

# Guidance Analysis of Precipitated Phases Based on ZL205A Alloy Main Cluster Model

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**Abstract:** ZL205A is a type of complex alloy with excellent comprehensive mechanical properties. As there is a lack of research into the origin of its phase composition, research into the composition design of the ZL205A alloy has faced difficulties. This paper qualitatively characterizes the near-programmed atomic arrangement structure of multi-element alloy solid solution based on the "first nearest neighbor cluster plus connected atoms" model, thereby accurately expressing the solid solution near-programmed cluster spatial structure of ZL205A alloy in a quantitative manner. The results show that the solid solution cluster model of ZL205A is

$\{[Al-Al_{12}]Al_2\}_{12}[Cu-Cu_{3.6}Mn_{0.4}Al_8]Ti_{0.233}Zr_{0.078}Al_{1.689}$ , this cluster model is accurate and reasonable, and the phase composition and element content of the model are consistent with the XRD verification results, SEM verification results and EDS verification results. The use of alloy solid solution near-program cluster model to guide the precipitation phase analysis of ZL205A alloy was realized.

**Keywords:** ZL205A; "Cluster Plus Connected Atoms" Model; Atomic Density; Solid Solution; Mixing Enthalpy

## 1. Introduction

In the process of researching metal materials, people often use the method of adding appropriate components to the metal element to form a solid solution to form a multi-component alloy to improve the physical properties of the metal. [1] However, due to

the lack of understanding of the origin of the alloy's phase composition, for most scientific researchers, the only way to complete the design of a new high-quality alloy is to carry out a large number of experiments.

ZL205A alloy has become the first choice material for manufacturing various large-scale stressed structural parts due to its excellent machining performance, high hardness and strength, good toughness and other comprehensive mechanical properties. It has been widely used in many fields such as aviation, aerospace, automobile and mold [2]. ZL205A is a kind of relatively complex alloy, and there is still less research on the origin of its phase composition. The study of the interatomic interaction mechanism based on the near-program spatial distribution structure of solid solution is the core of understanding the phase composition of alloys. Therefore, establishing effective alloying solid solution theory and microscopic solid solution analysis model plays a decisive role in guiding the component design of multi-component alloys.

Therefore, based on the "first nearest neighbor cluster plus connected atoms" model, this paper investigates the correlation between the radial density of atomic arrangement and the Friedel oscillation potential function caused by electronic interaction among solid solution atoms. The purpose of the correlation study is to express the near-program cluster model of the Al-Cu binary system solid solution in a quantitative manner. Then, a qualitative construction of a near-program cluster model for the solid solution of the five-element ZL205A alloy was carried out after adding trace strengthening elements, taking into account the criteria of solid solution solubility

and atomic mixing enthalpy. The homologous atomic content of the near-program cluster model of the ZL205A alloy solid solution after the addition of trace elements is determined using the "maximum atomic density defines the first nearest neighbor cluster in the alloy phase" method. Finally, the validation process involves the integration of element mass conservation, atomic spatial arrangement principles, and atomic conservation. The constructed cluster model confirms accuracy and rationality, thereby accurately expressing the solid solution near-program cluster spatial structure of ZL205A alloy in a quantitative manner, and establishes a basis and guarantee for future alloy component design and development.

## 2. Proposal of Construction Method of ZL205A Alloy Solid Solution Near-program Cluster Model

In view of the high content of solutes (elements other than Al) in ZL205A, a solid solution short-range cluster model can be constructed to provide a theoretical basis and research support for the design and development of future alloy components. Table 1 shows the distribution of each component of ZL205A alloy. In combination with the ZL205A alloy formation process [3], due to the content of Cu element is the highest among non-Al elements. And the Cu element and Al matrix have the same crystal structure, both are face-centered cubic structures (FCC). And the ratio of the radius of the solute atom Cu to the radius of the solvent atom Al is 0.895, which is greater than 0.59 ( $R_{Al}$ : 0.143nm,  $R_{Cu}$ : 0.128nm). In addition, it is also considered that the difference in radius between the solute atoms of Cu and the atoms of the Al matrix is only 10.5%, which is less than 15% (only when  $\Delta r < 15\%$ , the solute can form an infinite solid solution with the solvent). Combined with the solid solution solubility criterion [4], the Cu element will create an infinite solid solution in the Al matrix, causing elasticity due to the difference in atomic dimensions. The influence of mechanical stress on the arrangement of atoms in solid solution alloys is extremely minimal, hence the distribution of neighboring atoms in the alloy is primarily influenced by the mixing energy. Consequently, this research initially focuses on investigating the near-program

cluster model for the binary system solid solution by utilizing the Al element matrix. This model is further utilized to analyze the alloy of the quinary system after the incorporation of trace strengthening elements including Mn, Zr, and Ti. Near-program cluster model to precisely delineate the solid solution state of the selected ZL205A alloy.

