A conductance model for kinetics studies when more than two phases are involved

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Received 4 August 2004; received in revised form 14 September 2004; accepted 17 October 2004

Abstract

A general model of electrical conductance, which takes into account the contribution of various phases encountered during a transformation, is described. The case when more than the initial and the end phases are observed during the resistance measurement is discussed. In particular, the general case reduced to the presence of three phases during the sequence of some phase formation, is considered in the light of available experimental data. The conductance model provides a relationship between the measured resistance and the fraction of the new phase formed. The shapes of the curves derived on the basis of the model are discussed in terms of the relative resistivities of the phases that might be involved in some reaction. Transformations in the Co–Si, Ni–Si, Pt–Si and the (Ti,Ta)Si 2 systems are tested and related to the model. The fractions derived by the model on the basis of the suggested method can then be used to evaluate some kinetic parameters such as the activation energy for the formation of a phase of interest. Effective activation energy can be obtained by defining the time needed at each temperature to obtain a constant resistance at a certain fraction of the new phase formed. The activation energies obtained by using the model are in good agreement with the experimental values.

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PACS: 73.61.–r; 68.55.Jk; 68.18.Jk

Keywords: Conductivity; Multiphase; Kinetics; Thin film silicides

1. Introduction

One of the easiest methods to follow the progress of a reaction between two substances or between two constituents of a material is by measuring the change in the resistance, which accompanies the reaction. Such measurements
have been used to identify some feature of the reaction, particularly the activation energy. Often a linear dependence between the resistivity and the volume fraction of an isothermally transformed material is assumed in order to relate the change in resistivity to the progress of the reaction [1–5]. In many cases however, this approach is not adequate. In a previous publication [1] a nonlinear conductance model was suggested for the use of the experimentally measured resistivity data for kinetic purposes. The validity of the conductance model was tested for the Ti–Ta–Si system and it was found to describe better the relation between measured resistivity and the fraction of the end phase formed than the linear resistivity model. Sometimes however, additional phases might be present before the end phase formation, which is dependent on experimental conditions. This, for example, might be the case in the near noble metal silicides [6–15]. It would be of interest to extend our earlier model [1] to such a case when simultaneously more than one phase is present in the system while the resistivity data are collected. It is expected that the relation between the fraction of the end phase (or the phase of interest) formed in the progress of a reaction might be related to the measured resistivity more correctly.

The purpose of this communication is to present the conductance model for the more general case than the earlier approach [1] and relate it to experimental observations. It is also suggested that resistivity measurements as a function of time and temperature should be included into the experiments designed if the aim is to get kinetic information also. Resistivity measurements is a well-established method and the change in its magnitude with anneal time can be related to the evolution of phase transformation. The applicability of the model suggested in this communication to those few cases of thin film silicides where resistivity data as a function of time and temperature are available despite the still existing controversy regarding the simultaneous presence of more than one phase. It is clear however, that the application of the model is valid for a variety of different material systems as well.

2. Comparison between the models

Let us assume that \( n \) phases are involved in a reaction such as a phase transformation and they are connected in parallel. Lien et al. [16] in their conductance model had also assumed that the silicide films are connected in parallel electrically. The conductance of each of the phases \( c_i(t) \), with concentrations \( X_i \), can be assumed to be additive according to

\[
c(t) = \sum_{i=1}^{n} c_i(t) = \frac{1}{R(t)} = \sum_{i=1}^{n} \frac{1}{R_i(t)},
\]

where \( R_i(t) \) are the resistances of the phases. If the thickness, \( t \), across the sheet is constant, the conductance of the \( i \)th phase is proportional to the area of its cross-section and therefore to its fraction according to:

\[
c_i(t) = X_i(t)c_i^*,
\]

where \( c_i^* \) is the conductance of a film consisting in its entirety of this phase. Therefore,

\[
c(t) = \sum_{i=1}^{n} X_i(t)c_i^* \quad \text{or} \quad \frac{1}{R(t)} = \sum_{i=1}^{n} \frac{X_i(t)}{R_i^*},
\]

where \( R_i^* \) is the resistance of the \( i \)th phase of the film.

