The existing forms of Zr in Mg-Zn-Zr magnesium alloys and its grain refinement mechanism

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Abstract
The formation of the Zr-containing phases during the solidification of Mg-Zn-Zr alloy is simulated, the structure of the Zr-containing compounds and the solid solution amount of Zr in α-Mg solid solution as well as the grain size of the as-cast alloy are measured. Based on this, the existing form of Zr element in Mg-Zn-Zr alloy and its action mechanism of grain refinement are discussed. The results show that either α-Zr or α-Mg solid solution precipitates first from melt of Mg-Zn-Zr alloy at the beginning of solidification due to the different Zr content, then some Zn-Zr phases with different Zn/Zr atomic ratios form in the alloy melt during solidification. The Zr element in Mg-Zn-Zr alloy mainly exists in the form of compounds, its solid solution amount in α-Mg is not large and is inhibited by Zn element. The Zr in Mg-Zn-Zr alloy has the effect to refine grain, the reason is that the α-Zr phase and α-Mg formed by peritectic reaction or α-Mg formed from Zr atomic clusters can be used as the nucleus of subsequent α-Mg crystals. In addition, the Zr-containing compound formed during solidification can prevent the growth of grains, the enrichment of Zr in the crystallization front can also promote nucleation by component undercooling.

Magnesium alloy has the advantages of high specific strength and specific rigidity, easy to recycle, etc. It is the lightest metal structural material and green environmental protection material currently in practical application [1–3]. However, the mechanical properties of magnesium alloys are relatively low, the deformability is poor, and the solidification process is prone to defects such as shrinkage porosity and pore cracks. Grain refinement is an important measure to improve its mechanical properties [4–7]. Alloying is a commonly used method for refining the grains of magnesium alloys, and Zr is an important alloying element in many alloys systems, It can not only refine the grains, but also has a significant effect on the strengthening and toughening of the alloy and the improvement of the corrosion resistance and heat resistance of the alloy [8–12].

In terms of grain refinement, it is generally believed that Zr as a grain refiner of magnesium alloy is based on the peritectic reaction mechanism proposed by Emley [13], Emley pointed out, at the peritectic temperature, Zr particles separate out from the melt and react with the melt to form a Zr-rich solid solution, the peritectic product provides an effective nucleus for the crystallization of Mg. Therefore, the Zr content should be greater than 0.61% of the Zr particles that can be precipitated first, to play the role of grain refinement. Moreover, only those Zr particles which precipitated near the peritectic temperature can serve as the core to promote the nucleation of the melt. Tamura et al. [14] pointed out, when the content of Zr added to the magnesium alloy by the Mg-Zr master alloy reaches 0.4%, it can play the role of grain refinement. The reason is that the added Zr has two states of dissolved and undissolved in the melt, undissolved Zr is surrounded by magnesium solid solution, which becomes the crystal nucleus of alloy crystal. Therefore, undissolved Zr particles play a very important role in grain refinement. Ma et al. [15] adopted a method of sampling from the top of the melt before and after stirring, the effect of soluble Zr and total Zr on the grain refinement of pure magnesium was investigated. It is found that the grains of the sample before stirring have been refined, and Zr mainly exists in the dissolved state,
indicating that the soluble Zr has the effect of grain refinement; Although the amount of soluble Zr does not change much after stirring, the grain refinement is more obvious, and the grain refinement is related to the total Zr content of the sample. Because there are undissolved Zr particles precipitated at the bottom of the solution before stirring, it shows that the dissolved Zr and undissolved Zr particles after stirring play the role of crystal grain refinement at the same time. Lee [16] and others found that adding Zr to pure magnesium can effectively refine the grains, but the maximum amount of Zr added in the experimental alloy is 0.32%, which is much lower than the composition of peritectic point (0.61%), in this case, Zr seems impossible to exist in the form of particles. Through calculation, the growth restriction factor (GRF) of Zr is larger, that is, Zr has a strong segregation at the front of the solidification interface. Therefore, the grain refinement achieved by the addition of Zr is due to the enrichment of Zr at the front of the solid-liquid interface hindering the growth of grains, and at the same time promoting the nucleation of the composition in the supersaturated zone. Liu Rui [17] used first principles to construct the Mg/Zr interface, it can be seen from the results of the convergence analysis of the surface model, it shows that the HCP stacking interface is the most stable interface of Mg/Zr, at the same time, the calculated Mg/Zr interface energy is smaller than the solid-liquid interface energy between the α-Mg/Mg melt where α-Mg is directly nucleated from the Mg melt, so α-Mg can nucleate on the surface of Zr (0 0 0 1).

