Effects of solution time and cooling rate on microstructures and mechanical properties of 2219 Al alloy for a larger spun thin-wall ellipsoidal head

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\textbf{A B S T R A C T}

The effects of solution time and cooling rate on microstructures and mechanical properties of 2219 Al alloy for a larger spun thin-wall ellipsoidal head are investigated. It is found that the Al\textsubscript{3}Cu phases are greatly affected by the solution time. The content of Al\textsubscript{3}Cu phases first decreases and then stabilizes with increasing the solution time. Moreover, the effects of solution time on the transformation of precipitates are obvious. As the solution time is increased from 35 min to 60 min, almost all the precipitates transfer from GP zones to $\theta^\prime$ phases. When the solution time is further increased to 110 min, some $\theta^\prime$ phases appear. Meanwhile, the size of $\theta^\prime$ phases increases, while the density of $\theta^\prime$ phases drops. These microstructure changes greatly influence the mechanical properties, i.e., the hardness and tensile strengths first increase and then slightly decrease with the continuous increase of the solution time. In addition, if the cooling rate is decreased, the precipitation of coarse equilibrium $\theta^\prime$ phases is enhanced, but the precipitation of strengthening phases ($\theta^\prime$, $\theta$) is restricted. It significantly deteriorates the mechanical properties. Based on the comprehensive analysis, the suitable solution time and cooling method are about 60 min and water cooling.

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\textbf{1. Introduction}

The large thin-wall ellipsoidal heads are the critical structural components of nuclear power plants, propellant tank of rockets, etc. [1,2]. The thin-wall ellipsoidal heads are mainly fabricated by complex forming processes such as spinning, friction stir welding, stamping, etc. [3,4]. In the forming process, the material flow and microstructure changes such as the evolution of grains and the transformation of phases are usually complex due to the complicated and time-variant stress fields [5–10], which greatly influence the mechanical properties of alloy components. Usually, the proper heat treatments can be designed to optimize the microstructures and improve the properties of components formed by spinning, forging, welding, etc. [11–16]. Therefore, it is important to investigate the effects of heat treatment on the microstructural evolution and mechanical properties of spun larger thin-wall alloy components.

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Up to now, some researchers have investigated the effect of spinning parameters and heat treatment on thin-walled components. For example, Xia et al. [17] found that the tubes with ultrafine grains can be obtained by annealing treatment and spinning process. Xu et al. [18] concluded that the annealing treatment can improve the bonding strength of the 3A21/5A03 composite tube. Hu et al. [19] investigated that the grains of T250 maraging steel tube can be refined by solution treatment, and the temper microstructures can be obtained by aging treatment. Lin et al. [5] investigated the influences of feed rate and wall thickness reduction on the microstructures of a thin-walled Hastelloy C-276 cylinder during staggered spinning, and found that the uniform deformation and grain distribution can be obtained when the feed rate is about 0.8 mm/r or the wall thickness reduction is about 44.1%. Mohabbi et al. [20] found that the grains of pure aluminum can be refined by annealing treatment and spinning process, and the mechanical properties are improved with increasing spin-bonding cycles. Meanwhile, some studies have focused on the influence of heat treatment on the microstructures and properties of Al-Cu alloys and their thin-wall parts. For example, Lin et al. [21–23], Zhu et al. [24], Liu et al. [25] and Liu et al. [26] analyzed the stress-aging on the precipitation mechanisms and mechanical/Corrosion properties of different Al-Cu alloys. These investigations are very useful for manufacturing larger thin-wall complex aeronautical vehicles parts, such as fuselage, landing gear, etc. Paolotti et al. [27] demonstrated the creep behaviors of Al-Cu-Mg alloys strengthened by precipitates, and established one physically-based creep model to describe the creep features of an AA2024-T3 alloy. Also, Regev et al. [28] comprehensively discussed the microstructure stability such as the secondary precipitation and coarsening of nano-precipitates within grains during creep of FSW AA2024-T3 alloy. Chang et al. [29] found that the high dislocation density formed in spinning process can enhance the precipitation of fine phases in the aging treatment, which improves the mechanical properties of 2024 aluminum alloy thin tube. Wang et al. [30] discussed the competitive relationship between grain boundary precipitates and thermal effect on the ductility of an Al-Cu-Mn alloy.