**Table 1. Distribution of Various Components of ZL205A**

Main element composition standards of ZL205A			
Elements	wt.%	Elements	wt.%
Cu	4.6 ~ 5.3	Ti	0.15 ~ 0.35
Mn	0.3 ~ 0.5	Al	Bal.
Zr	0.05 ~ 0.2		
The main element composition of ZL205A in this article			
Elements	wt.%	Elements	wt.%
Cu	5.09	Ti	0.21
Mn	0.414	Al	93.738
Zr	0.134		

## 3. Expression of Near-programmed Cluster Model of Binary System Al-Cu Solid Solution

### 3.1 Qualitative Expression of Near-programmed Cluster Model of Binary System Al-Cu Solid Solution

The atomic spatial distribution structure of the matrix Al, which has FCC structure, can be represented as  $[Al-Al_{12}]-Al_y$  (where  $[Al-Al_{12}]$  refers to the central atom combined with the coordination polyhedral cluster formed by its first nearest neighbors, and  $Al_y$  is the cluster external connecting atoms).

Combined with the analysis of the atomic solid solution mixing enthalpy criterion, considering that the Cu element has the highest content among the non-Al elements, the Cu atoms and Al matrix have the same crystal structure, both are FCC structures, and the mixing enthalpy between Cu atoms and Al matrix is negative mixing enthalpy ( $\Delta H_{Cu-Al} = -1 kJ/mol$ ). Thus, the spatial distribution structure of  $[Cu-Cu_xAl_{12-x}]-Al_y$  will be formed.

### 3.2 Quantitative Expression of Near-program Cluster Model of Binary System Al-Cu Solid Solution

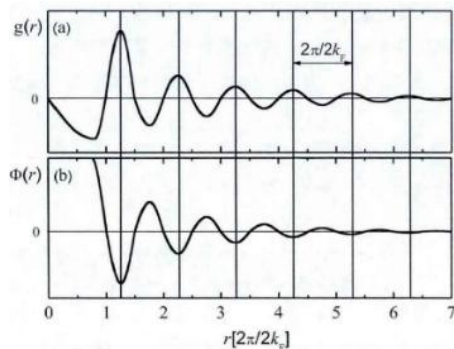
The influence of the electronic factors in the

interaction between atoms in the alloy is taken into account. This paper combines the gel model and the Friedel oscillation [6], as shown in equation (1) and Figure 1, and introduces the radial distribution function of the overall atomic number density across various shells, as shown in equation (2). Furthermore, a comparison is made with the corresponding Friedel oscillation potential function in order to effectively regulate the precision and rationality of the alloy cluster model construction [7,8].

$$\phi(r) \propto \cos(2k_F \cdot r + \Theta) / r^3 \quad (1)$$

$$g(r) = N(r) / (4\pi r^3 / 3) \quad (2)$$

In the formula:  $g(r)$  is the total atomic distribution density;  $r$  is the distance between the cluster center atom and the shell atom;  $N(r)$  is the sum of atoms present in the cluster;  $k_F$  is the Fermi wave vector;  $\Theta$  is the phase deviation Shift ( $\Theta$  takes  $\pi/2$  [9]), so equation (1) can be marked as:  $\phi(r) \propto \sin(2k_F \cdot r) / r^3$ , and define  $\lambda_{Fr} = 2\pi / 2k_F$ .



