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Abstract

The structural stability of nanocrystalline aluminum-manganese (Al-6.5 at.%. Mn) alloys is studied in the temperature range of 200 to 400 °C. Transmission electron microscopy shows that grain growth in this alloy is subdued by the presence of Mn, such that 100 nm or finer grain sizes can be retained at 200 and 300 °C even after 1 month of annealing. In contrast, the principal mode of instability in the alloy is the precipitation of the equilibrium Al_6Mn phase, which was observed to form at much shorter time scales and is present at 300 and 400 °C after just 30 minutes. Differential scanning calorimetry was used to study the kinetics of the Al_6Mn reaction using Johnson-Mehl-Avrami-Kolmogorov analysis and construct a time-temperature-transformation (TTT) diagram for this process. It is found that this Al-Mn single-phase nanostructured alloy can be stable against forming the Al_6Mn phase and against grain growth for several months below 200 °C and for short thermal excursions up to 300 °C.

Keywords:

1. Introduction

Conventional aluminum-manganese alloys are widely used for manufacturing foil, roof sheets, cooking utensils, and rigid containers, because of their high ductility, good mechanical strength, and excellent corrosion resistance[1,2]. Beyond the conventional Al-Mn alloys, it has been suggested that electrodeposition of Al-Mn from room temperature ionic liquids could be a scalable way to produce nanostructured and amorphous alloys in this system, with superior mechanical properties[3]. In particular, the solid-solution Al(Mn) FCC phase can be deposited with a nanoscale grain size for compositions up to about 8 at.% Mn[4,5], and this phase can be both very hard and ductile[6]. This combination of properties is useful for applications requiring high specific strength and wear resistance, and the electroforming route is amenable to many product forms including foils, sheets, and thin-section net-shaped parts [6,7]. For these reasons, in the present work we explore the Al-6.5 at% Mn alloy specifically, which adopts a solid solution FCC nanocrystalline structure.

However, as with all nanostructured materials, the high proportion of grain boundary area in electrodeposited Al-Mn alloys raises questions of thermal stability. Nanostructured materials can suffer from grain coarsening at relatively low temperatures [8–10], and nanostructured aluminum in particular has been shown to exhibit grain growth from the nanoscale to the microscale when heated above 170 °C within one hour [11]. It is not yet established how the presence of Mn affects nanostructure stability in the Al-Mn system. In our recent work[5], we showed with high-resolution transmission electron microscopy and atom probe tomography that the grain boundaries in Al-6.5at%Mn are preferentially decorated with excess Mn solute, even in the as-deposited condition. This is a positive attribute of the system: grain boundary segregation suggests that the grain boundary energy is lowered as compared with an unsegregated boundary,

and segregation also should involve attendant solute drag forces that oppose grain boundary motion. On the other hand, Mn enrichment at the boundaries to levels as high as 12.5 at.% places the local composition well beyond the bulk solubility limit of 0.62 at.% and could facilitate decomposition of the system into FCC Al and second-phase intermetallic Al_6Mn. As with other nanocrystalline alloys such as Ni-P or Ni-W [12–15], the stability against not only grain growth but also phase separation is a question of practical concern for a proposed engineering material.

It is therefore our purpose in this work to explore the structural evolution of nanocrystalline solid solution Al-6.5 at% Mn alloys during post-deposition heating. We consider a broad range of times and temperatures, including both short, high-temperature excursions, as would be relevant for post-processing thermal budgets (i.e., for forming, joining, etc.), and long-term stability at lower temperatures, which would be relevant in usage. After first exploring the basic structure of the as-deposited alloys, Al-6.5at%Mn samples are subjected to calorimetry and annealing under various conditions to study grain growth and the eventual phase separation into the equilibrium solution-plus-intermetallic structure. The kinetics of the transformation process are analyzed using a Johnson-Mehl-Avrami-Kolmogorov (JMAK)-like kinetic model, and a time-temperature-transformation diagram is developed to guide thermal processing and usage of the alloy.

2. Experimental methods

A sheet of electrodeposited Al-Mn alloy was provided by Xtalic Corporation (Marlborough, MA). While the details of the electrodeposition process for this commercial alloy

The sheet was received still adhered to a 5 by 5 cm^2 brass panel. The deposit had a thickness of about 300 μm, and was removed from the substrate using concentrated nitric acid (79%, Sigma Aldrich) before being cut into small square specimens of about 25 mm^2 in area for composition measurement using calibrated energy-dispersive spectroscopy (EDS). Some of the specimens cut from the edges exhibited compositions away from the target composition of 6.5 at.% Mn by as much as 1-2 at.%. Accordingly, only specimens with concentrations close to the target of 6.5±0.4 at.% Mn were grouped together for further study in this paper; these generally came from the center of the deposited sheet.

