MOLTEN SALT PHASE DIAGRAMS CALCULATION USING ARTIFICIAL NEURAL NETWORK OR PATTERN RECOGNITION-BOND PARAMETERS①

PART 3. ESTIMATION OF LIQUIDUS TEMPERATURE AND EXPERT SYSTEM

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ABSTRACT The temperatures of the liquidus lines or surfaces in some binary or ternary systems have been estimated using artificial neural network(ANN) with the chemical bond parameters of ions and the melting points, and using the compositions of the constituents as inputs and the properties of phase diagrams as outputs. The computerized values are in good agreement with the experimental ones. Moreover, an expert system has been built up, which consists of two parts, one is the database produced by the experimental data of the various known phase diagrams and chemical parameters for the retrieval of the features of the existing phase diagrams; the other is the knowledge base produced by the trained ANN for the estimation or prediction of some features of the unknown phase diagrams.

Key words phase diagram calculation artificial neural network bond parameter molten salt system expert system

1 INTRODUCTION

The experimental data on the liquidus lines or surfaces in binary or ternary systems from references are always finite. Sometimes the data which we need to use in practical work are unmeasured for some points of liquidus in the known phase diagrams, so, some linear regression equations were used to express the known data in general. The method can estimate the data of the unmeasured points, but meanwhile it produces large error as it substitutes an approximate linear equation for a real nonlinear boundary equation. Because artificial neural network (ANN) is an information processing technique which can express nonlinear problems[1, 2], so, ANN can be used to express the knowledge of the liquidus. We can predict or retrieve the temperatures of any points of the unmeasured or measured liquidus using ANN method.

In this paper, the estimation of the temperatures of the liquidus lines or surfaces of some binary or ternary systems were reported by ANN with the chemical bond parameters of ions and the melting points, the compositions of constituents as the inputs. An expert system which

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we had built up based on the series work was also reproted, including its principle, structure, functions and flowsheet.

2 ESTIMATION OF TEMPERATURES OF LIQUIDUS LINES OF BINARY SYSTEMS

Thirty two eutectic type phase diagrams[3-5], including $CuCl$-$SnCl_2$, UCl_4-$MgCl_2$, $TaCl_5$-$HgCl_2$, KF-NaF, KF-LiF, LiF-PuF_3, AgI-NaI, NaF-CdF_2, NaF-LiF, LiCl-UCl_3, AgBr-KBr, LiBr-KBr, $CdBr_2$-NaBr, NaBr-$BaBr_2$, NaBr-$MgBr_2$, LiCl-RbCl, LiCl-TiCl, LiCl-$BaCl_2$, LiCl-$PuCl_3$, LiCl-$PbCl_2$, LiBr-$BaBr_2$, NaI-TeI_4, NaCl-RbCl, NaCl-TiCl, NaCl-$PbCl_2$, $PbCl_2$-$BeCl_2$, $CdCl_2$-$SnCl_2$, $CaCl_2$-$PbCl_2$, NaCl-$SrCl_2$, KCl-AgCl, $PbCl_2$-AgCl, AgCl-$BeCl_2$, were used as training set, the T_1^0, T_2^0 (T^0 denotes the melting points of two constitutents, definite $T_1^0 > T_2^0$), $|\Delta Z/r|$ (absolute difference of the ionic charge-radius ratio of A, B metallic ion), $|\Delta X|$ (absolute difference of the electronegativity of two metallic ions), r_-, $(Z/r)_A$, X_A, x_1 (composition of the first constituent, mole fraction) were used as the inputs of ANN, the temperatures of liquidus lines were used as the output. About twenty points taken from each liquidus of phase diagram were used as the learning samples, the learning set was 631 samples, hidden nodes were eight. After training, the liquidus temperatures of NaCl-CsCl system were predicted by the trained ANN. The cross point of two liquidus lines is the eutectic point. Computational results of the system are plotted in Fig. 1. It can be seen that the predicted results are in agreement with experimental ones. The predicted cross point (66.5%, 487 ℃) of two liquidus lines is also close to experimental eutectic point(64.6%, 490 ℃).