**Figure 1. The correlation between atomic distribution and the corresponding Friedel oscillation (the abscissa is changed to  $r/\lambda_{Fr}$ )**

Combining formula (3) and structural homology [10-12], it is known that the constraints in formula (3) can be used to calculate and analyze the atomic weight of the Al-Cu solid solution cluster constructed previously. The Al-Cu solid solution cluster model of the above-mentioned ZL205A high-strength cast aluminium alloy is  $[\text{Cu-Cu}_x\text{Al}_{12-x}]_n\text{-Al}_y$ . This model has an FCC structure. The close packing degree of the FCC structure is 0.74. So combined with the energy of atomic space stacking, the minimum principle and the atomic conservation theorem give the relationship shown in equation (4).

$$Z = c \cdot \rho_a \cdot r_1^3 \quad (3)$$

$$13+y = \frac{c \cdot (R_{Al} + R_{Cu})^3}{\left[ \frac{1+x}{13+y} \cdot \left( \frac{4\pi/3 \cdot R_{Cu}^3}{0.74} \right) + \frac{12-x+y}{13+y} \cdot \left( \frac{4\pi/3 \cdot R_{Al}^3}{0.74} \right) \right]} \quad (4)$$

In the formula:  $Z$  is the number of atoms,  $\rho_a$  is the average atomic density,  $r_1$  is the cluster radius, and  $c$  is a constant of 11.476 [13].

Solving equation (5) shows that it has many different sets of solutions. Combining the atomic content (at%) of the constructed cluster model should be consistent with the element mass content (wt%) of the selected alloy in Table 1. It can be concluded that the number of Al atoms in the shell of the cluster is 8 and the number of Cu atoms is 4. The number of external connecting Al atoms is 2 each. Therefore, the corresponding Al-Cu alloy solid solution cluster for the optimal solution of equation (4) is obtained as:  $[\text{Cu-Cu}_4\text{Al}_8] \text{Al}_2$ . Based on the cluster model formed by stacking during the solid solution stage, it can be seen that the alloy mainly forms the  $\text{Al}_2\text{Cu}$  phase during the solidification and precipitation stage.

Then based on the above method, the solid solution cluster model construction of ZL205A alloy after introducing trace elements Mn, Zr, and Ti was studied.

#### 4. Expression of Near-programmed Cluster Model of quinary system ZL205A Alloy Solid Solution

##### 4.1 Construction of Near-program Cluster Model of Five-element ZL205A Alloy Solid Solution

On the basis of the binary system Al-Cu solid solution constructed above, when adding trace elements Mn, Zr, and Ti ( $R_{Mn}$ : 0.132nm,  $R_{Zr}$ : 0.160nm,  $R_{Ti}$ : 0.145nm) Mn has a similar atomic radius to the first shell atom  $\text{Cu}_4\text{Al}_8$  in the above-mentioned Al-Cu cluster  $R_{\text{Cu}_4\text{Al}_8} = 0.138\text{nm}$ . And the ratio of the radius of the Mn atom to the first shell atom  $\text{Cu}_4\text{Al}_8$  is 0.96 (only when the ratio of the solute atomic radius to the solvent atomic radius is less than 0.59, an interstitial solid solution is easily formed). The atomic radius difference between the Mn atom and the first shell atom  $\text{Cu}_4\text{Al}_8$  is  $\Delta r$ : 2.4% (only when  $\Delta r < 15\%$ , the solute can form an infinite solid solution with

the solvent). The atomic radius of Zr and Ti is quite different from the radius of the first shell atom  $\text{Cu}_4\text{Al}_8$  in the above-mentioned Al-Cu cluster, and it is difficult to dissolve in the first shell atom of the cluster. But it has a similar atomic radius ( $R_{\text{Al}}$ : 0.143nm) to the connecting atom  $\text{Al}_2$ , and the ratio of the Zr atomic radius to the connecting atom  $\text{Al}_2$  radius is 1.12. The ratio of the Ti atomic radius to the connecting atom  $\text{Al}_2$  radius is 1.01. The atomic radius difference between the Zr atom and the connecting atom  $\text{Al}_2$  is Zr-Al:11.9%. The atomic radius difference between the Ti atom and the connecting atom  $\text{Al}_2$  is Ti-Al:1.4%. Consider

that  $\Delta H_{\text{Al-Cu}} = -1 \text{ kJ/mol}$ ,  $\Delta H_{\text{Al-Mn}} = -19 \text{ kJ/mol}$  (The latter has a more negative value, so Mn has a stronger interaction with Al than Cu),  $\Delta H_{\text{Al-Zr}} = -44 \text{ kJ/mol}$ ,  $\Delta H_{\text{Al-Ti}} = -30 \text{ kJ/mol}$ ,

the principle of minimum binding energy, trace elements Mn will replace the Cu atoms in the first shell  $\text{Cu}_4\text{Al}_8$  in the Al-Cu solid solution cluster  $[\text{Cu-Cu}_4\text{Al}_8] \text{Al}_2$ , and the trace elements Zr and Ti will replace the connecting atoms  $\text{Al}_2$  in the Al-Cu solid solution cluster  $[\text{Cu-Cu}_4\text{Al}_8] \text{Al}_2$ , forms solid solution clusters with lattice distribution.

