Journal of Alloys and Compounds 664 (2016) 351–362

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Compositional dependent high temperature crystalline phase formation on manganese–silicon thin film combinatorial libraries in controlled oxidizing atmospheres

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ARTICLE INFO

Article history:
Received 31 August 2015
Received in revised form
10 December 2015
Accepted 20 December 2015
Available online 23 December 2015

Keywords:
High temperature oxidation
Water content
Thin films
Vapor deposition
Diffusion

ABSTRACT

Wide compositional range Mn–Si thin film combinatorial libraries were used for studying the influence of the oxidation potential of the annealing atmosphere (510–12,500 ppm H_2O at 900 °C) on phase formation. For all annealing conditions, the formation of silicide phases was evidenced. A threshold for O incorporation in newly formed crystalline phases was found to be related to water contents between 510 and 2880 ppm. In spite of the influence of high potential for oxidation on phase formation, silicide phases were identified for Si-rich alloys. The formation of higher manganese silicide (HMS) phases was identified in the compositional zone ranging from 56 at.% to 80 at.% Si and the exact phases were determined to be influenced by the annealing conditions. With higher water content in the atmosphere, the formation of Mn_4Si_7 was favored. However, independent on the increase in the water content the HMS formation was generally not inhibited by the applied annealing atmosphere. Given the wide range of possible application of HMS, this is highly relevant for the formation of HMS bulk or thin film materials.

1. Introduction

The binary system Mn–Si is of wide scientific interest due to the numerous applications of these alloys, their good availability and low costs. Both, aluminum and steel industries are major users of Mn, Si and their alloys. The specific mechanical and/or electrical properties of steels [1–5] or aluminum alloys [6–8] are much improved upon alloying with these elements. The microstructure of such alloys plays an important role for following reactions which can be either thermodynamically or kinetically controlled resulting often in an unexpected behavior [9]. Moreover, the use of Mn containing silicides is highly relevant due to their good thermoelectric and optoelectric properties [10–14]. Additionally, the corrosion resistance of different silicides especially at higher temperatures is described as excellent due to the formation of a stable silica layer on the surface, protecting therefore the bulk material [15–17]. This led to the particular subject of silicide formation to be in the focus of recent investigations. Higher manganese silicides (HMS) with the general formula $MnSi_{1.75-x}$ ($x \leq 0.05$) is one main class of materials which are under investigation. These phases can either be formed as bulk materials or as thin films but the preparation methods are always extensive [11,18–23]. Additionally, a specific heat treatment at temperatures above 300 °C is necessary in order to form the desired silicide phases [12,14,24–28]. These materials are usually produced in very narrow concentration ranges (62–66 at.% Si, residual Mn) in order to successfully prepare the desired phases during subsequent annealing treatments in vacuum or under inert Ar atmosphere [21,29–32].

Recently, various studies regarding metal alloys and their oxides are performed on thin film combinatorial libraries rather than on bulk samples due to the clear advantages mainly represented by the identical alloy formation history, ease of fabrication and possibility

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http://dx.doi.org/10.1016/j.jallcom.2015.12.155
0925-8388/

of fast identification of relevant compositions by screening with appropriate tools. The possible application fields are extensive including high impact topics from thin film corrosion science [33], high-k electronics [34], photoelectrochemistry [35] and electrocatalysis [36]. Both Si and Mn are easily deposited from vapor phase being suitable as sources in co-deposition vacuum systems due to their thermally accessible evaporation temperatures and reasonably low volatility. Moreover, their good adhesion on metallic substrates (e.g. steel or Fe) allows obtaining model samples suitable for investigations of high temperature phase formation.

In the current work, a thin film combinatorial library with a wide compositional spread (Si-20 at.% Mn to Si-62 at.% Mn) was produced via thermal physical vapor co-deposition. This fast, easy and cost efficient preparation method helped to investigate the phase formation on this wide compositional spread upon heat treatment. To the best of our knowledge, for the first time the used heat treatment was performed in H_2O-containing atmosphere in order to subject the as-prepared Mn–Si compositional spread to severe but well-defined oxidizing conditions [37].

2. Experimental

A self-developed state of the art thermal co-evaporation chamber with a base pressure in the range of 10^{-5} Pa was used for the co-deposition of Mn–Si thin film combinatorial library. The special design of the co-evaporator ensures the geometrical requirements for co-deposition [38]. Two independent thermal baskets (W wire) holding BN crucibles containing high purity Mn or Si (>99.9%, Alfa Aesar) were simultaneously heated for this purpose via Joule effect using high DC currents. The Mn and Si sources were positioned off-center with respect to the substrate leading to a compositional gradient along the substrate due to the cosine law of evaporation governing the spatial distribution of individual atomic species [39,40]. The deposition distance was set to 120 mm for both sources. The Mn–Si library was deposited on industrial grade Fe substrates (99.6% purity, supplied by voestalpine Stahl GmbH). The substrate material was cold rolled and subsequently annealed in order to achieve a thickness of 1.4 mm and a grain size of around 20 μm. In a follow-up step, the Fe substrates were precut in rectangular shapes of 10 × 77 mm^2 and five of them at a time were inserted in the vacuum chamber aligned with the deposition sources. In this way, virtually identical compositional spreads were obtained on the substrates during the same deposition process. The surfaces of the substrates were sequentially ground before being used as substrates for thin film deposition and in a last stage diamond paste with 1 μm particle size was used.