For two phases, Eq. (3) is reduced to the expression [1] given by

\[
\frac{1}{R} = \frac{X}{R_f} + \frac{1 - X}{R_0},
\]

\( X, R_0 \) and \( R_f \) are the fraction of the end phase, the resistances of the original and the end phases, respectively.

In the presence of an additional phase having a concentration \( X_a(t) \), relation. Eq. (4) should be
replaced according to Eq. (3) by
\[
\frac{1}{R(t)} = \frac{X(t)}{R_f} + \frac{X_a(t)}{R_a} + \frac{1 - X(t) - X_a(t)}{R_0}.
\] (5)

If the third phase is an intermediate compound, and is absent in the beginning and at the end of the reaction, and its concentration, \(X_a\) is unknown, a simple approximation is
\[
X_a = 4X_{a,\text{max}}X(1 - X),
\] (6)

where \(X_{a,\text{max}}\) is the maximal value of \(X_a\). Let us note that since the concentration of the original phase \(X_0\) should not be negative, one obtains from \(1 - X - 4X_{a,\text{max}}X(1 - X) > 0\) for \(X_{a,\text{max}}\) the condition \(X_{a,\text{max}} \leq 1/4X\). Furthermore, since this condition should hold for all values of \(1 > X > 0\) (not only \(X = 0.5\)), one obtains that \(X_{a,\text{max}}\) should not exceed 0.25. Substituting Eq. (6) into (5) (and dropping the dependence of \(X\) on \((t)\)) one obtains:
\[
\frac{1}{R} = \frac{X}{R_f} + \frac{4X_{a,\text{max}}X(1 - X)}{R_a} + \frac{1 - X - 4X_{a,\text{max}}X(1 - X)}{R_0}.
\] (7)

The above approximation is based on an expansion of \(X_a\) in terms of a product of the original and the end phase concentrations \(X_0\) and \(X_f\), respectively, as seen in Appendix A.

It is obvious that, when the fraction is small the influence of the third term is greater when the resistances are of the same order, but with increasing \(X\), the first term becomes dominant. At intermediate concentrations the numerator of the second term is not influenced by the amount of \(X\) formed because the expression contains the term \(X(1 - X)\). The functional dependence of \(R(X)\) of Eq. (7) coincides with Eq. (4) in the following two cases: (i) \(X_{a,\text{max}} = 0\) and (ii) when \(X_{a,\text{max}} \neq 0\) but \(R_a = R_f\).

In other cases, there is a spread in the \(X\) vs. \(R(X)\) plots for different \(X_{a,\text{max}}\) values. In general the various shapes of the curves and the spread between them can be understood on the basis of Eq. (7). The influence of the numerators in Eq. (7) is associated with the fraction formed during the progress of the transformation, while relative magnitudes of the denominators of the right-hand side have a significant influence on \(1/R\). Thus,

(a) for the same value of \(X\), the first term of Eq. (7) on the right is greater than the other two terms when \(R_a\) and \(R_0\) are \(> R_f\);
(b) when \(R_a\) and \(R_0\) are considerably \(< R_f\), the contribution of the second and third terms are not negligible and affect the spread of the curves. However, the extent of the spread in the plots due to the influence of the additional phase present in the system is truly large for small \(R_a\) relative to the values of \(R_0\) and \(R_f\). Otherwise, the two-phase approximation [1] can be used. Furthermore, the plots are convex when \(R_0 < R_f\) and they are concave otherwise.

3. Evaluation of the model and its application for kinetic studies

It is rather problematic to choose a test case for the model presented above. Two main reasons could be noted:

(a) The literature contains contradictory statements about the growth kinetics of thin film silicides and the simultaneous growth of phases is still a controversial problem. All the three near-noble silicides considered below, fall into this category of controversy, see for example, Refs. [9,12–23].
(b) The required parameters, i.e. resistivity measurements as a function of time and temperature to test the model, are not readily available.

