I - Solid state reactions

The elaboration of materials requires the synthesis of solid phases from available starting chemicals (oxides, carbonates, natural ores ....) and the precise shaping in order to satisfy the material function. This procedure can be performed in one or several steps. Examples are found in the synthesis of ferrites (magnetic AB_2O_4 spinels A,B=main group transition metals; $A_3B_5O_{12}$ garnets A=Ga, rare earth, B= main group transition metals) or ferroelectric ABO_3 perovskites (A=Ba, Sr, Pb ; B=Ti, Zr).

Generally, the chemical path involves decomposition, precipitation or other reactions, in order to obtain one or several starting powders. When possible, fine grained powders must be prepared in order to increase the contacts between the grains and their reactivity. Then, the appropriate amounts of the starting phases are weighted and intimately homogenised by grinding (pollution is frequently encountered at this stage).

Shaping and mechanical strength are obtained by solid state reaction and sintering at high temperature and, eventually, under pressure. An inert container must be found, the atmosphere must be carefully controlled and the thermal treatment must be accurately applied. This last step needs the former investigation of the phase diagrams, especially when the stoechiometry and the properties, depend strongly on the partial pressure of a reacting gas (oxygen, hydrogen, frequently). It is the case of $Y_3Fe_5O_{12}$ (figure 4.b), high T_C-superconductors or $UO_{2.00}$, for example.

1. Precursor method

When the diffusion of the species is very slow, the last two steps of solid state synthesis, grinding and heating, must be repeated. Therefore, it is very convenient to find a solid precursor which allows for the formation of a few nanometer size grains. A large decrease of the reaction temperature results, together with a better control of stoechiometry. Reactivity is enhanced by the large surface/volume ratio and the favourable surface state of the grains.
Chromite or ferrite spinels are prepared at 200-300°C below the normal heating temperature :

Spinels	Precursor	Sintering temperature
$NiFe_2O_4$	$Ni_3Fe_6(CH_3COO)_{17}O_3OH$, 12 C_5H_5N	1000°C
$MnCr_2O_4$	$MnCr_2O_7$, 4 C_5H_5N	1100°C
$NiCr_2O_4$	$(NH_4)_2Ni(CrO_4)_2$, 6 H_2O	1100°C

Mineral or organic (acetate, oxalate, pyridinate...) precursors must be decomposed at low temperature (200-300°C), prior to the high temperature treatment.

2. Solid state reactions, the diffusion process

The formation mechanism of double salts was extensively studied during the last decades. Spinel or garnet ferrites, perovskites, silicates (Mg_2SiO_4, $CaSiO_3$ ...), double sulfides or halides were investigated. Their synthesis from simple salts shows that diffusion occurs between adjacent A and B solids. A first quantitative study of spinel formation was proposed by C. Wagner in 1938. The evolution of the $NiAl_2O_4$ layer thickness $\Delta\xi$ at the boundaries of NiO and Al_2O_3 (figure 5) was followed as a function of time.

Counter diffusion of the cations $(2j_{Ni^{2+}} = -3j_{Al^{3+}})$ occurs in the immobile anionic subnetwork and no oxygen uptake was observed. This mechanism, which explains that one quarter of the spinel layer forms at the $NiO/NiAl_2O_4$ interface and three quarters are formed at the other interface, was confirmed for $MgAl_2O_4$ and $MgFe_2O_4$.
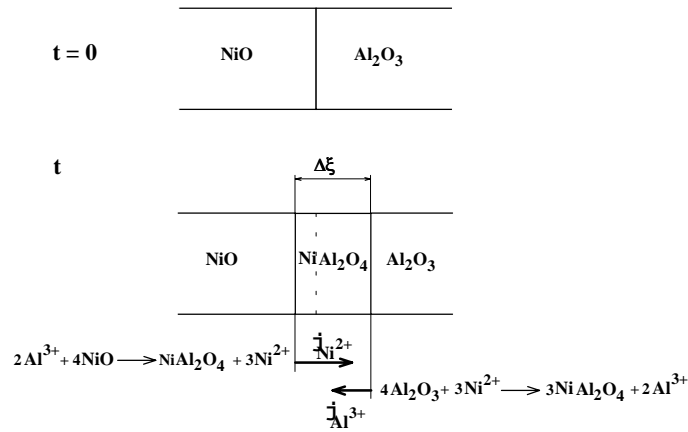
Figure 5. - Formation of NiAl$_2$O$_4$ from NiO and Al$_2$O$_3$

In this hypothesis, the limiting flux is : $j_{Ni^{2+}} = -c_{Ni^{2+}} b_{Ni^{2+}} \nabla\eta_{Ni^{2+}} = D_{Ni^{2+}} \nabla c_{Ni^{2+}}$ {4}

c, b, $\nabla\eta$, D represent respectively the concentration, the mobility, the driving force (gradient of the electrochemical potential) and the diffusion coefficient.

