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The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Reaction-Diffusion in Co_2Si/Zn Diffusion Couple

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(Received: 2025/11/23, Revised: 2025/11/25, Published online: 2025/11/27)

Abstract
Periodic layered structures were examined in the Co_2Si/Zn diffusion couple annealed at 390 °C. SEM, TEM, EPMA, and XRD analyses revealed alternating Co–Si–rich and Zn–rich layers composed of CoSi, γ_1, and γ_2 phases with cell-to-cell variations in wavelength. The reaction zone thickness followed a parabolic time dependence, confirming diffusion-controlled growth governed by the Kirkendall effect. Three-dimensional FIB reconstruction showed complex layer morphologies, including branching and misalignment influenced by local diffusion pathways and grain orientations. EBSD measurements suggested no clear correlation between Co_2Si grain orientation and layer periodicity. These findings provide insight into multiphase reaction-diffusion mechanisms and the origin of periodic microstructures in the Co–Si–Zn system.

Introduction
In solid-state reactions, materials undergo transformations at the atomic level. These processes can include diffusion, chemical reactions, and phase transformations between solid reactants. Periodic layered structures are a specific type of morphology that emerges during such reactions. They are recognized by alternating layers (bands) of different phases arranged in a regular and repeating pattern. Periodic layer formation during solid-state reactions was first discovered in the early 1980s [1]. Over the past decade, several researchers have reported this phenomenon [2,3,4], proposing various explanations [5,6], though none have proven entirely satisfactory. This kind of morphologies can emerge during solid-state reactions in some ternary and higher-order systems [7]. These structures are characterized by regularly spaced layers (bands) of one reaction product embedded within a matrix phase of another. In this paper, we present our observations on the reactions between Co, Si, and solid zinc. The composition and crystal structure of the constituents forming the periodic layered microstructure during the solid-state reaction between Co_2Si intermetallic and zinc at 390 °C were examined using scanning electron microscopy (SEM), transmission electron microscopy (TEM), electron-probe microanalysis (EPMA) and electron backscatter diffraction (EBSD). We also present the 3D image and 3D analytical map of the reaction zone. The paper systematizes experimental findings from a diffusional and structural point of view. The development of reaction zone morphologies that are periodic in both time and space is attributed to the Kirkendall effect accompanying solid-state interdiffusion. The observed patterning during multiphase diffusion results from diverging vacancy fluxes within the interaction zone. These fluxes can lead to the formation of multiple Kirkendall planes, which, by attracting in-situ formed inclusions of a secondary phase, produce a highly patterned microstructure [8].

Methodology
Co (99.99), Si (99.98) and Zn (99.97) were used as initial materials. The compound was prepared by arc-melting method. The alloy ingots were melted several times and later annealed in Ar filled quartz ampoules at 950 °C for 168 h to improve their homogeneity. After standard metallographic processing, diffusion couples were made and heat-treated in a dynamic Ar atmosphere for different periods under uniaxial external load. Following the annealing, the specimens were prepared for LM, SEM, EPMA, X-ray diffraction (XRD) and EBSD investigations. Samples for EBSD studies were further polished with 0.04µm colloidal silica slurry for 20 min on a special polishing cloth. The selected area was finely polished with Ar-ion milling method.

Results

Light Microscope (LM) and SEM imaging reveal the existence of periodic, repeating layered structure. The Zn-Co_2Si solid state reaction exhibits certain unique characteristics. The reaction zone contains several cells with various morphologies. While some are irregular but still exhibit some degree of periodicity, others are regular and comprise parallel alternating layers with slightly wavy dark bands. From cell to cell, the band spacing – also known as the "wavelength" – varies. The varying wavelength is thought to be related to the mother phase of Co_2Si's crystallographic orientation. A mixture of reaction products forms the structure, where the composition also changes periodically. Light regions contain CoSi, γ_1 (Co_2Zn_{15}) and γ_2 ($CoZn_{13}$) phases, the black 'bands' are two-phase regions, CoSi precipitates in γ_1 and γ_2 parent phases. XRD measurements also confirmed the presence of these phases (Fig. 1.).