3 ESTIMATION OF TEMPERATURES OF LIQUIDUS SURFACES OF TERNARY SYSTEMS

3.1 Prediction of temperature of unmeasured points on liquidus surface

Table 1 lists the predicted and the experimental results of the "unmeasured" points of the liquidus surface in Li, Na, K|F system[3]. We used x_{LiF}, x_{NaF} (the compositions of LiF, NaF) as the inputs of ANN, the temperatures of liquidus surface as the output. The hidden layer had ten nodes. Forty eight samples taken from the liquidus surface of Li, Na, K|F system were used as the training set. Then the trained ANN was used to predict the seven points which were not included in training set. The average predicted error is 16 ℃, the average relative error is 2.5%. The predicted results are in good agree-

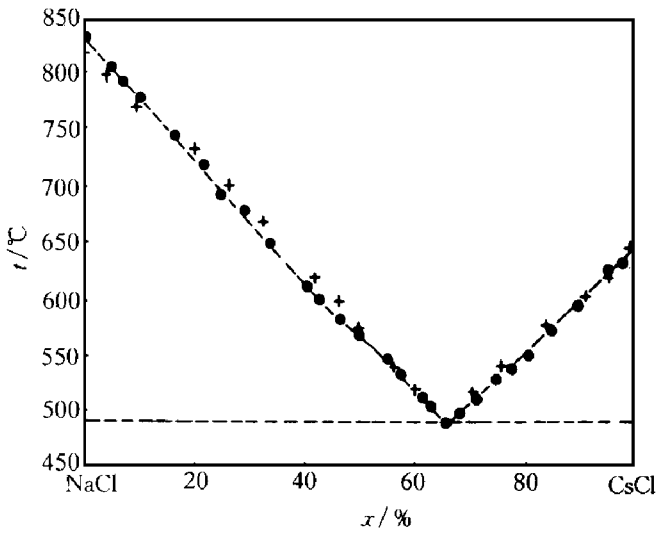

Fig. 1 Computerized prediction of liquidus temperatures in the NaCl-CsCl system
(+ —Experimental value[5]; ● —Predicted value)

Table 1 Computerized estimation of temperatures of liquidus surface in the Li, Na, K|F system

x_{LiF} /%	x_{NaF} /%	t_{exp} /℃	$t_{pre.}$ /℃	Error t/℃	Relative error/%
15.0	5.0	750	725	− 25	3.3
35.3	7.0	650	671	+ 21	3.2
20.6	22.7	600	614	+ 14	2.3
19.2	30.2	550	569	+ 19	3.4
24.6	61.1	700	701	+ 1	0.0
24.6	35.9	600	580	− 20	3.3
42.0	30.0	725	711	− 14	1.9

ment with experimental ones.

3.2 Prediction of temperatures of liquidus surface of unknown system

The ANN can be used for the prediction of the temperatures of any points on liquidus surfaces of the unknown phase diagrams by learning from the temperatures on the liquidus surfaces of the known same type phase diagrams. For example, we used the temperatures on the liquidus surfaces of the Cs, K, NaI I, Cs, K, TlI I, Na, K, TlI I, Rb, Cs, TlI I, Cs, Na, K I Br, Na, K, Rb I Cl, Rb, Na, TlI I, Li, Na, K I F phase diagrams[3], whose types are eutectic mixture, as training set. About seventy points were taken from each surface, the sum of samples was 547. The inputs of ANN were T_1, T_2, T_3 (T denotes the melting point of a constituent, subscript 1, 2, 3 represent constituents, definite $T_1 > T_2 > T_3$); r_A, r_B, r_C, (r denotes the radius of three metallic ions, subscript A, B, C denote metallic ions); χ_A, χ_B, χ_C (electronegativities of three metallic ions), r_-, and x_1, x_2 (x denotes composition of a constitutent, subscript 1, 2 represents the first and the second constituent). The temperatures of liquidus surfaces were used as the output, the mumber of hidden nodes was twenty. The trained ANN was used to predict the sixty two temperatures of the liquidus surface of the "unknown" Na, Cs, TlI I system (its type of phase diagram is also continuous solid solution). The predicted results are listed in Table 2. The results of prediction are good in general. The average relative error is 5.0%, but the errors of the predicted temperatures near the eutectic point are larger than those of the other points, the maximum relative error is 16.7%.

Moreover, the trained ANN can be used to predict the liquidus temperatures of any vertical section in ternary Na, Cs, TlI I system, such as the liquidus line for passing NaI and $x_{CsI}/x_{TlI} = 1$, and the liquidus line for paralleling CsI-TlI and $x_{NaI} = 60\%$[6].

