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Study on Dissolution of Al₂Cu in Al-4.3Cu and A205 Cast Alloys

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Abstract: Evolution of microstructure in a binary Al-Cu system (Al-4.3Cu) and a commercially alloyed Al-Cu system (A205) during solution heat treatment was investigated using optical microscopy (OM), scanning electron microscopy (SEM), wavelength-dispersive X-ray spectroscopy (WDS), and differential scanning calorimetry (DSC). The diversified coarseness of the microstructure was initiated by controlling the solidification rate. Different solution treatment temperatures were applied to identify a proper solutioning temperature. The larger microstructural scale required an increased solutioning temperature and prolonged holding time to obtain homogenized solutes in the α -Al matrix. The diffusion of Cu primarily controlled the solution heat treatment process. A diffusion-based model was applied and calibrated to determine the dissolution rate of an Al₂Cu particle in the matrix. The model operates on a similar time scale with the experimental results for the Al-4.3Cu and A205 alloys with various microstructural scales, different chemical compositions, and at different solution treatment temperatures. Three-dimensional (3D) reconstructed images from SEM images and energy dispersive spectroscopy (EDS) map of elements showed that TiB₂ particles shield the Cu-rich phases in the boundaries of α -Al grains, presumably acting as a physical barrier to the diffusion of Cu solutes toward α -Al grains. The model also suggests that the effective diffusion coefficient of Cu in Al, in the presence of TiB₂ particles, reduced by a factor of 2.0–2.5 in the A205 alloy compared with the binary Al-Cu alloy.

Keywords: Al-Cu alloy; A205; solution heat treatment; TiB₂ particles; diffusion-based model

1. Introduction

Aluminum has been utilized in the aerospace industry, primarily due to its high strength-to-weight ratio. Alloys of 2xxx class are Al-Cu based cast alloys, which can retain strength and hardness at temperatures up to 250 °C [1,2]. Alloys in this class rely on a combination of solid solution strengthening, precipitation hardening by θ'' and θ' precipitates, together with dispersion hardening by Al₂Cu intermetallics [3]. Al₂Cu particles precipitate mainly at the α -Al grain boundaries, however, the precise structure and distribution is determined by the cooling rate [4,5].

The A205 alloy claimed to have the highest tensile strength among the 2xxx class of alloys, is employed in aerospace industries to satisfy the demand for lightweight and high-performance material [5]. A205 is an Al-Cu based system alloyed with Mg, Ag, Ti, and B elements. The addition of Mg substantially strengthens the alloy through solid solution strengthening [6]. Small additions of Ag improve age-hardening response in Al-Cu-Mg alloys. During aging, Ag promotes precipitation of thin

plates of finely dispersed Ω phase formed on the $\{111\}$ α -Al planes instead of the θ'' and θ' phases formed on the $\{100\}$ α -Al planes [7–9]. Addition of Ti together with B results in grain refinement and formation of rigid reinforcing TiB_2 particles with a high level of continuity in the grain boundary [5], which significantly improves tensile strength and wear resistance. Presence of 4.5% TiB_2 in A205 classifies this alloy as a particulate reinforced Al matrix composite (AMC).

A substantial improvement in the strength of 2xxx alloy series is obtained by precipitating large amounts of θ' and Ω phases through a T6 heat treatment, which consists of solution heat treatment (SHT), quenching, and artificial aging [10]. The highest precipitation rate takes place when Al_2Cu secondary phases, formed during solidification, are dissolved entirely, and Cu solutes are evenly homogenized in the α -Al during the SHT process [11].

During solidification, the heat transfer is locally different in a cast component, which leads to variations in the size of microstructural features [12]. Homogenization kinetics is strongly influenced by the morphology of microstructural features, such as coarseness of Al_2Cu and size of α -Al secondary dendrite arms. An increased solidification rate results in a smaller microstructural scale (e.g., smaller α -Al grains and secondary particles). Zamani et al. [13] compared the dissolution rates of Al_2Cu particles in an Al-Si-Cu cast alloy with two different secondary dendrite arm spacing (SDAS) at 10 and 25 μm . The dissolution rate of Al_2Cu particles during heating at 500 $^\circ\text{C}$ was higher in the case of SDAS 10 μm , which comprises smaller Al_2Cu particles compared with the case of SDAS 25 μm . Another study [4] also showed that the dissolution rate of Al_2Cu particles in an Al-4.3Cu alloy significantly increases when reducing the coarseness of microstructure (i.e., the α -Al grain size reduces from 168 to 15 μm).

In Al-Cu systems, the majority of Al_2Cu particles precipitates at the α -Al grain boundaries. Smaller α -Al grains reduce the distance between the Al_2Cu particles, which therefore reduces the time required for homogenization due to the reduced diffusion distance [11].

