The approximate calculation of the MgO rich corner of the $MgO-Al_2O_3-CaO-SiO_2$ phase diagram by ESTPHAD method

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Abstract
The ESTPHAD (Estimation of Phase Diagrams) thermodynamically based phase diagram calculation method was developed by us in the University of Miskolc. The paper shows the writing up by ESTPHAD method of the MgO rich corner of the binary, ternary and quaternary phase diagrams of the $MgO-Al_2O_3-CaO-SiO_2$ oxide system. The differences between the calculated data and data from literature are less than 1% of the liquidus temperature values, which is near equal to the measurement error of the high temperature measuring.
Keywords: equilibrium phase diagram calculation, ESTPHAD method, oxide system

1. Introduction

In case of ceramic industries it is very important to know the liquidus temperature of multicomponent oxide system. By using of the ESTPHAD method the liquidus and solidus curves (binary systemí) or surfaces (multicomponent system) of the equilibrium phase diagrams can be calculated by simple equations. The ESTPHAD method has thermodynamic based equations and hierarchical structure. Used to the hierarchical structure, it is possible to approach the ternary liquidus surface (in case of high MgO concentration) on the basis of the binary phase diagrams even if the ternary system is not known. For the calculations we can use measured or calculated data from literature and with regression analysis we can determine easily the constants of the equations.

2. Calculation of liquidus temperature

The equation used in ESTPHAD method (Eq. 1) is based on thermodynamic principles. In equilibrium the partial molar free energy of the phases being in equilibrium are equal. After a long deduction [1,2], the liquidus temperature can be calculated as follows in case of binary A-B system:

$$T_L = \frac{T_0}{1+\sum_{i=1}^{\infty} A(i:0:0)(c_B)^i} = \frac{T_0}{1+F_{AB}(c_B)} \quad (1)$$

Where: T_0 melting point of pure element (K), c_B liquid phase concentration (wt%), A(i:0:0), *A(0:j:0) and A(0:0:k)* calculated coefficients, $F_{AB}(c_B)$ polynome which belongs to liquidus concentration.

The ESTPHAD algorythm has hierarchical structur, which means that we are able to use the calculated polynomes of binary systems (created in case of A-B and A-C systems) to approximate the ternary A-B-C liquidus temperature. The results would be more precise used the ΔF_{ABC} function determined from the measured or calculated ternary equilibrium phase diagram *(Eq.2.)*.

$$T_L = \frac{T_0}{1+F_{AB}(c_B)+F_{AC}(c_C)+\Delta F_{ABC}(c_B;c_C)} \quad (2)$$

The ΔF_{ABC} function includes mixed products of the concentrations of the components with sufficient powers:

$$\Delta F_{ABC}(c) = A(1;1;0)\cdot(c_B)\cdot(c_C) + A(2;1;0)\cdot(c_B)^2\cdot(c_C) + A(1;2;0)\cdot(c_B)\cdot(c_C)^2 + \ldots$$

$$= \sum_{i,j=1-\ldots} A(i;j)\cdot(c_B)^i\cdot(c_C)^j \quad (3)$$

The calculation of the liquidus temperature of quaternary system and the FABCD function can be set up by the aforementioned hierarchical way (Eq.4, Eq.5):

$$T_L = \frac{T_0}{1+F_{AB}+F_{AC}+F_{AD}+\Delta F_{ABC}+\Delta F_{ABD}+\Delta F_{ACD}+\Delta F_{ABCD}(c_B;c_C;c_D)} \quad (4)$$

$$\Delta F_{ABCD}(c) = A(1;1;1)\cdot(c_B)\cdot(c_C)\cdot(c_D) + A(2;1;1)\cdot(c_B)^2\cdot(c_C)\cdot(c_D) + \ldots =$$

$$= \sum_{i,j,k=1-\ldots} A(i;j;k)\cdot(c_E)^i\cdot(c_C)^j\cdot(c_D)^k \quad (5)$$

3. Results

The liquidus curves of the binary phase diagrams can be calculated with ±5 K variances (which is less than 0,3% of the liquidus temperature) by the ESTPHAD method. Due to the hierarchical structure of the ESTPHAD method, the liquidus surfaces of the ternary phase diagrams can be approximate with ±25 K difference (less than 1%), the quaternary liquidus temperature (above 80 wt% MgO content) ±25 K difference (less than 1%). On the following figures can be found the digitalized (which were used as base data for our calculations) and calculated liquidus curves and surfaces.

By using our equations and the following calculated coefficients (Table 1. to 3.) the liquidus temperature can be calculated easily. The T_0 initial value in Eq. (1) to (4) is equal to 3083 K.