Based on the above review, although some work on the heat treatment processing of some typical Al-Cu alloys and thin-wall components have been reported, there are few efforts to investigate the changes of microstructures and mechanical properties of 2219 Al alloy for a spun larger thin-wall ellipsoidal head during the heat treatment. Here, 2219 Al alloy is one typical Al-Cu alloy, which is often used in critical structural components such as the propellant tank of rockets [31–34]. In this work, a heat treatment processing including solution treatment, quenching and aging treatment are designed to optimize the microstructures and enhance the mechanical properties of 2219 Al alloy for a spun larger thin-wall ellipsoidal head. The effects of solution time and cooling rate on the microstructures and mechanical properties of the studied head are discussed in detail. The optimized heat treatment parameters are obtained.

### Table 2 - Heat treatment parameters.

<table>
<thead>
<tr>
<th>Case ID</th>
<th>Solution time (ST, min)</th>
<th>Quenching method (QM)</th>
<th>Aging treatment (AT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>35</td>
<td>WC</td>
<td>160 °C, 12 h</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>WC</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>85</td>
<td>WC</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>110</td>
<td>WC</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td>AC</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>60</td>
<td>FC</td>
<td></td>
</tr>
</tbody>
</table>

### Table 1 - Chemical composition of 2219 Al alloy ellipsoidal head (wt. %).

<table>
<thead>
<tr>
<th>Cu</th>
<th>Mg</th>
<th>Zr</th>
<th>V</th>
<th>Mn</th>
<th>Si</th>
<th>Fe</th>
<th>Ti</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.37</td>
<td>0.03</td>
<td>0.12</td>
<td>0.07</td>
<td>0.30</td>
<td>0.05</td>
<td>0.16</td>
<td>0.04</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

2. Material and experiments

In this study, the studied material was a commercial 2219 Al alloy, and its chemical composition (wt. %) was displayed in Table 1. Firstly, the thin wall ellipsoidal head was spun from the annealed 2219 Al alloy blank by mandrel-free spinning, as shown in Fig. 1(a). The thickness of annealed plate was 6 mm before spinning, while the thickness and diameter of the spun thin wall ellipsoidal were about 4 mm and 2.29 mm, as presented in Fig. 1(b). Fig. 2 presents the initial microstructure of the spun 2219 Al alloy thin wall ellipsoidal head. Clearly, some second phases are uniformly distributed in the aluminum matrix, and its volume fraction is evaluated as 8.46%. The shapes of these phases are various, including block-like, strip-like and equiaxed-like, as shown in Fig. 2(b). Moreover, it can be found that the second phases can be appropriately divided into two kinds, i.e., the first one is the coarse second phases, which is the primary second phases formed in the solidification process. While the second one is the fine dispersed second phases, which is produced in the solidification and air cooling processes [35, 36]. In general, the second phases are hard and brittle [26]. The stress concentration likely appears at the surface of second phases, leading to the crack source and deteriorating properties of material [22]. For the spun 2219 Al alloy without heat treatments, the hardness, ultimate tensile strength (UTS), yield strength (YS) and elongation (EL) are only 59 HV, 177.69 MPa, 145.73 MPa and 10%, respectively. Through the EDS experiment, the component of second phases is Al2Cu phases, as shown in Fig. 2(c). Fig. 2(d) gives the size distribution of Al2Cu phases. Obviously, the size of Al2Cu phases is relatively different, and the maximal coarse Al2Cu phases are nearly 20 μm. Therefore, a suitable solution treatment is highly necessary to refine the coarse Al2Cu phases and improve the mechanical properties of material.