Temperature and time are critical factors in the SHT process. Lowered SHT temperatures do not ensure complete dissolution of Al_2Cu intermetallics, while elevated temperatures lead to the incipient melting of the intermetallics. A brief SHT does not yield homogenized Cu atoms in the Al matrix; meanwhile, prolonged treatment is not energy efficient. Several detailed experimental studies were conducted on Al-Cu systems in order to find the proper SHT cycle. Masuku et al. [14] suggested a two-step SHT (5 h at 515 $^\circ\text{C}$, followed by 15 h at a temperature above 515 $^\circ\text{C}$) for an Al-5Cu-Mg-Ag alloy to prevent the incident of incipient melting and to ensure the dissolution of phases with a lower melting point. In another study, a two-step homogenization/solution heat treatment (24 h at 49 $^\circ\text{C}$, followed by 2 h at 520 $^\circ\text{C}$) was suggested to prevent the formation of incipient melting pores [15]. Daswa et al. [16] suggested controlled heating followed by two-step SHT for an Al-4.5Cu-Mg-Ag alloy with controlled heating from 400 to 513 $^\circ\text{C}$, followed by 2 h at 513 $^\circ\text{C}$ and 16 h at 525 $^\circ\text{C}$. Zamani et al. [4] showed that if the microstructure is refined by cooling (e.g., α -Al 11–17 μm) in an Al-Cu-(Mg-Ag) cast alloy, a single-step SHT at temperatures 10–20 $^\circ\text{C}$ below the onset temperature of the Al_2Cu phase melting peak results in a sufficiently solutionized and homogenized microstructure within 10–20 h.

Numerical modeling of the SHT process with the purpose of optimizing the solution treatment time and temperature for the alloys with different microstructural scales is of interest both for researchers and for process designers. Singh et al. [17] described the dissolution kinetics of Al_2Cu in a binary cast of Al-4.5Cu alloys by considering Cu having an initial sinusoidal concentration in the primary α -Al. The lowest Cu level was in the center of α -Al grains, while the highest Cu level was at the grain boundaries. The time required to completely dissolve Al_2Cu is dependent on the diffusion rate of Cu in the form of solid solution in α -Al. Liu et al. [18] applied a similar methodology to model segregation of Cu solute in Al-Cu-Mg-Ag alloys. Their numerical model of Al_2Cu dissolution, however, was not described based on the detailed underlying physics of the material.

Simplified one-dimensional diffusion-based models were successfully applied to model particle dissolution in the alloy matrix. Depending on the particle shape, different diffusion field geometries are introduced in the models, for example, planar, cylindrical and spherical [11,19–23]. It was shown

that dissolution time for cylindrical particles lies in-between the spherical and planar, but closer to the spherical shape [21]. Admitting that the actual Al_2Cu particle shape is complex in industrial castings, researchers highlighted that the assumption of a simplified particle geometry in the dissolution models makes the models simpler to implement, while still delivering reasonable agreement with experimental results [22]. Vermolen et al. [19,20] proposed a numerical model based on Scheil analysis to describe the dissolution and homogenization kinetics of planar, cylindrical, and spherical particles. The model is feasible for any combination of first-order reactions at the particle–matrix interface and long-distance diffusion within the matrix. Sjölander et al. [11] adapted the diffusion-based model and described the homogenization kinetics of Cu solute in the α -Al dendrites for an Al-7Si-3Cu cast alloy.

The ability to predict the time required to obtain the homogenized microstructure is essential for determining the proper SHT cycle for cast components, with various microstructural scales, which is of industrial interest. Moreover, in the case of the A205 alloy, where Al_2Cu phases are surrounded by large fractions of interconnected TiB_2 particles on the α -Al grain boundaries [24], it is of practical interest to understand the effect of TiB_2 , which remains stable at SHT temperatures [25], on the dissolution behavior of Al_2Cu phases.

The aim of this study is, therefore, to understand the influence of the microstructural scale and TiB_2 particles on the dissolution behavior of Cu-rich phases and homogenization kinetics of Cu-solutes over the α -Al grains during the SHT process, by comparing the microstructures of Al-4.3Cu and A205 cast alloys. Furthermore, we investigate whether a diffusion-based SHT numerical model can be applied to describe the homogenization kinetics of Cu solute over time, at different SHT temperatures and microstructural scales, for both Al-4.3Cu and A205 alloys.

First, the material, process, and methodology for microstructural analysis are described. Next, the detailed results of two-dimensional (2D) and 3D microstructure investigations are discussed. The choice of the SHT temperatures was then motivated for both alloys. The modeling assumptions and simplifications are elaborated, followed by the presentation of the model calibration procedure and both the simulation and measurement results for the Cu concentration in the α -Al matrix during the SHT process.

2. Experimental

2.1. Material and Process

Two Al-Cu based alloys were studied: a binary Al-4.3Cu alloy (in the following referred to as Al-Cu alloy) and a commercial A205 alloy (A205). The Al-Cu alloy was produced by melting pure Al ingots (99.9% purity) and pure Cu (99.99% purity) at 750 °C. No degassing treatment was applied during the melting process. The melt was gravity die-cast in a 250 °C preheated copper die having six cylindrical rods, 20 cm in length and 1 cm in diameter. The cast rods were then re-melted at 750 °C for 30 min in the Ar atmosphere in a Bridgman furnace and directionally solidified. The furnace was placed on a motorized lifting device while the rods were in a stationary position. The pulling speed of the furnace was prescribed to control the cooling rate. In this study, the pulling speed of the furnace was set to 0.03 and 0.3 $\text{mm}\cdot\text{s}^{-1}$, in order to generate diversified microstructural scales. In the Bridgman furnace-produced samples, the major part of the sample length solidifies under steady state, which results in a relatively homogenous microstructure. Samples for the material characterization were cut from the central part of the directionally solidified cylindrical samples. The A205 alloy was received in the form of a sand-cast multi-section structure. The geometry of the casting is provided in Figure 1. The castings had seven different wall thicknesses, from 5 mm to 39 mm. The specimens of A205 were prepared from the section with the largest wall thickness (39 mm), thus comprising the coarsest grains. The grain size of the A205 specimens was comparable with the grain size of the studied Al-Cu alloys. The specimens for the material characterization were cut from the center of the 39 mm section as a block with dimensions $10 \times 10 \times 39 \text{ mm}^3$ (see Figure 1). The surface of specimens for wavelength-dispersive X-ray spectroscopy (WDS) point analysis was prepared by mechanical

