

change in the temperature dependence of C_{44} at the $L_6^+ \rightarrow L_6^-$ band crossover could arise either from an appreciable change in either (i) carrier concentration or (ii) the deformation potential characteristics of the bands. However, measurements of Hall coefficient as a function of temperature do not reveal any appreciable change in the carrier concentration at the $L_6^+ \rightarrow L_6^-$ crossover. As the L_6^+ and L_6^- bands have mirror symmetry, parameters in the two bands should be of similar magnitude — the deformation potential constants should be similar for the two bands. Theoretical calculations show this to be so for SnTe [19]. The slope of C_{44} before and after the $L_6^+ \rightarrow L_6^-$ crossover depends upon E_u^2 ; thus the present experimental results suggest that the deformation potentials for the L_6^+ and L_6^- bands are almost equal for $Pb_{0.47}Sn_{0.53}Te$.

Furthermore, in general the elastic constants of the $Pb_xSn_{1-x}Te$ alloys do not depend markedly upon composition and do not evidence any marked degree of acoustic phonon mode softening even for alloys with composition in the band crossover region.

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Received 9 March
and accepted 2 April 1976

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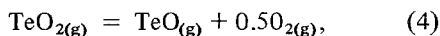
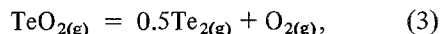
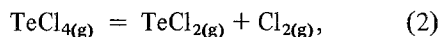
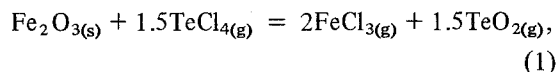
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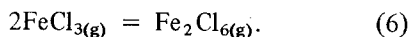
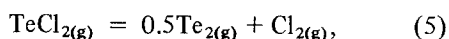
Growth of hematite single crystals by chemical transport with $TeCl_4$

Ferric oxide is the main component of ferrite materials which have various applications. For this reason, the study of the methods and conditions of preparation of α - Fe_2O_3 single crystals is of considerable interest.

In a previous paper [1] it was established by means of thermodynamic considerations that $TeCl_4$ should be one of the best carriers in the

chemical transport of hematite. In this case, the following reactions could take place when working in a closed system:





At 1000°C (1273.2 K), the equilibrium constants have the following values:

$$K_{p,1} = 1.48 \times 10^3, K_{p,2} = 93.2 [2],$$

$$K_{p,3} = 2.03 \times 10^{-3} [2], K_{p,4} = 1.10 \times 10^{-6} [2],$$

$$K_{p,5} = 2.20 \times 10^{-6} [2], K_{p,6} = 6.14 \times 10^{-5} [3].$$

Later, Reactions 4 to 6 will be neglected as the values of their equilibrium constants are very low.

Using data for ΔH_{298}° , S_{298}° and $c_p = f(T)$ and the method of calculation described in detail in a previous paper [4], the following expression for dependence $\log K_{p,1} = f(T)$ was obtained:

$$\begin{aligned} \log K_{p,1} &= -28785/T + 0.322 \cdot \log T \\ &\quad - 0.001146 \cdot T + 33661/T^2 + 26.219 \\ &= 1.5 \log P_{\text{TeO}_2} + 2 \log P_{\text{FeCl}_3} \\ &\quad - 1.5 \log P_{\text{TeCl}_4}. \end{aligned} \quad (7)$$

The corresponding expressions for the temperature dependence of $\lg K_{p,2}$ and $\lg K_{p,3}$ are deduced by Piekarczyk [2]:

$$\begin{aligned} \log K_{p,2} &= -2698/T + 2.667 \cdot \log T - 0.000361 \cdot T \\ &\quad - 6560/T^2 - 3.738 \\ &= \log P_{\text{TeCl}_2} + \log P_{\text{Cl}_2} - \log P_{\text{TeCl}_4}, \end{aligned} \quad (8)$$

$$\begin{aligned} \log K_{p,3} &= -7483/T - 0.931 \cdot \log T \\ &\quad + 0.0000645 \cdot T - 32780/T^2 + 7.481 \\ &= 0.5 \log P_{\text{Te}_2} + \log P_{\text{O}_2} - \log P_{\text{TeO}_2}. \end{aligned} \quad (9)$$