X-ray diffraction (XRD) was conducted using a zero-background holder with a PANalytical X'Pert x-ray diffractometer operated at 40 mA and 45 kV with a Cu Kα source. Phase identification was conducted using Rietveld refinement, with the refinement template calibrated on standard silicon powder 640b, with a slit size of 2° and a beam size of 4 mm, from 15° to 125° 2θ. The XRD data was used only for phase identification and not for grain size estimation, because although the as-deposited grain size is below 100 nm, and therefore accessible by line broadening measurements, many of the annealed samples had grain sizes beyond the resolution limit available (~100 nm) with the present apparatus. Instead, grain size and microstructure were characterized using a JEOL 2010F transmission electron microscope (TEM). TEM samples were prepared by first manually thinning down the freestanding deposited sheet using SiC paper from 400 to 4000 grit, and subsequently electrochemically polishing in an etching solution with 5% perchloric acid, 20% butoxyethanol, and 75% methanol at -20 °C with 25V and 15 mA using a Fischione twin-jet polisher. The TEM samples were from roughly the

For the measurement of grain size, multiple dark field images were taken to achieve better contrast between grains, and over 100 grains were counted in this manner to determine the grain size distribution and average grain size.

Multiple types of annealing tests were conducted. For kinetic studies, at least 1 mg of sample was placed into a TA Discovery differential scanning calorimeter (DSC) to be scanned over the temperature range between 50 and 550°C at a constant ramping rate ranging from 5 to 15 °C/min, under flowing nitrogen. The slow ramping rate and large amount of sample used were to ensure the heat released during transformation was distinguishable from the background. Selected samples were sealed in glass ampoules under a purified Ar atmosphere, and isothermally annealed at 200, 300, and 400°C for various lengths of time for phase transformation and grain growth studies. The isochronal DSC measurements were used to fit parameters for a kinetic model, as described in Section 4. To ensure unbiased curve-fitting in determining the model parameters, the background heat flow was subtracted, and the remaining signal curve was interpolated using a custom MATLAB program to make sure that each dataset had the same number of evenly spaced data points.

3. Grain growth and intermetallic precipitation

Figure 1 shows the structure of the Al-6.5 at.% Mn alloy in the as-deposited condition. The bright field image in Figure 1(a) reveals a grain size that is in the nanocrystalline range, and the inset electron diffraction pattern identifies a single phase FCC nanocrystalline solid solution, with the first few diffraction rings indexed as (111), (200), (220), and (311). The grain size statistics for this sample were measured from a series of dark-field images (as described in

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Section 2) and shown in Figure 1(b). The average grain size is about 66 nm, and the distribution is reasonably tight with a standard deviation of 16 nm. The as-deposited structure also shows evidence of additional structural debris through the mottled appearance of the individual grains and the lack of definition of grain boundaries; this is likely associated with additional defects such as dislocations that are naturally present in the as-deposited condition.

TEM micrographs of samples after annealing at 200, 300, or 400 °C isothermally from 30 minutes to 1 month are shown in Figure 2 and Figure 3. Figure 2 focuses on the first few hours of annealing, while Figure 3 shows results after a month. At 200 °C, the first few hours of annealing lead to a mild coarsening of the grain structure, but the mottled appearance of the grains remains. After 4 hours of annealing, the average grain size is around 100 nm, and this appears to be a relatively stable condition as the structure after annealing one month at 200 °C, shown in Figure 3(a), does not present substantial additional coarsening. Moreover, the samples annealed at 200 °C do not exhibit any indications of second phase precipitation, even after one month of annealing.

XRD data for these annealed samples are shown in Figure 4, where the position of the dominant Al_6Mn peak is denoted with a diamond, and no peak develops at 200 ℃ after even a month of exposure, further corroborating the lack of phase evolution. This result is noteworthy because at 200 °C, the nominal solubility limit for Mn in FCC Al is reported to be 0.62 at.%[16], while the present material is beyond that limit by about 6 at.%. We can suggest two contributing reasons that this solution would remain mixed at this temperature (which is about half of the absolute melting point of Al). First, we have recently demonstrated [5] that in the as-deposited condition, this alloy exhibits mild segregation of Mn to the grain boundaries. The combination of a nanoscale grain size (with its increased volume of grain boundary sites), and an apparent

preference for solute to occupy those sites can together lead to an apparently increased solubility limit for such nanostructured alloys,[17] as solute can sit in the grain boundary instead of in the FCC lattice. Second, it is possible that the decomposition of the solution is kinetically suppressed over the timescale of months; the kinetics of the transformation are more easily assessed at higher temperatures.

