Grain Refinement during Rapid Solidification of Aluminum–Zirconium Alloys Using Electrospark Deposition

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Electrospark deposition (ESD) was applied to Al–Zr binary system in order to study the possible change of solidification structure from the stable D022 tetragonal equilibrium phases to the cubic L12 when high cooling rates and undercooling conditions are involved. The results show that a supersaturated solid solution was formed for the alloy containing 0.5 at% Zr. These layers are composed of refined equiaxed grains, with a smaller particle size distribution for the region where the L12 precipitates were present.

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1. Introduction

Nanostructured materials can provide superior mechanical properties due to the reduced grain size, but manufacturing costs remain a serious hurdle for their commercial utilisation. In addition, some technical challenges in manufacturing processes, such as welding or freeforming for example, remain to be optimised to allow for their joining into assemblies or direct fabrication. Typical fusion welding processes will induce grain growth in the heat affected zone and result in a coarse micro-scale solidification structure, which will defeat the initial gain in properties through the loss of the nanograins from the parent material. Consequently, peritectic solidification, where typically Al3M are forming for aluminum alloys, becomes the key solidification scheme to aim at nano or ultra fine grains (UFG) directly from solidification. Elements for group 4 (Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W) all exhibit peritectic phase equilibria with Al as the terminal solidification phase.

Rapid solidification experiments have shown that additions of group 4 metals (Ti, Zr or Hf) to aluminum may be a promising approach for developing nano or UFG Al alloys directly from the liquid during the solidification process. These particular systems show the formation of an Al3M (M = Ti, Zr, or Hf) peritectic phase as the first solid under equilibrium conditions. The equilibrium structure of these Al3M trialuminides is tetragonal (Al3Ti,D022/Al1Zr,Hf,D023; see Fig. 1) when slow cooling conditions are used. However, for accelerated cooling rates, these systems can form a metastable cubic L12 phase as primary solidification phase, which due to the matching in the lattice parameter and surface energy, serve as ideal heterogeneous nucleation sites for solidification. In addition to this thermodynamic consideration, kinetics plays an important role during rapid solidification, as rate-limiting steps can influence suppression of events expected during equilibrium solidification. From this point of view, the degree of primary Al3M precipitation, which directly impacts the quantity of solute loss and consequently the grain refinement, is highly dependant on the initial solution content in the alloy, as well as the cooling rate imposed on the melt. The understanding of the kinetics of peritectic solidification and what are the possible deviations from the equilibrium sequence becomes key to reach the goal of nano or UFG solidification beads. Hori et al. have reported the relationship between the cooling rate and the solute content for Al–Zr alloys, which is shown in Fig. 2, and have identified processing conditions resulting in non-equilibrium solidification structure, i.e., supersaturated solid solution or L12 Al1Zr within Al.

Electrospark deposition (ESD) is a micro-arc rapid solidification welding process. It uses low heat-input, high energy density pulses with a typical duration on the order of several micro-seconds to transfer the metal from the working electrode. Due to the small amount of liquid formed and the short duration of the pulse, cooling rates approaching
10^5–10^8 K s^{-1} may be achieved, resulting in the development of metastable microstructures, such as nano-composites or amorphous deposits.22–25) This process has all the key features to allow for the solidification of the cubic L1_2 metastable phase in Al-transition metal alloys, hence a potential route to allow for the solidification of nanostructured weld beads.

In this paper, we investigated the Al-rich regions of the Al–Zr binary system for different compositions with the aim of controlling the formation of the cubic L1_2 metastable phase in Al-transition metal alloys, hence a potential route for the deposition of nanostructured weld beads.

In this paper, we investigated the Al-rich regions of the Al–Zr binary system for different compositions with the aim of controlling the formation of the cubic L1_2 metastable phase through the use of rapid solidification processing by ESD. The primary objective, therefore, is to report and discuss the differences in microstructure and grain size, for the rapidly solidified Al–Zr system using ESD.

2. Experimental Procedure

Binary Al–Zr alloys containing different solute compositions (0.5, 1.0, 1.25 and 1.5 at% Zr) were prepared by powder metallurgy. Commercially available Al (99.5%, -325 mesh) and Zr (98.5%, -325 mesh) powders were supplied by Alfa Aesar. Fully dense puck-type samples, as precursors to the ESD electrodes, were obtained by sintering the corresponding powder mixtures using a spark plasma sintering (SPS) technique.