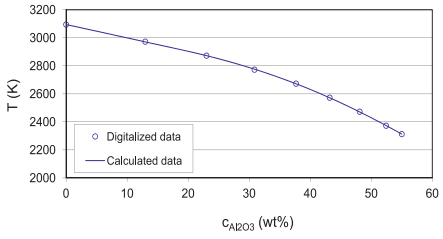

Fig. 1. The digitalized [4] and calculated liquidus curves of MgO phase in case of MgO-Al_2O_3 phase diagram
1. ábra Az MgO fázis digitalizált [4] és számított likvidusz vonala MgO-Al_2O_3 fázisdiagramban

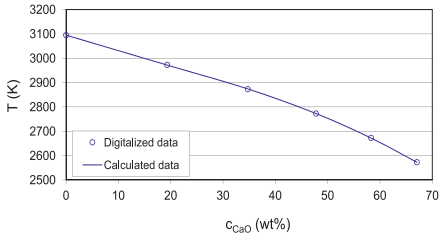

Fig. 2. The digitalized and calculated liquidus curves of MgO phase in case of MgO-CaO phase diagram [4].
2. ábra Az MgO fázis digitalizált és számított likvidusz vonala MgO-CaO fázisdiagramban [4]

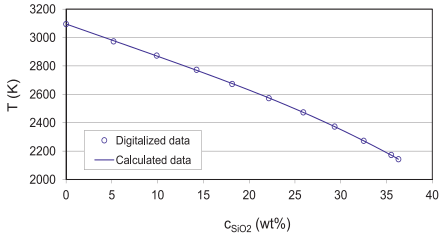

Fig. 3. The digitalized and calculated liquidus curves of MgO phase in case of MgO-SiO_2 phase diagram [3].
3. ábra Az MgO fázis digitalizált és számított likvidusz vonala MgO-SiO_2 fázisdiagramban [3]

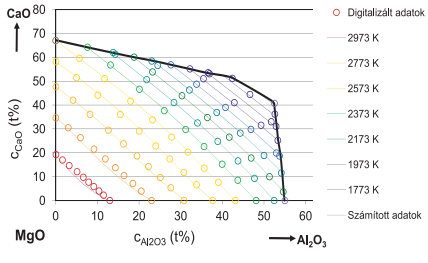

Fig. 4. The digitalized and calculated liquidus surface of MgO phase in case of MgO-Al_2O_3-CaO phase diagram [4].
4. ábra Az MgO fázis digitalizált és számított likvidusz felülete MgO-Al_2O_3-CaO fázisdiagramban [4]

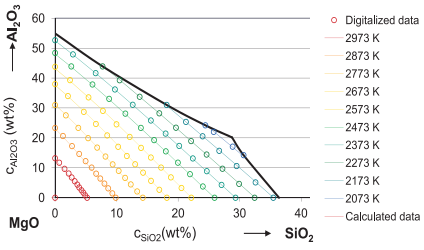

Fig. 5. The digitalized and calculated liquidus surface of MgO phase in case of MgO-Al_2O_3-SiO_2 phase diagram [3].
5. ábra Az MgO fázis digitalizált és számított likvidusz felülete MgO-Al_2O_3-SiO_2 fázisdiagramban [3]

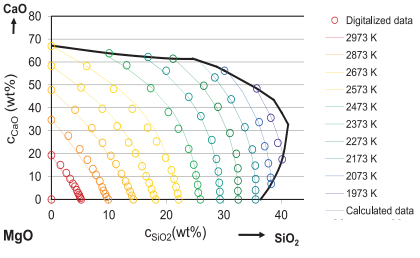

Fig. 6. The digitalized and calculated liquidus surface of MgO phase in case of MgO-CaO-SiO_2 phase diagram [3].
6. ábra Az MgO fázis digitalizált és számított likvidusz felülete MgO-CaO-SiO_2 fázisdiagramban [3]

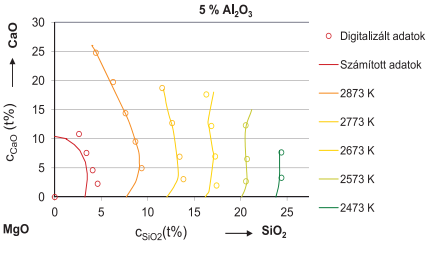

Fig. 7. The digitalized and calculated liquidus surface of MgO phase in case of MgO-CaO-SiO_2 phase diagram and 5% Al_2O_3 section of quaternary system [3].
7. ábra Az MgO fázis digitalizált és számított likvidusz felülete MgO-CaO-SiO_2 fázisdiagramban és a négyfázisú rendszer 5% Al_2O_3 metszete [3]

4. Conclusion

By using the ESTPHAD method we calculated the liquidus temperature of binary, ternary and quaternary systems with a sufficient precision. The differences between the calculated data and data from literature are less than 1%, which is near equal to the measurement error of the high temperature measuring.

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A MgO-Al_2O_3-CaO-SiO_2 fázisdiagram MgO-ban dús sarkának közelítő számítása ESTPHAD módszerrel

A kerámiaipari vállalatok számára rendkívül fontos a többalkotós oxid-rendszerek likvidusz hőmérsékletének minél pontosabb ismerete. Az ESTPHAD (Estimation of Phase Diagrams – Fázisdiagramok közelítő számítása) módszerrel két- és többalkotós rendszerek (legyen szó fémes vagy oxid) fázisainak likvidusz hőmérséklete számítható egy egyszerű egyenlet felhasználásával. Az ESTPHAD algoritmusát termodinamikai egyenletekből levezetve hierarchikus módon építettük fel annak érdekében, hogy többalkotós rendszerek számítására is lehetőség nyíljon. A számítások során szakirodalomból származó egyensúlyi fázisdiagramokat használtunk és regressziós analízissel határoztuk meg az ESTPHAD egyenlet paramétereit.
Kulcsszavak: egyensúlyi fázisdiagram számítás, ESTPHAD módszer, oxid-rendszer