The reaction rate, in a first approximation, decreases linearly with $\Delta\xi$: $\dfrac{d\Delta\xi}{dt} = k\dfrac{1}{\Delta\xi}$, therefore :

$$\Delta\xi^2 = 2kt, \text{ with } k = 8\frac{\overline{D_{Ni^{2+}}D_{Al^{3+}}}}{2D_{Ni^{2+}} + 9D_{Al^{3+}}}\frac{\Delta G^0_{AB_2O_4}}{RT} .$$ {5}

The study of numerous similar oxides has shown that non stoechiometry and/or oxygen uptake interfere. Then the derivation of the reaction rate is, in fact, more complicated.

3. Sintering

Good mechanical and thermal stability, corrosion resistance must be acquired by numerous industrial items. The stoneware pottery, discussed in the introduction is one of these objects ; numerous other examples are found in ceramic industry (furnace refractory lining, roof tiling...), magnet or nuclear industry. Cold-pressed moulded powders are progressively heated at subsolidus temperatures. An increase of the apparent density, linked to the shrinkage of the object, arises. Necking occurs at the grain contacts (figure 6.a) and the pores tend to collapse (figures 6.b and 7). Simultaneously, the mean grain size increases with time in order to reach a limit which is a function of temperature. The initial grain growth kinetics, at constant temperature, is generally expressed by :

$$(\overline{\Phi}(t))^n - \overline{\Phi}_0^n = k(T)\times t = k_0\left[\exp(-\frac{Q}{RT})\right]\times t$$ {6}

$\overline{\Phi}_0$ represents the initial mean diameter and Q is the activation energy of the growth process.

Grain growth results from interface migration in order to minimise the surface energy γ ($\gamma = \left(\dfrac{\partial G}{\partial A}\right)_{T,P,\mu_i}$).
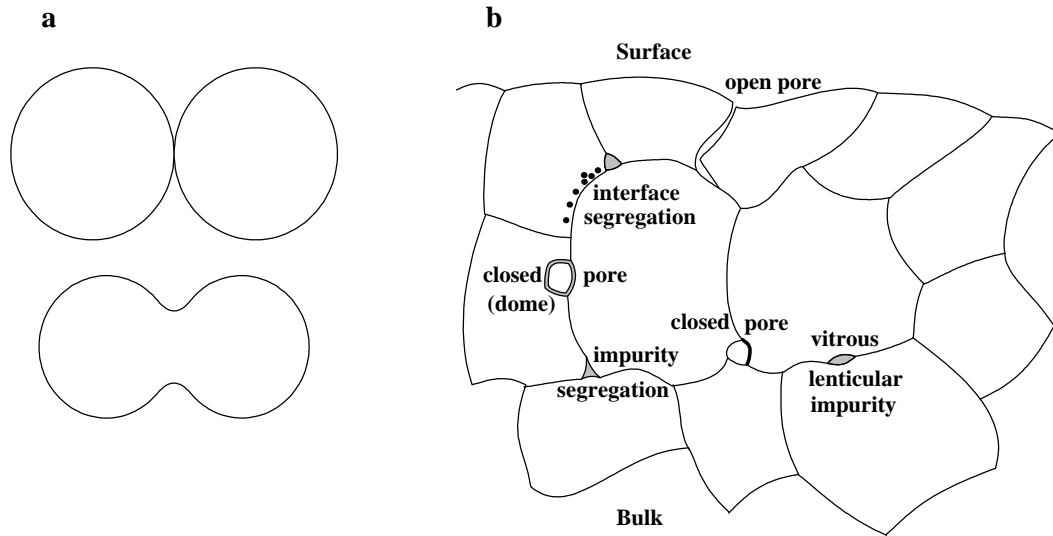
Figure 6. - Necking at grain contacts during solid state sintering (a) and crystallisation of the material (b).

The driving force F is related to the interface curvature R :

$$F = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \Omega^{\frac{2}{3}} , \qquad \{7\},$$

(Ω=molar volume, R_1,R_2 =main curvature radii) ,

and the interface displacement speed v is :

$$v = MF = \frac{D}{RT} \times F = \frac{D_0 [\exp - (Q/RT)]}{RT} \times F, \qquad \{8\} ,$$

(M=interface mobility, D=diffusion coefficient).

A strong curvature gives a large interface displacement speed.

Interface mobility is strongly influenced by the presence of impurities. Their dissolution in the grain volume (solid solution) favours the disorder and the formation of stacking faults, Schottky or Frenkel defects, which increase the interface mobility.

At the opposite, impurity segregation at the interface acts as a pinning of the interface (figure 6.b).