The ESD experiments were performed using a SparkDepo power supply. Model 300. The electrodes were deposited over a substrate with the same chemical composition as the electrode to avoid dilution effects between the electrode and the substrate. During the ESD process, multiple layers were deposited in order to yield an approximate thickness of 40 µm for the deposited layer. The deposition process was conducted in Ar atmosphere to prevent oxidation. The ESD parameters were kept constant for all compositions [100 µF, 100 V, 390 Hz, and a rotation speed of 5200 rpm].

The deposits were analyzed by X-ray diffraction (XRD) and Field Emission Electron Microscopy (FE-SEM). XRD was performed using a Phillips PW1070 diffractometer (Cu Kα λ = 1.54056 Å) to identify the different crystalline phases over the ESD deposited coatings. Cross-sections of the coatings were prepared by cutting using diamond slow cutting saw, followed with conventional metallographic sample preparation. The polished surfaces were analyzed using backscattered electron microscopy using a Phillips XL-30 FE-SEM. The average grain sizes for the Al–Zr coatings were calculated from equivalent-circle diameter measurements in BSE-SEM micrographs.

3. Results and Discussion

3.1 Modeling of the cooling rate in ESD

Prior to discussing the results obtained in this study, modeling results regarding the high cooling rate known for ESD will be presented in order to better understand the microstructures generated and the magnitude of deviation from the equilibrium concepts. Gould addressed the modeling of the cooling rate for ESD with different Ni-based superalloys by thermal balance of molten splats.24) He assumed a one-dimension heat transfer problem, in which the heat extracted from the molten splat is transferred to the metal substrate. Further refinement led to the prediction of the average cooling rate \( (dT/dt) \) as function of the deposit thickness \( (z) \), which is shown in eq. (1).

\[
dT/dt = 2αC_p ΔT^2/πz^2 H_m
\]

(1)

Where \( α \) and \( C_p \) are the thermal diffusivity and heat capacity of the substrate, \( H_m \) is the heat of fusion of the molten material, and \( ΔT = T_m - T_o \), where \( T_m \) represents the splat melting temperature and \( T_o \) is the substrate temperature. For the present work, eq. (1) was used to determine peak cooling rates for pure aluminum splats over pure aluminum substrate. The selection of pure Al for the treatment is based on the fact that very dilute alloys are used, hence limited deviation in \( α \), \( C_p \) and \( H_m \) would be expected. The thermal properties for pure Al used in this model are provided in Table 1.26)

<table>
<thead>
<tr>
<th>Thermal properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( α/m^2s^{-1} )</td>
<td>8.59 × 10^{-5}</td>
</tr>
<tr>
<td>( C_p/Jkg^{-1}K^{-1} )</td>
<td>862.5</td>
</tr>
<tr>
<td>( H_m/Jkg^{-1} )</td>
<td>3.9775 × 10^5</td>
</tr>
<tr>
<td>( T_m/K )</td>
<td>933</td>
</tr>
</tbody>
</table>

Fig. 2 Relationship between cooling rate and solute content in Al–Zr alloys on the solidified microstructure.19,20)
Figure 3 shows the calculated cooling rate ($dT/dt$) during solidification as a function of deposit thickness ($z$) for a substrate at room temperature. The graph predicts the peak cooling rates expected under ideal conditions for aluminum molten splats. Typical splat thickness produced by ESD ranges between 5–20 microns, hence cooling rates ranging between $2 \times 10^9$ to $10^8$ K s$^{-1}$ could be expected. However, it must be specified that this analysis does not take into account any kinetic rate limiting factor that could occur during solidification, which would have the tendency to reduce the cooling rate. Hence, the modeled values will be considered for the following analysis, but the actual cooling rates could be lower.