To separately study the effects of solution time and cooling rate on microstructures and mechanical properties, the detailed heat treatment process is designed, as depicted in Table 2. The samples are separated into two groups. One group (cases 1–4) was solution treated at 535 °C for different time, and then the samples were quenched in water. Finally, these samples were aging treated at 160 °C for 12 h. The other one group (cases 2, 5 and 6) was heated to 535 °C for 60 min, and quenched by water cooling (WC), air cooling (AC) and furnace cooling (FC).
cooling (FC), respectively. Then, the samples aged at 160 °C for 12 h. In addition, the samples were cut from the spun 2219 Al alloy thin-wall ellipsoidal head along spinning direction, i.e. circumferential direction.

To investigate the microstructure changes of the alloy during heat treatment, the optical microscope (OM), and scanning electron microscope (SEM), and transmission electron microscope (TEM) were carried out. Here, the TEM specimens were grinded into thin foils and thinned by double-jet electropolishing in 30% HNO₃ and 70% CH₃OH at −30 °C. To evaluate the effects of heat treatment on the mechanical properties, the micro-hardness was measured at a load of 0.2 kg for holding time of 15 s. The MTS test machine was employed to execute the uniaxial tensile tests at 25 °C. Here, the tensile tests were carried out at the constant speed of 2 mm/min. Meanwhile, non-contact measuring instrument ARAMIS was used to measure the elongation to fracture.

3. Results and discussion

3.1. Effects of solution time on microstructures and mechanical properties

3.1.1. Effects of solution time on microstructures

Fig. 3 shows the morphologies and size distribution of Al₂Cu phases in the alloy under cases 1–4, i.e., the solution time are different. It can be observed that the Al₂Cu phases are
Fig. 3 – The morphologies and size distribution of Al₂Cu phases in the alloy after the solution treatment-QM (WC)-AT (160 °C, 12 h) and the solution time of: (a–b) 35 min; (c–d) 60 min; (e–f) 85 min; (g–h) 110 min.
still evenly distributed in the matrix after solution treatment. When the solution time is increased to 35 min, the maximal size of the coarse Al$_2$Cu phases drops to 13 µm (drop to about 65% of the as-spun alloy), as shown in Fig. 3(a and b). It indicates that the solution treatment can effectively make coarse phases dissolve. Fig. 3(c and d) indicate that the coarse Al$_2$Cu phases are further dissolved and the maximal size drops to 9 µm when the solution time is increased to 60 min. The size distribution of Al$_2$Cu phases gradually stabilizes as the solution time is continually increased to 110 min, as shown in Fig. 3(e and f). The coarse Al$_2$Cu phases are stable due to their high surface energy [36]. It means that the coarse Al$_2$Cu phases are difficult to sufficiently dissolve into matrix. Therefore, as the solution time is increased, the size of coarse Al$_2$Cu phases firstly decreases and then stabilizes.

In addition, the content of Al$_2$Cu phases is also affected by the solution time. Fig. 4 presents the variations of Al$_2$Cu phases content at different solution times. When the solution time is 35 min, the content of Al$_2$Cu phases is about 1.92%. As the solution time is raised to 60 min, the content of undissolved Al$_2$Cu phases further decreases to 1.27%. However, as the solution time is further raised to 110 min, the content of Al$_2$Cu phases inconspicuously change. The reason is that the content of Cu in the 2219 Al alloy has surpassed the solubility limit [36]. Therefore, the content of second phases firstly decreases and then stabilizes with increasing the solution time.

