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Prediction of formation enthalpies for Al_2X-type intermetallics using back-propagation neural network

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ABSTRACT

A back-propagation artificial neural network (ANN) was established to predict the formation enthalpies of Al_2X-type intermetallics as a function of some physical parameters. These physical parameters include the electronegativity difference, the electron density difference, the atomic size difference, and the electron–atom ratio (e/a). The values calculated by the ANN method agree with experiments well to typically within 10%, indicating that the well-trained back-propagation (BP) neural network is feasible, and can precisely predict the formation enthalpies of Al_2X-type intermetallics. The method comparison based on the predicted formation enthalpies suggests that our ANN method is superior to Miedema's model. Some trends of formation enthalpies for Al_2X-type intermetallics were also observed from the ANN.

1. Introduction

Formation and transformation for alloy and compound has always been a hot topic in the field of physical metallurgy. In 1930s, Hume-Rothery et al. [1] experientially pointed out that the formation of intermetallics was largely affected by some physical factors, including size factor, electrochemical factor and valence factor. About the same time, Pauling [2] suggested formation enthalpy of ionic compounds could be quite accurately described by electronegativity difference. In 1980s, Miedema et al. [3] proposed a so-called macroscopic atom picture to predict the formation enthalpies of binary systems, which extended Pauling's scheme to alloys and compounds.

During the last decades, the semi-empirical Miedema's model has been developed and successfully applied to the prediction of formation enthalpies in binary intermetallics. Some experimental work through calorimetric measurements was also carried out to investigate the thermochemistry of these binary intermetallics, and found however that over 90% of these predicted values based on Miedema's model was more negative than the experiments [4]. To overcome this discrepancy, more recent research efforts have been focused on developing some extended Miedema's models by taking into account, for example, the important effect of the atomic size difference, which has led to some interesting results [5–7]. Nevertheless, there are still some disputations in these improved models, and the physical meaning of Miedema's theory is still missing [6,7]. It is well known that *ab initio* calculations based on density functional theory can provide accurate enthalpies of formation for these compounds [8], but require an enormous amount of computation time. Here we present a quite simple but accurate method from the artificial neural network approach. The theoretical activity within this work is not intended to compete with but instead to encourage and complement *ab initio* efforts (if available).

Artificial neural network (ANN) is an artificial intelligence approach inspired by simulating the biological nerve system [9]. An ANN consists of many interconnected neurons to simulate complex nonlinear relationships, and its geometry and functionality have been likened to that of the human brain. According to its capacities of self-adaptive, self-organization and self-learning, ANN technique has received extensive attention to solve multivariate problems and nonlinear ones, especially in pattern recognition and functional approximation. ANN have been also used widely in the fields of materials science, such as the prediction of mechanical properties [10–12], design of composition [13] and optimization of processing parameters [14–16], due to its ability to learn from limited experimental data and that it is much faster than other theoretical approaches.

Al_2X-type intermetallics have attracted considerable attention due to their outstanding physical and mechanical properties, and their thermodynamic data are valuable sources of information on

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Table 1
The formation enthalpies and some physical parameters of Al_2X-type intermetallics used in present study.

