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On the preparation of nickel ferrite single crystals by chemical transport

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A thermodynamic study of the process of close-spaced chemical transport of nickel ferrite with tellurium tetrachloride has been carried out. On the basis of computed data on the partial pressures of the species in the transport system, the temperature dependence of the change in the conversion degree of the transport reaction and of the supersaturation in the crystallization zone were plotted and used to determine the optimum experimental conditions. Stoichiometric nickel ferrite crystals with maximum edge dimensions of 5 mm were obtained.

1. Introduction

Nickel ferrite ($NiFe_2O_4$) is the main component of a large number of magnetic materials. Single crystals of the latter are preferred for many practical purposes and above all, for microwave devices. Nickel ferrite melts in air at 1640° C [1], and in an oxygen atmosphere, at 1740° C [2]. In both cases the melting is accompanied by the evolution of oxygen and the formation of a wustite phase, the equilibrium oxygen pressure being 1 atm at 1300° C [3]. For this reason, the usual methods for growing single crystals from melts are not suitable for the preparation of $NiFe_2O_4$ with a composition close to the stoichiometric one. This is confirmed by experimental results obtained by flame fusion [4, 5], and zone melting [6]. Obviously, the crystals should be grown at temperatures considerably lower than the melting point. This possibility is ensured by the flux method which has been used by a number of authors [7–17] with various fluxes.

Nickel and iron possess volatile halides because of which it is possible to obtain $NiFe_2O_4$ crystals at relatively low temperatures using chemical transport reactions. In the literature there are data on the application of HCl as a carrier [18–22]. In a previous paper of one of the authors [23], the disadvantages of this transport agent were shown, and Cl_2 and $TeCl_4$ were found to be more suitable carriers. The purpose of the present paper was to determine, on the basis of thermodynamic considerations, the optimum conditions for the preparation of $NiFe_2O_4$ single crystals using $TeCl_4$ as a carrier, and to check the results experimentally.

2. Theoretical considerations

During close-spaced chemical transport of nickel ferrite with tellurium tetrachloride, the following reactions may proceed:

$$NiFe_2O_4(s) + 2TeCl_4(g) = NiCl_2(g) + 2FeCl_3(g) + 2TeO_2(g), \qquad (1)$$

$$TeCl_4(g) = TeCl_2(g) + Cl_2(g), \qquad (2)$$

$$TeO_2(g) = 0.5Te_2(g) + O_2(g), \qquad (3)$$

$$TeO_2(g) = TeO(g) + 0.5O_2(g), \qquad (4)$$

$$TeCl_2(g) = 0.5Te_2(g) + Cl_2(g), \qquad (5)$$

$$2FeCl_3(g) = Fe_2Cl_6(g). \qquad (6)$$

The equilibrium constants of these reactions can be determined using van't Hoff's isotherm

$$\lg(K_p) = -\Delta G^\circ_T/4.575T. \qquad (7)$$

For preliminary approximate calculations, the ΔG°_T values are usually obtained by means of the expression

$$\Delta G^\circ_T = \Delta H^\circ_{298} - T\Delta S^\circ_{298}. \qquad (8)$$

TABLE I Thermodynamic data of the substances participating in Reaction 1

Substance	ΔH°_{298} (kcal mol^{-1})	S°_{298} (cal mol^{-1} deg^{-1})	a (cal mol^{-1})	$b \times 10^3$ (cal mol^{-1})	$d \times 10^{-5}$ (cal mol^{-1})	Reference
$NiFe_2O_4$(s)	−254.9	30.1	36.49	18.60	−3.55	[26], [27], [28]
$TeCl_4$(g)	− 49.4	83.5	18.5	3.5	–	[29], [30]
$NiCl_2$(g)	− 15.7	70.3	13.72	1.06	−2.91	[26], [28]
$FeCl_3$(g)	− 60.5	82.243	15.0	6.0	–	[30], [31]
TeO_2(g)	− 12.4	65.3	14.5	–	–	[29]

The equilibrium constants at 1000° C (1273.2 K) calculated in this way have the following values:

$$K_{p,1} = 2.1 \times 10^4,$$

$$K_{p,2} = 93.2 \text{ [24]},$$

$$K_{p,3} = 2.03 \times 10^{-3} \text{ [24]},$$

$$K_{p,4} = 1.10 \times 10^{-6} \text{ [24]},$$

$$K_{p,5} = 2.20 \times 10^{-6} \text{ [24]},$$

$$K_{p,6} = 6.14 \times 10^{-5} \text{ [25]}.$$

In our further calculations, only Reactions 1, 2 and 3 are taken into account as the equilibrium constant values for the remaining three reactions are negligibly low.