In conclusion, the ANN-chemical bond parameters method is a useful tool for the estimation temperatures of liquidus. The knowledge of ANN acquired from liquidus can not only retrieve and calculate the temperatures of any points of the known liquidus lines or surfaces, but also

Table 2 Computerized estimation of temperatures of liquidus surface of the Na, Cs, TlI I system

x_1/%	x_2/%	t_{exp}/℃	t_{pre}/℃	x_1/%	x_2/%	t_{exp}/℃	t_{pre}/℃	x_1/%	x_2/%	t_{exp}/℃	t_{pre}/℃	x_1/%	x_2/%	t_{exp}/℃	t_{pre}/℃
100.0	0.0	660	647	0.0	83.0	600	598	42.2	18.5	500	527	25.2	45.7	450	517
0.0	100.0	640	625	0.0	67.8	550	559	39.8	12.5	500	509	32.0	28.2	450	524
0.0	0.0	442	467	0.0	52.0	500	488	35.6	6.4	500	481	37.7	50.3	450	525
10.0	90.0	600	579	0.0	38.8	450	427	31.1	22.1	450	487	41.8	52.0	450	524
27.2	72.8	550	534	0.0	25.3	406	408	27.4	16.7	450	462	4.9	51.7	500	498
37.4	62.3	500	534	91.5	4.4	650	628	23.9	10.1	450	447	11.0	53.1	500	514
60.0	40.0	500	531	76.2	17.4	600	577	20.9	4.2	450	447	16.6	53.9	500	523
68.6	31.4	550	542	72.3	11.0	600	602	20.9	22.3	400	447	27.4	57.9	500	529
79.2	20.8	600	564	68.6	4.2	600	620	15.7	20.2	400	429	33.0	60.5	500	527
93.2	6.8	650	613	64.4	26.6	550	553	18.3	31.2	400	460	9.7	68.3	550	552
89.0	0.0	650	655	59.0	19.2	550	567	14.3	28.4	400	438	16.1	69.8	550	546
68.0	0.0	600	626	54.7	12.0	550	569	11.5	24.4	400	423	22.2	71.4	550	539
48.0	0.0	550	528	49.6	5.2	550	545	13.0	22.5	400	425	5.6	82.2	600	581
33.0	0.0	500	470	54.9	35.1	500	537	5.0	39.3	450	442	10.3	81.1	600	571
19.2	0.0	450	453	51.6	29.8	500	543	11.1	41.1	450	470				
14.6	0.0	426	453	48.3	26.7	500	542	18.8	43.6	450	501				

predict temperatures of any points of the unknown liquidus lines or surfaces reliably and plot the liquidus lines of various vertical sections rapidly. This calculated method can compensate the finiteness of the known experimental data and the lack of unknown experimental data and the lack of the unknown phase diagrams data. This method may be also useful for the estimation of the liquidus temperatures of the quaternary and high order systems.

4 EXPERT SYSTEM

4.1 Principle

Based on above discussions, including our previous two series papers[7, 8] and Ref. [9], the success of the prediction or estimation of the binary and ternary molten salt phase diagrams shows that the ANN-chemical bond parameters method can become a new tool for phase diagram calculation. The chemial bond parameters of ions and the melting points, the compositions of constituents are used as the inputs of ANN, the properties of phase diagrams as the output. ANN consists of three layers, the nodes of hidden layer are veried for different learning sets. Back propagation algorithm and transfer function $\tanh x$ are used. The trained ANN by the experimental data of the known phase diagrams is used for the prediction of the unknown phase diagrams. All data of phase diagrams used are quoted from the Refs. [3- 5, 10] and journal of inorganic chemistry (in Russian) after 1980, the chemical bond parameters from Ref. [11].

4.2 Structure

A prototype of the expert system of molten salt phase diagrams has been constructed. It is designed by modules, and is menu-driven. The expert system consists of two parts, one is the database which is produced by the experimental data of the various known phase diagrams and chemical bond parameters for the retrieval of the properties of the existing phase diagrams, the other is the knowledge base which is produced by the trained ANN for the prediction or estimation of some features of the unknown phase diagrams.

4.3 Function

The expert system of molten salt phase diagrams includes common anion binary systems $MeX\text{-}Me'X_n$ (Me, Me′ denote metallic elements, X halogen, n = 1, 2, 3, 4), additive ternary systems Me, Me′, Me″ | X (Me, Me′, Me″ denote metallic elements, X halogen or its radical) and some reciprocal ternary systems. It has the functions of retrieval and prediction. It can answer the questions as follows: (1) the formation of the intermediate compound of binary and ternary systems; (2) the stoichiometry of binary intermediate compound; (3) the melting type of binary intermediate compound (congruent or incongruent); (4) the melting point or decomposition temperature of binary intermediate compound; (5) the formation of the continuous solid solution or the eutectic mixture of some binary and ternary systems; (6) the composition and the temperature of the minima corresponding to the minimum point in minimum solid solution system (only for $MeX\text{-}Me'X$ system); (7) the composition and the temperature of eutectic point in the binary and ternary eutectic system; (8) the estimation of the temperatures of the liquidus of some binary and ternary systems (for no intermediate compound formation).