In order to obtain the specific number of  $\text{Cu}_4\text{Al}_8$  atoms in the first shell replaced by the above trace element Mn, and the specific number of connecting atoms  $\text{Al}_2$  replaced by trace elements Zr and Ti. This paper is based on the method of "defining the first nearest neighbor cluster in the alloy phase based on the maximum atomic density". And then infers the trace atomic content of the final ZL205A alloy solid solution formed after the introduction of trace elements based on the content proportion of each component [14]. Therefore, the cluster atomic arrangement is characterized by using the atomic arrangement information of each phase in Pearson Crystal Database and combining the atomic distribution at the maximum value of the radial atomic density distribution function proposed by Equation (4). The core idea is to establish the solid solution cluster model corresponding to the  $\text{Al}_{12}\text{Mn}_2\text{Cu}$  phase,  $\text{Al}_3\text{Ti}$  phase and  $\text{Al}_3\text{Zr}$  formed by introducing trace elements Mn, Zr and Ti as:  $[\text{Al-Al}_9\text{Mn}_2\text{Cu}]-\text{Al}_2$ ,  $[\text{Al-Al}_8\text{Ti}_4]-\text{Al}_2$  and  $[\text{Al-Al}_8\text{Zr}_4]-\text{Al}_2$  (if the atomic density is the same, the mixing

enthalpy relationship between the core atoms and the outer atoms will be further considered). Finally, the solid solution cluster models corresponding to the  $\text{Al}_{12}\text{Mn}_2\text{Cu}$  phase,  $\text{Al}_3\text{Ti}$  phase and  $\text{Al}_3\text{Zr}$  are converted into the atomic content proportional forms  $[\text{Al}_{2/3}\text{Mn}_{2/15}\text{Cu}_{1/15}]-\text{Al}_{2/15}$ ,  $[\text{Al}_{3/5}\text{Ti}_{4/15}]-\text{Al}_{2/15}$  and  $[\text{Al}_{3/5}\text{Zr}_{4/15}]-\text{Al}_{2/15}$ , and using equation (5) combined with atomic conservation to solve the solid solution cluster model of ZL205A alloy after introducing trace strengthening elements. ZL205A's solid solution cluster model is  $\{[\text{Al-Al}_{12}]\text{Al}_2\}_{12}[\text{Cu-Cu}_{3.6}\text{Mn}_{0.4}\text{Al}_8]\text{Ti}_{0.233}\text{Zr}_{0.078}\text{Al}_{1.689}$ .

## 4.2 Verification of Near-program Cluster Model of Quinary System ZL205A Solid Solution

### 4.2.1 Analysis of mass conservation

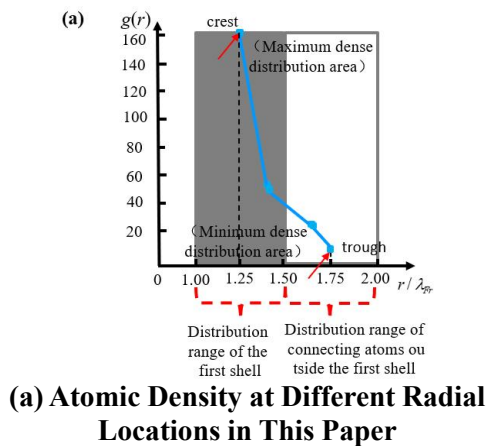
Because the near-program cluster model of the solid solution of the ZL205A alloy has ensured atomic conservation during the construction process, it only needs to be analyzed whether it satisfies mass conservation. Convert the atomic percentage (at%) of each component of the constructed cluster model into mass percentage according to Equation (5). And compare the obtained results with the measured contents in Table 1. It was found that it has high consistency, so it meets mass conservation.

$$A(\text{mass}\%) = \left\{ \frac{A(\text{at}\%) * Ar(A)}{[100 - A(\text{at}\%)] * Ar(B) + [A(\text{at}\%) * Ar(A)]} \right\} \quad (5)$$