The ideal case to study kinetics of some phase formation by the method described above would be in systems where no controversy exists regarding the simultaneous multiphase formation and their presence in the binary system such as bulk diffusion couples [24–29]. However, the required parameters of resistivity measurements were not performed in these works. The majority of investigations up to now were carried out using diffusion couples in which one of the components is limited in material supply, i.e. usually thin films. In thin film diffusion couples the phases present in the equilibrium phase-diagram are seldom
observed and only a limited number of them can be practically seen. In such experiments it is generally observed that only one phase grows at a time, and the appearance of a new phase is accompanied by the disappearance of another. This is not always the case when kinetic or other restrictions disturb the progress of a reaction. In some cases even three phases might be present, i.e. the initially as-deposited film and one or two intermediate compounds [18,30,31]. The second intermediate compound may be present before the consumption of the initial phase; it can be the phase of interest but not necessarily the end phase. Various experimental parameters can dictate the outcome of the experimental results, among these, the condition of the interfaces at the beginning of the reaction, the relative thickness of the components of the system, the presence of native oxide and in general impurity effects, the magnitude of the diffusion coefficients involved in the reaction, to mention some. Crystalline or amorphous structure of the components, which participate in the solid-state reaction, can be a decisive factor influencing the sequence of phase growth and their number present. Consequently, the results might be in variation with the expected phase sequence formation and the number of coexisting phases at some temperature. These are a reflection of the experimental conditions. Actual device fabrication occurs under conditions not necessarily the same as the careful study of ideal cases for fundamental purposes, and therefore, it might be of interest to get information from measurements relevant to the production environment and apply them for these practical cases. Testing the model is done with the available information from measurements relevant to the experimental environment, while being aware of the mentioned shortcoming and controversy.

3.1. Testing the model for a few cases

Of particular interest in thin film applications are the silicides. The theoretical model and the restrictions on the shape of the plots are tested with experimental data from the literature in the following:

Figs. 1–4 are graphical illustrations of the function expressed by Eq. (7). It takes into account the presence of an additional phase, which precedes some subsequent phase formation (not necessarily the end phase). The choice of the systems was based on the availability
of experimental data for testing the applicability of
the model (although resistivity measurements are
routinely performed in laboratories the $R$ vs. $t$
data at various temperatures required by Eq. (7)
are not readily found). Furthermore, it was required
to use data from systems where layer by layer growth
parallel to the surface occurs which is explicit in
the model. Three values were arbitrarily chosen for
$X_{a,\text{max}}$ to see the effect of the amount of a third
phase on the conductivity plots. The values are
$X_{a,\text{max}} = 0, 0.1$ and 0.2. When $X_{a,\text{max}} = 0$, Eq. (7)
reduces to expression (4) as noted in the previous
section. The resistivity values used in Eq. (7) to
express the relation between the fraction of a phase
formed during the silicidation reaction are:

(a) In the Co–Si system for the formation of the
final CoSi$_2$ phase during the process: $R_0 = 3.0\, \Omega/\Box$, $R_a = 13.5\, \Omega/\Box$ and $R_f = 0.9\, \Omega/\Box$
are the data used [17]. Here $R_0$ is the sheet
resistance of the initial phase, $R_a$ is related to
the intermediate CoSi and $R_f$ is the resistivity
of the CoSi$_2$ end phase. These values were
obtained by re-expressing the sheet resistance
ratios in terms of actual sheet resistance.
Tabasky [21] has found similar sheet resistance
values. The results in Ref. [22] show that Co$_2$Si
the first phase formed exists in a very narrow
temperature range during RTA, and at 850 K
it was observed that Co$_2$Si and CoSi formed
simultaneously. At 923 K it was found by
XRD that even after $\sim65$ s the 3 phases coexist.
Formation of CoSi$_2$ at 1223 K occurs in
such a fast time by RTA that any detection
of Co$_2$Si or Co could not be observed. In bulk
Co/Si diffusion couples simultaneous growth
of all three phases were observed [28,29] at
temperatures up to 1323 K. Refs. [28,29]
discuss the absence of some phases in thin film
couples compared to bulk ones, and the
deficiency in supply of materials during the
reaction of phase formation is one of the
reasons. Also, it is clear that the amount of a
particular phase of the system might be too
small to be detected experimentally but its
effect can be observed by its contribution to
resistivity.

