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High-throughput in-situ characterization and modeling of precipitation kinetics in compositionally graded alloys

F. De Geuser [a,b,*], M.J. Styles [c], C.R. Hutchinson [d], A. Deschamps [a,b]

[a] Univ. Grenoble Alpes, SIMAP, F-38000 Grenoble, France
[b] CNRS, SIMAP, F-38000 Grenoble, France
[c] CSIRO Manufacturing Flagship, Clayton, 3168 VIC, Australia
[d] Department of Materials Science and Engineering, Monash University, Clayton, 3800 VIC, Australia

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ABSTRACT

The development of new engineering alloy chemistries is a time consuming and iterative process. A necessary step is characterization of the nano/microstructure to provide a link between the processing and properties of each alloy chemistry considered. One approach to accelerate the identification of optimal chemistries is to use samples containing a gradient in composition, ie. combinatorial samples, and to investigate many different chemistries at the same time. However, for engineering alloys, the final properties depend not only on chemistry but also on the path of microstructure development which necessitates characterization of microstructure evolution for each chemistry. In this contribution we demonstrate an approach that allows for the in-situ, nanoscale characterization of the precipitate structures in alloys, as a function of aging time, in combinatorial samples containing a composition gradient. The approach uses small angle X-ray scattering (SAXS) at a synchrotron beamline. The Cu–Co system is used for the proof-of-concept and the combinatorial samples prepared contain a gradient in Co from 0% to 2%. These samples are aged at temperatures between 450 °C and 550 °C and the precipitate structures (precipitate size, volume fraction and number density) all along the composition gradient are simultaneously monitored as a function of time. This large dataset is used to test the applicability and robustness of a conventional class model for precipitation that considers concurrent nucleation, growth and coarsening and the ability of the model to describe such a large dataset.

1. Introduction

The process of designing engineering alloys requires finding an optimal point in a chemistry space, subject to relevant constraints of processing. In all major alloy families, the number of alloying elements typically ranges from 5 to 10 and optimizing a composition in such multicomponent space is an extremely challenging task. The traditional approach is to try to decouple the interactions between different solutes and study alloys of discrete compositions. In recent years, considerable efforts have been launched (e.g. the Materials Genome Initiative (MGI) [1] and the Accelerated Metallurgy Project [2]) to develop new alloy design strategies using combinatorial methods in both computational material science and related experimental approaches that accelerate this alloy design process. Materials containing compositional gradients have long been used to map the composition space of alloys. Specifically, diffusion couples or multiples have been used for determining the effect of composition on the material structure (phase diagram identification [3–7]), on the diffusion of solute species [8], and on various properties related to materials chemistry (e.g. modulus [9], thermal conductivity [10,11]) and sometimes more complex properties such as shape memory alloy identification [12] or metallic glass formability [13].

However, a key characteristic of engineering metallic alloys is that their main properties depend not only on chemistry, but also on microstructure. Therefore, their optimization with respect to a given property requires an understanding of the effect of chemistry on the kinetic path of microstructure development during thermal or thermo-mechanical treatments. Few studies have actually tried to determine the microstructure development in compositionally graded materials from the point of view of combinatorial experimentation. The community interested in phase transformations in steels have used this approach to study the compositional limits for certain types of phase transformations [14,15]: the limits for the massive transformation [16,17], acicular ferrite formation [18] and allotriomorphic ferrite formation [19,20] have all been

* Corresponding author at: Univ. Grenoble Alpes, SIMAP, F-38000 Grenoble, France.
E-mail address: frederic.de-geuser@simap.grenoble-inp.fr (F. De Geuser).

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examined using specially designed samples containing a macroscopic gradient in either carbon or substitutional solute such as Ni or Mn. Sinclair et al. [21] have even used a sample containing a gradient in Nb content in one direction and a gradient in temperature in an orthogonal direction to simultaneously probe the effect of temperature and Nb content on the recrystallization of Fe. Similar approaches have been used by to study the compositional limits for coherent versus incoherent precipitation [22], order/disorder transformations [22,23], competition between spinodal decomposition and nucleation and growth [22], nucleation in the vicinity of phase boundaries [22,24] and the effect of Cu and Mg content on the rapid hardening phenomenon in Al–Mg–Cu alloys [25].

In all of these studies, the alloys were observed ex-situ after a specific heat treatment, which provided a snapshot of the microstructure (and hence of the corresponding potential properties) as a function of chemical composition. However, composition interacts in a complex manner with microstructure development during heat treatments, and an alloy design strategy requires the characterization of the full kinetic path in composition space. If this is to be done, in a combinatorial manner, by exploiting samples containing a macroscopic composition gradient, the characterization strategy requires tools exhibiting the following characteristics:

- Fast, quantitative characterization of the microstructural feature of interest.
- Spatially resolved with a high resolution compared to the size of the composition gradient, yet probing a volume large enough to guarantee sufficiently good statistics on the measured microstructure features.
- Time resolved with a time resolution sufficient so the kinetics can be monitored simultaneously in the desired number of locations within the composition gradient.