Fig. 5 shows the precipitates and corresponding SAED patterns of the alloy at different tested condition. Generally, the dissolution of second phases has a great impact on aging precipitates [37,38]. The typical precipitated sequence of Al-Cu alloys in the aging treatment process is: supersaturated solid solution → quenched clustered → G.P.(I) → G.P.(II) → coherent θ' (independent of G.P. (II)) → semi-coherent θ' → stable θ [39,40]. From Fig. 5(a), when the alloy is solution treated for 35 min, the aging precipitate phases are uniformly distributed in the (001)$_{Al}$ planes. According to Fig. 5(b), the continuous streaks can be clearly found in the planes, which are the typical features of G.P. zones [41]. The small G.P. zone is formed by the aggregation of Cu atoms in the vacancies or dislocations. When the Cu atoms are aggregated at the interface between G.P. zone and matrix, the G.P. zone is coarsened and transformed into θ'' phases. From Fig. 5(c), when the solution time is raised to 60 min, many needle-like precipitates can be obviously observed. Combining with the corresponding SAED pattern shown in Fig. 5(d), it can be confirmed that the precipitates are composed of G.P. zone and a large amount of θ'' phases. The length of θ'' phases varies from 15 nm to 45 nm, and the thickness is less than 2 nm. However, the density of G.P. zone decreases due to the formation of θ'' phases. From Fig. 5(e and f), when the solution time is raised to 110 min, the size of precipitates slightly raises. The corresponding SAED pattern shows discontinues streaks at the {020}$_{Al}$ positions, indicating that the main precipitates are still θ'' phases. Moreover, the diffraction streaks at the {110}$_{Al}$ sites indicate a small amount of θ'' phases in the matrix. The length of precipitates varies from 25 nm to 55 nm and the thickness varies from 2 nm to 4 nm. However, the density of precipitates decreases due to the coarsen of precipitates. Summarily, the size of precipitates increases, but the density of precipitates decreases with increasing the solution time. Combining with the content of undissolved Al$_2$Cu phases at different solution times, which shown in Fig. 4, it can be found that the solubility of Cu content firstly increases and then stabilizes. The increasing solubility of Cu content can promote the transformation of precipitates. Therefore, the diameter of precipitates increases and transforms from G.P. zone to θ'' phases. However, when the solution time is increased from 60 min to 110 min, the solubility of Cu content stabilizes. Thus, the diameter of precipitates slightly increases, but the density decreases.

Fig. 6 shows that the grain boundary features in the alloy at different tested condition. From Fig. 6(a), the precipitation free zone (PFZ) in the grain boundary can be observed. The width of PFZ is evaluated as 53.37 nm. There are two main reasons for the formation of the PFZ. Firstly, a lot of vacancies diffuse to the grain boundary to form a low vacancy concentration zone in the solution process, which induces the appearance of PFZ. Secondly, the nucleation and growth of precipitate phases in the grain boundary consumes some solution atoms, which reduces super-saturation degree of solution atoms near grain boundaries. From Fig. 6(b), when the solution time is raised to 60 min, the width of PFZ drops to 39.36 nm. When the solution time is increased to 110 min, no distinct PFZ can be observed in grain boundaries, as shown in Fig. 6(c). So, it can be concluded that the width of PFZ decreases with increasing the solution time.

### 3.1.2. Effects of solution time on mechanical properties

Fig. 7 presents the variations of mechanical properties with the solution time. When the solution time is 35 min, the hardness, UTS and YS increase by 73.75 HV, 244.49 MPa and 71.9 MPa, respectively, compared with those of the as-spun alloy. It is generally known that the precipitation strengthening is the main strengthening mechanism of Al alloys [42]. The mechanical properties are not only related to the type and size of precipitates, but also to their content and density. Combining with Fig. 5(a) and Fig. 7(a–c), it can be concluded that the hardness and tensile strength is reinforced by fine G.P. zones. As solution time is raised to 60 min, the hard-
Fig. 5 – TEM images and corresponding SAED patterns of the alloy after the solution treatment-QM (WC)-AT (160 °C, 12 h) and the solution time of: (a–b) 35 min; (c–d) 60 min; (e–f) 110 min.
ness, UTS and YS further increase to 146.83 HV, 446.14 MPa and 260.69 MPa, respectively. This is because the main precipitates change from G.P. zones to $\theta''$ phases, leading to the increased content of $\theta''$ phases. The coherent strains around $\theta''$ phases effectively hinder the movement of dislocations and enhance the mechanical properties. As the solution time is raised to 110 min, there are only slight decrease in the hardness and tensile strengths. Combining with Fig. 5(e), the precipitates are mainly $\theta''$ phases, and accompanying with a few $\theta'$ phases. Although the size of precipitates is slightly increased, their density decreases. The effect of precipitation strengthening is weakened, inducing a slight decrease in hardness and tensile strengths. Therefore, as the solution time is increased, the hardness, UTS and YS firstly increase and then slightly decrease.