4.4 Flowsheet

The flowsheet of expert system is shown in Fig. 2. It works according to the following process: starting the system, selecting the molten salt type and inputting the name of elements existed in the molten salt phase diagram. Then, the system checks the database, if the phase diagram exists, the expert system gives some features of phase diagram; if not, the expert system produces automatically the suitable chemical bond parameters of ions and other data and inputs these parameters and data to the trained ANN to predict some unknown phase diagram features.

The expert system is written in Turbo C language. It has friendly interface and its operation is convenient. The performance of expert system is stable and rapid, and the database and the knowledge base are reliable. The expert system can be applied to the experimental measure-

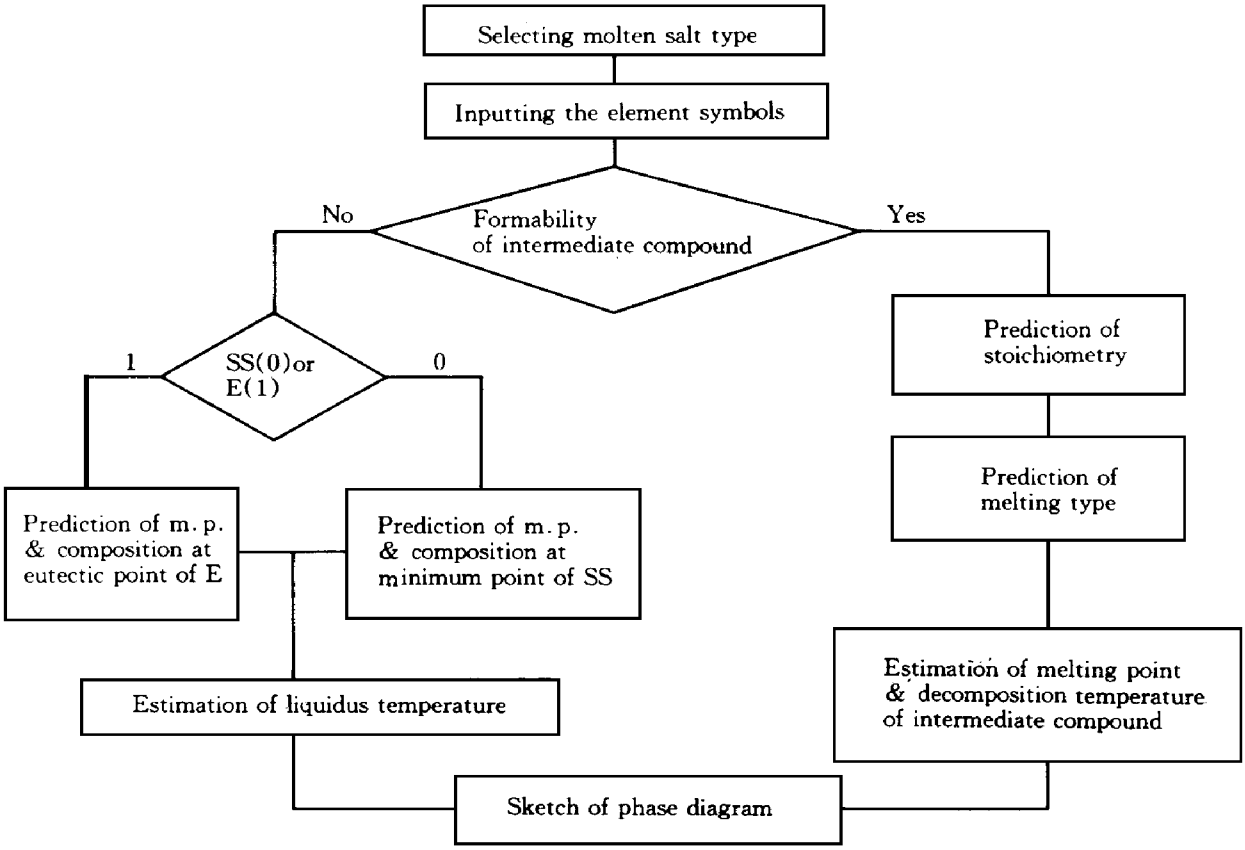

Fig. 2 The flowsheet of expert system

ments, thermodynamic calculation of phase diagrams and materials design as well.

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