3.2 Microstructure development during ESD of Al–Zr binary alloys

The Al-Group 4 alloys (Ti, Zr and Hf), are well known to form L1$_2$ structure possessing very similar lattice parameter when rapid solidification is imposed. Hence, the application of XRD for phase analysis becomes obsolete since no distinction between the Al and the Al$_3$Zr L1$_2$ peaks is possible. The observation of the microstructure of the deposited alloys reveals precipitates (see Fig. 9, which will be discussed later) and to confirm their metastable state, XRD patterns were acquired in the as-deposited state and following a heat treatment of 8 h at 823 K, after which, the equilibrium D0$_{23}$ structure should be observed. Figure 4 is presenting the collection of XRD patterns for the composition Al–1 at%Zr, where the upper spectrum represents the as-deposited and the lower one represents the heat-treated material. As expected, the pattern for the as-deposited only possesses reflections corresponding to Al, while the tetragonal Al$_3$Zr reflections are observed after the heat-treatment. The reflections for the D0$_{23}$ phase are in agreement with the results reported by Malek et al. While this result was expected, it further reinforces the concept that ESD is capable of creating the metastable $\beta$ phase during solidification, hence having a cooling rate categorized in the intermediate-to-high, based on Hori’s observations (see Fig. 2). Figure 5 shows backscattered electron micrograph of (a) 0.5 at%Zr and (b) 1 at%Zr deposits, respectively. The multilayer deposits show a high quality bond to the substrate with few visible defects and a smooth surface. They also displayed a consistent thickness ranging between 30 to 40 µm. The significant difference between the two deposits is the appearance of a single phase structure for the 0.5 at%Zr (see Fig. 5(a)), where a homogeneous columnar microstructure is present across the layer, without evidence of solute segregation or precipitates. On the other hand, for the deposit possessing 1 at%Zr (see Fig. 5(b)), a clear distinction can be observed through band-like precipitates developed with a certain periodicity, highlighting the boundary of the layer. All coatings with >1 at%Zr show a similar layering.
Figure 6 presents a back-scattered electron micrograph of the deposit containing 0.5 at% Zr. The microstructure is clearly composed of a mix between large columnar grains and some equiaxed grains. The grain size is in the micron range, indicative that grain refinement during solidification did not occur. Furthermore, few precipitates were observed. X-ray diffraction was conducted to measure if any shift in the lattice parameter had occurred, and the calculated value was compared to reported lattice parameter values. The measured lattice parameter was 0.40512 ± 0.00002 nm. By comparing with the work of Hori et al., the present combination of solute concentration and cooling rate suppresses the formation of the β phase, known to act as grain refiner, and a supersaturated Al solid solution possessing a typical columnar solidification structure forms. This is in fact the ideal situation for an aged hardening alloy, but is the worst condition in the situation to develop an alloy for nanostructured solidification grains.

Figure 7(a) presents a back scattered micrograph of the Al–1 at% Zr, showing a band-structure containing precipitates and a zone with a significantly lower precipitate concentration above. The white precipitates are believed to be the β (Al3Zr) phase with the L12 structure, known to favor grain refinement. Figure 7(b) shows grain size distributions for the two regions depicted in Fig. 7(a), i.e., within the region with the precipitates and in the precipitate-free one, respectively. The grain size distributions are showing that the region containing precipitates has a smaller grain size distribution, ranging between 300–600 nm, while the region free from precipitates has a grain size ranging between 500 nm to 1 μm. This result is indicating that UFG can be obtained upon solidification, conditional to the presence of the L12 metastable precipitates.

Similar observations with respect to a shifted grain size distribution was made for the sample possessing 1.25 at% Zr. A closer microstructure examination of this precipitate free zone was performed and a back scattered electron micrograph for the Al–1 at% Zr sample is shown in Fig. 9. One interesting feature observed is the presence of another type of precipitate, showing darker in contrast micrograph, suggesting a lower content in Zr than the L12 precipitates, suggesting that during solidification, a change in precipitate composition is occurring.

As demonstrated for the alloys ranging between 1 and 1.5 at% Zr, a two-layer structure is forming for each individual ESD layer deposited, initially with the β L12 metastable phase, followed by a region possessing another type of precipitate that could be sub-stochiometric to the L12 phase. Firstly, and as opposed to the Al–0.5 at% Zr, the...
Combination of solute concentration and cooling rate for the 1–1.5% alloys is sufficient to induce primary solidification of the β precipitates. These metastable Al12Zr precipitates, acting as heterogeneous nucleants, are the most desirable form of precipitate to induce grain refinement in Al alloys, which was observed in Figs. 7 and 8, respectively. However, as demonstrated within the current experimental parameter window tested, the ESD layers exhibited a change in grain size and microstructure, which are believed to be caused by the nature of the peritectic solidification reaction itself. The solidification of the primary β phase inevitably causes a reduction of the solute concentration at the solid/liquid interface, which could fall below the minimum necessary Zr concentration to form the L12 phase. Intuitively and based on the suggested solidification map of Hori (see Fig. 2), once below the threshold concentration, the formation of a supersaturated solid solution should develop. This assumption could be valid if the cooling rate during solidification would remain constant, but as demonstrated in the solidification model shown in Fig. 3, a significant reduction (2 to 3 orders of magnitude) in cooling rate is occurring during the solidification event, and hence creating an additional competitive interaction altering the microstructure. By comparing the microstructures shown in Figs. 6 and 7(a), we believe that when the Zr concentration ranges somewhere between 0.5 and 1 at%, the necessary solute concentration becomes too low to support continual development of the L12 precipitates. The presence of isolated β precipitates in Fig. 6 suggests that the critical Zr threshold required to support the formation of the L12 would be closer to 0.5 at% than 1 at%. However, further experiments would be required to precisely identify this critical Zr content.