Compounds	Type	Structure	T_m (K)	T_X (K)	X_X	ΔX	T_X (Å)	$\lvert R_a - R_b\rvert/R_a$ (%)	$\Delta(Z/(4\pi R^3/3))$	e/a	Formation enthalpy (kJ mol-atom^{-1})
Al_2Mg	Cu_2Mg	Cubic	–	922	1.31	0.30	3.20	11.9	0.128	2.67	−2.301 [20]
Al_2Ca	Cu_2Mg	Cubic	1352	1113	1.00	0.61	3.95	38.1	0.183	2.67	−33.981 [20]
Al_2Sc	Cu_2Mg	Cubic	1693	1814	1.36	0.25	3.25	13.6	0.078	3	−47.2 [21]
Al_2Ti	Ga_2Hf	Tetragonal	1706	1946	1.54	0.07	2.89	1.0	0.072	3.33	−37.1 [22]
Al_2Fe	Al_2Fe	Triclinic	1442	1811	1.83	0.22	2.48	13.3	0.757	2	−29.6492 [23]
Al_2Ni	CaF_2	Cubic	–	1728	1.91	0.3	2.49	12.9	0.993	2	−50 .[24]
Al_2Cu	Al_2Cu	Tetragonal	873	1358	1.90	0.29	2.56	10.5	1.008	2.33	−15.5359 [23]
Al_2Sr	Cu_2Mg	Cubic	1209.2	1042	0.95	0.66	4.30	50.4	0.197	2.67	−29.7 [25]
Al_2Y	Cu_2Mg	Cubic	1758	1801	1.22	0.39	3.55	24.1	0.117	3	−50.4 [26]
Al_2Zr	$MgZn_2$	Hexagonal	1933	2128	1.33	0.28	3.17	10.8	0.005	3.33	−52.1 [26]
Al_2Ru	TiS_2	Orthogonal	–	2527	2.20	0.59	2.65	7.3	0.576	2	−66.2743 [27]
Al_2Ba	Cu_2Mg	Cubic	1187	1002	0.89	0.72	4.35	52.1	0.199	2.67	−54.8 [28]
Al_2La	Cu_2Mg	Cubic	1678	1194	1.10	0.51	3.73	30.4	0.135	3	−49.9 [26]
Al_2Ce	Cu_2Mg	Cubic	1753	1072	1.12	0.49	3.65	27.6	0.088	3	−48.94 [29]
Al_2Pr	Cu_2Mg	Cubic	1753	1205	1.13	0.48	3.63	26.9	0.045	3	−54 .[30]
Al_2Nd	Cu_2Mg	Cubic	1733	1290	1.14	0.47	3.66	28.0	0.011	3	−54 .[30]
Al_2Pm	Cu_2Mg	Cubic	1753	1204	1.13	0.48	3.62	26.6	0.037	3	−49.88 [18]
Al_2Sm	Cu_2Mg	Cubic	1773	1346	1.17	0.44	3.59	25.5	0.085	3	−54.3 [30]
Al_2Eu	Cu_2Mg	Cubic	1573	1091	1.20	0.41	3.96	38.5	0.032	3	−36 .[30]
Al_2Gd	Cu_2Mg	Cubic	1798	1587	1.20	0.41	3.58	25.2	0.171	3	−51.4 [29]
Al_2Tb	Cu_2Mg	Cubic	1787	1632	1.20	0.41	3.52	23.1	0.237	3	−52.4 [30]
Al_2Dy	Cu_2Mg	Cubic	1773	1684	1.22	0.39	3.51	22.7	0.285	3	−52.7 [30]
Al_2Ho	Cu_2Mg	Cubic	1803	1745	1.23	0.38	3.49	22.0	0.339	3	−52.5 [30]
Al_2Er	Cu_2Mg	Cubic	1728	1797	1.24	0.37	3.47	21.3	0.395	3	−49 .[29]
Al_2Tm	Cu_2Mg	Cubic	1895	1820	1.25	0.36	3.54	23.8	0.401	3	−51 .[30]
Al_2Yb	Cu_2Mg	Cubic	1633	1098	1.1	0.51	3.88	35.7	0.278	3	−39.5 [31]
Al_2Lu	Cu_2Mg	Cubic	1773	1938	1.27	0.34	3.43	19.9	0.560	3	−52.6 [26]
Al_2Hf	$MgZn_2$	Hexagonal	1923	2504	1.30	0.31	3.13	9.4	0.877	3.33	−43.8 [26]
Al_2Os	$MoSi_2$	Tetragonal	–	3306	2.20	0.59	2.68	6.3	1.939	2	−44.9 [26]
Al_2Pt	$CaFe_2$	Cubic	–	2045	2.28	0.67	2.77	3.1	1.913	2	−82 .[32]
Al_2Au	CaF_2	Cubic	1333	1338	2.54	0.93	2.88	0.7	1.755	2.33	−39.2 [33]
Al_2Th	AlB_2	Hexagonal	–	2031	1.30	0.31	3.6	25.9	0.122	3.33	−46.8 [34]
Al_2U	Cu_2Mg	Cubic	1893	1406	1.38	0.23	2.75	3.8	0.306	3.33	−30.8 [35]
Al_2Np	Cu_2Mg	Cubic	–	910	1.36	0.25	2.62	8.4	0.499	3.33	−37.3 [35]
Al_2Pu	Cu_2Mg	Cubic	1813	913	1.28	0.33	3.10	8.4	0.268	3.33	−47.3 [36]

thermal properties of these condensed matter phases. In fact, most Al_2X-type intermetallics including all the Al_2RE intermetallics (RE – rare earth) are Laves phase, and their formation enthalpies have been partly reported in the early time [17,18]. As mentioned above, it has been found that these calculated formation enthalpies for Al_2X-type intermetallics from Miedema's model are not very satisfactory, and those values are about 1.3 times of the experiments [18,19].

In our study, an ANN with back-propagation learning algorithm was developed to predict the formation enthalpies for Al_2X-type intermetallics as a function of some physical parameters including the electronegativity difference, the electron density difference, the atomic size difference, and the electron–atom ratio. These microcosmic parameters can be directly related to macroscopic thermodynamic properties of the intermetallics. The ANN was verified by comparing with available experiment data. The values calculated by the ANN method were also compared with the Miedema's results, to assess each method's predictive ability. Using the ANN method, we revealed some trends of formation enthalpies of Al_2X-type intermetallics.

2. Some trends of formation enthalpies for Al_2X-type intermetallics – the selection of the input variables

The available formation enthalpies of Al_2X-type intermetallics from literature [20–36] were summarized in Table 1. The required physical parameters can be found in some handbooks [37,38].

2.1. Miedema's model

According to Miedema's approach, the formation enthalpy of a binary alloy consists of a negative contribution from the electronegativity difference between the two components, a positive contribution from the electron density difference between the two components, and a correction of hybridization if one component is a transition element. The detailed description of Miedema's model can be referred to Refs. [3,39,40].

The Miedema's model results and the experimental values of formation enthalpies for Al_2X-type intermetallic compounds are shown in Fig. 1 for a comparison. It is seen that the calculated formation enthalpies based on Miedema's model are not very satisfactory ($R^2 = 0.4679$). There exist some obvious differences between these calculated values and those obtained by the most accurate experimental techniques: most of the calculated values based on Miedema's model are about 1.3 times more negative. A disagreement of as large as 20 kJ mol-atom^{-1} (or a relative error of as large as 25%) is found as typical. In some cases, errors even culminate to about 30 kJ mol-atom^{-1} and relative errors to 80%. As we show later, this large deviation is possibly due to the neglected but important effect of the atomic size difference.

As we know, the formation of intermetallics is affected primarily by three physical factors, i.e. the electrochemical factor, size factor, and valence factor. All these factors are useful for the investigation of the formation enthalpy regularities of intermetallics. The relations between these factors and formation enthalpies are discussed separately in the following sections.