polishing as follows: 1—abrasive grinding using SiC paper of grit size 320, 800, and 1200, for 3 min each; 2—polishing pad (The commercial polishing pads by Struers, Cleveland, OH, US) Lrago, Mol, Nap using diamond suspensions lubrication with a particle size of 9 μm , 3 μm , and 1 μm , respectively, for 5 min each; 3—fine polishing pad (Chem) using a suspension of colloidal silica with a particle size of 0.04 μm for 5 min.

Figure 1. The A205 cast component with varied wall thicknesses (all the dimensions are provided in mm) and the typical specimen for the characterization of the microstructure.

The composition of the alloys was determined with the SPECTROMAXx optical emission spectroscope (Spectro, Kleve, Germany). The average chemical composition obtained from six measurements is presented in Table 1.

Table 1. The detailed composition of alloys in wt.%.

Alloys	Cu	Mg	Ag	Ti	B	Zn	Fe	Si	Other	Al
Al-4.3Cu	4.33	-	-	-	-	-	0.07	0.05	<0.01	balanced
A205	4.36	0.39	0.59	3.54	1.54	0.03	0.05	0.07	<0.01	balanced

Differential scanning calorimetry (DSC) analyses were carried out with the Netzsch 404C Pegasus[®] instrument (NETZSCH Holding, Selb, Germany) in the Ar atmosphere, with a scanning rate of 5 $^{\circ}\text{C}/\text{min}$, and temperature range from 30 $^{\circ}\text{C}$ to 600 $^{\circ}\text{C}$. The Nabertherm LE2/11-R7 furnace (Nabertherm GmbH, Lilienthal, Germany) was employed for solution heat treatment. The temperature of the specimens was controlled by thermocouples inserted in each specimen. Water at 40 $^{\circ}\text{C}$ was used as quenching media.

2.2. Microstructural Analysis

The microstructure was characterized using optical microscopy (Olympus GX71, Olympus Corporation, Tokyo, Japan) and scanning electron microscope (SEM, JEOL 7001F, JEOL, Tokyo, Japan) equipped with an energy dispersive spectrometer (EDS). In order to measure Cu solute concentration in the α -Al grains, an SEM (TESCAN Lyra3, TESCAN, Brno, Czech Republic) equipped with wavelength-dispersive X-ray spectroscopy (WDS) was employed. In order to measure the Cu concentration during the SHT process, WDS technique was preferred over the EDS techniques because it offered a better energy/wavelength resolution and peak/background ratio, which resulted in more precise measurements of the concentration of an element in the matrix [13]. The chemical resolution of WDS, depending on the element, reaches ppm, while EDS chemical resolution is between ~0.1 and 0.5 wt.%. An electron beam voltage of 20 kV was set for Cu measurement. The analysis points were selected in the center of each α -Al grain during SHT, and at least 15 points were measured on the surface of the specimen along the specimen length (Figure 1) for each sample. Three samples were analyzed for each SHT condition (see Figure 2a). The measurements were performed on the surface of the specimen after mechanical polishing.

Figure 2. (a) An example of the measured Cu-solute level in the center of α -Al grains using wavelength-dispersive X-ray spectroscopy (WDS) technique. (b) Scanning electron microscopy (SEM) micrograph (secondary electron) on the trench with focused ion beam (FIB) milled around the bulk which undergoes serial FIB cross-section milling.

The α -Al grain size was quantified using Olympus Stream Motion image analyzer software, and grain sizes were reported through different measurement methods. Some ~ 250 grains over three fields of view of 0.4 mm^2 were counted for each condition from three sections.

In order to demonstrate the 3D configuration of Cu-rich phases and Ti_2B particles in the boundary of α -Al grains, high-resolution focused ion beam (FIB) 3D tomography technique, using a plasma Xe source (XEIA 3, TESCAN, Brno, Czech Republic) was utilized. The FIB-SEM provides a sub-micron position resolution (or spatial resolution) of 2.5 nm to reveal 3D architecture of the microstructural features. It was combined with chemical analysis using EDS technique. Firstly, the region of interest (ROI), $20 \times 20 \mu\text{m}^2$, of the sample's surface was selected using SEM imaging. Then, a trench with a depth of 22 μm near the ROI was milled (see Figure 2b). A slice thickness of 25 nm, along with 80 milling steps, was applied. The milling direction is shown in Figure 2b. An electron beam voltage of 15 keV was chosen for EDS analysis. TEAM 3D IQ software, (EDAX, Mahwah, NJ, USA) was utilized to reconstruct the 3D map of elements. For the FIB-SEM characterization, fine polishing and slicing of the ROI were conducted using a FIB current of $\sim 2 \mu\text{A}$ at 30 keV. This led to around 100 two-dimensional slices, each with a thickness of 20 nm. Slice SEM imaging was done at 15 keV using a high-sensitivity in-beam secondary electron detector, and 3D reconstruction of the SEM images was carried out using ORS visualization software package v.1.9 (ORS, Montreal, Quebec, Canada).

