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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 investigated in this work, i.e. to determine the regions from which some compositions can show phase separation. For this we went through the conditions of thermodynamic equilibrium, which were translated later by mathematical equations to find an approximate solution. The latter has been translated in a simulation which was established thereafter to find the immiscibility regions in this type of special glasses.

***Keywords*—**Sodium borosilicate, heat-resistant, isothermal treatments, immiscibility, thermodynamics four.

I. Introduction

THE principal interest of the application of immiscibility phenomena in the glasses industry is that of the synthesis of microporous glass. It was noted that the most suited chemical compositions to decomposition is that of alkaline borosilicate. However, this is caused by the boron anomaly by involving the formation of two phases, one rich in alkaline silica and the other borate rich phase. This latter phase is easily dissolved under acidic conditions. The acidic medium results in a network of pores inter-connected, whereas-the consolidation of microporous glass results in a vitrified structure, which approaches that of glass from silica forming a glass known as Vycor® [1]-[3]. In the ternary system soda-borosilicate, Elmer et al defined the optimal line of glass lixiviated for the Vycor® industry [4]. Recently, Aboutaleb et al. were showed that the effect of chemical composition on the rate of leaching showed that boron and sodium are dissolved much more quickly than silicon [5]-[8]. These authors also noted that the greater the content of Na_2O and B_2O_3 in glass, the more soluble the glass becomes. However, addition of silica results a decrease in glass solubility [5]. The obtained results of their work indicate that substitution of sodium by calcium induces an acceleration of the kinetics of deterioration.

For this, the aim of this study is to determine the areas of immiscibility in glasses prepared in laboratory. These glasses have subjected subsequently isothermal treatments at different times, 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.

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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-resisting 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 (SiO_2-B_2O_3-Na_2O) 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)

	SiO_2 (%wt)	B_2O_3 (%wt)	Na_2O (%wt)	SiO_2 (%wt)	B_2O_3 (%mol)	Na_2O (%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

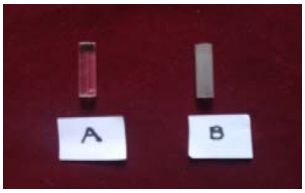

Fig. 1 Samples SBN1 (A: Before Annealing, B: After Annealing)

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 (μ_i) of the components are the same ones in all the phases:

$$\begin{cases} \mu_x^1 = \mu_x^{\ 2} = ... = \mu_x^f \\ \mu_y^1 = \mu_y^{\ 2} = ... = \mu_y^f \\ \vdots \\ \mu_k^1 = \mu_k^{\ 2} = ... = \mu_k^f \end{cases} \quad (1)$$

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:

$$\begin{cases} \Delta\mu_x = \Delta G_m + (1-x)\left(\frac{\partial \Delta G_m}{\partial x}\right)_{T,P} \\ \Delta\mu_y = \Delta G_m - x\left(\frac{\partial \Delta G_m}{\partial x}\right)_{T,P} \end{cases} \quad (2)$$

For three components of the system, one will have:

$$\begin{cases} \Delta\mu_x = \Delta G_m + (1-x)\left(\frac{\partial \Delta G_m}{\partial x}\right)_{y,T,P} - y\left(\frac{\partial \Delta G_m}{\partial y}\right)_{x,T,P} \\ \Delta\mu_y = \Delta G_m + (1-y)\left(\frac{\partial \Delta G_m}{\partial y}\right)_{x,T,P} - x\left(\frac{\partial \Delta G_m}{\partial x}\right)_{y,T,P} \\ \Delta\mu_z = \Delta G_m - x\left(\frac{\partial \Delta G_m}{\partial x}\right)_{y,T,P} - y\left(\frac{\partial \Delta G_m}{\partial y}\right)_{x,T,P} \end{cases} \quad (3)$$

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

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

μ_i : Chemical potential of component i in the solution

$\mu_i^{\ 0}$: Chemical potential of the standard state.

ΔG_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:

$$\begin{cases} F_1 = a_{xy}(y_1 - y_2) + a_{xz}(z_1 - z_2) + a_{xy}(x_2y_2 - x_1y_1) + a_{xz}(x_2z_2 - x_1z_1) + a_{yz}(y_2z_2 - y_1z_1) + RT\ln\frac{x_1}{x_2} = 0 \\ F_2 = a_{xy}(x_1 - x_2) + a_{yz}(z_1 - z_2) + a_{xy}(x_2y_2 - x_1y_1) + a_{xz}(x_2z_2 - x_1z_1) + a_{yz}(y_2z_2 - y_1z_1) + RT\ln\frac{y_1}{y_2} = 0 \\ F_3 = a_{yz}(y_1 - y_2) + a_{xz}(x_1 - x_2) + a_{xy}(x_2y_2 - x_1y_1) + a_{xz}(x_2z_2 - x_1z_1) + a_{yz}(y_2z_2 - y_1z_1) + RT\ln\frac{y_1}{y_2} = 0 \end{cases} \quad (4)$$