On the basis of the stoichiometry conditions the following equations can be written:

$$P_{\text{TeCl}_2} = P_{\text{Cl}_2} \quad (10)$$

$$\text{and} \quad 1.5P_{\text{FeCl}_3} = 2P_{\text{TeO}_2} \quad (11)$$

$$P_{\text{O}_2} = 2P_{\text{Te}_2}. \quad (12)$$

The equation for carrier balance has, after the necessary transformations, the following form:

$$C_{\text{TeCl}_4}^\circ = 3.283(P_{\text{TeCl}_4} + P_{\text{TeCl}_2} + 0.75P_{\text{FeCl}_3})/T, \quad (13)$$

where $C_{\text{TeCl}_4}^\circ$ is the initial concentration of the carrier in g cm^{-3} .

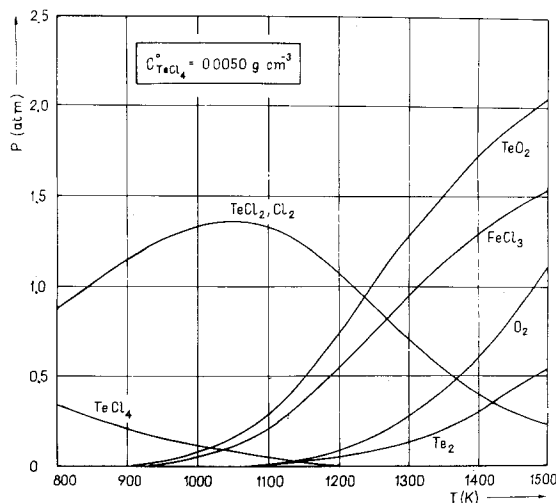


Figure 1 Partial pressures of the gaseous species as a function of temperatures.

Equations 7 to 13 form a system which may be used for the determination of the gaseous species partial pressures at various preset values for T and $C_{\text{TeCl}_4}^\circ$. This system was solved by a computer for the temperature range 800 to 1500 K (in steps of 50 K) and for TeCl_4 concentrations between 0.0005 and 0.0100 g cm^{-3} (in steps of 0.0005 g cm^{-3}). Fig. 1 (given as an example), shows the change in the partial pressures of the gaseous components in the transport system for $C_{\text{TeCl}_4}^\circ = 0.0050 \text{ g cm}^{-3}$.

The conversion degree for the main reaction 1 at a given temperature and carrier concentration is expressed by the ratio

$$\alpha = 0.75P_{\text{FeCl}_3}^{(T)}/P_{\text{TeCl}_4}^{(T)}$$

where $P_{\text{TeCl}_4}^{(T)}$ is the pressure of TeCl_4 when hematite is absent from the ampoule.

The values of α in the two zones of the ampoule are different and the rate of the transport is proportional to the difference in the conversion degrees, $\Delta\alpha$. Fig. 2 shows the correlations between $\Delta\alpha$ and the temperature T_1 in the crystallization zone at a temperature gradient $\Delta T = 50^\circ \text{C}$ and several concentrations of TeCl_4 . They have the form of curves with a maximum which is shifted towards the higher temperatures of crystallization when increasing the carrier concentration. At other temperature gradients, the curves have the same character but with increasing ΔT and at the same carrier concentrations, $\Delta\alpha$, and hence the rate