3. Experimental Results and Discussion

3.1. Microstructure

SEM micrographs of the Al-Cu alloys are shown in Figure 3a,b, which were cast at solidification rates of 0.3 and $0.03 \text{ mm}\cdot\text{s}^{-1}$, respectively. The microstructure comprised the two main phases: α -Al and Al_2Cu phases. An increased solidification rate leads to a more refined microstructure. The solidification rates of 0.3 and $0.03 \text{ mm}\cdot\text{s}^{-1}$ resulted in “fine” and “coarse” microstructures, respectively. Figure 3c shows the microstructure of the A205 alloy corresponding to the 39 mm wall thickness of the cast component. Principal microstructural features, in this case, were α -Al phases and continuous Cu-rich and Ti-rich phases on the grain boundaries. These phases were identified as Al_2Cu and TiB_2 phases. The element concentration map is provided in Figure 3d–f. The EDS analysis revealed the scarce presence of TiAl_3 particles in the α -Al grains (see Figure 3c).

Figure 3. SEM micrographs of Al-Cu alloy cast at (a) 0.3 mm s^{-1} and (b) 0.03 mm s^{-1} solidification rates. (c) Micrographs of the A205 alloy. (d–f) Concentration map of Cu and Ti in the inter-dendritic region of the A205 alloy.

The 3D configuration of Al_2Cu and TiB_2 particles in the ROI in the α -Al grain boundaries (Figure 4a) was reconstructed using serial FIB-sectioned SEM micrographs (see Figure 4b). Figure 4a shows the region chosen for FIB-SEM tomography. TiB_2 is seen in the form of a continuous rigid network of particles, which are built along the α -grain boundary regions. Although the Al_2Cu particles are diversified in size, their morphology is in the form of either continuous or isolated sectorial plates (see Figure 4b). It seems that the majority of plates have a curvature face.

Figure 4. (a) Scanning electron image showing the region of interest (ROI) in the as-cast A205 alloy, obtained by image slicing. (b) Three-dimensional (3D) reconstructed Al_2Cu and TiB_2 particles in the selected bulk from 80 serial-sectioned SEM micrographs. (c–e) Expanded local regions in the selected bulk.

The 3D tomography reveals that Al_2Cu and TiB_2 particles are three-dimensionally connected to a certain extent in the boundary of the α -Al grain. The extended interfaces of Al_2Cu and TiB_2 in

Figure 4c–e show that particles are touching each other, which is also seen in the 2D micrographs in Figure 3. The sufficient level of connectivity and contiguity of Al_2Cu and TiB_2 was realized qualitatively as the interface area shared by them, and the interfacial area was estimated to be 10–20%. However, no quantitative analysis was carried out. The level of connectivity between Al_2Cu and TiB_2 and the coverage rate of Al_2Cu by TiB_2 are different from particle to particle as shown in Figure 4c–e.

Since Al_2Cu and TiB_2 had similarities in color and morphology in both secondary electron (SE) and backscattered electron (BSE) imaging (Figure 5), a 3D view of Al_2Cu and TiB_2 agglomerations at the α -Al grain boundary was reconstructed (Figure 6a). Serial EDS maps of elements in another ROIs were obtained, in order to understand the internal architecture of Al_2Cu and TiB_2 particles in the α -Al grain boundary. 3D configuration of Al_2Cu and TiB_2 particles in α -Al grain boundary was visualized in a video is available in the Supplementary Materials.

Figure 5. (a) SEM micrographs of secondary electron (SE) image and (b) backscattered electron (BSE) image of the ROI for the as-cast A205 alloy.

The configuration of Al_2Cu and TiB_2 particles was reconstructed based on the Cu and Ti concentration maps. Figure 6b shows the reconstructed 3D volume of interest obtained from 80 EDS slice-maps with ~ 250 nm spacing. The orange zones represent the Cu-rich phases (i.e., Al_2Cu and $\text{Al}_7\text{Cu}_2\text{Fe}$ particles). The dark green zones show Ti-bearing phases. Since TiAl_3 particles are located in the center of α -Al grains [3] (Figure 3), the Ti-rich regions (the dark green zones) in the α -Al grain boundaries were identified as TiB_2 particles. Figure 6b shows three-dimensionally interconnected Cu-rich and TiB_2 particles in the boundary of the α -Al grain. The internal architecture of Al_2Cu and TiB_2 particles in the α -Al grain boundary is quite similar to the results from the FIB-SEM analysis (see Figure 4b). In order to better understand the configuration of Cu-rich phases and TiB_2 particles, a section of the 3D tomography was expanded (see section 1 in Figure 6c). Section 1 shows that Cu-rich phases and TiB_2 particles have a relatively high degree of inter-connectivity, particularly in the vicinity of α -Al grains, where TiB_2 particles are abundant. The TiB_2 particles are accommodated in the form of a continuous band along the α -Al grain boundaries. The other sections (i.e., sections 2–4), presented in Figure 6c, also confirm that the TiB_2 particles encompass the regions in the grain boundaries where Al_2Cu particles are located. The 3D configuration of Al_2Cu shows quite complex morphology that cannot be simply treated as plate or spherical particles. It is reasonable to assume Al_2Cu as platelets of different sizes, where the diffusion mainly occurs from the facets during dissolution.