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)

$$\begin{cases} F_1(x_2^0 y_2^0 y_1^0) + \left(\frac{\partial F_1}{\partial x_2}\right)\Delta x_2 + \left(\frac{\partial F_1}{\partial y_2}\right)\Delta y_2 + \left(\frac{\partial F_1}{\partial y_1}\right)\Delta y_1 = 0 \\ F_2(x_2^0 y_2^0 y_1^0) + \left(\frac{\partial F_2}{\partial x_2}\right)\Delta x_2 + \left(\frac{\partial F_2}{\partial x_2}\right)\Delta y_2 + \left(\frac{\partial F_2}{\partial y_1}\right)\Delta y_1 = 0 \\ F_3(x_2^0 y_2^0 y_1^0) + \left(\frac{\partial F_3}{\partial x_2}\right)\Delta x_2 + \left(\frac{\partial F_3}{\partial y_2}\right)\Delta y_2 + \left(\frac{\partial F_3}{\partial y_1}\right)\Delta y_1 = 0 \end{cases} \quad (5)$$

The initial arbitrary values x_2^0, y_2^0 and y_1^0 are chosen and the stages of the equations. The solution obtained for Δx_2, Δy_2 and Δy_1 ;

Computed values Δx_2 , Δy_2 and Δy_1 are adjusted with the initial values x_2^0, y_2^0 and y_1^0 giving ($x_2^0 + \Delta x_2$)… 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 (x1y1 - x2y2) is not easily expressed, it is necessary to use numerical methods or solutions [12], [13].

The value of x1 is on the other hand selected the corresponding value (y1- x2y2) is calculated according to the solution of (5)

Calculation is repeated during the stages of change of x1, until the combined lines recover the totality of the area section of immiscibility. (See Fig. 2; linens combined).

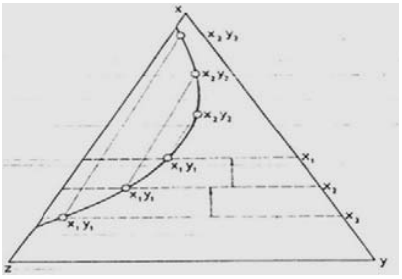

Fig. 2 Diagram of the construction of the lines combined by solution numerical of (5) [8]

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
%**********************************************
*****
[jc1,jc11,jc111,jc2,jc22,jc222,jc3,jc33,jc333]=jacob(0.405,0.1
91,0.127);
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);
  y1=XX(2);
   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+2*axz*x2-
axz*x2.^2+(axy-axz-ayz)*y1+ayz*y1.^2+(axy-axz-
ayz)*x2*y2-ayz*y2.^2+(-axy+axz+ayz)*y2+r*t*log(x1/x2);

f2=(axy-ayz-axz)*x1+axz*x1.^2 +(-axy+ayz+axz)*x1*y1+(-
axy+ayz+axz)*x2-axz*x2.^2-2*ayz*y1+ayz*y1.^2+(axy-ayz-
axz)*x2*y2+2*ayz*y2-ayz*y2.^2+r*t*log(y1/y2);

f3=axz*x1.^2+(-axy+axz+ayz)*x1*y1-
axz*x2.^2+ayz*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+ayz+axz)-2*axz*x2+(axy-ayz-axz)*y2;
j3=-2*axz*x2+(axy-axz-ayz)*y2;

j11=(-axy+axz+ayz)*x1+(axy-axz-ayz)+2*ayz*y1;
j22=(-axy+axz+ayz)*x1-2*ayz+2*ayz*y1+r*t*1/y1;
j33=(-axy+axz+ayz)*x1+2*ayz*y1+r*t*1/y1;

j111=(axy-axz-ayz)*x2-2*ayz*y2+(-axy+axz+ayz);

j222=(axy-axz-ayz)*x2+2*ayz-2*ayz*y2-r*t*1/y2;
   j333=(axy-axz-ayz)*x2-2*ayz-y2-r*t*1/y2;
```

3. Graphical Presentation

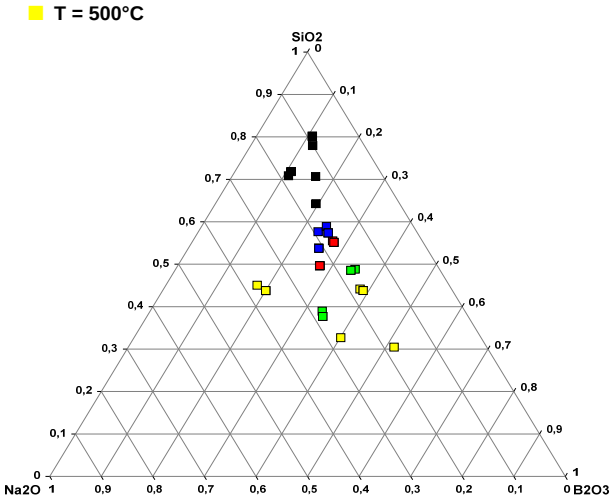

Fig. 3 Representative diagrams of the immiscibility areas in the system (SBN) for temperatures 500,550,600,650 and 700°C (Obtained by the software ProSim Ternary Diagram)

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).

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