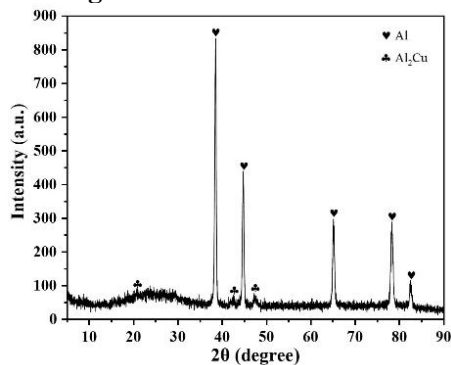
### 4.2.2 Energy analysis of atomic stacks

When the homologous cluster structure or phase is formed, strong interatomic interactions will occur. This kind of strong interatomic interaction will result in crystal structure (or cluster structure) with the tightest atomic stacking. Therefore, combining the relationship between the two functions shown in Figure 1, the spatial distribution structure of the cluster model constructed in this article and formula (2), the radial distribution function of the atomic density of each shell of the solid solution near-program cluster of the ZL205A alloy shown in Figure 2a is plotted. From Figure 2a, it can be seen from the analysis that the abscissa coordinate of the densest stacking part of the first shell of the cluster model is nearly 1.25. The homologous abscissa of the most sparse stacking part of the

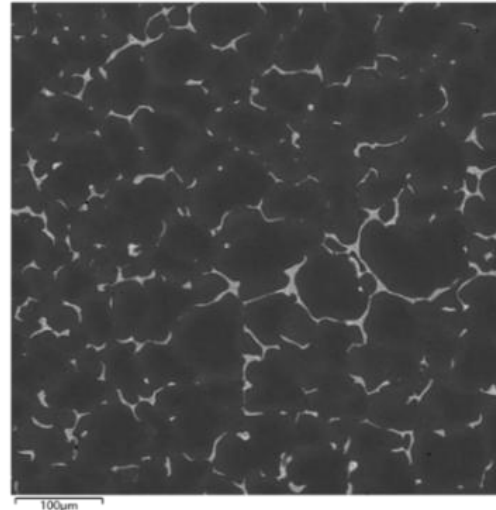
external connected atoms is nearly 1.75. And the curve obtained from the analysis in this article is very close to the structure of the ideal cluster model, as shown in Figure 1. Hence, the ZL205A alloy's solid solution cluster model exhibits the lowest overall system energy, and it's the most stable. And can quantitatively reflect the solid solution atomic distribution and occupancy of the selected ZL205A alloy reasonably and accurately, and obtain the final cluster structure shown in Figure 2b. The XRD phase analysis of ZL205A is shown in Figure 3. The SEM analysis of ZL205A is shown in Figure 4. The EDS analysis results is shown in Figure 5. And the total number of distribution diagrams is shown in Table 2.



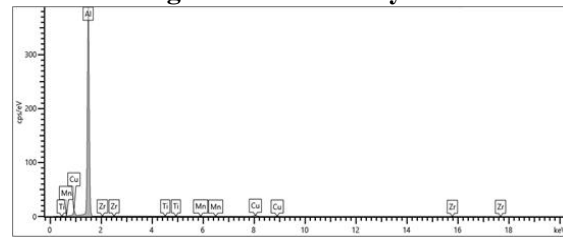
(a) Atomic Density at Different Radial Locations in This Paper  
 (b) The Final Cluster Structure  
**Figure 2. Verification of Solid Solution Near-Program Cluster Model of ZL205A**



**Figure 3. Phase Analysis Results**



**Figure 4. SEM Analysis**



**Figure 5. SEM Image**

**Table 2. Total Number of Distribution Diagrams**

Elements	Signal type	wt. %	wt. % Sigam
Al	EDS	94.15	0.08
Cu	EDS	5.08	0.06
Mn	EDS	0.37	0.03
Ti	EDS	0.27	0.02
Zr	EDS	0.13	0.05
Total		100.00	

**5. Conclusion**

Based on the "first nearest neighbor cluster plus connected atom model", a ZL205A alloy solid solution cluster model was qualitatively constructed. The cluster formula is  $\{[Al-Al_{12}]Al_2\}_{12}[Cu-Cu_{3.6}Mn_{0.4}Al_8]Ti_{0.233}Zr_{0.078}Al_{1.689}$ , the ZL205A solid solution cluster model constructed is accurate and reasonable, and verified with XRD, SEM and EDS. The results remain consistent.

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