From the two aspects of interface atomic structure and bonding characteristics, the paper provides strong theoretical support for the Zr particles as the heterogeneous nucleation core of α-Mg to refine the magnesium alloy grains. It can be seen that although researchers believe that Zr can produce significant crystal fineness, moreover, it is believed that the generation of crystal refining and the effect of refining are related to the existence of Zr, however, different researchers hold different views on which form of Zr mainly plays a role in crystal fineness, different explanations are given to the fine crystal mechanism of Zr. This question suggests that if you want to accurately grasp the mechanism of Zr’s mechanism of fine crystal, and then guide the alloy composition design, smelting and solidification process formulation, an exact understanding of the form of Zr in the alloy is a necessary prerequisite, in addition, knowing exactly how Zr exists in alloys is also an important basic work for analyzing other functions of Zr.

For this reason, this article chooses the currently widely used ZK alloy as the research object, Scheil-Gulliver non-equilibrium solidification model is used to simulate the precipitation of Zr-containing phase and the solute distribution coefficient of Zr during the alloy solidification process, The solid solution content of Zr in the experimental alloy sample is measured and the phase containing Zr compound is identified and analyzed, on this basis, the grain refinement mechanism of Zr in the research alloy is discussed.

1. Experimental materials and research methods

The composition of the experimental alloy is designed with reference to ZK31 and ZK61 magnesium alloys, using pure magnesium, nominal Mg-30wt.%Zn and Mg-3wt.%Zr master alloys as raw materials, use graphite crucible as a container to melt in a resistance furnace, After melting at 900 °C, cooling down to 750 °C and stirring, and then pour into a φ20 mm steel mold. In order to compare and analyze the grain refinement effect of Zr, meanwhile a Mg-Zn series experimental alloy with the same Zn content as ZK31 and ZK61 but without Zr was designed. The actual chemical composition of the sample was measured with OPTIMA 2X00/5000 inductively coupled plasma emission spectrometer (ICP), and the actual added amount and measured results are shown in table 1.

Determination of Zr solid solution content in alloy based on chemical phase separation, the phase separation solution uses methanol as the solvent, use ammonium benzoate, 2,2’-bipyridine, salicylic acid and dioxane as solutes, Respectively as compound surface passivator, complexing agent of Zn ion, inhibitors of hydrolysates and chemical corrosion inhibitor for magnesium alloy. The chemical solution can accurately separate the solid

| Sample code | Designed composition | Actual added amount (wt%) | Measured composition (wt%) |
|-------------|----------------------|---------------------------|---------------------------|
|             | Zn Zr                | Zn Zr                     | Mg                        |
| ZK-I        | Mg-3%Zn-0.5%Zr       | 3.50 0.60                 | 3.41 0.54 Bal.            |
| ZK-II       | Mg-6%Zn-0.5%Zr       | 6.50 0.60                 | 5.86 0.57 Bal.            |
| Z-I         | Mg-3%Zn              | 3.50 0                  | 3.33 — Bal.               |
| Z-II        | Mg-6%Zn              | 6.50 0                  | 5.36 — Bal.               |

Table 1. The main chemical composition of samples.

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solution and compound of Mg-Zn series magnesium alloy at low temperature. separation of solid and liquid by centrifugation + filter membrane method. The liquid phase is converted into inorganic matter and used to determine the content of Zn and Zr elements in solid solution. The solid phase is used for the phase identification and morphology observation of the compound.

Observe the metallographic sample with an optical metallographic microscope (Axiolmager, Germany), and use the grain size measurement software attached to the microscope to determine the grain size of the experimental alloy; Use SU8220 field emission scanning microscope (HITACHI, Japan) to observe the phase morphology, and use OXFORD energy spectrometer (UK) to analyze the composition; Use Talos F200X transmission electron microscope (FEI, USA) to observe the phase morphology, obtain high-resolution images and perform phase calibration after Fourier transform (FFT); Use Scheil module of Thermo-calc thermodynamics software (Sweden) to calculate the phase precipitation in the non-equilibrium solidification process of the alloy.