With a view to an exact determination of the temperature dependence of the equilibrium constant, one has to know, in addition to the ΔH°_{298} and S°_{298} values of the reagents, the temperature dependence of their specific heats, which usually are of the kind

$$c_p = a + bT + d/T^2. \tag{9}$$

$\Delta G'_T$ is calculated from the expression

$$\Delta G^\circ_T = \Delta H^\circ_O - 2.303 \Delta a T \lg(T) - 0.5 \Delta b T^2 - 0.5 \Delta d T^{-1} + IT, \tag{10}$$

where ΔH°_O and I are constants. ΔH°_O can be calculated from the equation

$$\Delta H^\circ_T = \Delta H^\circ_O = \Delta a T + 0.5 \Delta b T^2 - \Delta d T^{-1} \tag{11}$$

on carrying out the corresponding substitutions for a temperature $T = 298.2$ K. Using the ΔH°_O value obtained and the other values for the same temperature, one can determine the constant I in Equation 10.

Then, the following general equation is obtained for the temperature dependence of the equilibrium constant:

$$\lg(K_p) = -\Delta H^\circ_O/4.575\,T + \Delta a \lg(T)/1.987 + \Delta b T/9.15 + \Delta d/9.15\,T^2 - I/4.575. \tag{12}$$

Using the data from Table I, one obtains for Reaction 1 the expression:

$$\log(K_{p,1}) = -42230/T - 0.387 \log(T) - 0.00137\,T + 6994/T^2 + 40.425. \tag{13}$$

The corresponding dependences for Reactions 2 and 3 have been deduced by Piekarczyk [24]:

$$\log(K_{p,2}) = -2698/T + 2.667 \log(T) - 0.000361\,T - 6560/T^2 - 3.738, \tag{14}$$

$$\log(K_{p,3}) = -7483/T - 0.931 \log(T) - 0.0000645\,T - 32780/T^2 + 7.481. \tag{15}$$

The equilibrium constants of Reactions 1, 2 and 3 expressed by the partial pressures may be written as:

$$K_{p,1} = P_{NiCl_2} P^2_{FeCl_3} P^2_{TeO_2} / P^2_{TeCl_4}, \tag{16}$$

$$K_{p,2} = P_{TeCl_2} P_{Cl_2} / P_{TeCl_4}, \tag{17}$$

$$K_{p,3} = P^{0.5}_{Te_2} P_{O_2} / P_{TeO_2}. \tag{18}$$

After taking the logarithm and making a substitution in Equation 13, 14 and 15, respectively, one obtains:

$$-42230/T - 0.387 \log(T) - 0.00137\,T + 6994/T^2 + 40.425 = \log(P_{NiCl_2}) + 2\log(P_{FeCl_3}) + 2\log(P_{TeO_2}) - 2\log(P_{TeCl_4}). \tag{19}$$

$$-2698/T + 2.667 \log(T) - 0.000361\,T - 6560/T^2 - 3.738 = \log(P_{TeCl_2}) + \log(P_{Cl_2}) - \log(P_{TeCl_4}), \tag{20}$$

$$-7483/T - 0.931 \log(T) + 0.0000645\,T - 32780/T^2 + 7.481 = 0.5 \log(P_{Te_2}) + \log(P_{O_2}) - \log(P_{TeO_2}). \tag{21}$$

