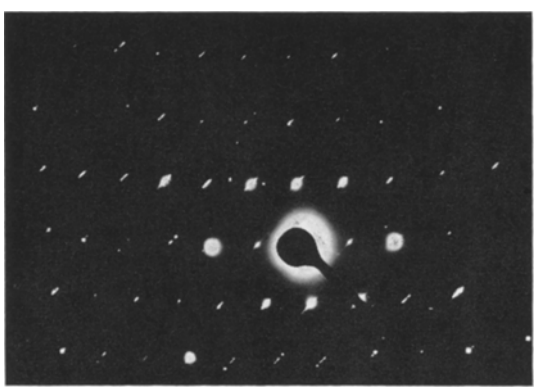

Figure 3 Selected area electron diffraction pattern of the low-temperature phase.

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