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Combining thermodynamic modeling and 3D printing of elemental powder blends for high-throughput investigation of high-entropy alloys – Towards rapid alloy screening and design

Christian Haase[a,*], Florian Tang[b], Markus B. Wilms[c], Andreas Weisheit[c], Bengt Hallstedt[b]

[a] Department of Ferrous Metallurgy, RWTH Aachen University, 52072 Aachen, Germany
[b] Institute for Materials Applications in Mechanical Engineering, RWTH Aachen University, 52062 Aachen, Germany
[c] Fraunhofer Institute for Laser Technology ILT, 52074 Aachen, Germany

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ABSTRACT

High-entropy alloys have gained high interest of both academia and industry in recent years due to their excellent properties and large variety of possible alloy systems. However, so far prediction of phase constitution and stability is based on empirical rules that can only be applied to selected alloy systems. In the current study, we introduce a methodology that enables high-throughput theoretical and experimental alloy screening and design. As a basis for thorough thermodynamic calculations, a new database was compiled for the Co–Cr–Fe–Mn–Ni system and used for Calphad and Scheil simulations. For bulk sample production, laser metal deposition (LMD) of an elemental powder blend was applied to build up the equiatomic CoCrFeMnNi Cantor alloy as a first demonstrator. This production approach allows high flexibility in varying the chemical composition and, thus, renders itself suitable for high-throughput alloy production. The microstructure, texture, and mechanical properties of the material processed were characterized using optical microscopy, EBSD, EDX, XRD, hardness and compression testing. The LMD-produced alloy revealed full density, strongly reduced segregation compared to conventionally cast material, pronounced texture, and excellent mechanical properties. Phase constitution and elemental distribution were correctly predicted by simulations. The applicability of the introduced methodology to high-entropy alloys and extension to compositionally complex alloys is discussed.

1. Introduction

Most alloys used for structural components are based on one principal element that is alloyed with additional elements to improve the overall performance of the material. In contrast to this classical approach, alloys without a predominant base element but high concentrations of multiple elements have opened an emerging field in materials science and gained high interest of the research community during the last years, resulting in constantly increasing numbers of publications per year since 2004 [1,2]. This new material concept originates from the pioneering studies by Cantor et al. [3] and Yeh et al. [4] and has been termed as high-entropy alloys (HEAs). HEAs contain five or more principal elements, which have a concentration in the range between 5 at% and 35 at% [4]. In these materials, the selection of elements and their high mixing entropy may lead to the formation of non-ordered single-phase solid solution with simple crystal structures, such as body-centered (bcc) or face-centered cubic (fcc) instead of multi-phase alloys containing intermetallic phases. In addition to the high-entropy effect, also the inherent slow diffusion kinetics, the severe lattice distortion, as well as the so-called 'cocktail effect' were identified as the core effects that influence the properties of HEAs. Due to the multi-component alloy concept, HEAs exhibit property combinations not found in conventional alloys, such as high hardness, strength and wear resistance, exceptional high-temperature strength, and high corrosion and oxidation resistance [5–9].

Although HEAs have now been under intensive investigation during the past 10 years, rules and approaches to predict phase constitution and phase stability in HEAs are still mainly based on empirical equations. The majority of approaches to describe the formation of non-ordered single-phase solid solutions or contrariwise the formation/suppression of intermetallic phases is based on three parameters: the entropy of mixing, ΔS_{mix}, enthalpy of mixing, ΔH_{mix}, and the

* Corresponding author.
E-mail address: christian.haase@iehk.rwth-aachen.de (C. Haase).

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atomic size difference, δ.[1] For instance, a non-ordered single-phase solid solution is likely to be formed when $12 \leq \Delta S_{mix} \leq 17.5$ J/Kmol, $-15 \leq \Delta H_{mix} \leq 5$ kJ/mol, and $\delta \leq 4.3\%$ [7,10,11]. However, other parameter ranges [12,13] as well as additional parameters [11,14–17] have also been suggested. Nevertheless, these guidelines do only hold for some selected alloy systems but often fail to predict phase formation for other alloys within the wide space of possible systems [18–20]. As recently summarized by Miracle and Senkov [21], a better thermodynamic understanding of HEAs is desirable in this respect. More importantly, focusing on formation rules for non-ordered single-phase solid solutions disregards the major opportunity opened by multi-principle element alloys, i.e. advancing from single-phase HEAs to multi-phase compositionally complex alloys (CCAs) with superior properties. In order to address this opportunity, the focus of this study was put on preparation of a thermodynamic database and evaluating the Calphad method for this system based on existing descriptions previously untested with HEAs. The corresponding predictability of chemistry- and temperature-related phase constitution allows to identify suitable alloy systems and heat treatment parameters depending on the requirements of the final application [22].

