Full length article

Kinetics and morphological evolution of liquid metal dealloying

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ABSTRACT

Liquid metal dealloying (LMD) has recently emerged as a novel technique to fabricate bulk nanostructures using a bottom-up self-organization method, but the literature lacks fundamental studies of this kinetic process. In this work, we conduct an in-depth study of the kinetics and fundamental microstructure evolution mechanisms during LMD using Ti—Ta alloys immersed in molten Cu as a model system. We develop a model of LMD kinetics based on a quantitative characterization of the effects of key parameters in our system including alloy composition, dealloying duration, and dealloying temperature. This work demonstrates that the dealloying interface is at or near equilibrium during LMD, and that the rate-limiting step is the liquid-state diffusion of dissolving atoms away from the dealloying interface (diffusion-limited kinetics). The quantitative comparison between theoretically predicted and measured dealloying rates further reveals that convective transport and rejection of the dissolving element during coarsening of the structure also influence the dealloying kinetics.

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1. Introduction

Liquid metal dealloying (LMD) has recently emerged as a facile technique to fabricate bulk nanoporous and nanocomposite materials for a variety of applications including electrolytic capacitors, Li-ion battery anodes, and high-strength structural materials [1—5]. Dealloying is a corrosion process in metallic systems where one or more components are selectively dissolved from an alloy [6]. Historically, dealloying has been restricted to electrochemical corrosion where the less noble component(s) are removed, but the concept is now generalized to any embodiment of liquid-mediated dissolution. In electrochemical dealloying, the dissolving component(s) are removed by applying a potential which is above their standard reduction potential but below the standard reduction potential of the remaining component(s) [7—9]. During dissolution the remaining component(s) diffuse along the metal/liquid interface, self-organizing into a topologically complex, high surface area porous material. Analogously, LMD relies on enthalpies of mixing to facilitate dissolution [10,11]. Specifically, the liquid metal is chosen to have a negative enthalpy of mixing with the dissolving

component(s) and a positive enthalpy of mixing with the remaining component(s). The analogous critical potential in LMD is the concentration of the dissolving component in the liquid bath: the highest driving force for dealloying is when the concentration of the dissolving component in the liquid bath is zero, and there should be no driving force for dealloying when the liquid bath is saturated with the dissolved component.

While a majority of the work on this subject has focused on the characterization and properties of nanomaterials made by LMD, a recent phase field modeling study has shed light on fundamental mechanisms of structure formation [12]. This study also briefly addressed the kinetics of the dealloying process, but focused primarily on explaining the variety of topologically distinct morphologies formed during LMD as a function of alloy composition [12]. The goal of the present manuscript is to comprehensively characterize the dealloying kinetics and morphological evolution during LMD. We present an in-depth analysis of dealloying kinetics that examines the effects of diffusive transport, convective transport, and coarsening of the structure, all of which influence the dealloying rate. Our results provide a quantitative framework for optimizing the fabrication of nanocomposite and nanoporous materials.

For this study we chose our model LMD system of Ti—Ta alloys immersed in molten Cu. Ti and Ta form a solid solution with a body

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centered cubic (bcc) symmetry across the entire composition range at all processing temperatures, Ta is immiscible with Cu, and molten Cu has a high Ti solubility (approximately 75 at% for the temperature range in this study). During dealloying, molten Cu selectively dissolves Ti out of the alloy while Ta diffuses along the metal/liquid interface and reorganizes into a porous bicontinuous network. Copper remains inside the pores and fills the dealloyed-phase volume as it penetrates further into the alloy, and a dense Ta/Cu nanocomposite is formed upon cooling. A nanoporous structure can be excavated by chemically or electrochemically dissolving the Cu phase. The surface mobility of Ta at room temperature in an electrolyte is very low so the refractory phase remains undisturbed during chemical etching (as well as forming a passive oxide). Additionally, the Ti–Ta system is not limited to dealloying in molten Cu, and later in this manuscript we briefly examine LMD of Ti–Ta alloys in molten baths containing Cu, Ag, and Bi.

2. Experimental methods

Experiments were carried out by immersing Ti–Ta alloy samples into Cu baths; we varied the alloy composition, immersion time and reaction temperature to investigate how these parameters affected the dealloying depth, ligament size, and concentration profile in the liquid phase.