At higher temperatures, the TEM observations reveal the emergence of second phase precipitation, as expected at this level of supersaturation. Close inspection of Figure 2 shows that within 30 minutes, the samples annealed at 300 and 400 °C already showed precipitates of the intermetallic Al_6Mn phase; some of these are marked with arrows. The XRD patterns of these samples are shown in Figure 5, revealing more clearly the emergence of the intermetallic phase after 30 minutes of annealing. Furthermore, the sample annealed at 400 °C exhibits higher intensity peaks, which means that the precipitation of Al_6Mn has occurred more rapidly and the reaction at 300 °C is not complete after 30 minutes.

Figure 6 shows the grain sizes as a function of time at 200, 300 and 400 °C. The grain size at 300 °C, after a slight relaxation at the earliest annealing time, stabilized at around 110 nm, which is close to the grain size of roughly 100 nm measured in the 200 °C sample after annealing. At 400 °C the increment of grain growth in the first 30 minutes of annealing is larger than for the other specimens, with an average grain size of greater than 150 nm. While we did not explore times-at-temperature beyond 30 minutes for 400 °C, this data point suggests sufficient mobility for the system to be evolving quickly to equilibrium and for grains to continue growing.

The presence of solute and its preference for grain boundary sites in particular is likely responsible for the stability of the grain structure at 200 °C; nanocrystalline pure aluminum at a

comparable temperature would have coarsened to the micrometer scale in about an hour [18–21]. Mn atoms in solution should provide kinetic stability through the conventional solute drag mechanism, and solute segregation at grain boundaries also lowers the excess energy of the grain boundaries and the driving force for grain growth[22–27].

Interestingly, at 300 °C, the grain size after 1 month of annealing is roughly unchanged even though precipitation of the Al_6Mn phase has occurred. There are a number of possible reasons for this dual-phase apparently stable nanostructural configuration. First, it is possible that the precipitation reaction has occurred only to a limited degree as compared with what would be expected for a bulk alloy, leaving some solute in the grain boundaries in equilibrium. Alloys in which phase separation is the ground state but grain boundary segregation is the first activated state (vis-à-vis a solid solution) are referred to as "nano-duplex"[28]. In the case of Al-Mn, the enthalpy of the intermetallic compound is -16.7 kJ/mol[29], the enthalpy of grain boundary segregation is roughly 1.5 kJ/mol[5], and the enthalpy of mixing is -102 kJ/mol[30]; it is therefore reasonable to expect some grain boundary segregation in equilibrium with the second phase at finite temperatures[27,31]. In this case the mechanism providing stability at 200 °C, i.e., grain boundary segregation and/or solute drag, is still in effect and is not entirely removed due to the precipitation of the second phase. Second, the formation of second-phase Al_6Mn is also expected to provide grain structural stabilization through Zener pinning. This new mechanism could effectively replace grain boundary segregation as a source of grain size stabilization, especially at lower temperatures where such pinning is kinetically effective.

It is not until the temperature is increased up to 400 °C that the grain boundaries are released. At high enough temperatures, we would expect both grain boundary segregation to be lessened, second phase precipitates to coarsen, and kinetic barriers associated with grain boundaries

detaching from either solute or second phase pinning points to be lowered [32]. It is encouraging that for all of the annealing conditions studied here, grain growth does not appear to be running away as is often seen in unalloyed nanocrystalline materials, and at 200 to 300 °C the grain size appears to stabilize around 100 nm for a duration of several months.