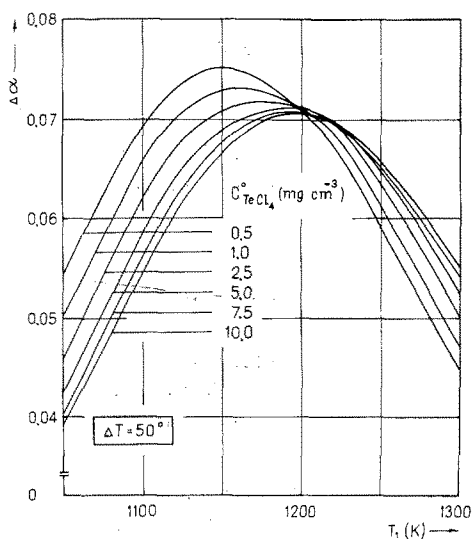


Figure 2 Plots $\Delta\alpha$ versus T_1 ($\Delta T = 50^\circ\text{C}$).

of transport increases. From a spherical point of view it would be better to work at values of T_1 around the maxima of the curves since small changes in the temperatures during the experiment have practically no effect on the constancy of the substance flow towards the growing crystal.

At a given temperature gradient, the expression

$$\beta = \frac{P_{\text{FeCl}_3}^{(T_2)} - P_{\text{FeCl}_3}^{(T_1)}}{P_{\text{FeCl}_3}^{(T_1)}} = \Delta P_{\text{FeCl}_3} / P_{\text{FeCl}_3}^{(T_1)}$$

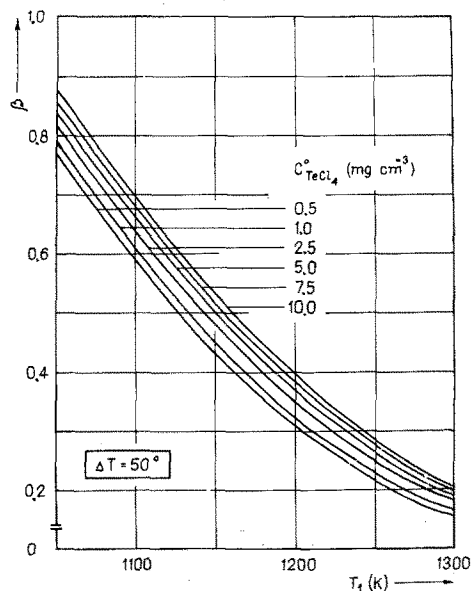


Figure 3 Plots β versus T_1 ($\Delta T = 50^\circ\text{C}$).

gives an idea about the supersaturation. Fig. 3 (given as an example) shows the dependence $\beta = f(T_1)$ for $\Delta T = 50^\circ\text{C}$ and the same concentrations of TeCl_4 as in Fig. 2. It is evident that the supersaturation changes very little even with a large change in TeCl_4 concentration and increases quickly with the decrease in T_1 . Since crystallization should be carried out at low supersaturation, one could expect to obtain better quality crystals at higher temperatures which, as follows from Fig. 2, are the optimum ones for higher carrier concentrations.

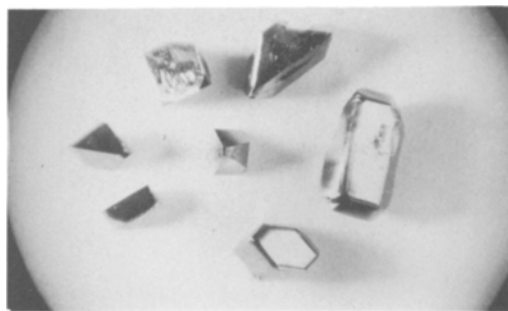


Figure 4 $\alpha\text{-Fe}_2\text{O}_3$ crystals.

Powdered $\alpha\text{-Fe}_2\text{O}_3$ (99.99%, Koch Light) and laboratory reagent purity TeCl_4 (Merck) were used for the experiments. The transport was carried out in ampoules of transparent quartz glass having 20 mm o.d. and a length of 100 mm. The introduction of the carrier was performed in a dry box.

