Formation kinetics study of the Tl-2223 phase in bulk samples

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Abstract. An isothermal kinetics study of the transformation of Tl−2212 into Tl−2223 has been carried out at four different temperatures. The Tl−2223 and Tl−2212 weight fraction have been deduced from Rietveld analysis of XRD patterns and the transformed fraction α has been calculated for each sample. The results indicate that the transformation is limited by diffusion and particularly by the thickening of large plates after lateral impingement.

1. Introduction
One of the more interesting copper based superconductor is the Tl2Ba2Ca2Cu3O9 (Tl−2223) phase. With an expected weak surface resistance and a critical temperature 15 K higher than the critical temperature of Tl-2212, Tl-2223 films are indeed good candidates for microwave applications. Films are generally prepared in a two step process. A precursor film with composition “Ba2Ca2Cu3O7” is first deposited on a buffered single crystal substrate and is subsequently thallinated by an ex situ treatment in either a closed or an open system. However, most authors come to the conclusion that it is very difficult to fabricate pure Tl−2223 films whereas the preparation of pure Tl-2223 ceramics is rather easy. Most of the time a mixture of Tl-2212 and Tl−2223 is obtained with small amounts of Tl-1223 when the thallium content is not kept to the required value [1].

It has been shown that the pathway for the formation of Tl−2223 implies the Tl−2212 phase according to the sequence: precursor oxides → Tl2BaO4 → Tl6Ba4O13 → Tl−2212 → Tl−2223 [2]. The difficulty mentioned above must therefore be related to the kinetics and to the mechanism of the transformation of Tl−2212 into Tl−2223. In order to identify this mechanism, we have undertaken an isothermal study of the kinetics of the transformation of Tl-2212 into Tl-2223 in bulk samples. In the following, we give the experimental procedure, a brief theoretical overview, the results and our interpretation.

2. Experimental
2.1. Sample preparation
Samples have been prepared from a mixture of Tl2O3 and pre-reacted BaCuO2 and Ca2CuO3. They have been reacted at four different temperatures, 1137K, 1144K, 1151K and 1158K, in a sealed quartz tube (p(O2) = 500 mbars at room temperature). The thallium content, sample volume, and tube volume have been defined to give only Tl-2223 at equilibrium. In order to achieve isothermal conditions, the samples in their quartz tube have been introduced in the furnace at the working temperature and, after the required time, 30 min to 2880 min, removed and cooled in air.
2.2. Sample characterisation
The weight fraction of each phase \( w_i \) in each sample has been deduced from complete Rietveld analyses of the X ray diffraction patterns collected in the \( \theta/2\theta \) mode between 3.5° and 70° (reliability factor: \( 8.0\% \leq R_{wp} \leq 12.7\% \)) with a Philips PW1150 goniometer (Cu K\( \alpha \), \( 2\theta \) step = 0.3°). The transformed fraction \( \alpha \) has been deduced with the relation: \( \alpha = w_{2223} / (w_{2223} + w_{2212}) \). The figure 1 shows the X-ray diffraction pattern of the sample treated at 1144 K for 360 min and the transformed fraction as a function of time at 1144K.

![X-ray diffraction pattern](image)

**Figure 1.** X-ray diffraction pattern of a sample treated at 1144 K for 360 min (left): calculated (full curve), observed (+ symbols), and difference (bottom), the vertical bars indicate the peak positions of (1) Tl-2212, (2) Tl-2223, (3) BaCO\(_3\) (traces), (4) (Ca,Tl\(_{1-x}\)CuO\(_z\) (< 10%); transformed fraction as a function of time for the samples treated at 1144K (right).

3. Data analysis and results

3.1. Theoretical background

Theoretical analysis of reactions in the solid state is based on mathematical models where the reaction rate \( d\alpha/dt \) is expressed as the product of a function of time \( t \) by a function of \( \alpha \) [3].

\[
\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (3.1)
\]

\[
k(T) = k_0 \exp\left(\frac{E_a}{RT}\right) \quad (3.2)
\]

\( \alpha \) is the fraction transformed from Tl–2212 to Tl–2223 defined by \( \alpha = w_{2223} / (w_{2223} + w_{2212}) \) (Fig. 1). \( k(T) \) is the temperature dependent time constant of the reaction and is given by an Arrhenius law implying the activation energy \( E_a \).

\( R \) is the perfect gas constant, \( k_0 \) a constant linked to the lattice vibrations (s\(^{-1}\)), and \( T \) the temperature.

The form of \( f(\alpha) \) gives information on the reaction limiting mechanism. The mathematical treatment of our data has been made using the integral method (equation 3.3).