Since rapid solidification is a non-equilibrium transient process, the relationship between the thickness of the layer possessing the L12 precipitates, the cooling rate as a function of deposit thickness extracted from Fig. 3, and the solute composition was studied. The results are presented in Fig. 10. It is worth mentioning that for the current analysis, the lower interface of the L12 banded structure was used as lower (bottom) weldment interface and that only the upper layer from the deposit was analysed to ensure the measured thickness is that of a single deposit. The results indicate that for the tested compositions and deposition parameters employed, the thickness of the layers containing the β precipitates are statistically similar, which translates into similar critical cooling rates within the range of $2 \times 10^7$ K s$^{-1}$ for the break down in the β precipitation. We can then infer that due to the similarity in the composition, the interfacial Zr content would also be very similar.

With respect to the formation of the sub-stoichiometric phase in the β free region, we believe that the cooling rate
has reduced to a point too low to form a supersaturated solid solution and that the solute concentration is too low to form the $\beta$ phase, favoring the formation of these precipitates. Metastable sub-stoichiometric (Al-rich) precipitates were observed in the Al–Ti system by several groups, but a controversy remains with respect to the actual composition. Particularly, the following sub-stoichiometric phases were observed: $\text{Al}_7\text{Ti}_0.2$, $\text{Al}_3\text{Ti}_0.2$, $\text{Al}_8\text{Ti}$, $\text{Al}_5\text{Ti}$, and $\text{Al}_7\text{Ti}$. In the case of the Al–Zr system, Clout et al. have modeled the formation energy of several sub-stoichiometric Al-rich phases and found that the following compounds can be present: $\text{Al}_2\text{Zr}$, $\text{Al}_7\text{Zr}$, $\text{Al}_8\text{Zr}$, $\text{Al}_1\text{Zr}$, and $\text{Al}_1\text{Zr}$. It is worth mentioning that no experimental evidence was provided. Hence, we believe that Al–Zr sub-stoichiometric phase are present in the upper part of the deposited layer, which would form because of an insufficient concentration of Zr solute to sustain the L1$_2$ precipitates at the given cooling rate. As illustrated by the numerous possible stoichiometries for these compounds, the actual determination of the composition will require a significantly more in-depth analysis than what was done for this work, to provide a controversy-free composition for the observed precipitates. With respect to grain refinement, we believe that the volume fraction of these sub-stoichiometric precipitates is too low to yield nucleation efficiency similar to what was observed from the L1$_2$ precipitates.

Finally, with respect to the objective of producing refined grain size weldments, the results are indicating that the deposit thickness must be controlled to a maximum of 5 microns per pass for Al–Zr alloys containing 1–1.5 at%, assuming a similar characteristic in the discharge during the micro-arc deposition. This control would allow for the development of the L1$_2$ structure, which is the ideal heterogeneous nucleation site, while maintaining a Zr concentration at the termination of solidification higher than the concentration allowing for the breakdown in precipitation of the L1$_2$. Similar solute concentration for the substrate and the electrode will need to be used to facilitate the control of the solidification structure.

4. Conclusion

It has been shown that the electrospark deposition is able to produce multilayered deposits with the presence of the metastable cubic phase L1$_2$ Al$_3$Zr precipitates due to the high cooling rates and undercooling that could be achieve by this micro-welding process. The presence of the L1$_2$ proeutectic precipitates during the rapid solidification of Al–Zr promotes the formation of UFG equiaxed Al grains. It was also observed that the solidification morphology is altered and sub-stoichiometric precipitates are forming towards the termination of the solidification, resulting in larger solidified grains.

Acknowledgments

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REFERENCES

26) T. S. Sudarshan: Rapid Solidification Technology, (Technomic publishing company, United States, 1993).