4. Kinetic analysis

Based on the above results, it is clear that during thermal exposure of nanocrystalline Al-6.5 at% Mn, grain growth is not the principal instability of the system. Rather, phase separation is the first major structural change to occur in these alloys upon heating, and this in turn may play a role in de-segregating the grain boundaries and potentially unlocking grain growth. Accordingly, the phase transformation represents the key degradation mechanism, and it is necessary to develop a quantitative picture of its kinetics. We approach this by using a Johnson-Mehl-Avrami-Kolmogorov (JMAK) analysis, such as has been used extensively for solid-state precipitation [33–36] and crystallization [37–42] reactions. The analytical JMAK solution for an isochronal process by Mittemeijer *et al.* is used here [43–46]. The so-called "extensive volume" in the JMAK analysis (i.e., the transformed volume without impingement of the transformation product precipitates) can be written as:

$$V_e = \int_0^t V \, \dot{N}(T(t)) Y(T(t)) \mathrm{d}\tau \tag{1}$$

in which V is the sample volume, $\dot{N}(T(t))$ is the nucleation rate as a function of time, t, and temperature, T, and $Y(T(t))$ is the time- and temperature-dependent growth rate. The transformation product can only form if there is parent phase left in which to form it, and if there

is solute left to feed it. These factors slow the transformation, and can be captured using the conventional relationship between the extended volume and the true transformation product volume, V_t:

$$dV_t = \frac{aV - V_t}{aV} dV_e \tag{2}$$

The parameter a represents the volume fraction at which the transformation saturates or completes. In the present case there is not expected to be any impingement of Al_6Mn precipitates because their equilibrium volume fraction is below $a = 25\%$ at temperatures ranging from 200 to 400 °C, with specific values at any temperature being easily calculable from the phase diagram[16] using the lever rule; instead the saturation of the reaction occurs by loss of solute from the matrix.

In what follows below, we will calibrate the parameters of the JMAK analysis using constant heating-rate DSC experiments. For such an isochronal condition, Mittemeijer *et al.* derive the following JMAK expression (adapted to include the equilibrium volume fraction, a)[47]:

$$f = 1 - \exp\left(-\frac{V_e}{aV}\right) = 1 - \exp\left(-\left(\frac{RT^2}{b}\right)^n \frac{k^n}{a} \exp\left(-\frac{nQ}{RT}\right)\right) \tag{3}$$

where $f = V_t / aV$ is the fraction of the transformation that has occurred at a temperature, T, given the (constant) heating rate, b, where, k is a pre-exponential factor accounting for nucleation rate effects, n is the growth exponent determined by dimensionality and growth mode, Q is the activation energy, and R is the gas constant.

The heat released during a DSC scan is proportional to the transformed fraction:

$$\frac{dH}{dT} = \Delta H \frac{df}{dT} \tag{4}$$

in which $\frac{dH}{dT}$ is the heat flow in the isochronal DSC experiment, ΔH is the total heat of transformation, i.e., the total area under the DSC curve after background subtraction to isolate the transformation peak.

Substituting Eq. (3) into Eq. (4), the heat flow during a constant thermal ramp is given as:

$$\frac{dH}{dT} = \Delta H \frac{1}{ab} nk^n (Q + 2RT) \left(\frac{RT^2}{b}\right)^{n-1} \exp\left[\left(\frac{RT^2}{b}\right)^n \frac{k^n}{a} \exp(-\frac{nQ}{RT}) - \frac{nQ}{RT}\right] \tag{5}$$

The DSC experimental results are shown in Figure 7 as black solid lines along with the least-squares best-fit form of Eq. (5), with heating rates from 5 to 15 °C/min. The black lines are the experimental data, and the red dashed best-fit lines achieve a very satisfactory coefficient of determination of $R^2 = 0.98$. The fitting here used exactly three unknowns, namely k, Q, and n, and all of the data sets in Figure 7 were fitted simultaneously with the same values of these parameters. The fitted reaction constant k = 99.2 s^{-1} is not of immediate physical significance, but the values of n and Q are mechanistically important.

First, the activation energy is fitted as Q = 126.9 kJ/mol. In the literature, the precipitation activation of Al$_6$Mn formation from 3 at.% Al-Mn alloys, Al-Mn-Mg alloys, and 3003 Al alloys were measured between 80 and 167 kJ/mol[48–50]. The present value is quite in line with these values. It is also appropriately lower than the activation energy for bulk diffusion of Mn in FCC Al, which is given as roughly 200 kJ/mol[51], as we expect the nanostructure and excess concentration of Mn at grain boundaries to access short-circuit grain boundary diffusion preferentially during the precipitation reaction.

Second, the fitted value of the kinetic exponent is n = 1.6, which in the JMAK analysis is defined as[47]

$$n = \frac{d}{m} + c \qquad (6)$$

where d is the dimensionality of the transformation, $m = 1$ for interface limited growth and 2 for diffusion controlled growth, and c is a constant that lies between 0 to 1, suggesting a more or less site saturation nucleation process (c = 0) vis-à-vis a continuous nucleation process (c = 1). From the volume and condition of the sample, the Al_6Mn is a 3-dimensional process, so we may assume that d = 3. Since n is measured to be 1.6, we can further conclude that growth is a diffusion controlled process (m = 2) and nucleation is likely site-saturated (c = 0.1). These conclusions are eminently reasonable in light of the physics of the process, which involves slow solid-state diffusion to collect solute to the precipitates, and starts from grain boundaries that are segregated with solute, with an abundance of viable nucleation sites.