For the particular case of strengthening precipitation, the microstructural features of interest are the size, volume fraction and number density of precipitates. In most metallic systems the precipitate radius for maximum strength occurs at the nanoscale (often 2–5 nm). The only experimental technique that satisfies the three conditions above is small-angle X-ray scattering (SAXS). Reviews discussing the manner in which it can be used to provide a fast, quantitative characterization of precipitates can be found in [26–30]. The spatial resolution of these measurements is equal to the X-ray beam size, which is typically greater than 1 mm for laboratory sources and 100 μm for synchrotron experiments. Several studies have demonstrated the capability of SAXS to map the distribution of nanoscale precipitates in heterogeneous microstructures such as in welds [31–33]. Furthermore, SAXS is particularly well suited to be performed in-situ during heat treatments, along isothermal or more complex thermal paths (e.g. [34,35]). Depending on the particular contrast of scattering factors between the precipitates and matrix, acquisition times on synchrotron beamlines can be as low as 1–10 s, which opens the possibility to couple spatially and time-resolved experiments.

The aim of this contribution is to demonstrate the feasibility of in-situ, combinatorial studies of the effect of alloy composition on precipitation kinetics, and to use the acquired database as a tool for assessing the capability of a simple precipitation model in a wide range of compositions and temperatures. For the experimental proof-of-concept study, we have chosen a model system, Cu–Co. This system offers a number of advantages, including:

- This system is relatively dilute (a maximum of 2 wt.%Co is used), and the precipitates formed are almost pure Co [36]. These two conditions will make it possible to apply relatively simple precipitation models.
- At relatively low temperatures, the precipitates form as spherical particles [37–39], which simplifies the interpretation of the SAXS data;
- Cu–Co has been used several times as a model system (ie. spherical precipitates of pure Co exhibiting negligible strain with the matrix) to assess the capability of classical nucleation theory and more generally to provide a comparison with precipitation models [40,41].

As will be detailed below, the experiments involved preparing diffusion couples between pure Cu and Cu–2 wt.%Co, performing a solution heat treatment on the composition gradient material, and subsequently performing heat treatments at three temperatures (450, 500 and 550 °C) in-situ at a synchrotron SAXS beamline (BM02 – D2AM at ESRF) while measuring the SAXS signal at different positions along the composition gradient (Fig. 1). Co undergoes an allotropic phase transformation at 422 °C which is below the lowest temperature studied in this work. As a result Co precipitates as fcc particles under all conditions considered in this contribution. Experimental difficulties were yet encountered. They included some loss of Co during diffusion couple preparation that must be accounted for. The grain structure within the sample was such that double Bragg scattering interfered with the measured SAXS signal, and it was necessary to develop a specific methodology to deconvolute the two signals. Finally, a challenge was to link the observed precipitation kinetics to the local alloy composition where the X-ray measurement was made. A specific procedure was used to obtain an in-situ composition measurement with the help of the X-ray beam.

The precipitation kinetics, as a function of time, temperature and solute content has been modeled using the so-called numerical Kampmann–Wagner class model [42,43]. In relatively simple systems, such as that studied here, this model has been shown to provide a robust and efficient framework which compares satisfactorily with experimental results [43–46]. One advantage of this modeling technique is its good computational efficiency, which makes it possible to apply to a large set of experimental conditions with varying temperature and alloy composition, so that the results can be compared to the full dataset that is produced from the combinatorial experiment shown in Fig. 1. One of the interests here is to assess the limitations (and therefore the robustness) of this model when applied to situations where all parameters (e.g. diffusivity, driving force) vary widely.

2. Materials and preparation of the diffusion couple

The diffusion couples were prepared from pieces of Pure Cu and Cu–2.0Co (wt.%) produced by AMES Laboratory and contained impurity levels below 0.01%, as measured by ICP-AES. Pieces of pure Cu and Cu–2Co were first sectioned into cubes ~14 mm × 14 mm × 14 mm. To help the bonding between the alloys, pieces of each alloy were held together for ~10 min at ~500 °C using a hot compression machine before being encapsulated in a quartz tube and transferred to a tube furnace for 15 days at 1000 °C (above the solvus boundary for Cu–2Co). Diffusion calculations suggest that the Co gradient would be 500–600 μm after such a heat treatment. To further spread the compositional gradient, each diffusion couple was subsequently hot compressed in a channel die that constrained the deformation to the direction of the diffusion zone. This channel die hot compression was performed at 700 °C with a strain rate of $2 \times 10^{-3}\ s^{-1}$. The samples were reduced in height from ~15 mm to 7 mm which approximately doubled the length of the diffusion zone.

Samples were then solution treated at 1000 °C for 1 h, water quenched and sectioned into thin slices using a precision saw.