Solid Solubility of $CoSi_2$ in β–$FeSi_2$

The thermal conductivity κ of $FeSi_2$-rich polycrystalline $FeSi_2$–$CoSi_2$ alloys was determined as a function of the $CoSi_2$ content by Ware and McNeill [1]. They found that $CoSi_2$ lowers the thermal conductivity according to the expected solid solution effect up to 6 mol % $CoSi_2$. The increase in κ above 6 mol % $CoSi_2$ was ascribed to a second phase which appears after exceeding the maximum solid solubility at 6 mol % $CoSi_2$. The minimum in κ has recently been confirmed [2]. In the present work we have checked the above interpretation by a direct determination of the solid solubility of $CoSi_2$ in β–$FeSi_2$. For this purpose specimens were prepared as described by Hesse [2]. The $\alpha \rightarrow \beta$ phase transformation was performed at 750° C in view of the transformation hysteresis [3, 4], and checked by X-ray diffraction. The length changes of the three orthorhombic axis of β–$FeSi_2$ were measured as described by Bucksch [5]. The results are plotted in fig. 1 against the $CoSi_2$ content of the alloy. A

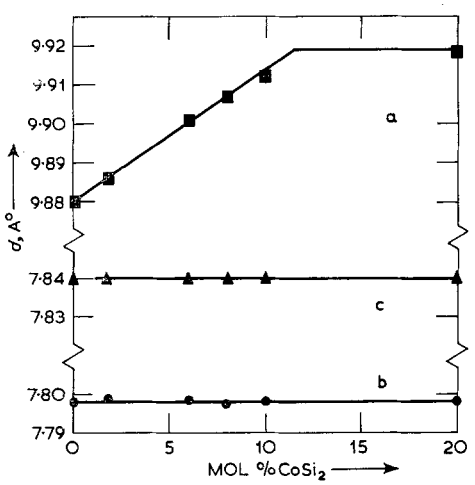

Figure 1 Lattice constants in $FeSi_2$–$CoSi_2$ alloys.

marked increase in the length of the *a*-axis up to approximately 12 mol % $CoSi_2$ was observed. Above this value lines of cubic $CoSi_2$ containing small amounts of $FeSi_2$ appear in the X-ray patterns, indicating the solid solubility of $FeSi_2$ in $CoSi_2$ [6]. The observations mean that 12 mol % $CoSi_2$ are dissolved in β–$FeSi_2$ at 750° C. Consequently, the former explanation of the minimum in κ at 6 mol % $CoSi_2$ cannot be correct. This conclusion is supported by Hall effect measurements (fig. 2) indicating that up to

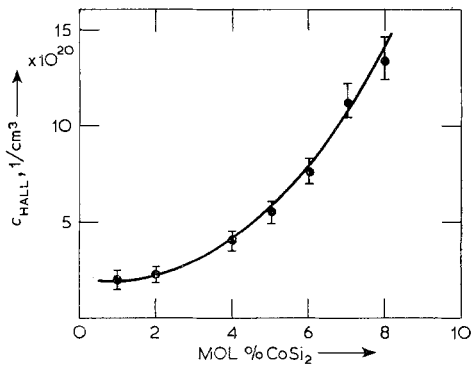

Figure 2 Carrier concentration c_{Hall} at room temperature versus $CoSi_2$ content in $FeSi_2$–$CoSi_2$.

at least 8 mol % $CoSi_2$ (in our case the upper limit for Hall voltage measurements) the number of free charge carriers, which is proportional to the number of dissolved cobalt atoms, increases with increasing cobalt content. In our opinion the position of the minimum in κ arises because above 6 mol % $CoSi_2$ the electronic part κ_e of the thermal conductivity increases more strongly with increasing $CoSi_2$ content than the lattice part κ_l decreases. This behaviour is illustrated schematically in fig. 3 together with experimental data.

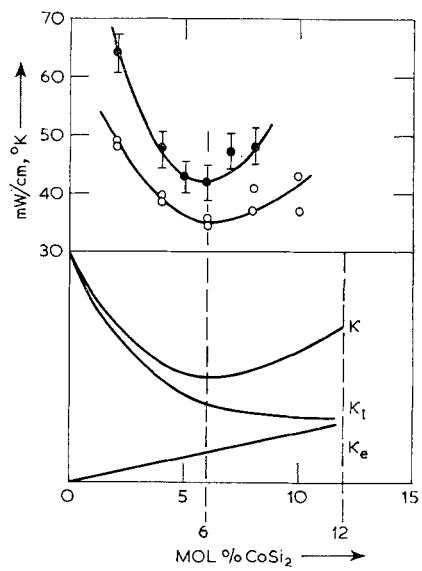

Figure 3 Thermal conductivity κ at room temperature versus $CoSi_2$ content in $FeSi_2$–$CoSi_2$ (open circles from [1]).

We shall now discuss briefly the sign of the observed change in one of the lattice constants. Since the atomic radius of cobalt is about 2% smaller than that of iron, a lattice contraction was expected with increasing x in $Fe_{1-x}Co_xSi_2$ and not a dilatation, as observed. Similar results were found for germanium in copper [7, 8]. If however interstitial sites were occupied in β–$FeSi_2$ one could perhaps explain the observed change. The dilatation of the *longest* axis in β–$FeSi_2$ supports this argument. But an electronic effect could also be responsible for the observed increase of the *a*-axis. Unfortunately, the atomic positions in β–$FeSi_2$ are still unknown [5, 9], preventing a more exact analysis. For the same reason it is unknown why both the *b*- and the *c*-axis are unaffected by alloying. As previously reported [10], the determination of these atomic positions is also desirable for a better understanding of the lamellar structure of the β-phase.

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