Figure 6. (a) Scanning electron image showing the volumetric ROI in the as-cast A205 alloy. (b) 3D reconstruction of Cu-rich phases and TiB_2 particles from energy dispersive spectroscopy (EDS) maps of the selected ROI. (c) Four 3D cross-sections with 5 μm spacing between each other (Section 1 is expanded).

3.2. Grain Size Measurement

Based on the two-dimensional micrographs, the grain size was termed by three different descriptors— D_L , D_A , and D_H . Descriptor D_L is measured by the linear intercept method (per the recommendation of ASTM E1382), D_A is the equivalent circular diameter estimated as $2 \cdot (A/\pi)^{0.5}$, and D_H is the hydraulic diameter calculated as $4A/P$, where A and P are the 2D area and the perimeter of grains, respectively. The grain size frequency distribution for the as-cast A205 alloy measured as D_L , D_A , and D_H is presented in Figure 7a. The frequency distributions slightly differ depending on the measurement method. As can be seen from the figure, D_L ranges from 18 to 114 μm . At least 50% of the grains had a diameter between 60 to 100 μm , irrespective of the measurement method. The frequency distribution of grain size (D_L) for the as-cast Al-4.3Cu alloy with different microstructural scales is displayed in Figure 7b. At least 70% of grains had a size between 120 and 240 μm in the case of fine microstructure. Similarly, at least 70% of grains had a size range of 160–280 μm for the case of coarse microstructure.

Figure 7. (a) Frequency distribution of grain size for A205 alloy through different size descriptors. (b) Frequency distribution of grain size measured by the linear intercept method for Al-Cu alloy with fine and coarse microstructures.

The reason for determining grain size frequency distribution in the cast alloys was to provide a valid input for the mathematical model. Since the SHT model assumes that the microstructure consists of mono-size grains, it is reasonable to choose the grain diameter from the range with the highest population.

3.3. Solution Heat Treatment

Figure 8 shows the single endothermic peak, irrespective of the microstructural scale, which corresponds to the melting of Al_2Cu phase in the typical DSC curves for the Al-Cu alloy and A205 alloy during heating up to 600°C [14].

Figure 8. Al_2Cu melting peaks on the typical differential scanning calorimetry (DSC) heating curves of the as-cast Al-Cu and A205 alloys (the curves are offset for clarity).

Although both microstructural scales of the Al-Cu alloy (fine and coarse) show melting peaks with similar onset temperature, 540°C , the peak area, which is proportional to the enthalpy of Al_2Cu melting with respect to the calorimetric constant, is larger for the alloy with the coarse microstructure. The onset temperature of the melting peak was lower for the A205 alloy, which is primarily due to the presence of Mg in the A205 alloy, as pointed out in the work of Birbilis [26]. The average onset

temperatures of the melting peak, the peak area, and the selected temperature for SHT are collated in Table 2.

Table 2. The average onset temperatures, endothermic peak areas corresponding to Al_2Cu melting derived from the DSC heating curves, and solution heat treatment (SHT) temperatures.

Alloys	Onset Temperature ($^{\circ}\text{C}$)	Peak Area (J/g)	Selected SHT Temperature ($^{\circ}\text{C}$)
Al-Cu (Fine)	540	5.1	520
Al-Cu (Coarse)	540	8.3	520
A205	531	4.2	520 and 535

In the binary Al-Cu alloy, the equilibrium Cu concentration in $\alpha\text{-Al}$ at 520°C was equal to 4.55 wt.%, whereas for A205, the values were 4.5 wt.% at 520°C and 4.6 wt.% at 535°C , according to Thermo-Calc material modeling. The Cu concentration in the center of $\alpha\text{-Al}$ grains for the Al-Cu alloy with fine and coarse microstructures as well as for the A205 alloy was measured with the WDS technique. The actual equilibrium Cu concentration, which is the solubility limit of Cu in Al at a given temperature, was achieved via heating the alloys for 200 h at a given temperature (i.e., 520°C and 535°C). The experimentally determined solubility limit of Cu at 520°C in the Al-Cu alloy was $3.98 (\pm 0.09)$ wt.% and $4.05 (\pm 0.11)$ wt.% for coarse and fine microstructures, respectively. The corresponding values for A205 were measured to $4.35 (\pm 0.13)$ wt.% and $4.46 (\pm 0.09)$ wt.% at 520°C and 535°C , respectively. The reported measured values of the equilibrium Cu concentration were employed in the numerical modeling of the SHT process.

In the Al-Cu alloy, the Cu concentration in the matrix after 20 h solution treatment at 520°C was equal to 3.7 wt.% and 3.4 wt.% for fine and coarse microstructural scales, respectively. In fact, despite having identical onset melting temperatures of Al_2Cu ($\sim 540^{\circ}\text{C}$) for both microstructures, the dissolution rate of Al_2Cu particles differed. This was primarily due to the size of Al_2Cu particles and diffusion distance [11], which was larger for the case of coarse microstructure (slower solidification rate, 0.03 mm.s^{-1}). Different dissolution rates of Al_2Cu particles were also reflected in the area under the peak of melting the Al_2Cu phase (Figure 8). In fact, the area under the peak is an indication of the fraction of Al_2Cu particles that melted. A larger area under the peak for the case of coarse microstructure compared with the fine microstructure (see Table 2) suggests a larger fraction of undissolved Al_2Cu particles, which were melted when heating at 535°C and beyond. Therefore, it is plausible that coarser Al_2Cu requires a relatively higher temperature to dissolve. Zamani et al. [4] present a detailed methodology of identifying an optimized heat treatment cycle and evolution of microstructure. Choosing an SHT temperature of 535°C for the A205 alloy, which is slightly higher than the melting temperature of Al_2Cu particles (531°C), would ensure dissolution of the majority of Al_2Cu particles.