2. Experimental results and discussion

2.1. Simulation results of alloy solidification process

Because the content of Zr in the ZK series magnesium alloy is usually between 0.3–2.1 [18], Therefore, use Scheil-Gulliver solidification model to simulate the solidification process of Mg-3%Zn-x%Zr and Mg-6%Zn-x%Zr (x = 0.3–0.9) alloys, among them. The Zr content in Mg-3%Zn-x%Zr alloy is 0.4% and 0.8%, figure 1 shows the temperature range of the Zr-containing phase in Mg-3%Zn-x%Zr and the calculated results of the mass percentage of Zr in each phase. Calculations proves that, for alloys with Zr content less than 0.77% (see figure 1(a)), the α-Mg phase containing Zr solid solution is precipitated at the beginning of solidification, which is of hcp structure, and then Zn2Zr is precipitated(When the Zn2Zr phase precipitates, the mass percentage of Zr in the liquid phase decreases, and it is determined that the Zn2Zr phase precipitates out of the liquid phase.). The number of two phases increases with the progress of solidification until the end of solidification. The calculation results also show that the mass percentage of Zr in the first precipitated α-Mg phase is much greater than its content in the alloy, and it increases with the increase of the Zr content of the alloy. For example, in an alloy containing 0.4% Zr, when the mass fraction of the precipitated α-Mg phase is 0.0001, the mass percentage of Zr is about 1.17%, When the alloy with 0.8% Zr is precipitated with the same mass fraction of α-Mg, the mass percentage of Zr is about 2.46%. However, as the solidification progresses, the mass percentage of Zr in the α-Mg phase gradually decreases, when the solidification is over, it is only 10⁻⁷ orders of magnitude. For alloys with a Zr content greater than 0.77% (see figure 1(b)), at the beginning of solidification, the α-Zr phase of hcp structure first precipitates, and then the α-Mg phase begins to precipitate. As the alloy solidification continues, the amount of α-Mg phase continues to increase, and then ZnZr2, Zn2Zr, and Zn2Zr appear one after another (When these phases are precipitated, the mass percentage of Zr in the liquid phase decreases, which confirms that these phases are all precipitated in the liquid phase.), until the end of solidification. The calculation results show that the content of Zr in the α-Mg phase is always low during the solidification process, and it is also only 10⁻⁷ orders of magnitude when the solidification is over. The above calculation results show, for the Mg-3%Zn-x%Zr alloy used in this research, at the beginning of solidification, there is a hcp structure α-Mg phase or hcp structure α-Zr phase with a higher Zr content in the system, Zn-Zr compound exists during solidification. Therefore, if Zr dissolves in the melt and the grains are refined by promoting nucleation during alloy solidification, then from the calculation results, these phases are possible sources of crystal nuclei.
This study also made similar calculations for the solidification process of Mg-6%Zn-x%Zr alloy, shows a similar precipitation process of Zr-containing phase to Mg-3%Zn-x%Zr alloy, however, the minimum Zr content of the alloy corresponding to the precipitated $\alpha$-Zr phase is about 0.85%, when the $\alpha$-Mg phase with a mass fraction of 0.0001 is precipitated, the mass percentage of Zr decreases slightly, while the precipitation temperature of various Zn-Zr compounds increased slightly.

2.2. Experimental analysis of the existence of Zr element
According to the aforementioned simulation results, the existing form of Zr after alloy solidification is mainly reflected in the solid solution in the $\alpha$-Mg phase and the formation of Zn-Zr compounds. Table 2 shows the measurement results of the solid solution content of Zr and Zn in the experimental alloys and the calculation results of the Scheil-Gulliver solidification model. The results show that the solid solution amount of Zr in the magnesium alloy is very small, much less than the content in the alloy, while Zn has a larger solid solution amount, reaching about half of its content. The results also show that the amount of solid solution of Zn increases with the increase of its content, but the solid solution content of Zr and Zn has an inhibitory effect on each other. Comparing the measurement and calculation results, it can be seen that the measured values of the solid solution amounts of Zr and Zn are far greater than the calculated values.