(b) The values for the Ni–Si system were taken
from Lien et al. [16] and are given as
$R_0 = 24\, \mu\Omega\, \text{cm (Ni}_2\text{Si)}$, $R_a = 14\, \mu\Omega\, \text{cm (NiSi)}$
and $R_f = 34\, \mu\Omega\, \text{cm (NiSi}_2)$.

(c) The sheet resistance data for Pt–Si are [18]:
$R_0 = 3.23\, \Omega/\Box$, $R_a = 4.22\, \Omega/\Box$ and $R_f = 2.83$
$\Omega/\Box$. Here, $R_0$ refers to the as deposited Pt
film; \( R_a \) and \( R_f \) are the crystallized \( Pt_{12}Si_5 \) and the \( Pt_2Si \) phases, respectively. According to Tsui [18], \( Pt_{12}Si_5 \) is the first phase to form from as deposited Pt reaction with Si when the films are thin. The normalized sheet resistance–time relation data of Fig. 1 in Ref. 18 were converted to sheet resistance values. Normalized sheet resistance data (normalized with that of the as-deposited value) are given as a function of time for temperatures in the range of 453–573 K. In the first stage of the graph, the increase is explained by the formation of \( Pt_{12}Si_5 \), and the low sheet resistance point at the second stage where there is a decrease of the sheet resistance, is associated with \( Pt_2Si \). For the use of Eq. (7) it would be advisable to have the corresponding data as sheet resistances. Naem [19] indicates an as-deposited sheet resistance value of Pt as 3.1 \( \Omega/\square \). This value was used to scale the sheet resistance data of Tsui [18], and thus convert the normalized values to actual sheet resistance.

(d) For the construction of the plot of Fig. 4 for \( (Ti, Ta)Si_2 \) the data of Ref. [32] were used. The sheet resistance values are: \( R_0 = 13.7 \Omega/\square \), \( R_a = 17.7 \Omega/\square \) [34] and \( R_f = 2.23 \Omega/\square \). Here the value of \( R_a \) refers to \( Ti_5Si_3 \) and was estimated following Ref. [33] on the basis of the work of Murrarka and Fraser [34]. Although in Ref. [32] more than one additional phase is present, the use \( Ti_5Si_3 \) only was based on two assumptions, namely: (a) \( Ti_5Si_3 \) and \( Ta_5Si_3 \) has almost the same properties and on the basis of the XRD diffraction cards is difficult to distinguish between them [35–36]. This was indicated in Ref. [32] also, and (b) current flows through the most conductive phase, and thus the very small amount of \( C54TiS_2 \) was considered as equivalent to the final phase of \( (Ti, Ta)Si_2 \) regarding its current carrying capacity.

The shapes of the curves depend on the resistivity values of the phases involved in accordance with the conclusions of the analysis given at the end of the previous section as follows: The curve of Fig. 1 for the Co–Si system is concave as predicted for \( R_0 > R_f \). When \( R_0 < R_f \) the curve is convex as seen in Fig. 2 for the Ni–Si system. The shape of the Pt–Si system is also convex but with an opposite orientation to that of the Ni–Si case. The extent of the spread between the individual curves for different values of \( X_{a,max} \) is appreciable only in the Ni–Si case where \( R_a \) is much smaller than both, \( R_0 \) and \( R_f \). Furthermore, for the same value of \( R_a \) if \( R_f > R_0 \) but their values are reasonably close to each other the shape of the lines is convex as mentioned, but the spread between the lines is very large. When \( R_a ~ R_0 \) the lines almost coincide. \( R_a \) affects directly the spread between the lines, and for the same values of \( R_0 \) and \( R_f \) if its magnitude is smaller, the spread is appreciable (i.e., when the resistivity of \( R_a \) is low compared to the resistivities of \( R_0 \) and \( R_f \)). The lower the value of \( R_a \) the greater is the spread between the lines.