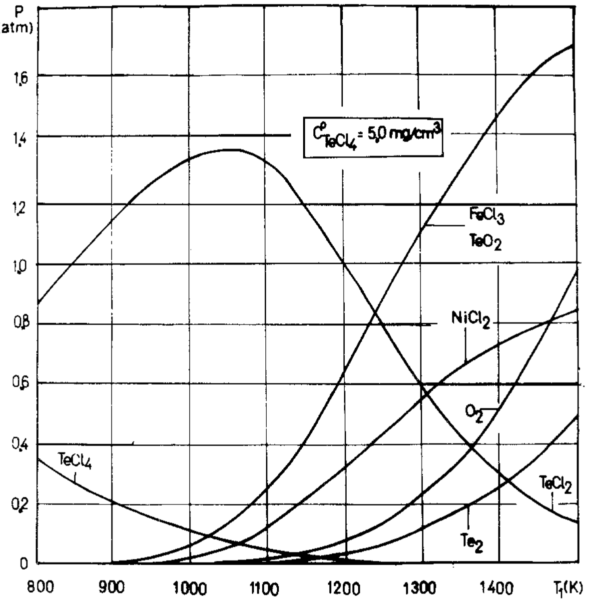

Figure 1 Partial pressures of the gaseous species as a function of temperature.

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

$$2P_{\mathrm{NiCl_2}} = P_{\mathrm{FeCl_3}}, \tag{22}$$

$$P_{\mathrm{TeCl_2}} = P_{\mathrm{Cl_2}}, \tag{23}$$

$$P_{\mathrm{FeCl_3}} = P_{\mathrm{TeO_2}}, \tag{24}$$

$$P_{\mathrm{O_2}} = 2P_{\mathrm{Te_2}}. \tag{25}$$

The material balance for the carrier $TeCl_4$ is given by the expression

$$\overset{\circ}{n}_{\mathrm{TeCl_4}} = n_{\mathrm{TeCl_4}} + n_{\mathrm{TeCl_2}} + 0.5\,n_{\mathrm{NiCl_2}} + n_{\mathrm{FeCl_3}}, \tag{26}$$

where $\overset{\circ}{n}_{\mathrm{TeCl_4}}$ is the initial number of $TeCl_4$ moles; $n_{\mathrm{TeCl_4}}$ the number of moles of unreacted $TeCl_4$; $n_{\mathrm{TeCl_2}}$, $n_{\mathrm{NiCl_2}}$ and $n_{\mathrm{FeCl_3}}$ the number of moles in $TeCl_2$, $NiCl_2$ and $FeCl_3$ obtained as a result of the dissociation of $TeCl_4$ and of the interaction of $NiFe_2O_4$ with $TeCl_4$.

Using the equation for an ideal gas, one can write this expression as

$$\overset{\circ}{n}_{\mathrm{TeCl_4}}/V = (P_{\mathrm{TeCl_4}} + P_{\mathrm{TeCl_2}} + 0.5P_{\mathrm{NiCl_2}} + P_{\mathrm{FeCl_3}})/RT. \tag{27}$$

On the multiplying both sides of this equation with $M_{\mathrm{TeCl_4}}$, one obtains

$$\overset{\circ}{n}_{\mathrm{TeCl_4}}M_{\mathrm{TeCl_4}}/V = M_{\mathrm{TeCl_4}}(P_{\mathrm{TeCl_4}} + P_{\mathrm{TeCl_2}} + 0.5P_{\mathrm{NiCl_2}} + P_{\mathrm{FeCl_3}})/RT, \tag{28}$$

or

$$C^{\circ}_{\mathrm{TeCl_4}} = 3.283(P_{\mathrm{TeCl_4}} + P_{\mathrm{TeCl_2}} + 0.5P_{\mathrm{NiCl_2}} + P_{\mathrm{FeCl_3}}), \tag{29}$$

where $C^{\circ}_{\mathrm{TeCl_4}}$ is the initial carrier concentration in g cm^{-3}.

Equations 19 to 25 and 29 form a system which can be used for determining the partial pressures of the gaseous species in the system in a range of preset temperatures and concentrations of the carrier. This system was solved by a computer for the temperature range 800 to 1500 K (in steps of 50 K) and for concentrations of $TeCl_4$ 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 pressure of the gaseous components in the transport system at an initial $TeCl_4$ concentration of 0.0050 g cm^{-3}.

The degree of conversion, α, for Reaction 1 at a given temperature and concentration of the transport agent is expressed by the ratio

$$\alpha = 0.66(P^{(T)}_{\mathrm{NiCl_2}} + P^{(T)}_{\mathrm{FeCl_3}})/P^{\circ(T)}_{\mathrm{TeCl_4}}$$

where $P^{(T)}_{\mathrm{NiCl_2}}$ and $P^{(T)}_{\mathrm{FeCl_3}}$ are the equilibrium partial pressures of $NiCl_2$ and $FeCl_3$ at a temperature T, and $P^{\circ(T)}_{\mathrm{TeCl_4}}$, the pressure of $TeCl_4$ at the same temperature when nickel ferrite is absent from the ampoule.