3.4. Numerical Modeling of SHT Process

3.4.1. Modeling Assumptions and Simplifications

A simplified mathematical model of the SHT process was developed for the Al-4.3Cu and A205 alloys. A diffusion-controlled dissolution of Al_2Cu particles located in the grain boundary of the $\alpha\text{-Al}$ grains was assumed for SHT modeling with the Vermolen approach [19]. The 2D and 3D microstructural characterizations revealed detailed information on the morphology of Al_2Cu particles, where they were found to be diversified in size. Their shape resembled either continuous or isolated sectorial plates. Therefore, in the model, the planar geometry of the particles was preferred over cylindrical or spherical geometry, which is a valid assumption.

The diffusion field implemented in the dissolution model of the eutectic Al_2Cu phases and homogenization of the Cu solute across the matrix was thus assumed to have planar geometry.

A planar particle with an initial half-thickness r_0 dissolves in a matrix of half-size $L/2$, where L corresponds to the matrix grain diameter (see Figure 9).

Figure 9. Schematic representation of one-dimensional planar particle half-geometry and the diffusion field; $C_{Cu,eut}$, $C_{Cu,M}$, and C_F are the Cu concentrations in the Al_2Cu particle, alloy matrix, and the interface, respectively.

The initial distribution of Cu in the matrix was taken from the solidification modeling results, under the assumption of the Al_2Cu equilibrium eutectic transformation. Solidification was modeled by Fick's 2nd law, including diffusion in the solid fraction. The results were found to be similar to the Scheil segregation model. Infinite diffusion in the liquid was assumed. The modeling approach is described elsewhere (see [11,19]). The concentrations from the solidification calculations were transferred to the SHT model as well as the fraction of Al_2Cu particles in the matrix. The concentration at the matrix–particle interface, C_F ($r = r_0$), was set to the actual measured equilibrium Cu concentration, provided in Section 3.3. Zero flux boundary condition was set on the boundary of the diffusion field ($r = L/2$). The initial size of the planar particle was considered as 3 μm (A205), 10 μm (Al-Cu fine), and 12 μm (Al-Cu coarse) corresponding to the mean size of Al_2Cu particles.

In the diffusion calculation, the movement of the Al_2Cu particle–matrix interface was achieved via the mass balance approach expressed in Equations (1) and (2), finally leading to Equation (3) for the mass fraction of eutectic Al_2Cu phases in the matrix. Equations (1)–(3) are written on the example of the A205 alloy. Once the Cu concentration in the matrix increases, the fraction of the Cu-rich phases decreases.

$$\omega_M + \omega_{Al_2Cu} + \omega_{TiB_2} = 1 \quad (1)$$

$$C_{Cu} = C_{Cu,M} \cdot \omega_M + C_{Cu,eut} \cdot \omega_{Al_2Cu} \quad (2)$$

$$\omega_{Al_2Cu} = \frac{C_{Cu} - C_{Cu,M} \cdot (1 - \omega_{TiB_2})}{C_{Cu,eut} - C_{Cu,M}} \quad (3)$$

where C_{Cu} is the alloy concentration of Cu, wt.%; ω_{TiB_2} is the mass fraction of TiB_2 in the as-cast alloy; ω_M is the instant mass fraction of the matrix including Al and all the dissolved elements; ω_{Al_2Cu} is the instant mass fraction of Al_2Cu phases in the alloy; $C_{Cu,eut}$ is the concentration of Cu in the eutectic Al_2Cu phase (eutectic composition), wt.%; $C_{Cu,M}$ is the instant total concentration of Cu in the matrix, wt.%. When the Al_2Cu particle is dissolved, the boundary condition at the matrix–particle interface is released. Homogenization was modeled based on Fick's 2nd law, with the boundary condition $\partial C / \partial r = 0$ at $r = 0$ and $r = L/2$. The model inputs are collated in Table 3.

Table 3. Model inputs.

Quantity (Units)	Alloy	Value	Ref. and Comments
ρ_{Al} (kg/m ³)	-	2700	Thermo-Calc
ρ_{Cu} (kg/m ³)	-	8960	Thermo-Calc
ρ_{TiB_2} (kg/m ³)	-	4520	Thermo-Calc
Diffusion coefficient of Cu in Al at 520 °C, $D_{Cu-in-Al}$ (m ² /s)	-	6.7×10^{-14}	[11]
Diffusion coefficient of Cu in Al at 535 °C, $D_{Cu-in-Al}$ (m ² /s)	-	9.8×10^{-14}	[11]
Solid-liquid partition coefficient	-	0.172	Thermo-Calc
Eutectic composition (wt.%)	-	32	Thermo-Calc
Liquidus temperature (°C)	Al-4.3Cu	650	Thermo-Calc
	A205	649	Thermo-Calc
Cu content in the alloy (wt.%)	Al-4.3Cu	4.33	Measured
	A205	4.38	Measured
Concentration of TiB ₂ (wt.%)	A205	5.9	Measured