Figs. 1–4 show some of the above aspects: Fig. 1 illustrates the case where the separation between the lines is the smallest since \( R_0 \) or \( R_a > R_f \). Fig. 2 represents the case where \( R_a ~ R_f \) and the separation of the lines is significant. Fig. 3 illustrates the situation when the lines are with small separation between them, since \( R_f > R_0 \) or \( R_a \). In Fig. 4 no separation at all exists between the lines. It differs from Fig. 1 by the fact that the assigned value of \( R_a \) is greater by \( \sim 24\% \) than the respective value in the Co–Si system (Fig. 1). Also the value of \( R_0 \) is substantially larger than \( R_f \). Basically, the difference in the shape of the lines, the separation distance between them and their orientation, depend on the relative magnitudes of the respective resistivity values. In these graphs the resistivities (or sheet resistance) at \( X=0.5 \) are also shown and compared with the value obtained in the linear model.

The effect of \( X_{a,max} \) of the second term of Eq. (7) and its contribution to the spacing between the lines can be understood on the following physical grounds. The current carrying capacity of a phase is associated with its conductivity. The phase having the highest conductivity is dominating the system, since preferential current passage in the system occurs through that phase. Only negligible current can flow through a high resistivity phase. The final phase often forms in the presence of another phase. In the metal silicon systems, in many instances a high resistive, Si lean silicide,
precedes the end phase and its current carrying capacity is negligible compared to the highly conductive component. In such cases the amount of the higher resistive phase (its presence is expressed through $X_{a,\text{max}}$) does not effect significantly the separation of the lines even at a 0.5 fraction transformed level. Irrespective to the fraction of this phase, current will flow preferentially through the highly conductive phase compared to the high resistive material. It is thus expected that the lines might even coincide (Fig. 4), or having a negligibly small separation. One can on the basis of the resistivity values given in the literature predict qualitatively if the presence of a phase before the end phase formation is expected to have a minor or a significant contribution to the overall resistivity. If its contribution is small, as mentioned above, one might use the simpler conductivity model for the case when only two phases, the initial and the end phases are present in the system [1].

3.2. The use of the model for kinetic studies

Any of the above figures can be used to evaluate apparent activation energy, $E_{\text{app}}$, by evaluating a volume fraction of a phase formed according to the model suggested. The temperature dependence of the rate of a phase formation can be obtained by defining a time constant $\tau$, at which some fraction of the phase under consideration is obtained. Usually, $X(\tau) = \frac{1}{2}$ is chosen for this relation according to

$$\ln(\tau_{0.5}) = E_{\text{app}}/kT + \text{constant.} \quad (8)$$

In order to determine the time constant $\tau_{0.5}$, the change in resistivity with time at various temperatures is needed. The ratio of sheet resistance plots of isothermally annealed Co–Si specimens from Fig. 6 of Ref. [17] were converted to sheet resistance to construct resistance vs. time curves shown in Fig. 1. The spread between the lines in terms of the sheet resistance representing the three values of $X_{a,\text{max}}$ is relatively small. The distance between the lines relative to the linear graph is however, significant (a difference of ~26%). Since the lines were sufficiently close to each other an average value of $1.44 \, \Omega/\Box$ for $X(\tau) = \frac{1}{2}$ was used.

This value had to be converted back to its equivalent in terms of sheet resistance ratio, i.e., 0.48, to read of the appropriate time values at the temperatures shown in Fig. 6 of Ref. [17]. Fig. 5 is a graph obtained for the Arrhenius relation resulting in an activation energy of 2.11 eV for the formation of CoSi$_2$. The activation energy listed for the growth of CoSi$_2$ is 2.3 eV [37].