The values of α will be different in the two zones of the transport ampoule. When disregard-

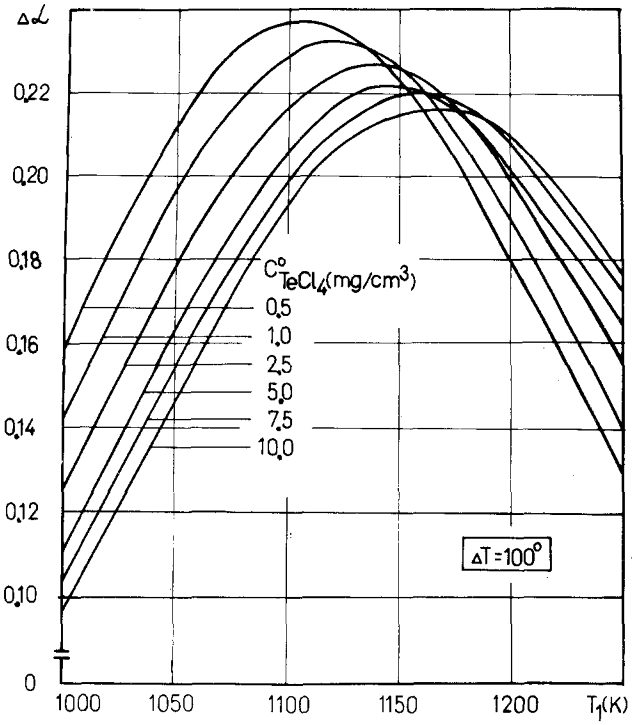

Figure 2 Plots Δα versus T_1 ($\Delta T = 100°$ C).

ing the mechanism of transfer of the gaseous products along the ampoule, one could assume that the rate of transport is, as a first approximation, proportional to the change in the degree of conversion $\Delta\alpha = \alpha(T_2) - \alpha(T_1)$.

Fig. 2 shows the curves of change in $\Delta\alpha$ depending on temperature in the crystallization zone, T_1, at a temperature gradient $\Delta T = 100°$ C and different initial carrier concentrations. The curves have a maximum which becomes flatter and is shifted towards the higher temperatures when increasing the $TeCl_4$ concentration. Hence, the crystallization should be carried out at values of T_1 close to the maximum of the curves. In this case, the changes in $\Delta\alpha$ will be negligible even with certain temperature fluctuations, i.e. the flow of substance towards the growing crystal will be practically constant, which will ensure a higher structural perfection of the crystals.

With other temperature gradients, the shape of the curves remains the same. At the same concentrations of the carrier, $\Delta\alpha$ (and the rate of transport, respectively) increases or decreases with increasing or decreasing ΔT.

From the data on the partial pressures at a given temperature gradient, ΔT, one may determine the ratio

$$\beta = \frac{(P_{\mathrm{NiCl_2}} + P_{\mathrm{FeCl_3}})^{(T_2)} - (P_{\mathrm{NiCl_2}} + P_{\mathrm{FeCl_3}})^{(T_1)}}{(P_{\mathrm{NiCl_2}} + P_{\mathrm{FeCl_3}})^{(T_1)}}$$

This ratio of the difference between the sums of the partial pressures of $NiCl_2$ and $FeCl_2$ in the source and crystallization zones of the sum of their partial pressures in the cyrstallization zone gives an indication of the supersaturation. Fig. 3 shows the dependence $\beta = f(T_1)$ for $\Delta T = 100°$C and the same concentrations of $TeCl_4$ as in Fig. 2. It is evident that at the same temperature of crystallization, the change in the supersaturation is small even with a 20-fold change in the carrier concentration. With decreasing T_1, the value of the supersaturation increases quickly at all $TeCl_4$ concentrations. Therefore, irrespective of the temperature gradient, crystallization should be carried out at higher temperatures, which, as follows from Fig. 2, are the optimum ones for higher concentrations of $TeCl_4$. The above method enables one to foretell the results for a wide range of experimental conditions.