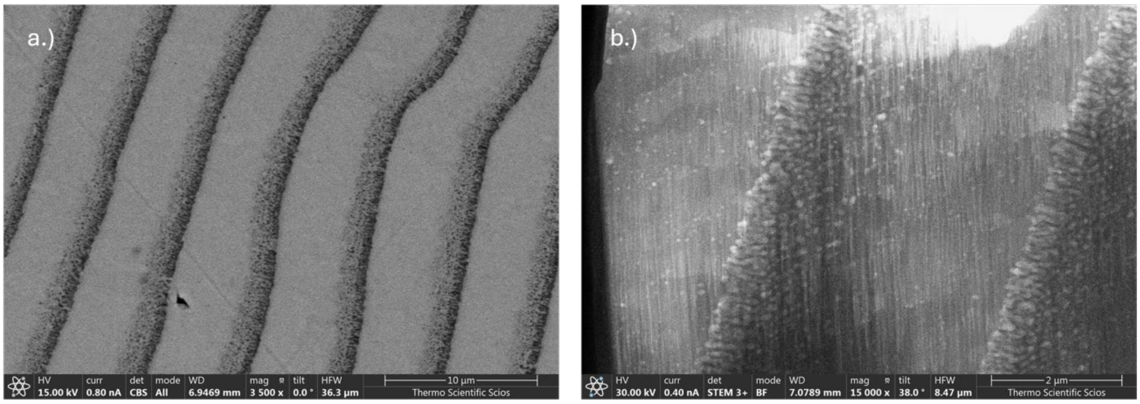

Fig. 1. Co_2Si/Zn diffusion couple annealed at 390°C for 72h. Scanning Electron Microscope (SEM) image on the left and TEM image on the right. Both images show that one reaction product embedded within a matrix phase of the another.

EPMA and line scan measurements also reveal alternating compositions. Fig. 2. shows that A and D regions are composed of CoSi phase, while region B is a mixture of CoSi and γ_2. Region C is a mixture of CoSi, γ_1 and γ_2 phases, in agreement with literature data [9].

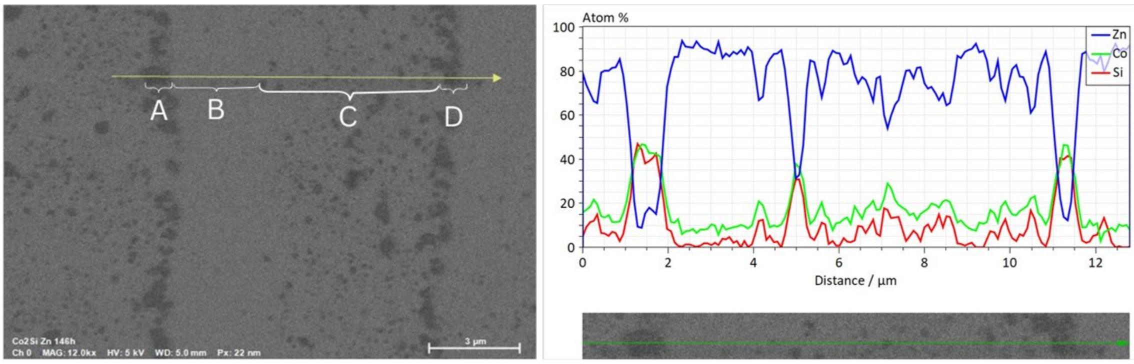

Fig. 2. Periodic Layers formed in Co_2Si/Zn diffusion couple (a.) SEM and (b.) linescan. (390 °C, 72 h)

The overall thickness of the reaction zone, as well as the number of the appearing bilayers follow a parabolic time dependence. It means that the process is completely diffusion controlled as it is displayed on Fig. 3.

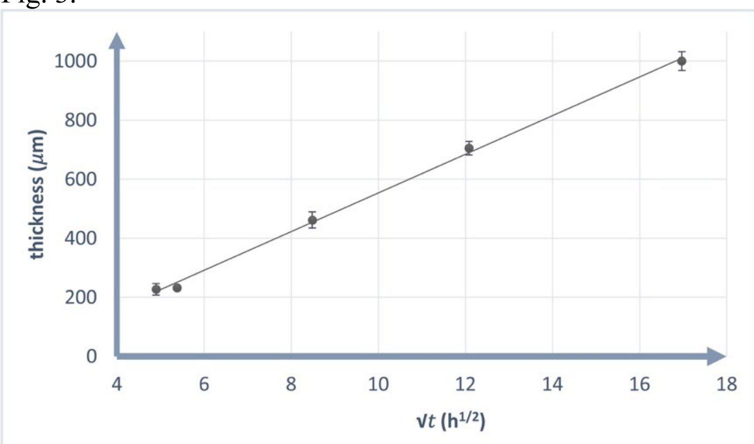

Fig. 3. Linear trend between the layer thickness and the square root of annealing time highlights a diffusion-controlled process.