Within the pores, impurity segregation plays a double role :

- pore migration is favoured when a liquid (or a gas) forms at the sintering temperature. It is the case, probably, when a small amount of LiF (T_m=845 °C) is added to MgO (T_m=2800 °C). LiF volatilises during sintering at T=1400-1700 °C and leaves a non porous transparent solid. Dissolution (or evaporation) of the matrix leads to a characteristic dome like shape of the pores (figure 6.b).

- pinning of the pores occurs when the impurity gives a non soluble or non volatile solid (figure 6.b).

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The technological importance of sintering is illustrated by the $UO_{2.00}$ ceramic (figure 7) which constitutes the nuclear fuel of PWR reactors. Cylindrical pellets of $UO_{2.00}$ (T_m=2858 °C) are prepared at 1700 °C under hydrogen atmosphere during four hours. The mean grain diameter is 8-10 μm. This process leads to a solid with no open porosity and the apparent density is close to 98 % of the theoretical density. Large grain diameter and no open porosity prevents the diffusion of the fission products during the nuclear cycle, while the swelling of the ceramic ($\approx$3 %) is partly compensated by the closed porosity.
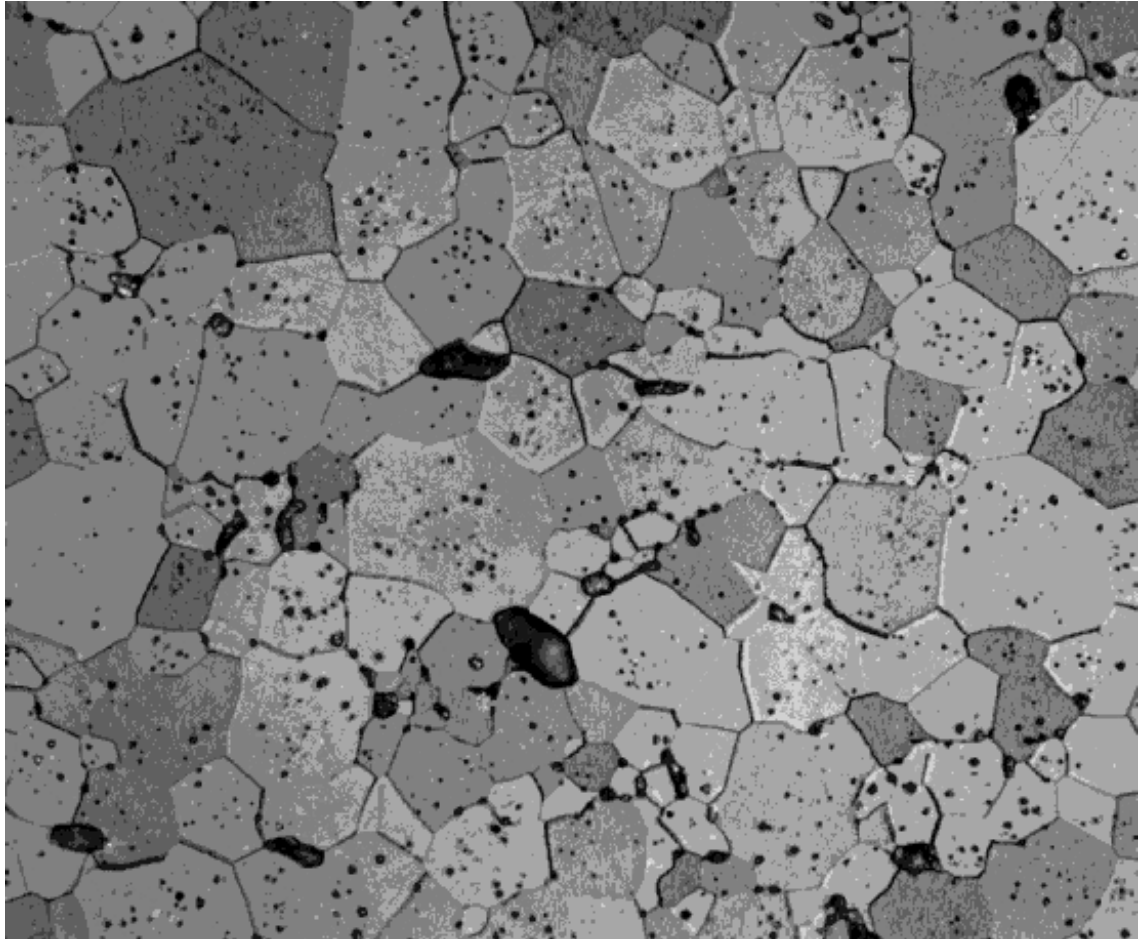
Figure 7. - UO$_{2.00}$ ceramic (1700°C, H$_2$, 4hours)
(by courtesy from P. Dehaudt, CEA Grenoble , France).