3. Experimental

Stoichiometric amounts of Fe_2O_3 (99.99%, Koch Light) and NiO obtained by thermal dissociation of $NiC_2O_4 \cdot 2H_2O$ at 1000° C were used for the

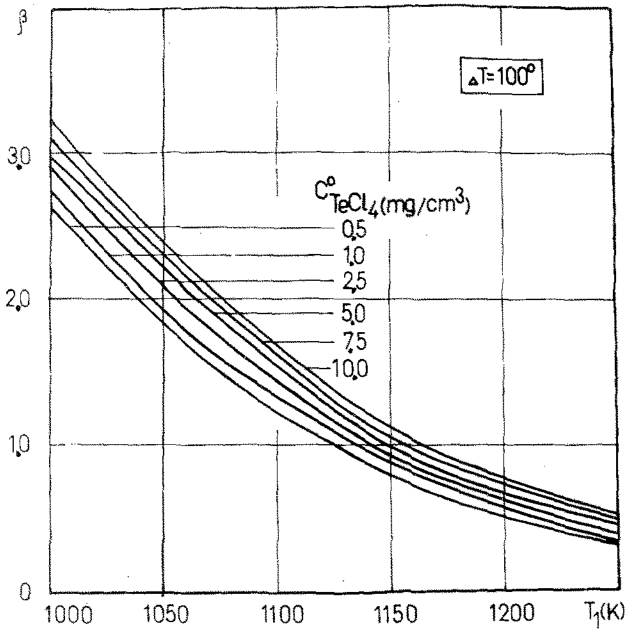

Figure 3 Plots β versus T_1 ($\Delta T = 100°$ C).

preparation of $NiFe_2O_4$ during back transport in the reaction ampoule. The chemical transport was carried out in ampoules of transparent quartz glass having 20 mm o.d. and a length of 100 mm. The carrier (laboratory reagent purity $TeCl_4$, Merck) was introduced into the system by means of thin-wall glass ampoules which were filled in a dry box.

On the basis of the above considerations, a relatively high carrier concentration, $C^{o}_{TeCl_4} = 5\,mg\,cm^{-3}$, was chosen.

The best-shaped single-crystal octahedra of nickel ferrite with maximum edge dimensions of 4 to 5 mm (Fig. 4) were obtained at $T_1 = 880°$ C (i.e., at a temperature corresponding to the maximum in Fig. 2) and $T_2 = 980°$ C. When the temperature gradient increases, the values of β increase considerably and the number of the crystals obtained becomes larger, but their size diminishes. The mean rate of transport under the optimum conditions was $9.4\,mg\,h^{-1}$.

The crystals obtained were subjected to X-ray phase and fluorescence analysis. Their Mössbauer spectrum was also taken. The X-ray analysis revealed the presence of a single spinel phase with a lattic parameter of 8.34 Å, which coincides with the data available in the literature on stoichiometric nickel ferrite. The same coincidence was found with the Mössbauer spectrum. No inclusions of other phases, in particular of hematite, were detected.

The X-ray fluorescence determinations were made with a Rigaku Denki KG-X spectrometer using a crystal analyser of LiF, a proportional counter and a tungsten tube. The crystal composition obtained was: NiO, 31.98 wt% (theoretical content, 31.87%) and Fe_2O_3, 68.02 wt% (theoretical content, 68.13%), i.e. a composition which is very close to the stoichiometric one.

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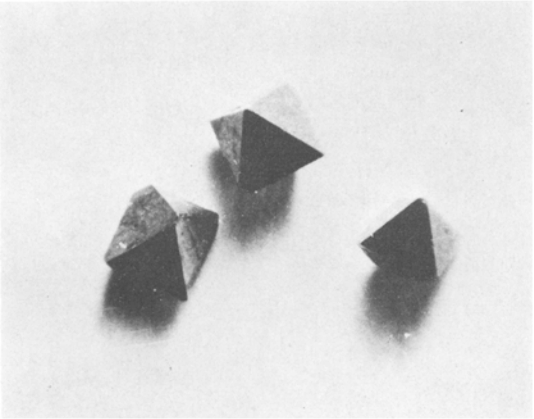

Figure 4 $NiFe_2O_4$ crystals.

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