Intermetallics 66 (2015) 56–66

Contents lists available at ScienceDirect

Intermetallics

journal homepage: www.elsevier.com/locate/intermet

Alloy design for high-entropy alloys based on Pettifor map for binary compounds with 1:1 stoichiometry

A. Takeuchi*, K. Amiya, T. Wada, K. Yubuta

Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

ARTICLE INFO

Article history:
Received 4 January 2015
Received in revised form
20 April 2015
Accepted 13 June 2015
Available online 29 June 2015

Keywords:
High-entropy alloys
Alloy design
Phase stability
Prediction
Microstructure

ABSTRACT

Pettifor map for binary compounds with 1:1 stoichiometry was utilized as an alloy design for high-entropy alloys (HEAs) with exact or near equi-atomicity in multicomponent systems. Experiments started with selecting GuGd binary compound with CsCl structure from Pettifor map, followed by its extensions by selecting the binary compounds with the same CsCl structure to CuDyGdTbY equi-atomic quinary alloy and to Cu_4GdTbDyY and Ag_4GdTbDyY quinary alloys and Cu_2Ag_2GdTbDyY senary alloy in sequence. X-ray diffraction revealed that CuDyGdTbY alloy was formed into a HEA with mixture of bcc, fcc and hcp structures, whereas the Cu_2Ag_2GdTbDyY HEA was a single CsCl phase. The results suggest a potential of Pettifor map for the development of HEAs by utilizing its information of crystallographic structures. The further analysis was performed for composition diagrams of multicomponent systems corresponding to simplices in a high dimensional space. The present results revealed that a strategy of equi-mole of compounds instead of conventional equi-atomicity also works for the development of HEAs.

1. Introduction

Recently, more and more scientific and industrial interest has been paid to high-entropy alloys (HEAs) [1–3], which have grown up as an outstanding advanced metallic material in the last decade. By definition, the HEAs in a class of multicomponent system are complex for the number of constituent elements (N) comprising five or more, but are principally simple in many other aspects. For instance, HEAs are formed into a simple crystalline structures from solid solutions consisting of a bcc and fcc, or its mixture phases as well as their chemically ordered phases [3] or a hcp phase [4,5] without appearance of intermediate compound phases. Furthermore, alloy compositions of the HEAs are principally as simple as exact or near equi-atomicity, which provides the origin of the terminology of HEA due to the fact that the configuration entropy (S_{config}) is maximized at the equi-atomic composition in an alloy. Thermodynamically, the stabilization of a solid solution in HEA is explained by the maximized S_{config} due to equi-atomicity that decreases Gibbs free energy (G) formulated as "$H-TS$" with enthalpy (H) minus the product of absolute temperature (T) and entropy (S). In actual alloy designs for HEAs, there are a couple of important quantities besides S_{config}. For instance, HEAs have been developed based on factors from physical, thermodynamic and electronic quantities, such as delta parameter (δ) [6], mixing enthalpy (ΔH_{mix}) [7] and valence electron concentration (VEC) [8]. These small numbers of quantities and resultant simple numerical calculations greatly enhance the development of HEAs.

The alloy designs for HEAs are principally simple and can be processed with numerical calculations. However, it should be noted that alloy designs of HEAs based on ΔH_{mix} do not include the information of crystalline structure, since the values of ΔH_{mix} [7] provided and frequently used for the development of HEAs are the ones for a liquid binary alloy with equi-atomicity for non-crystalline solids, such as amorphous and glassy alloys. Thus, ΔH_{mix}'s for bcc, fcc and hcp phases should be calculated instead of the ones for amorphous and glassy alloys as a function of composition in a binary alloy. However, the resultant ΔH_{mix}'s for the crystalline phases, if obtained, are extremely complicated and cannot be used for an alloy design for HEAs directly and efficiently. In this sense, the alloys designs for HEAs based on VEC has an advantageous aspect over those based on ΔH_{mix}, since it was reported [8] that conventional HEAs with bcc, bcc + fcc and fcc structures can be assessed with the values of VEC of alloys. This approach based on VEC for the alloy design for HEAs has something related to

* Corresponding author. 2-1-1, Katahira Aoba-ku, Sendai 980-8577, Japan.
E-mail address: takeuchi@imr.tohoku.ac.jp (A. Takeuchi).

http://dx.doi.org/10.1016/j.intermet.2015.06.014
0966-9795/

an approach to consider the crystalline structures of the constituent elements of pure metals, since the values of VEC for each element depends on the group of the periodic table. In reality, it is widely accepted that crystalline structure of pure elements changes in accordance of the group of the periodic table as well as VEC. Here, it should be noted that even binary alloys at equi-atomic composition ($A_{50}B_{50}$) can exhibit completely different crystalline structures to those of constituent elements. For example, binary phase diagrams [9] demonstrate that two pure elements with hcp structure, such as Mg, Y, Hf, Os and Zr, can yield a equi-atomic binary alloy with CsCl structure in Mg–Y, Hf–Os and Os–Zr systems. The change in crystalline structure of compounds from pure elements makes it difficult to predict a crystalline structure of HEAs in a multicomponent alloy systems.

These circumstances around HEAs mentioned above motivated the authors to consider a different approach for the development of HEAs depending on pure elements. Specifically, the authors hit on an idea to include to the crystalline structure at the $A_{50}B_{50}$ composition in A-B binary alloys by referring to the concept of HEAs with equi-atomicity. Here, binary phase diagrams [9] would provide the most reliable crystallographic information at the $A_{50}B_{50}$ composition, but this kind of crystallographic information of $A_{50}B_{50}$ phases from binary phase diagrams is neither well summarized in a simple form nor provided as a digitized source to utilize them as database for the development of HEAs. Besides, crystallographic database, such as Person's crystal data [10], is considerably awkward for this purpose and without versatility to handle for practical usage for it as the alloy design. As a result of the preliminary surveys, the authors have determined to utilize Pettifor map for compounds [11] for the following advantageous aspects. First, Pettifor map has its wide applicability in terms of the information of structure of binary compounds comprising over 70 elements, which has been summarized in accordance with the same scope of the mixing enthalpy (ΔH_{mix}) in a framework of Miedema's model [7,12]. Second, Pettifor map can compensate for the lack of the information of crystalline structure for the alloy design for HEAs based on ΔH_{mix}. Third, Pettifor map provides crystallographic information for binary AB compounds with 1:1 stoichiometry, which directly relates to HEA based on a concept of equi-atomicity, together with the several other set of stoichiometry.

The purposes of the present study are to establish an alloy design for HEAs based on Pettifor map for AB compounds with 1:1 stoichiometry, to apply it to find out new HEAs and to examine its applicability.

2. Methods

First, Pettifor map [11] for compounds with a set of stoichiometry of 1:1, and 1:2, 1:3, 2:3, 3:4 and 3:5 and their opposite ratios were digitalized in spread sheet for computations in advance for the subsequent usage as a database. An especial attention was paid to Pettifor map for AB compounds with 1:1 stoichiometry because

Table 1
Pettifor Map for AB compounds with 1:1 stoichiometry between elements with atomic numbers of (a) 1–46 and (b) 46–94 where the data lack for Pm. Reproduced with permission from the original literature of Pettifor map [11].