Simulation of Immiscibility Regions in Sodium Borosilicate Glasses

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Abstract—In this paper, sodium borosilicates glasses were prepared by melting in air. These heat-resistant transparent glasses have subjected subsequently isothermal treatments at different times, which have transformed them at opaque glass (milky white color). Such changes indicate that these glasses showed clearly phase separation (immiscibility). The immiscibility region in a sodium borosilicate ternary system was determined according to the compositions which have transformed them at opaque glass (milky white color). The immiscibility region in sodium borosilicate ternary system was determined according to the compositions can show phase separation.

II. EXPERIMENTAL AND NUMERICAL STUDY

A. Preparation of Studied Glasses

Sodium borosilicates glasses (SBN) were prepared of which the chemical composition represented in Table I. These glasses were worked out by fusion with the air. These heat-resistant transparent glasses underwent thereafter isothermic treatments various temperatures and time, this transformed them into opaque glasses (milky white colors as represented in the Fig. 1. [5], [6]. Such transformations indicate that these glasses presented separations of quite clear phases (immiscibility). The separation of the phases in glasses is a well-known thermodynamic phenomenon in the systems borosilicate of sodium (SiO2-B2O3-Na2O) and which can be of very important industrial interest which is the manufacture of glasses of the type Vycor® [1].

TABLE I

| Chemical Compositions of Studied Glasses (SBN) |
|-----------------|-----------------|-----------------|
| SiO2 (%wt)      | B2O3 (%wt)      | Na2O (%wt)      |
| SiO2 (%mol)     | B2O3 (%mol)     | Na2O (%mol)     |
| SBN1            | 55.00           | 35.00           | 10.00           | 57.95 | 31.84 | 10.21 |
| SBN2            | 60.00           | 30.50           | 09.50           | 62.80 | 27.56 | 09.64 |
| SBN3            | 65.00           | 26.00           | 09.00           | 67.60 | 23.32 | 09.08 |
| SBN4            | 70.00           | 21.50           | 08.50           | 72.34 | 19.14 | 08.52 |

Fig. 1 Samples SBN1 (A: Before Annealing, B: After Annealing)

One thought thereafter, to determine the zone of immiscibility in a ternary system sodium borosilicate, i.e. the areas from which certain compositions can present a separation of phase.

B. Simulation Part

1. Determination of the Immiscibility Regions

According to the thermodynamic criteria general, each system test (at temperature and pressure constants) to reach the most stable state, this will be accomplished with a reduction in the free energy of the system (G < 0) and reached...
a minimum with balance (dG = 0). One considers a formed system of f phases and K component [9].

From the equilibrium conditions, the arbitrary chemical potentials (μi) of the components are the same ones in all the phases:

$$\mu_i^1 = \mu_i^2 = \ldots = \mu_i^f$$

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If a mole of the mixture is considered, the chemical potential of the two components of the system (x, y) can be described by the relation:

$$\Delta \mu_x = \Delta G_m + (1-x) \left( \frac{\partial \Delta G_m}{\partial x} \right)_{y,z}$$

$$\Delta \mu_y = \Delta G_m - x \left( \frac{\partial \Delta G_m}{\partial x} \right)_{y,z}$$

For three components of the system, one will have:

$$\Delta \mu_x = \Delta G_m + (1-x) \left( \frac{\partial \Delta G_m}{\partial x} \right)_{y,z} - y \left( \frac{\partial \Delta G_m}{\partial y} \right)_{x,z}$$

$$\Delta \mu_y = \Delta G_m + (1-y) \left( \frac{\partial \Delta G_m}{\partial y} \right)_{x,z} - x \left( \frac{\partial \Delta G_m}{\partial x} \right)_{y,z}$$

$$\Delta \mu_z = \Delta G_m - x \left( \frac{\partial \Delta G_m}{\partial x} \right)_{y,z} - y \left( \frac{\partial \Delta G_m}{\partial y} \right)_{x,z}$$

or x, y and z are the molar fractions of the components.

$$\Delta \mu_i = \mu_i - \mu_i^0$$

where, \( \mu_i \): Chemical potential of component i in the solution

where, \( \mu_i^0 \): Chemical potential of the standard state.

\( \Delta G_m \): Molar free energy of the mixture.

where, \( x_1y_1 \) and \( x_2y_2 \) are equilibrium compositions of the phases 1 and 2 after substation of the equations and introduction of the symmetry condition. There are three components x, y and z and two phases 1 and 2.

After, the development of the equations in the equilibrium conditions, of three equations with four unknown \( x_1y_1, x_2y_2 \).

Or : \( z_1 = 1 - x_1 - y_1 \)

\( z_2 = 1 - x_2 - y_2 \)

One then the system of following equations:

$$F_1 = a_1(x_1y_1) + a_2(x_2y_2) + a_3(x_2y_1) + a_4(x_2y_1) + R = 0$$

$$F_2 = a_1(x_1y_1) + a_2(x_2y_2) + a_3(x_2y_1) + a_4(x_2y_1) + R = 0$$

$$F_3 = a_1(x_1y_1) + a_2(x_2y_2) + a_3(x_2y_1) + a_4(x_2y_1) + R = 0$$

The numerical interactive method of Newton is useful for the numerical equations or the solution is made by using the linear equations [10], [11]: (5)

$$F_1(x_1^0, y_1^0) + \frac{\partial F_1}{\partial x_1} \Delta x_1 + \frac{\partial F_1}{\partial y_1} \Delta y_1 + \frac{\partial F_1}{\partial y_2} \Delta y_2 = 0$$

$$F_2(x_1^0, y_1^0) + \frac{\partial F_2}{\partial x_1} \Delta x_1 + \frac{\partial F_2}{\partial y_1} \Delta y_1 + \frac{\partial F_2}{\partial y_2} \Delta y_2 = 0$$

$$F_3(x_1^0, y_1^0) + \frac{\partial F_3}{\partial x_1} \Delta x_1 + \frac{\partial F_3}{\partial y_1} \Delta y_1 + \frac{\partial F_3}{\partial y_2} \Delta y_2 = 0$$

The initial arbitrary values \( x_1^0, y_1^0 \) and \( y_1^0 \) are chosen and the stages of the equations. The solution obtained for \( \Delta x_1, \Delta y_2 \) and \( \Delta y_1 \).