When temperature is constant (isothermal method) the equation (3.3) transforms into (3.4):

\[
\int_{u_0}^{u} \frac{d\alpha}{f(u)} du = g(\alpha) = \int_{t_0}^{t} k(T) dt \quad (3.3)
\]

\[
\int_{u_0}^{u} \frac{d\alpha}{f(u)} = g(\alpha) = k(T)(t-t_0) \quad (3.4)
\]

In this expression, \( t_0 \) is time necessary for the Tl–2212 phase to be formed from the precursor oxides. In some cases, it must be considered as an adjustable parameter since its experimental determination would require the preparation of many more samples. Many kinetics models have been proposed to describe solid state reactions [4].
3.2. Results
We first worked with functions for which \( t_0 \) does not need to be adjusted and found that a second order reaction gave the best fit to our experimental data:

\[
f(\alpha) = (1-\alpha)^2 \quad \text{or} \quad \frac{\alpha}{1-\alpha} = k(t-t_0)
\]

Such a model is adapted to a large number of reactions and therefore cannot be associated to a particular mechanism. \( k(T) \) values were deduced from the plots of \( \alpha(1-\alpha) \) versus \( t \) (Fig. 2) and the related activation energy estimated to \( E_a = 980\pm127 \text{kJ/mol} \) (Eq. 3.2). This is a very high value, two times higher than the activation energy of the transformation of Bi-2212 into Bi-2223 for which the limiting mechanism is nucleation [5], and four times higher than the activation energy of the transformation from Tl-2223 into Tl-1223 [6]. Although the model is far from being satisfactory, it expresses the fact that a small increase in temperature results in a significant increase in the reaction kinetics (Fig. 2).

\[\text{Figure 2.} \quad \alpha(1-\alpha) \text{ versus } t \text{ for the four studied temperatures. The points have been shifted for clarity (500 min for 1151 K, 1000 min for 1144 K and 1500 min for 1137K).}\]

Other models where \( t_0 \) must be adjusted have been tested and the best results were obtained with the Avrami-Erofeev law:

\[1-\alpha = \exp\left(-k(t-t_0)^n\right)\]

with \( n < 1 \). This model describes reactions where the growth mechanism is limited by the diffusion of species from the initial phase to the nucleation centers. The Avrami exponent depends on both the shape of the growing particles and the time dependence of the nucleation rate. One finds 1/2 when the limiting mechanism corresponds to the thickening of large plates after lateral impingement [7].

To evaluate \( n \) from our experimental data, we performed linear fits of \( \log(-\log(1-\alpha)) \) versus \( \log(t-t_0) \) (Fig. 3), \( t_0 \) being considered as an adjustable parameter and we found \( n = 0.82 \) (1137K), 0.38 (1144K), 0.65 (1151K) and 0.79 (1158K). Considering these results, we propose that the Avrami-Erofeev law with \( n = 1/2 \), which corresponds to the growth of plate like grains in thickness after lateral impingement. This model is further supported by the fact the Tl-2223 grains indeed have the shape of large plates with their \( c \) axis parallel to the small dimension. We can deduce from these results that:

- \( \checkmark \) after nucleation, the growth of Ti-2223 grains takes place in the basal \((a,b)\) plane until lateral impingement occurs. This first step is very fast as demonstrated by the high value of the transformation rate \( d\alpha/dt \) at the early stage of the reaction.

- \( \checkmark \) then, Ti–2223 plate-like grains can only grow in thickness which is by far slower and implies the diffusion of species perpendicularly to the basal plane \( i.e. \) through planes of different nature (CuO$_2$, BaO, CaO, TIO).

The consequences for the preparation of Ti-2223 films are not straightforward. But additional informations come from other experiments on bulk ceramics. A sample prepared directly from
BaCuO₂, Ca₂CuO₃ and Tl₂O₃ at 1151 K contains about 70% in weight of Tl-2223 after a 6h treatment. However, when the starting mixture contains pre-reacted Tl-2212, CaO and CuO, no Tl-2223 can be detected in the sample after 6h at 1155 K. This means that if the Tl-2212 grains are already large, then the transformation becomes extremely slow or even does not occur. Our interpretation is the following. We believe that the nucleation of the Tl-2223 phase occurs at the edges of the Tl-2212 grains (boundaries parallel to c) so that the number of possible nucleation centers is considerably reduced after grain growth of Tl-2212. In films, the situation is even worsened by the texturing of Tl-2212 which further reduce the number of nucleation sites. In the limiting case of a well-textured Tl-2212 layer with large grains, the transformation into Tl-2223 hardly happens. This is precisely what we observe. These results and hypotheses led us to thallinate our films at higher temperature to accelerate the transformation process and therefore to avoid the grain growth and the texturing of intermediate Tl-2212. The resulting films have a higher proportion of Tl-2223 and, in some cases, are almost pure. However, the superconducting properties are poor because of partial melting.

Figure 3. Linear fits of Log(-Log(1-α)) versus Log (t-t₀) for the four studied temperatures.

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