Thin Solid Films 520 (2012) 5491–5499

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

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

Critical review

Combinatorial thin film materials science: From alloy discovery and optimization to alloy design

Thomas Gebhardt *, Denis Music, Tetsuya Takahashi, Jochen M. Schneider

Materials Chemistry, RWTH Aachen University, Kopernikusstr. 10, D-52074 Aachen, Germany

ARTICLE INFO

Available online 28 April 2012

Keywords:
Combinatorial approach
Alloy discovery
Alloy optimization
Alloy design

ABSTRACT

This paper provides an overview of modern alloy development, from discovery and optimization towards alloy design, based on combinatorial thin film materials science. The combinatorial approach, combining combinatorial materials synthesis of thin film composition-spreads with high-throughput property characterization has proven to be a powerful tool to delineate composition–structure–property relationships, and hence to efficiently identify composition windows with enhanced properties. Furthermore, and most importantly for alloy design, theoretical models and hypotheses can be critically appraised. Examples for alloy discovery, optimization, and alloy design of functional as well as structural materials are presented.

Using Fe-Mn based alloys as an example, we show that the combination of modern electronic-structure calculations with the highly efficient combinatorial thin film composition-spread method constitutes an effective tool for knowledge-based alloy design.

Contents

1. Introduction

Combinatorial materials science, also referred to as combinatorial approach, aims at rapid discovery and optimization of known and new materials by combining efficient synthesis of a large number of different material compositions and high-throughput property screening methods to delineate composition–structure–property relationships [1,2] and hence to identify compositions with desired properties [1]. The combinatorial approach is also a powerful tool to appraise theoretical models and hypotheses [3–5]. Pioneering experiments in the field of combinatorial materials science were published in the 1960s [6,7]; Kennedy et al. [6] synthesized samples with composition gradients to rapidly determine isothermal sections of ternary phase diagrams and Hanak et al. [7] combined the deposition of compositionally-graded

* Corresponding author. Tel.: +49 2418025892; fax: +49 2418022295.
E-mail address: gebhardt@mch.rwth-aachen.de (T. Gebhardt).

0040-6090/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2012.04.062

thin films and high-throughput property screening in the search for new superconducting materials. Combinatorial techniques on a larger scale were applied in the pharmaceutical industry [8,9], where concepts of high-throughput synthesis of small organic molecule libraries and high-throughput screening for lead structures were combined, inspiring in the mid-1990s a resurgence of interest in combinatorial materials science to efficiently discover new functional solid-state materials [10–12]. In spite of skepticism in the academic community due to a popular perception of combinatorial materials science as a trial and error approach [3], it is today a well established fact that it has accelerated the discovery and optimization of inorganic materials [1].

Combinatorial bulk materials can be fabricated as diffusion multiples [13] as well as by solution-based methods [14]. The synthesis of combinatorial thin film samples can be carried out by physical vapor deposition [15], chemical vapor deposition [16], various electrochemical methods [17–19], and ion implantation [20]. Combinatorial thin film synthesis processes can be subdivided into two main groups: continuous and discrete composition methods. In the latter case, depositions are carried out sequentially utilizing masks [10], whereas the most common combinatorial thin film synthesis process, the continuous composition technique, is based on co-deposition, and therefore also known as the composition-spread method [15]. A schematic experimental setup of this synthesis method is presented in Fig. 1.

The increasing interest in, and hence use of, the combinatorial approach in materials science and engineering within the last decade is also highlighted by numerous reviews on this topic, focusing on the historical evolution and state-of-the-art of the combinatorial approach [2,3,14,21], on different synthesis methods for combinatorial samples [2,3,14,21–26] and corresponding characterization tools [14,22,24,27], as well as on specific materials classes such as functional materials [1,22,28]. All of these reviews conclude that the combinatorial approach constitutes a powerful tool for the delineation of composition–structure–property relationships, and hence for materials discovery and optimization.

In the present paper, we review the development of metallic alloys utilizing thin film composition-spreads in combination with efficient property screening methods for various applications. The focus is on the significance of this research strategy for identifying the underlying materials science. Hence, we distinguish among alloy discovery, alloy optimization, and alloy design. The latter has to include, according to our understanding, theoretical guidance and hence knowledge of the underlying materials science. Alloy discovery and optimization however, do not necessarily involve detailed information regarding the underlying material science; enforced serendipity and the systematic delineation of composition–structure–property relationships enable discovery and optimization within the boundaries of the studied composition-spread. Using Fe-Mn based alloys as an example, we report that the combination of modern electronic-structure calculations with the highly efficient combinatorial approach constitutes an effective tool for knowledge-based alloy design.