Computed values \( \Delta x_1, \Delta y_2 \) and \( \Delta y_1 \) are adjusted with the initial values \( x_1^0, y_1^0 \) and \( y_1^0 \) giving \( (x_1^0 + \Delta x_1, y_1^0 + \Delta y_1) \) still used as initial information of the equation above.

This procedure is repeated until, \( F_1, F_2 \) and \( F_3 = 0 \) with the necessary precision.

In (5), the composition of balance \((x_1y_1 - x_2y_2)\) is not easily expressed, it is necessary to use numerical methods or solutions [12], [13].

The value of \( x_1 \) is on the other hand selected the corresponding value \((y_1 - x_2y_2)\) calculated according to the solution of (5)

Calculation is repeated during the stages of change of \( x_1 \), until the combined lines recover the totality of the area section of immiscibility. (See Fig. 2; linens combined).

Fig. 2 Diagram of the construction of the lines combined by solution numerical of (5) [8]

One used programming on Matlab and one had the model nearest to the solution sought with use of the ProSim software for the chart (modeling).
2. Numerical Simulation

Resolution of (5)
/* the Principal*/
program
global r t axy axz ayz x1
r=input('give R  ')
t=input('give the temperature')

% calcul des coefficients axy axz ayz
axy=(2400.5*r)-(0.152*r*t);
axz=4027.3*r-0.3*r*t;
ayz=-373*r+0.67*r*t;

% initial values
x1=0.173;
x20=0.405;
y20=0.127;
y10=0.191;
X0=[0.405 0.191 0.127 ]

[F1,F2,F3]=f(0.405,0.191,0.127);
F=[F1 F2 F3];

% calcul of the equation solutions for given x1
% using the Newton iterative method

% ****************************
*****
jacobien=[jc1,jc11,jc111,jc2,jc22,jc222,jc3,jc33,jc333];
nbit=0;
yy=X0-(F/jacobien);
while nbit~=5
  yy=X0;
  XX=X0-(F/jacobien);
  x2=XX(1);
  y2=XX(3);
  [F1,F2,F3]=f(x2,y1,y2);
  F=[F1 F2 F3];
  [jc1,jc11,jc111,jc2,jc22,jc222,jc3,jc33,jc333]=jacob(x2,y1,y2);
  jacobien=[jc1,jc11,jc111,jc2,jc22,jc222,jc3,jc33,jc333];
  X0=XX
  nbit=nbit+1
end

* The system of equation (the function F) *
function [f1,f2,f3]=f(x2,y1,y2)
global r t axz axy ayz x1
f1=-2*axz*x1+axz*x1.^2+(-axy+axz+ayz)*x1*y1-axy*x2.*2+axy*y1.*2+(axy-axz-ayz)*x2*y2-ayz*y2.^2+r*t*log(y1/y2);
f2=(axy-ayz+axz)*x1+axy*x1.*2+axy*x2.*2+y2.*(axy+axz+ayz)*x2*y2+axy*y2.*2+(axy-ayz-axz)*x2*y2+axy*y2.*2+r*t*log(y1/y2);
f3=axz*x1.^2+(-axy+axz+ayz)*x1*y1-axy*x2.*2+axy*y1.*2+(axy-axz-ayz)*x2*y2-ayz*y2.^2+r*t*log(y1/y2);

/* Jacobien (the function Jacob) */
function [j1,j2,j3,j11,j22,j33,j111,j222,j333]=jacob(x2,y1,y2)
global r t axz axy ayz x1
j1=2*axz-2*axz*x2+(axy-axz-ayz)*y2-r*t*1/x2;
j2=(-axy+axz+ayz)-2*axz*x2+(axy-axz-ayz)*y2;
j3=2*axz*x2+(axy-axz-ayz)*y2;

j11=(-axy+axz+ayz)*x1+(axy-axz-ayz)*y1+rt*1/x1;
j22=(-axy+axz+ayz)*x1+2*axy*y1+rt*1/y1;
j33=(-axy+axz+ayz)*x1+2*axy*y1+rt*1/y1;
j111=(axy-axz-ayz)*x1-2*axy+y2+(-axy+axz+ayz);
j222=(axy-axz-ayz)*x1+2*axy-2*axy*y2-rt*1/y2;
j333=(axy-axz-ayz)*x1+2*axy*y2-rt*1/y2;

3. Graphical Presentation

Fig. 3 Representative diagrams of the immiscibility areas in the system (SBN) for temperatures 500, 550, 600, 650 and 700°C
(Obtained by the software ProSim Ternary Diagram)

III. CONCLUSION

We determined the zone of immiscibility in the ternary system sodium borosilicate per calculation. One started initially with a calculation in the equilibrium conditions, and then one determined the compositions of the combined lines. That was translated thereafter by mathematical equations solved using the use of the numerical methods of analysis and finally, one used programming on Matlab and one had the model nearest to the solution sought with use of the software ProSim (Process Simulation SOFTWARE).
REFERENCES


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