The rates used for the simultaneous deposition of Mn and Si were 0.4 and 0.25 nm s^{-1}, respectively, as calculated aiming at a composition of Mn-50 at.% Si at the middle of the substrates. In order to achieve constant evaporation during deposition, an in-house-developed LabView software was used. The individual deposition rates were measured in real time by crystal quartz microbalances (QCMs) positioned above each thermal source and this information was feed-backed to the software for adjusting the evaporation sources DC power levels accordingly. The final thickness of the Mn–Si thin film library was approximately 200 nm at the middle of the substrate. Since the deposition sources used for Mn and Si were thermally heated (via Joule heating), heat was also transferred to the substrates during deposition by radiation. The substrate temperature increased to 130 °C as measured in vacuum directly on the sample holder at the end of the deposition.

After their deposition, the thin films were annealed using a resistively heated furnace. Due to the particularities of the setup, within the furnace it was possible to vary the annealing conditions in terms of temperature, atmosphere and water content. The water amount during annealing directly influences the potential for oxidation and throughout the present work this will also be referred to as oxidation potential not to be mixed up with same term in electrochemistry where the oxidation potential refers to an electrochemical potential. All annealing temperatures and atmospheres used are displayed in Table 1 and indexed as C1–C4. The heating and cooling rates were 10 °C s^{-1} and 5 °C s^{-1}, respectively. Usually, for precisely defining the O_2 partial pressure during an annealing sequence, the water content in the atmosphere is adjusted and controlled accordingly. For this reason the annealing conditions presented in Table 1 indicate both the content of H_2O and the calculated O_2 partial pressure. In order to observe the expected correlation between the partial pressure of O_2 and the temperature, an Ellingham-type diagram was used. The metal-oxide equilibrium partial pressure for the elements Fe, Mn and Si were thermodynamically calculated using specialized software (Factsage 6.3) and the results are plotted in Fig. 1. Additionally, the annealing conditions C1–C4 with varying water contents (described in Table 1) were also calculated. For all curves the calculations were performed using the thermodynamically most stable phases within the database.

The analysis of microstructure, composition and crystallographic particularities of the Mn–Si thin film combinatorial library were performed using scanning electron microscopy (SEM), energy-dispersive X-Ray (EDX) spectroscopy and grazing incidence X-Ray diffraction (GIXRD). The SEM surface imaging was performed using a Field Emission Gun Microscope Supra35 from ZEISS equipped with a secondary electron (SE) detector working at an acceleration voltage of 2 kV. An EDX system from EDAX with a Si(Li)-detector of 10 mm^2 and an acceleration voltage of 5 kV was used for determination of the chemical composition along the library by measuring at different equidistant points. The GIXRD characterization was performed at an incidence angle of 0.5° using an X'Pert Pro system (PANalytical) with a Co Kα anode which provides a wavelength of 178 pm. The Mn–Si thin film combinatorial library surface topography was visualized using an atomic force microscope (AFM) Nanosurf Easyscan 2 working in contact mode. The scanning Kelvin probe (SKP) is a very sensitive tool for the investigation of sample surfaces. Various changes, such as in morphology, chemical composition as well as adsorption phenomena can be tracked at micrometer resolution, with the advantage of a non-contact and non-destructive probing system. Since this is not a commercially well-established technique like SEM and XRD a short introduction is given in the following. The measurement principle has been invented over one hundred years ago and continuously improved to be applied in many scientific fields [41]. The technique is based on measuring the contact potential difference (CPD) between the probe tip and the sample. If two metals of different work function are brought in close vicinity and connected via an external circuit, their Fermi levels equalize resulting in oppositely charged surfaces. The electric field formed is nullified by an external voltage which magnitude is equal to the CPD [42–44].

In order to investigate the compositional dependence of the Mn–Si library surface potential, SKP measurements were performed using a commercial system (Wicinski & Wicinski GbR) equipped with a custom made measurement chamber allowing fully automatic monitoring and control of the atmosphere (e.g. oxygen content and humidity). The probe tip is made of a CrNi-alloy (90.1 wt.% Ni and 9.9 wt.% Cr) with a diameter of 300 μm and vibrated with fixed amplitude at 960 Hz. Scanning function is conducted via movement of the sample holder by software controlled DC stepper motors for X, Y and Z direction. Automatic height control via an external DC voltage applied to the AC coil voltage operates at a fixed displacement of 110 μm between probe tip and sample. Scanning parameters depended on sample size and