The α -Al grain size is a process-dependent parameter, and it has a key influence on homogenization kinetics of Cu in the matrix. The choice of the grain size, L , for calculation of the diffusion field is complicated by the presence of grains of various sizes in the microstructure. Since the assumption in the model was a microstructure with mono-size grain diameter, it was plausible to choose the grain diameter found in the majority of the population, as seen in Figure 7. For the A205 alloy the L values were selected from the range 60–100 μm , for the Al-4.3Cu alloy with coarse microstructure the range was 160–280 μm , and for the Al-4.3Cu alloy with fine microstructure, the values of interest were between 120 and 240 μm . Therefore, the grain size can be considered as the model calibration parameter. The total Cu concentration in the matrix during SHT calculated in the process of the model calibration was compared with the experimental results.

3.4.2. Simulation Results

The calibrated values of the grain size, which yielded the best agreement between calculated and measured Cu concentration in the α -Al matrix during SHT are summarized Table 4.

Table 4. Grain size values adopted from the measured range.

L (μm)		
Al-Cu Coarse	Al-Cu Fine	A205
240	160	80

Model calibration results for the binary Al-4.3Cu alloy are provided in Figure 10. The calibrated models largely reproduced the trend revealed by the measurement and delivered a good agreement to the measured total concentration of Cu in the matrix during SHT. The model operates well on the alloys with both coarse and fine microstructures, thereby increasing the confidence in the chosen modeling approach. Additionally, the dashed profile in the figure is provided for a hypothetical binary Al-4.3Cu alloy, with grain size of 80 μm (i.e., corresponding to the A205 grain size), applied in the SHT model (see Table 4). As can be seen from the simulation results, the Al₂Cu particles in such an alloy dissolved long before 20 h.

Figure 10. Simulated and measured Cu concentration in the matrix during solution heat treatment at 520 °C for the Al-4.3Cu alloy with various microstructures.

Figure 11 presents the results of the A205 simulation with the typical diffusion coefficient, $D_{\text{Cu-in-Al}}$. The modeled diffusion process was relatively fast, compared to the experimental results. The Al_2Cu particles were dissolved in the simulation before 20 h, which does not agree with the measurement results (4.2 wt.% Cu concentration in the matrix after 20 h).

Figure 11. Simulated and measured Cu concentration in the matrix during solution heat treatment at 520 °C for the A205 alloy; the typical value of diffusion coefficient, $D_{\text{Cu-in-Al}}$, from Table 3 is applied in the model.

There are two reasonable ways to fit the modeling results for the A205 alloy to the measured data: either changing the grain size parameter, L , in the model or modifying the diffusion coefficient of the Cu in Al for the A205 alloy to embed the effect of TiB_2 on the dissolution rate of Al_2Cu particles. Figure 12 demonstrates the first model calibration approach.

The simulation results demonstrate the effect of variation of the grain size on the simulated total Cu concentration in the matrix of the solution heat-treated A205 alloy. Indeed, the quicker dissolution of Al_2Cu particles is observed for the cases with a smaller grain size. Calibrating the value of the grain size parameter, L , enabled the fitting of the SHT A205 simulated curve to the measured data. However, the “successful” L value (105 μm) was out of range of the dominating grain size values

observed in the measurements (Figure 7a). The following discussion attempts to provide the reasons for the modification of the diffusion coefficient of Cu in Al in the SHT model of the A205 alloy.

Figure 12. The effect of parameter, L , variation on the simulated Cu concentration in the matrix during solution heat treatment at 520 °C for the A205 alloy, at the typical value of diffusion coefficient.

The DSC heating curves for the as-cast Al-4.3Cu and A205 alloys (Figure 8) indicate the lower dissolution rate of Al_2Cu particles in the $\alpha\text{-Al}$ matrix of the A205 alloy. This observation is in agreement with a previous statement [5], regarding A205 alloy, where Al_2Cu is surrounded by a high-volume fraction of TiB_2 in the grain boundaries, and therefore, the diffusion is impeded by TiB_2 particles. One way to take this phenomenon into account in the model is to adjust the diffusion coefficient in the dissolution model for the A205 alloy, in order to fit the simulation results to the measured data. This measure may give an indication of the magnitude for the single effective diffusion coefficient of Cu towards Al matrix in the presence of the impeding TiB_2 particles. Introduction of the effective diffusion coefficient, D_{eff} , with a value about two times lower than the typical diffusion coefficient, $D_{\text{Cu-in-Al}}$, provided in Table 3, resulted in a good agreement between the measured and simulated total Cu concentration in the matrix of A205 alloy during SHT at two different temperatures, as presented in Figure 13. The dissolution of Al_2Cu is controlled by the diffusion of Cu into the surrounding Al matrix [27]. The discovered particle configuration suggests that TiB_2 particles, which are thermally stable [25], surround the Al_2Cu phases at the grain boundaries and hence retard the diffusion of Cu into the Al matrix within grain boundaries as well as across the $\alpha\text{-Al}$ grains (see blue arrows in Figure 6c, which show diffusion paths of Cu solutes). The 3D visualization of Al_2Cu and TiB_2 particle configuration agrees with the remarkably smaller value of the effective diffusion coefficient for Cu in the SHT model for the A205 alloy compared to the Al-4.3Cu alloy, which was mentioned elsewhere [5]. The authors of an experimental study [4] investigated the role of the addition of Mg and Ag on the dissolution rate of Al_2Cu particles and homogenization kinetics of Cu solute during the solution heat treatment. The comparison was made between Al-4.3Cu and Al-4.3Cu-0.7Mg-0.7Ag alloys. It was found that Mg and Ag, which are accommodated up to 0.6 wt.% each in the matrix (in the form solid solution) had no indicative effect on the dissolution kinetics of Al_2Cu and homogenization rate of Cu solute across the matrix, which is mainly determined by the coarseness of microstructure. It is therefore expected that the lowered dissolution rate of Al_2Cu particles in the A205 alloy, as compared to the Al-4.3Cu alloy, is primarily determined by the thermally stable network of TiB_2 particles. The mechanism of reduced diffusion kinetics of solute atoms which are covered or surrounded by a relatively large fraction of thermally stable phases (particles that have fairly higher melting point than dissolved particles) was pointed out in other studies [28,29]. Asghar et al. [29] studied a similar phenomenon for a continuous rigid network of Al_3Ni , which had sufficient entanglement with eutectic