The next example, the Ni–Si system, shows a different feature of the $X$ vs. $R$ relation. This can be seen in Fig. 2. The lines are convex since the resistivity of Ni$_2$Si (the initial phase) is smaller than the end phase. An additional feature should be noted which is related to the contribution of the amount, $X_{a,\text{max}}$, to the spread of the curves. The larger is the value of $X_{a,\text{max}}$, the further away (apart) is the line from the plot representing the linear model. In the line labeled by F, $X_{a,\text{max}} = 0.2$. When $X_{a,\text{max}} = 0$ (line I), the graph practically coincides with the linear model of $X$ vs. $R$. Thus, the contribution of $X_{a,\text{max}}$ depends only on the relative values of the initial and final phases compared to the intermediate phase between them. In the Ni–Si system, NiSi is the most conductive phase with resistivity differences of 141% and 71% from the initial and the end phases, respectively. Despite the extensive studies of the phase sequence for Ni/Si reactions and the kinetics of Ni$_2$Si and NiSi formation, no $R$ vs. $t$ data at various temperatures (useful directly to test the model in
this case), are known to exist by the authors. The activation energy for NiSi$_2$ formation could not be evaluated.

In this system the phases are formed sequentially with increase in temperature as follows: Ni$_2$Si, NiSi and NiSi$_2$. However, NiSi does not form until all the Ni has been converted to Ni$_2$Si and similarly NiSi$_2$ does not form until all the Ni$_2$Si has been converted to NiSi. Only two phases can be present at any time [12]. The literature contains contradictory statements about the growth kinetics of NiSi or the other near-noble metal silicides. For example, Föll et al. on the basis of transmission electron microscopy [9] indicate that: “it is a basic finding that at 673 K Ni$_2$Si and NiSi are present. The layered structure of the silicide at 673 K is very clear. On Si (1 1 1) the layered structure is seen at 573 K and it is reminiscent of the 673 K case in Si (1 0 0)”. Colgan, however states [38] that typically Ni$_2$Si forms initially and after all the Ni is consumed by the formation of Ni$_2$Si, Ni Si is subsequently formed. Many examples could be quoted to show differences in the observations recorded. In the view of the authors in most of the reported cases these are apparent differences, reflecting the difference in experimental conditions and they come to manifest the importance of the experimental conditions. For all those cases where, for different reasons whatever they might be, two phases are simultaneously present in parallel, the model suggested in this communication is applicable.

An additional case where our conductance model provides kinetic information is the Pt–Si system [18]. The initial phase was Pt, followed by Pt + Si reaction to form Pt$_{12}$Si$_5$ before Pt$_2$Si or the end phase PtSi are produced. Fig. 3 illustrates the curves according to Eq. (7) for three values of $X_{a,\text{max}}$, and for comparison the linear relation between $X$ and the sheet resistance is also shown. As can be seen, the lines are convex since $R_f < R_0$ and the spread between them in terms of sheet resistance representing the three values of $X_{a,\text{max}}$ is relatively small since $R_S$ is almost of the same magnitude as $R_0$. The resistance values in the Pt–Si system are not too different but the value of $R_f$ (i.e., in this case that of Pt$_2$Si) is the lowest. Therefore, a contribution to the conductivity of each phase is expected, but the current is carried mainly through the Pt$_2$Si phase. Fig. 6 shows the Arrhenius relation according to Eq. (8). To obtain the fraction at 50% transformation the sheet resistance data from Fig. 3, corresponding to $X(\tau) = \frac{1}{2}$, were converted back to the normalized values indicated in Fig. 1 of Ref. [18] to get the respective $\tau_{0.5}$ times. The activation energy derived from the slopes of the lines in Fig. 6 are 1.84 and 1.48 eV. To obtain the time data at four temperatures [18], extrapolation of the $R_S$ vs. $t$ line at 498 K had to be used to the required resistance value corresponding to $X(\tau) = \frac{1}{2}$. The three point Arrhenius curve was derived without the need for extrapolation, and therefore, we believe, that the 1.48 eV activation energy is preferred. The activation energy results reported for the growth of Pt$_2$Si span a range of 1.04–1.6 eV [37]. There are three 1.3 eV values [15,39,40] and one 1.4 eV [41], but the closest activation energies with our 1.48 eV are 1.5 and 1.6 eV in Refs. [13,42], respectively. Non of the techniques used for evaluating the activation energies was by resistivity measurement and the very good agreement between the reported and the evaluated values by our method, provides credibility to the model.