Table 2. The result of solid solution amount of Zr and Zn(wt%).

| Sample code | Designed composition | Measured value | Calculated value |
|-------------|----------------------|----------------|------------------|
|             |                      | Zn  | Zr  | Zn   | Zr   |
| ZK-I        | Mg-3%Zn-0.5%Zr      | 1.42| 0.075| 0.78 | 3.75E−10 |
| ZK-II       | Mg-6%Zn-0.5%Zr      | 3.23| 0.070| 1.28 | 3.74E−10 |
| Z-I         | Mg-3%Zn             | 1.62| —   | 0.79 | —    |
| Z-II        | Mg-6%Zn             | 3.67| —   | 1.29 | —    |

Figure 2. The morphology and composition analysis results of the separated Zr-containing phase.
The solid phase powder separated from the ZK-II alloy by the chemical phase separation method, the scanning electron microscope (SEM) topography and energy spectrum (EDS) composition analysis results of the Zr phase are shown in figure 2. From the above analysis results, we can see that there are different proportions of Zn-Zr phase and even Mg-Zn-Zr ternary phase in the alloy, these phases are of different sizes, but they all appear as squares with relatively regular geometric shapes. There are also many kinds of Zn-Zr compounds in ZK-I alloy, and the atomic ratio of Zn/Zr is quite different.

The selection electron diffraction analysis of many particles in the alloy containing Zr shows that there are mainly four intermetallic compounds containing Zr in the alloy. Figure 3 shows the transmission electron microscopy (TEM) brightfield image of the compound particles with higher Zr content in the ZK-II alloy, and the calibration result of the compound by the diffraction pattern obtained by the Fourier transformation of the high-resolution image. The compound in figure 3(a) is located at the grain boundary and has a larger size; Energy spectrum analysis the compound is mainly composed of Zn and Zr elements, the atomic ratio of Zn and Zr is about 2:0.76, the distance and included angle of the adjacent spots of the diffraction pattern are similar to those of (110), (311), (220) crystal planes of Zn$_2$Zr, so the compound is judged to be Zn$_2$Zr, it is a cubic crystal system, and the standard lattice constant is $a = 7.39$. The compound in figure 3(b) is located in the crystal near the grain boundary, the atomic ratio of Zn and Zr is about 2:3.88, the distance and included angle of its neighboring diffraction spots are similar to those of (111), (220), (311) crystal planes of Zn$_2$Zr$_3$, so the compound is judged to be Zn$_3$Zr$_3$, which is a tetragonal crystal system, and the lattice constant is $a = 7.6$, $c = 6.965$. The compound in figure 3(c) is also located in the crystal near the grain boundary, composed of three elements: Mg, Zn and Zr, the atomic ratio of the three is 3:6.64:1.07, the distance and included angle of its neighboring diffraction spots are similar to those of (330), (510), (220) crystal planes of Mg$_3$Zn$_6$Zr, so the compound is judged to be Mg$_3$Zn$_6$Zr, it is a cubic crystal system, and the standard lattice parameter is $a = 13.71$. The compound in figure 3(d) is inside the crystal, composed of three elements: Mg, Zn and Zr, the atomic ratio of the three is 1:2.71:0.46, the distance and included angle of its neighboring diffraction spots are similar to those of (110), (002), (112) crystal planes of MgZn$_2$, and the ratio of the sum of Mg and Zr atoms to Zn is 1:1.83, therefore, the compound should have the structure of MgZn$_2$, and because Zr and Mg have the same crystal

![Figure 3](image_url)
structure and the atomic radius is closer, it is judged that the compound is \((\text{Mg, Zr}) \text{Zn}_2\) formed by partial replacement of Mg by Zr, the crystal structure of the compound is hexagonal, and the unit cell parameters are \(a = 5.22\), \(c = 8.57\).

From the above analysis, it can be seen that Zr in the as-cast alloy at room temperature is basically not dissolved in \(\alpha\)-Mg, it constitutes compounds of different structures or exists in the compound in the form of replacement solid solution. With reference to the simulation calculation results of the alloy solidification process, \(\text{ZnZr}_2\) and \(\text{Zn}_2\text{Zr}_3\) in the formed compound are formed in the early stage of alloy solidification. Therefore, if Zr can refine grains in a way that promotes nucleation, they are possible sources of crystal nuclei. No element of Zr was found in actual observations, it shows that the Zr added with Mg-Zr master alloy is basically dissolved and distributed in the alloy melt at the melting temperature, it also shows that the experimental alloy did not form \(\alpha\)-Zr or disappeared due to peritectic reaction.