A detailed volumetric reconstruction of the reaction zone was performed using Focused Ion Beam equipment (FIB). A specimen of about 15×15×10 μm^3 was prepared for the study, with slices of 20 nm thickness removed using the FIB. 473 slices were sequentially eroded and BSE images were captured after each erosion step. The AVIZO program was used to reconstruct the 3D structure of the sample from the acquired images. During this process, image alignment was required due to the shifts introduced by the milling process. Additionally, the contrast and brightness settings of successive images also needed to be fine-tuned. Several segmenting techniques were tested, and the most effective approach was using inverted contrast and brightness settings. This method along with cropping and filtering the images successfully separated the Co-Si rich bands from the surrounding Zn-based layers. The three-dimensional reconstruction allowed us to visualize the true morphology of the reaction layers and their transition between the neighboring cells (Fig. 4.). They revealed that some segments detach from their primary band and instead bridge to an adjacent band. These are interpreted as the result of local variations in the diffusion pathways and different grain boundary orientations. Furthermore, because the Co-Si layers are not perfectly aligned, we can say that the cross-sections taken perpendicular to the diffusion direction exhibit circular or oval patterns, which is consistent with the observations of literature data [7].

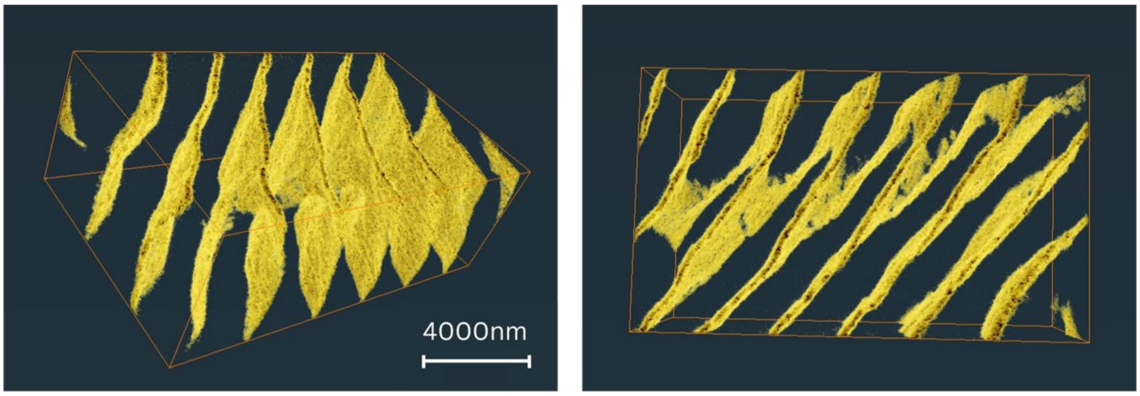

Fig. 4. 3D representation of the Co-Si intermetallic network, capturing branching dynamics from alternative layers.)

EBSD (Electron Backscattered Diffraction) measurements were performed to focus on the structural analysis of the reaction layer with a special attention of a possible connection of the Co_2Si orientations of the grain and the corresponding reaction layer's wavelengths. Two samples with different annealing times are chosen: 72h and 146h. This process detects Co_2Si in a chosen area of the sample and explores the different crystallographic orientations in different grains. For a deep analysis a Matlab based ATEX software package was used [10]. To find out if different patterns in the reaction layer correlate to different grain orientations, the crystal orientations for each unique grain in contact with the reaction layer was compared. After measuring more than 40 different grains we can say that the results were rather inconclusive, more data or single crystals of the Co_2Si with some known orientation is needed.

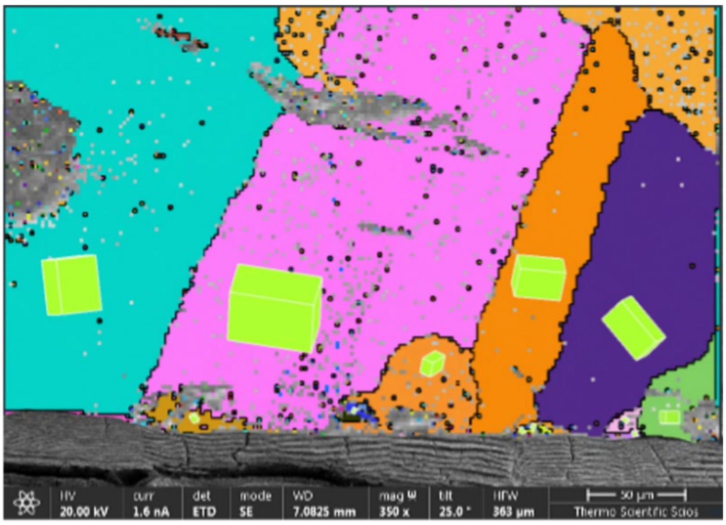

Fig. 5. EBSD post-processed Euler angle map together with crystal orientations in the orthorhombic Co_2Si grains)

Acknowledgement
This work was supported by the Development and Innovation Office NKFIH, Grant No.: OTKA. K143724.

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