The activation energy of (Ti,Ta)Si$_2$ formation determined on the basis of the above model is 2.6 eV. The Arrhenius plot constructed from the
The resistivity data summarized in Fig. 4 is shown in Fig. 7. In the simple two-phase conductivity model [1] the same activation energy was obtained, i.e., 2.55 eV. This should not be surprising, since in Fig. 4 the lines completely coincide. Nevertheless, the line of Fig. 7 is more well-defined than a similar curve in Ref. [1] and the concept of considering the additional phase present is physically also more correct. Furthermore, the experimental points of the fraction transformed vs. sheet resistance in Fig. 1 of [1] has a large scatter along the theoretical curve. However, as indicated earlier the contribution of $R_a$ is negligible when its value relative to $R_f$ is large and the two-phase approximation [1] can be used.

The major error in the evaluation of activation energies originates from the method to evaluate the variation of $R$ vs. $t$ data from the respective plots published in the literature.

4. Conclusion

A simple conductivity model is suggested to describe the resistivity changes occurring during the transformation in thin film reactions. The model is applicable when more than the initial and end phases are present in a system assuming parallel growth of the layers. The model was tested with experimental results observed during a silicidation process in noble metal–silicon systems. The main points of the model can be summarized as follows:

(a) The contribution of a third phase present in a system was taken into account in the model suggested. Thus for example in the Ni–Si system, two phases the Ni$_2$Si and NiSi, were observed simultaneously after heat treatment at some temperature interval for some time while the resistivity data were measured (at room temperature). Similarly in the Co–Si system, for example, Co$_2$Si and CoSi start to form simultaneously and only when all the Co$_2$Si is consumed to form CoSi, CoSi$_2$ starts to form.

(b) Even when simpler models such as the linear resistivity or the conductivity model [1] are used for kinetic purposes, the application of the more general model is physically more appropriate, since the contribution of each phase is taken into account.

(c) The progress of a phase formation can be related to the change in the resistivity in a system by measuring the appropriate resistivity values at various temperatures and for various times. Evaluating a volume fraction according to one of the models suggested can then be applied for kinetic purposes, for example to evaluate the activation energy of a phase formed.

Acknowledgments

The authors would like to thank Mrs. A. Pelleg for proofreading the manuscript.

Appendix A

The approximation of Eq. (6) is based on an expansion of $X_a$ in terms of a product of the original and the end phase concentrations $X_0$ and $X_f$, respectively.

Since the additional phase of concentration $X_a$ is absent in the system in the beginning and at the
end of the reaction, a simplified approximation for the expansion could be
\[ X_a = X_0 + \frac{dX_a}{dX_0} \bigg|_{X_0=0} X_0 + \cdots \approx K_0 X_0 \quad (A.1) \]
and
\[ X_a = X_f + \frac{dX_a}{dX_f} \bigg|_{X_f=0} X_f + \cdots \approx K_f X_f, \quad (A.2) \]
where \( K_0 \) and \( K_f \) are coefficients relevant to the two conditions in the system, the initial and the final stages of the reaction, respectively. By an additional assumption of the symmetry with respect to the original and the end phases, \( K_0 = K_f = K \) the two equations can be combined as
\[ X_a = K X_0 X_f = K X_0(1 - X_0) = KX(1 - X). \quad (A.3) \]
It can be seen that this equation holds for the case when \( X \sim 0 \) or when \( X \sim 1 \) with respect to the additional phase. Since the above equation provides a maximal concentration of the additional phase, \( X_{a,\text{max}} = 0.25 K \) at \( X = 0.5 \), the relation given below is obtained
\[ X_a = 4X_{a,\text{max}}X(1 - X). \quad (A.4) \]
This is a simplified approximation which can be applied if the concentration \( X_a \) is unknown. This corresponds to Eq. (6).

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