Fig. 7(d) demonstrates the effects of solution time on the elongation to fracture (EL). When the solution time is increased from 35 min to 110 min, the EL drops from 24.28% to 14.69%. It can be found that the elongation decreases with increasing the solution time. This is because the size of precipitates increases with the increased solution time, which effectively to hinder the motion of dislocation. In addition, the plastic deformation easily occurs in the PFZs. In other words, the PFZs are conductive to relax the stress in the plastic deformation process, and the wider PFZs can improve the ductility. Therefore, the alloy with fine precipitates and wide PFZs exhibits the better elongation.

3.2. Effects of cooling rates on microstructures and mechanical properties

3.2.1. Effects of cooling rates on microstructures

Fig. 8 shows the morphologies in the alloy at different tested conditions. Here, for the cooling speed ranges, the water-cooling (WC) is about 150–170 °C/s, the air-cooling (AC) is about 1.5–1.7 °C/s, and furnace cooling (FC) is about 0.5–0.6 °C/s. In Fig. 8(a), when the solution-treated alloy is cooled by WC, the granular Al$_2$Cu phases evenly distribute in the matrix. When
the alloy is cooled by AC (Fig. 8b), it can be found that many long and thin strips precipitates appear on grain boundaries. These grain-boundary precipitated phases are equilibrium \( \theta \) phases [43]. The reason for the precipitation of \( \theta \) phases is that the formed solid solution is not stable at slow cooling rate, which easily decomposes at grain boundaries. As shown in Fig. 8(c), the \( \theta \) phases continuously distribute at grain boundaries. In addition, the content and size of precipitated \( \theta \) phases significantly increases, compared with those of case 5. This is because of the long precipitation time for \( \theta \) phases under case 6. Therefore, the content and size of \( \theta \) phases increase with the decreased cooling rate.

Fig. 9 shows the precipitates and corresponding SAED patterns of the alloy under case 5. As presented in Fig. 9(a), the coarse undissolved \( \Al_2\Cu \) phases are observed in the matrix. There are few precipitates in the region of undissolved \( \Al_2\Cu \) phases. This is because the coarse \( \Al_2\Cu \) phases insufficiently dissolve into matrix, making the content of \Cu atoms too less to form fine intermediate precipitates. Combining with Fig. 9(c), the corresponding SAED pattern shows discontinues streaks at \( \{020\}_{\Al} \) and \( \{200\}_{\Al} \) positions, indicating the existence of \( \theta' \) phases in the matrix. Additionally, the diffraction streaks at the \( \{110\}_{\Al} \) sites indicate that \( \theta' \) phases also exist in the matrix. The length of these phases is between 25 nm and 55 nm, and the width is less than 3.5 nm, as shown in Fig. 9(b). It is noticed that the long needle-like \( \theta \) phases can be found in the matrix. Usually, the \( \theta \) phases are formed through the transformation of \( \theta' \) phases [37,44]. The well-grown \( \theta' \) phases form in the slow air cooling, and further form \( \theta \) phases in the subsequent aging treatment [37]. Additionally, some non-decomposed solid solution can be directly transformed into \( \theta \) phases in the air cooling process [37]. Moreover, there are few fine precipitates surrounding \( \theta \) phases. Because the precipitation of \( \theta \) phases consumes plenty of \Cu atoms, reducing the content of fine intermediate precipitates. Therefore, these results demonstrate that slow cooling rate can restrict the precipitation of fine \( \theta' \) phases and \( \theta \) phases.