2.3. Analysis of Zr’s grain refinement mechanism

Figure 4 is an optical microscope photo of the four alloy samples listed in Table 1, it can be seen that for alloy samples with basically the same Zn content, the crystal grains containing Zr are smaller. respectively the grain sizes of the Mg-3\%Zn and Mg-6\%Zn alloy samples are 121 \(\mu\)m and 117 \(\mu\)m, while the average grain size of the Mg-3\%Zn-0.5\%Zr and Mg-6\%Zn-0.5\%Zr alloy samples are 81 \(\mu\)m and 74 \(\mu\)m, it can be seen from the above results that the addition of Zr to the alloy will produce the effect of grain refinement.

Zr also achieves grain refinement through the above mechanism in Mg-Zn-Zr alloy, produce component overcooling, and prevent grain growth. The mechanism of Zr’s grain refinement in the Mg-Zn-Zr alloy is nothing more than the above-mentioned mechanism.

In recent years, Zhang, MX [19–22] and others proposed an edge-to-edge matching model (E2EM), it can effectively predict whether the second phase particles in the alloy can be used as effective heterogeneous nucleation particles to promote nucleation, and has been verified through a large number of experiments. The E2EM model believes that if the particles in the alloy can become heterogeneous nucleation point to promote the nucleation of the alloy and cause the refinement of the alloy grains, then the primary crystal nucleus of the particle and the alloy needs to satisfy a certain crystal degree relationship, one is the degree of mismatch between the atomic spacing of the two phases in the closely packed direction, the second is the mismatch of the interplanar spacing mismatch of close-packed planes including the pair of close-packed direction. Generally speaking, when the interatomic distance mismatch between the particles and the primary phase is less than 10\%, and the interplanar distance mismatch is less than 6\%, it is believed that particles can be used as heterogeneous nucleation particles to promote nucleation.

The degree of interatomic distance mismatch and the degree of interplanar distance mismatch can be calculated by the following formulas respectively.

\[
f_r = \left| \frac{r_M - r_P}{r_M} \right| \times 100\%; \quad f_d = \left| \frac{d_M - d_P}{d_M} \right| \times 100\%
\]

In the formula, \(r_M\) and \(r_P\) are the atomic distance between the matrix atoms and the second phase particle atoms, \(d_M\) and \(d_P\) are the interplanar distances between the matrix and the second phase, respectively.

Thermodynamic calculations and experimental observation analysis have show, The Zr-containing second phase formed during the solidification in Mg-Zn-Zr alloys may include \(\alpha\)-Zr, \(\text{ZnZr}_2\), \(\text{Zn}_2\text{Zr}_3\), \(\text{Zn}_2\text{Zr}\), Mg\(_3\text{Zn}_6\)Zr,
etc apply edge-edge matching model (E2EM) to Mg-Zn-Zr alloy, calculate the degree of atomic mismatch and interplanar distance mismatch between each second phase and Mg, the calculation results are shown in table 3.

According to the calculation results in the above table, there is a very good lattice matching relationship between $\alpha$-Zr and Mg, possess the crystallographic conditions as a heterogeneous $\alpha$-Mg crystal nucleus. Therefore, if the Zr in the alloy is in elemental form during batching, the undissolved Zr can be directly used as the foreign crystal nucleus of $\alpha$-Mg crystals. In addition, the lattice matching relationship between other second phases and Mg is poor, and formed in the middle and late stages of $\alpha$-Mg crystallization, it is unlikely to be a heterogeneous nucleus of $\alpha$-Mg crystals. However, since these second phases are precipitated from the liquid phase and they are formed at the solid-liquid interface, they can prevent the growth of crystal grains. In addition, the effective solute distribution coefficient of the Zr element in the early stage of $\alpha$-Mg crystallization is greater than 1, that is, enrichment at the front of the grain boundary (See figure 5), therefore, it will also promote nucleation through ingredients undercooling and play a role in grain refinement.