Si particles, thereby reducing the spheroidization rate of Si, acting as a physical barrier and retarding the diffusion of Si solute.

Figure 13. Simulated and measured Cu concentration in the matrix during solution heat treatment of A205 (a) at 520 °C and (b) at 535 °C; in the models: $L = 80 \mu\text{m}$, $D_{\text{eff}} = 0.45 \cdot D_{\text{Cu-in-Al}}$.

Alternatively, adopting the reasonable measured grain size $L = 75 \mu\text{m}$ in the SHT model of the A205 alloy, led to the calibrated value of the effective diffusion coefficient 2.5 times lower than the typical diffusion coefficient, $D_{\text{Cu-in-Al}}$ provided in Table 3. The computed Cu solute levels for $L = 75 \mu\text{m}$ had the same degree of agreement with the measured data as those shown in Figure 13, for $L = 80 \mu\text{m}$. The modeling results show that the finer grain size and the presence of TiB_2 particles counteract each other in terms of the effect on the Al_2Cu dissolution rate in the matrix of the A205 alloy. Indeed, finer grain size results in the higher Al_2Cu dissolution rate, and the presence of the TiB_2 particles embedded in the effective diffusion coefficient result in lower Al_2Cu dissolution rate. Future research will cope with the complexity of the co-location between the Al_2Cu and TiB_2 particles experimentally discovered on the grain boundaries, to reach an understanding of how such a grain boundary geometry contributes to the degradation of dissolution rate of Al_2Cu particles. It will allow building a more advanced model of Cu diffusion in the conditions when Al_2Cu particles of different complex shapes are surrounded by TiB_2 particles.

4. Conclusions

Dissolution of Al_2Cu in Al-4.3Cu and A205 cast alloys was studied both experimentally and by modeling. A diffusion-based model was developed and calibrated to describe the dissolution of Al_2Cu phases during the solution heat treatment process for Al-4.3Cu and A205 cast alloys. The simulation model was experimentally validated for different alloys, a diversified microstructural scale, and different solution heat treatment temperatures, which contribute to the robustness of the presented modeling approach. The α -Al grain size, an input parameter of the model, was chosen from the highest population obtained from the grain size measurements, which yielded the best agreement with the experimental results. Detailed 3D characterization techniques were used to map the complex morphology of Al_2Cu phases in combination with TiB_2 particles in the A205 alloy. The results increased the understanding of the effect of the TiB_2 particles on the dissolution kinetics of the Al_2Cu phases. The conclusions are summarized, as follows:

- Al_2Cu particles located mainly on the α -Al grain boundaries in A205 are different in size, with a morphology resembling continuous or isolated sectorial plates, most often with a curvature face.
- TiB_2 particles are three-dimensionally connected, thereby forming a nearly continuous rigid network of particles located along the α -grain boundaries.

- The Al₂Cu and TiB₂ particles are interconnected, with the interfacial area roughly estimated to 10–20%.
- TiB₂ network encompasses the Al₂Cu particles, however, the degree of coverage differs between the particles. It elucidates the shielding effect of TiB₂ particles, retarding the diffusion of Cu-solutes toward α -Al grains.
- The experimental and simulation results showed that the solution heat treatment time is a function of the microstructural scale. In the case of large scatter in the grain diameter of as-cast microstructure, the model needs to be calibrated based on the local microstructure scale.
- Analysis of modeling and experimental results provided an indication of the relatively lower dissolution rate of Al₂Cu particles in the matrix of the A205 alloy compared to the binary alloy (Al-4.3Cu) alloy. This was understood via the introduction of the effective value of the diffusion coefficient of the Cu in the α -Al grain.
- Modeling results supported with the measurements of the Cu concentration in the Al matrix show that the impeding effect of TiB₂ particles on the dissolution of the Al₂Cu phases on the grain boundaries can be quantified in terms of effective reduction of the diffusion rate of Cu by a factor of 2.0–2.5.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-4701/10/7/900/s1>, Video S1: 3D configuration of Al₂Cu and TiB₂ particles in α -Al grain boundary.

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