Taking into account the above theoretical considerations, a relatively high constant carrier concentration, $C_{\text{TeCl}_4}^0 = 5 \text{ mg cm}^{-3}$, was used. Investigations were carried out at $\Delta T = 50, 150, 200$ and 250°C and temperatures in the crystallization zone corresponding to the maxima of the curves $\Delta\alpha = f(T_1)$ and varying between 920 and 830°C . Under these conditions, the values of β ranged from 0.40 to 4.10. The mean duration of the transport was 90 h. It was established that with the increase of ΔT the rate of transport increases but at the same time the crystals obtained become smaller and not well shaped (Fig. 4). The best single crystal polyhedra of $\alpha\text{-Fe}_2\text{O}_3$ with maximum dimensions of 7 to 8 mm were obtained at $\Delta T = 50^\circ\text{C}$ and a temperature in the crystallization zone of 920°C . The rate of transport in this case was 6.7 mg h^{-1} . As the Mössbauer spectra showed, these crystals contained no admixtures of bivalent iron.

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Received 10 March
and accepted 30 April 1976

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Influence of vacancies on the precipitation of germanium in an Al-4.0 wt % Ge alloy

Precipitation phenomena in Al-Ge alloys have recently been studied by X-ray, electronmicroscopic and resistivity methods [1-11]. These studies show that the quenched-in vacancies play an important role in the formation of Ge nuclei and the subsequent growth of the Ge precipitates. The present study deals with the influence of quenched-in vacancies on the precipitation of germanium in an Al-4.0 wt % Ge alloy. Measurements were made using X-ray and microhardness methods and the specimens were prepared from super-purity aluminium and germanium (99.999%, Koch Light Laboratories Ltd, UK). The final specimens were homogenized for 24 h at 390, 420, 450, 480 and 510°C, and then quenched in ice-water; the ageing temperature was 160°C. Small-angle X-ray diffraction measurements were performed, using a Kratky X-ray camera in combi-

nation with a programmed step scanning device [10]. Some preliminary wide-angle measurements were also carried out by using a Si(Li) semiconductor detector. The microhardness of a specimen was measured using a Reichert apparatus: the surface of a testing specimen was electrolytically polished before the hardness measurements were taken. Each Vickers hardness number in Fig. 1 is the mean value of 20 measurements. All X-ray and hardness measurements were performed at room temperature.

It is known that the age-hardening of an alloy depends on the volume fraction and the mean size of precipitates. Fig. 1 shows that the increase in microhardness of an Al-4.0 wt % Ge alloy with ageing time is greater for higher solution-treatment temperatures. According to our small-angle X-ray measurements, the mean size of small precipitates is practically independent of the solution-treatment temperature, although the total intensity increased with the solution-treatment

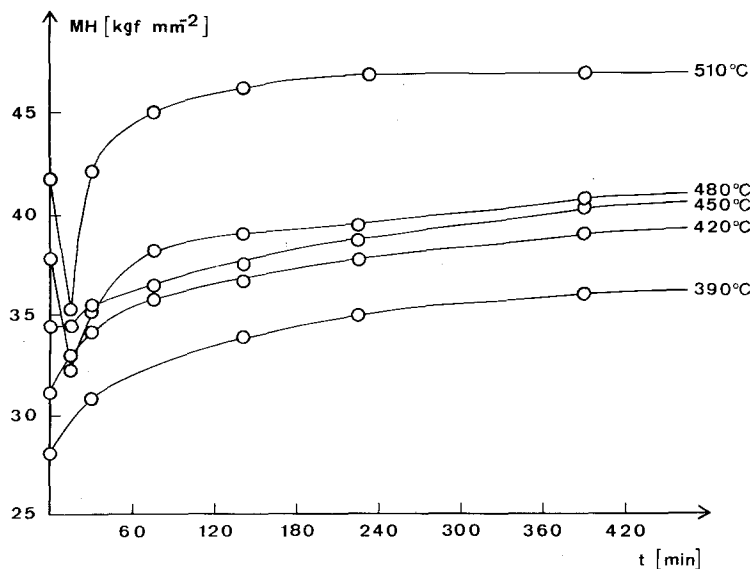


Figure 1 The microhardness of Al-4.0 wt % Ge alloy as a function of ageing time at 160°C. The solution-treatment temperatures are 390, 420, 450, 480 and 510°C.