However, for alloys with higher Zr content, the pre-phase is $\alpha$-Zr, although according to the calculation results of the Scheil-Gulliver non-equilibrium solidification model, the precipitated $\alpha$-Zr will remain until the end of solidification, however, since this model assumes that the solid phase has no diffusion (fast solidification rate), it limits the formation of $\alpha$-Zr without decomposition or transformation. According to the Mg-Zn-Zr equilibrium phase diagram, the precipitated $\alpha$-Zr will be decomposed in the subsequent peritectic reaction, the peritectic product formed at the same time has the same structure as the subsequent crystalline $\alpha$-Mg. Therefore, depending on the solidification rate, the alloy may be either $\alpha$-Zr or a peritectic reaction product, which provides a nucleus for subsequent $\alpha$-Mg crystallization. For the alloys with lower Zr content and the first phase being $\alpha$-Mg, calculations show that the concentration of Zr in the initially formed $\alpha$-Mg is much greater than its content in the alloy. The calculation results also show that the higher the Zr content of the alloy, the higher the starting temperature of $\alpha$-Mg formation. Based on this speculation, there may be a large number of Zr clusters in the alloy melt due to concentration fluctuations, these clusters first form $\alpha$-Mg with Mg atoms at a higher temperature, and have the hcp structure, and they will become the nuclei of subsequent $\alpha$-Mg crystals. In other words, even if the content of Zr in the alloy is less than the composition conditions required to form $\alpha$-Zr, Zr still has the effect of promoting nucleation.

![Figure 5. The calculation results of effective solute distribution coefficient of Zr.](image)

| Second phase | Crystal orientation relationship | Misfit degree |
|-------------|----------------------------------|---------------|
| $\alpha$-Zr | $\langle 11\overline{2}0 \rangle_{Zr} / \langle 11\overline{2}0 \rangle_{Mg}$ | 0.68% 1.20% |
| ZnZr | $\langle 11\overline{1} \rangle_{ZnZr} / \langle 11\overline{2}0 \rangle_{Mg}$ | 123.6% 12.24% |
| Zn2Zr | $\langle 11\overline{2} \rangle_{ZnZr} / \langle 11\overline{2}0 \rangle_{Mg}$ | 21.69% 40.91% |
| Zn4Zr | $\langle 11\overline{0} \rangle_{ZnZr} / \langle 11\overline{2}0 \rangle_{Mg}$ | 38.61% 22.01% |
| Mg3Zn6Zr | $\langle 11\overline{0} \rangle_{Mg3Zn6Zr} / \langle 11\overline{2}0 \rangle_{Mg}$ | 66.87% 34.20% |

Table 3. The crystal orientation relationship between Zr-containing second phase and Mg
In summary, Zr added to the alloy can increase the number of crystal nuclei and promote grain refinement in theory. In addition, if there are undissolved Zr particles in the melt during alloy smelting, they will surely function as heterogeneous crystal nuclei.

3. Conclusion

1. Scheil-Gulliver solidification model calculation display, Mg-Zn-Zr alloys are first formed as $\alpha$-Zr or $\alpha$-Mg solid solutions at the beginning of solidification due to different Zr content, among them, the concentration of $\alpha$Zr in $\alpha$-Mg solid solution is higher; during solidification, Zn-Zr phases with different Zn/Zr atomic ratios are precipitated in the liquid phase, at the end of solidification, there are two Zr-containing phases in the alloy structure at the end of solidification: $\alpha$-Mg phase and Zn2Zr compound.

2. In the as-cast alloy, the solid solution of Zr in $\alpha$-Mg is not large, and the solid solution of Zr is inhibited by the solid solution of Zn element; a variety of Zr-containing compounds such as ZnZr2, Zn2Zr3, Mg3Zn6Zr, (Mg, Zr)Zn2, etc were actually detected, they have regular geometric shapes and exist in the grain boundaries or within the grains close to the grain boundaries.

3. Zr in Mg-Zn-Zr alloy has the effect of grain refinement. first analysis of the $\alpha$-Zr phase, $\alpha$-Mg formed by peritectic reaction and $\alpha$-Mg formed by Zr clusters all have the hcp structure, can be used as the nucleus for subsequent $\alpha$-Mg crystallization; The Zr-containing compound formed during solidification can prevent the growth of grains, The enrichment of Zr in the crystallization front can also promote nucleation by component undercooling.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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