3.2.2. Effects of cooling rates on mechanical properties

Fig. 10 presents the variation of mechanical properties of the alloy at different cooling rates. Obviously, the cooling rates have significantly effects on the mechanical properties of the alloy, as shown in Fig. 10. The hardness, UTS and YS obviously increase with increasing the cooling rate. When the cooling method is changed from FC to WC, the hardness, UTS and YS increases by 93.92 HV, 313.78 MPa and 199.65 MPa, respectively. The elongation (EL) first slightly increases and then decreases with decreasing the cooling rate. Usually, the hardness and tensile properties have close relationships with microstructures [45]. As the discussed above, the solid solutions are easily to decompose and form \( \theta \) phases at a slow cooling rate. Especially, these \( \theta \) phases always precipitate at grain boundaries, deteriorating the mechanical properties of material [46,47]. In addition, the nucleation of \( \theta \) phases consumes a large num-

**Fig. 7** – Effects of the solution time on: (a) hardness; (b) UTL; (c) YS; (d) EL.
ber of Cu atoms, hindering the precipitation of strengthening phases (θ'' phases and θ' phases). Therefore, the hardness and tensile strengths decrease, while the elongation slightly increases. When the cooling method is transferred from AC to FC, the content and size of θ phases increase. Meanwhile, the θ phases are segregated at the grain boundaries, which will deteriorate the comprehensive mechanical properties. Thus, in order to obtain the ideal mechanical properties, a high cooling rate is needed in the quenching process.

4. Conclusions

The effects of the solution time and cooling rate on microstructures and mechanical properties of a spun 2219 Al alloy ellipsoidal head are discussed in detail. Some summarized conclusions can be drawn:

1) The Al₂Cu phases are strongly sensitive to the solution time. As the solution time is increased, the content of Al₂Cu phases firstly decreases and then stabilizes. When the solution time is increased from 35 min to 60 min, the content of Al₂Cu phases decreases from 1.92% to 1.27%. While the solution time is further increased to 110 min, the content of Al₂Cu phases stabilizes. Meanwhile, the solution time has significant effect on aging precipitates. Aging precipitates firstly transform from G.P zone to θ'' phases. Then, θ'' phases slightly grow up and partly transform to θ' phases with increasing the solution time.

2) The solution time has visible effect on the mechanical properties. The hardness and tensile strengths first increases and then slightly decreases, while the elongation decreases with increasing the solution time. This phenomenon can be attributed to the distribution of precipitates and the width of PFZ.

Fig. 8 – SEM images of the alloy after ST (60 min)-QM-AT (160 °C, 12 h) and the quenching method of: (a) WC; (b) AC; (c) FC.
Fig. 9 – TEM images and corresponding SAED patterns of the alloy after ST (60 min)-QM (AC)-AT (160 °C, 12 h): (a) undissolved $\text{Al}_2\text{Cu}$ phases; (b) coarse $\theta$ phases; (c) corresponding SAED patterns.

3) The cooling rate has greatly influences on microstructures of the alloy. When the alloy is cooled by WC, sufficient $\theta''$ phases precipitate in the matrix. While cooled by AC and FC, $\theta$ phases appear in the grain boundaries, restricting the precipitation of strengthening phases ($\theta'$ phases and $\theta''$ phases). Moreover, with the decreased cooling rate, the size of $\theta$ phases increases, which deteriorates the comprehensive mechanical properties.

4) The proper solution time and cooling method are about 60 min and water cooling, respectively.
Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References


Fig. 10 – Effects of cooling rate on: (a) hardness; (b) UTS; (c) YS; (d) Elongation.