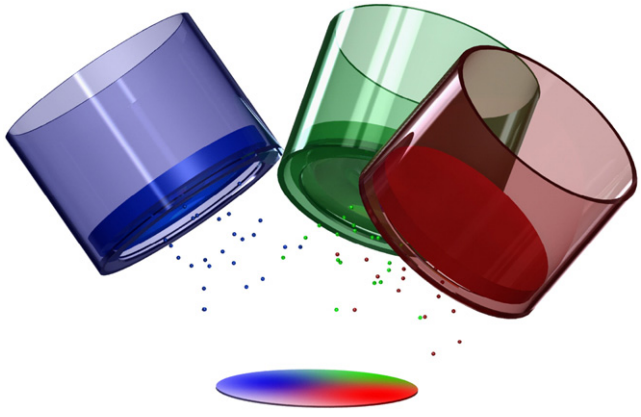

Fig. 1. Schematic experimental setup of the composition-spread method with three vapor sources.

2. Applications

2.1. Transducer materials

Transducer materials such as magnetostrictive, piezoelectric, and shape-memory materials, which directly convert electrical into mechanical energy and vice versa, present an interesting materials platform for realizing new actuators and sensors in microsystems as they can easily be scaled to small lateral dimensions, especially if they are synthesized by thin film deposition techniques [29]. Furthermore, thin film transducers are of special interest as they are suitable for cost-effective mass-production and compatible with microsystem or microelectronic process technologies. In this section, we focus on the discovery, optimization, and design of shape-memory, ferromagnetic shape-memory, and magnetostrictive alloys utilizing the composition-spread method.

2.1.1. Shape-memory alloys

Shape-memory alloys (SMA) are characterized by forward and reverse transformation between martensite and the austenite phases [29]. The shape-memory effect (SME) is a phenomenon, in which the application of a load leads to a change in microstructure from austenite to martensite. The load-induced phase transformation can be completely reversed upon heating to a temperature above the transformation temperature [30]. Ti-Ni based alloys are the most prominent and actively investigated SMAs [30]. Two major drawbacks associated with SMAs are the temperature/stress hysteresis and the limitation to low frequency applications due to slow cooling [30,31]. The temperature/stress hysteresis characterizes the reversibility of the martensite–austenite transformation and is also understood to be a limiting factor controlling the fatigue properties of SMAs [32].

A modified wedge-type composition-spread method, where elemental layers with a thickness gradient are sequentially deposited, followed by a heat treatment resulting in a gradient in chemical composition [31], has proven beneficial for the discovery and optimization of Ti-Ni based alloys [31,33–35]. Zarnetta et al. [33,34] and Lobel et al. [31] systematically mapped the phase transformation characteristics of Ti-Ni-Cu and Ti-Ni-Pd shape-memory thin film composition-spreads for microactuator applications by correlating the transformation temperatures, the thermal hysteresis, and the temperature interval of transformation and/or the recovery stress with the chemical composition to develop optimized Ti-Ni based SMAs. Fig. 2 displays the thermal hysteresis in $Ti_{51}Ni_{49-x}Cu_x$ alloys as a function of the chemical composition. With increasing Cu content up to ~6.5 at.%, the thermal hysteresis rapidly decreases from >20 K to reach an almost constant value of ~7.5 K for higher Cu contents. This observation is known to be linked to a change of the transformation pathway.

To enable the design of SMA with optimized fatigue properties, Cui et al. [4] investigated the applicability of the geometric nonlinear theory of martensite, a theory of the origin of reversibility of phase transformations [36–39], using the combinatorial approach. The theory describes the fundamental cause of large transformation hysteresis and predicts that the hysteresis can be drastically reduced by improving the geometric compatibility of the martensite and austenite phases. Hence, geometric compatibility is a possible design criterion for SMAs with improved fatigue properties. According to this theory, the middle eigenvalue λ_2 of the transformation stretch tensor that maps the martensite to the austenite lattice of SMAs, and that can be derived if the lattice parameters of both the austenite and the martensite phases and their symmetries are known, should be equal to one. Since the substitution of Ni by Cu in Ti-Ni-Cu alloys is known to be effective in decreasing the transformation temperature