Ti–Ta alloys were prepared in-house by radio-frequency (RF) induction using an Ambrel Ekoheat 45 kW system by melting Ti (99.995 wt%), and Ta (99.95 wt%) pellets from Kurt Lesker in a water-cooled copper crucible from Arcast Inc. under flowing Ar (99.999 wt%). After casting the ingots were annealed under flowing Ar (99.999 wt%) for approximately 10 h and compositional homogeneity was confirmed using energy-dispersive X-ray spectroscopy (EDS). Master ingots of ~30 g were made of the following compositions: $Ti_{70}Ta_{30}$, $Ti_{65}Ta_{35}$, $Ti_{55}Ta_{45}$, $Ti_{40}Ta_{60}$, $Ti_{30}Ta_{70}$, and $Ti_{20}Ta_{80}$. Approximately 1 g samples (roughly $6 \times 2 \times 10$ mm) were cut for LMD from the master ingots using wire electrical discharge machining (wire EDM). After cutting, the samples were lightly sanded with 600 grit to remove the recast layer from wire EDM and Ta wires were spot-welded onto one end of each sample for the immersion experiments.

Prior to immersion, a 40 g molten Cu (99.99 wt%) bath was prepared [for each sample] in a high-purity alumina crucible cast in-house with materials from Cotronics at a preset temperature (1160, 1240, 1305, or 1360 °C). Temperature measurements were made using an infrared camera set to the emissivity of molten Cu. Prior to immersion, the sample was preheated by bringing it inside the RF coils –without touching the bath – to avoid thermal gradients between the sample and the bath. The sample was then immersed into molten Cu for a fixed time (between 10 and 120 s) and then removed from the bath, cooling the sample and solidifying the Cu inside the pores, halting the dealloying process.

Cross sections of the nanocomposites were mounted, polished, and characterized using a JEOL scanning electron microscope (SEM) in order to determine the average ligament size and measure the dealloying depth as a function of time, temperature and composition. ImageJ was used to measure dealloying depth and average ligament sizes. The dealloying depth was determined by averaging ~40 measurements taken from four images, which were from different regions of the sample. Fig. 1 shows a panel of SEM images with typical cross sections (here, of $Ti_{55}Ta_{45}$ dealloyed for 20 s at four different temperatures), illustrating our measurements of dealloying depth. The average ligament size was determined by averaging over ~20 measurements for a given depth. We included both the ligament diameters and nodes in our measurements of the ligament size. Additionally, EDS was used to determine the

composition of each phase as a function of depth. The composition for a given depth was determined by averaging over an area with a 1–5 μm diameter.

3. Results and discussion

3.1. Dealloying depth data

Fig. 2 shows raw data for the dealloying depth as a function of time for three different compositions and four different temperatures. Error bars are not included, but all depth measurements had a standard deviation below 30 μm and the majority had a standard deviation below 15 μm. Three obvious trends are apparent: the dealloying depth increases with time and temperature, and decreases with increasing Ta composition. The data also appears to follow a power-law relationship with time. We now introduce a dissolution model to interpret our data and understand the dealloying depth's functional dependence on time and temperature.

3.2. Dissolution model

Previous work on LMD systems have suggested the reaction is diffusion-limited and dependent on diffusion of the dissolving component (here, Ti) away from the dealloying interface [11,12], but have not introduced and rigorously tested a quantitative model. The concept of LMD in nobel metal systems was first introduced, and briefly explored, in 1959 by Harrison and Wagner who had also performed some of the initial work on electrochemical dealloying [13]. In this work they introduced a similar analytical model to the one described below, however their approach was heavily approximated because they were unable to measured concentration profiles and did not examine multiple temperatures. Consistent with previous work, here we assume that the dealloying kinetics are limited by diffusion of the dealloyed element in the liquid metal and further validate this hypothesis by quantitative comparison of theoretical predictions based on this assumption and experiments. Before we can introduce a dissolution model, however, we need to address two key points.

First, we need to assess the Ti concentration in the Cu phase at the dealloying interface. Specifically, we need to establish that the interface is at (or near) equilibrium during dealloying. This requires a direct measurement of the Ti concentration profile in the Cu phase in the dealloyed region, which we were able to accomplish because the Cu remains inside the pores and solidifies after dealloying. It is readily apparent in Fig. 3 that the Ti concentration at the interface is unique for a given parent alloy composition, Ti_xTa_{1-x}. This suggests that the interface is in chemical equilibrium and that the Ta composition at the interface has an influence on the equilibrium concentration, governed by the Ti–Ta–Cu ternary diagram and not the Ti–Cu binary diagram. Additionally, Fig. 3 illustrates that the interface concentration is relatively constant across the timescales and temperature range we are studying; for both parameters we did not observe a significant difference outside the error of our measurement (±5 at%).

Second, we need to address the dimensionality of this kinetic problem. In principle, the dissolving element is able to diffuse in three dimensions, but we are able to neglect lateral transport because the thickness of the diffusive boundary layer (of order 100 μm) – where the concentration of the dissolving element varies appreciably – is much larger than the pore size (of order 1 μm). As a result the LMD process can be simplified to a one-dimensional Stefan problem, the general class of free boundary problems where a phase boundary can move with time through a diffusion-limited process [14]. Since diffusion in the parent alloy is very slow at these temperatures, the velocity of the dealloying front