5. Isothermal transformation kinetics

The above experiments were all based on a constant thermal scan rate in DSC, but they calibrate the kinetic model for the transformation more generally. With the resulting fitting parameters, a conventional isothermal time-temperature-transformation (TTT) diagram can be constructed for the Al_6Mn precipitation reaction using Eq. (5). This construction requires that the isochronal transformation data be converted to isothermal data, which can be accomplished using the inverse additive rule[52]:

$$\tau(f,T) = \left(\frac{dT}{db}\right)_f \qquad (7)$$

where $\tau(f,T)$ is the time to reach a fraction transformed, f, at temperature, T, which can be determined from the derivative of the temperature (at which the same fraction transformed would be reached isochronally) with respect to the heating rate. This derivative is performed numerically on Eq. (3) using the fitted parameters.

The resulting TTT diagram is shown in Figure 8, with contour lines for 1%, 50% and 99% transformed states. The TTT diagram derived from the isochronal experiments compares reasonably well with the independent experimental results based on isothermal annealing. In the TTT diagram, the reaction begins at roughly 30 seconds and completes after about 45 minutes at 400˚C, which is roughly in line with the observation of intermetallics after 30 minutes in the isothermal experiment (see Figures 2 and 5). At 200˚C ($T = 0.5T_m$), it was experimentally observed that no transformation occurred after 1 month, which is on the same order of magnitude as the time predicted in the TTT diagram for the transformation to begin (roughly 27 days). The TTT diagram seems to slightly overestimate the time required to start the transformation at 300 and slightly underestimate the time at 200˚C, which is a result of using the fitted form of Eq. (3) at heating rates outside of the 5 ˚C/min to 15 ˚C/min window, but still provides a reasonably accurate result. The strong correspondence between the kinetics attained from DSC and observations from microscopy suggests that the TEM microstructures are representative of the overall film.

This TTT diagram can serve as a general guideline for heat treatment processes. For example, a rapid thermal excursion at 300˚C without transformation is possible for post-processing operations such as soldering. It also suggests that the alloy can have a reasonable

stable service lifetime at temperature below 200°C, which is of practical engineering use. Interestingly, the time-to-transformation increases dramatically below 200 °C, growing to 4 months at 175 °C.

6. Conclusion

In conclusion, the nanostructure evolution for Al-6.5 at.% Mn, including grain growth and phase transformation, was explored. The alloy is a single-phase solid solution alloy with a grain size of approximately 65 nm in the as-deposited condition, with Mn segregated at grain boundaries and a supersaturation of Mn in the grains. Whereas grain growth is generally suppressed in the solid solution phase, the phase separation that produces Al_6Mn is the principal instability in this system. Grain growth is restrained to average grain sizes of roughly 100 nm up to 300 °C even after 1 month of annealing.

By studying the Al_6Mn precipitation reaction using isochronal differential scanning calorimetry, we evaluate the JMAK parameters underlying the phase transformation. The resulting kinetics are consistent with a three-dimensional diffusion-controlled process with an activation energy of 127 kJ/mol, which is reasonable in light of prior work on the same reaction in other (non-nanocrystalline) alloys in this family. These transformation kinetics allowed for the construction of a conventional isothermal TTT diagram across a large temperature and time range. Through extended isothermal annealing experiments, the TTT diagram was verified to be reasonably predictive. Experimentally at 200 °C, which is one-half of the melting temperature of Al, the alloy can retain its nanostructure over a month of annealing, without significant formation of intermetallic phases. The TTT diagram further predicts that the alloy can sustain longer

annealing times for at least several months without formation of intermetallics at 175 °C, which makes the alloy amenable to some downstream engineering processes such as soldering, and possibly for extended use at modest elevated temperatures.

7. Acknowledgements

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(a) 200 nm

(b)
Mean = 66
STD = 16

Counts

Cumulative Percent

Grain Size (nm)

30 min   1 hr   2 hrs   4 hrs

200°C   100 nm   100 nm   100 nm   100 nm

300°C   100 nm   100 nm   100 nm

400°C   100 nm

As-deposited

100 nm