In order to validate the thermodynamic calculations, screen the materials properties, and build up materials libraries, high-throughput production of bulk samples with varying chemical composition is desirable [23,24]. Although there have been attempts for rapid alloy prototyping based on casting [25], this method is still limited in flexibility. In contrast we apply a powder-based approach using blends of elemental powders combined with consolidation by laser metal deposition (LMD). This technique offers several advantages that are utilized here [26,27]. (i) Usually expensive pre-alloyed powders are used for metal additive manufacturing (AM) to guarantee chemical and microstructural homogeneity. However, using elemental powder blends offers not only saving costs but also maximal degrees of flexibility in chemical composition. In addition, the possibility to further modify the composition of the powder blend by in-situ alloying during LMD, e.g. adding different amounts of Al to a CoCrFeMnNi elemental powder blend, allows even higher flexibility and throughput production. (ii) The rapid solidification and cooling during LMD-processing facilitates strong reduction of element segregation, which is of particular importance in highly alloyed systems, and thus may reduce/eliminate the necessity for homogenization annealing. (iii) LMD, as one of the most widely used metal additive manufacturing methods [together with selective laser melting (SLM) and laser beam melting (LBM)], is a promising production method for manufacturing components, e.g. for high-temperature aerospace applications [28–30]. As a method for rapid alloy development and a future manufacturing technique, the possibility to produce HEAs from elemental powders by LMD is investigated in this work.

In this study, we introduce a methodology that will allow high-throughput computation and experimental screening of HEAs/CCAs and facilitate easier design of new alloy systems. The methodology is schematically illustrated in Fig. 1. First, a new database was compiled from extensive literature review and re-calculation of all binary systems and sections of ternary systems to perform thorough Calphad calculations. This was done for the Co–Cr–Fe–Mn–Ni system. Second, the equiatomic Cantor alloy, i.e. CoCrFeMnNi, was produced using an elemental powder blend and LMD, as a first demonstrator. Third, the material was characterized with respect to microstructure, texture, and mechanical properties and compared to conventionally processed material. The applicability of the methodology will be discussed.

[1] $\Delta S_{mix} = -R \sum_i c_i \ln c_i$, $\Delta H_{mix} = \sum_{i=1, i \neq j}^{N} 4 \Delta H_{AB}^{mix} c_i c_j$, $\delta = \sqrt{\sum c_i \left(\frac{1 - r_i}{\bar{r}}\right)^2}$. Here R denotes the gas constant R=8.3144598(48)Jmol^{-1}K^{-1}, $c_{i,j}$ the concentration of element i and j, and r_i the atomic radius of i, and $\bar{r}$ the mean atomic radius.

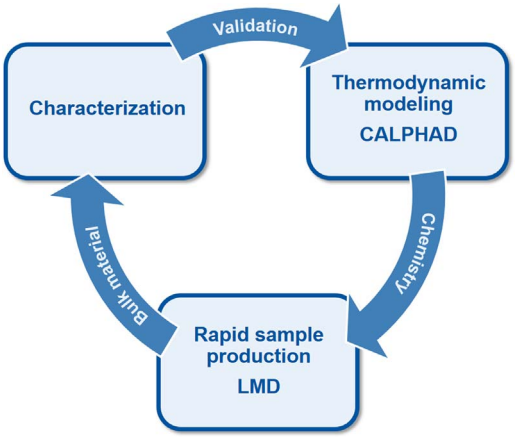

Fig. 1. Schematic illustration of the methodology used in the present study.

2. Applied methods

2.1. Material and processing by laser metal deposition

The nominal composition of the alloy investigated is given in Table 1. The equiatomic CoCrFeMnNi alloy was produced from a mixture of the five elemental powders (Co, Cr, Fe, Mn, Ni) that were acquired with technical purity (≥99.6% of the respective element). The size of the powder particles was in the range between 45 and 90 µm. The powders were mixed by means of a tumbling mixer Turbula 2 F for 30 min to achieve a homogeneous powder blend.

The LMD process was conducted on a 3 axis handling system by Schuler Held equipped with a fiber coupled diode laser system LDF 2000-30 by Laserline with a maximum output of 2 kW. This laser system emits laser radiation with two specific wavelengths of 900 and 1070 nm with a beam parameter product of 30 mm*mrad. The beam is led through an optical fiber with a core diameter of 600 µm into the optical system. The optical system consists of a collimation lens with a focus length of f_c=200 mm and a focusing lens with a focus length of f_f=400 mm resulting in a beam diameter of 1.2 mm in the focus point. The powder mixture is fed by means of a disc-based feeding system GTV PF 2/2, where the metal powder particles are conveyed by Argon carrier gas (purity≥99.996%) and subsequently injected into a coaxial powder nozzle (Fraunhofer ILT, Aachen, Germany). More information about the laser metal deposition process can be found elsewhere [31].

Bulk samples were produced on a hot-working steel substrate (1.2365/32CrMoV12-28) by using a bidirectional scan strategy, depositing 28 single tracks (track length of 20 mm) next to each other with a constant track offset of 700 µm (approximately 50% overlap). 57 layers were deposited in total with a constant height offset of 350 µm resulting in a cube of 20×20×20 mm^3. A parameter adaption was carried out based on experience to ensure fully melting of the powder and to produce dense layers. From this the final parameter set was chosen. The laser power of 370 W, deposition speed of 800 mm/min, and powder mass flow of 2 g/min were also kept constant in every layer. Argon was used as a shielding gas fed through the beam path in the powder feed nozzle. This provides an additional shielding of the melt pool from the atmosphere besides the carrier gas.

Table 1
Chemical composition of the investigated alloy.

Element	Fe	Mn	Cr	Co	Ni
(at%)	20	20	20	20	20
(wt%)	19.92	19.58	18.55	21.02	20.93