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Effects of electric pulse modification on liquid structure of Al−5%Cu alloy

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Abstract: The electric pulse modification (EP, EPM) of liquid metal is a novel method for grain refinement. The structure of EP-modified Al−5%Cu melt was characterized by high-temperature X-ray diffractometry. The results show that the Cu-containing Al clusters remarkably increase in the EP-modified melt, furthermore, these clusters in that case tend to contract due to the decrease of relevant atomic radius and the co-ordination number. This kind of liquid-phase structure leads to a more homogeneous Cu-rich phase distribution in the final solidification structure. Differential scanning calorimetry (DSC) tests indicate that the solidification super-cooling degree of the EP-modified liquid phase is 2.36 times that of the unmodified. These facts suggest that the atom cluster changes in EP-modified Al−5%Cu melt would disagree with that by EPM model previously proposed in liquid pure metal.

Key words: electric pulse modification; Al−Cu melt; atomic cluster; liquid structure

1 Introduction

With the rapid development of solidification technology and cluster physics, the effects of melt structure on the final solidification structure attract more attention [1,2]. Recently, researchers have found that the imposed electric pulse (EP) on metal melt could refine grains, reduce segregation of solute elements and improve mechanical properties of the alloys [3−5]. It is generally considered that the interesting results stem from a certain structural change in liquid metal [6,7]. However, due to the difficulty of liquid structure tests requiring elevated temperature combined with pulse electric field, the past investigations on the above EP-modified melt were mostly carried out using so-called post-mortem examination methods such as metallographic examination [8], performance test [9]. As a result, the mechanism of EP treatment is still a hypothetical theory and far from being understood. Fortunately, the outstanding structure heredity of the EP-modified liquid aluminum has been reported [10,11]. It is indicated that for the EP-modified aluminum casting, its liquid structure after once remelting could roughly substitute for that in the EP-modified duration. Based on the significant heredity characteristics, previous researches were done for investigations of the structure transformation in EP-modified liquid aluminum [12,13]. However, the responses for EP should have some discrepancies between the binary alloy melt and pure metal melt [14]. The present work will examine the changes of EP-modified Al−5%Cu melt according to the method in Ref. [12], in order to illuminate the EP treatment mechanism for binary alloy system.

2 Experimental

The Al−5%Cu alloy was smelted from pure aluminum (99.99%) and pure copper (99.99% in mass fraction) raw materials in an electric resistance furnace, then appreciable amount of the prepared Al−5%Cu alloy was heated to 750 °C and melted. After holding at this temperature for 5 min and the subsequent refining procedure (C_2Cl_6 was here adopted as refining agent), two columnar graphite electrodes with dimensions of *d*5 mm × 200 mm were vertically inserted 50 mm into liquid alloy and EP treatment was performed. The EP parameters were optimized as follows: 500 V peak

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voltage, 3 Hz frequency and 30 s treating time. Then the molten alloy was poured into a metal mold by a manipulator at room temperature. The unmodified specimen used for comparison was also prepared under the same cooling conditions. The tested cuboid specimens with dimensions of 20 mm × 16 mm × 12 mm for high temperature X-ray diffraction were wire-cut at the same central section of the castings. The EP treatment experimental setup is schematically shown in Fig. 1.

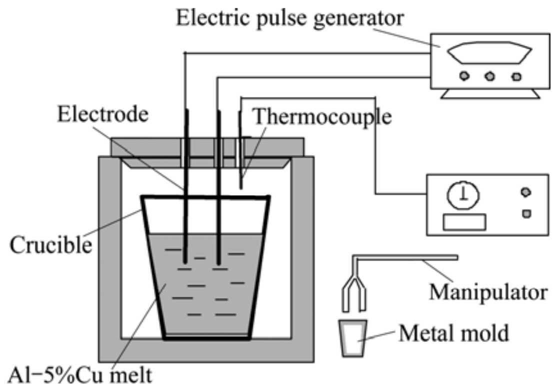

Fig. 1 Schematic pattern of EP treatment setup

The melt structure tests were carried out using a high temperature X-ray diffractometer with Mo K_α radiation (wavelength λ=0.071 nm). A graphite single crystal was used for monochromatisation of X-ray scattered by the specimens. The accuracy of the angle was 0.001°, and the scattering angle 2θ ranged from 5° to 90°. The magnitude of wave vector Q (Q=4πsinθ/λ) was then from about 0.2 to 120 nm^{-1}. The scanning step was 0.02º within the region of principal peak and 0.5° at rest values of wave vectors. During heating, diffraction measurements were made at 700, 750, 800 and 1000 °C, and at each temperature, the liquid Al−5%Cu alloy was held for 30 min before test. Differential scanning calorimetry (DSC) was performed respectively on specimens without EPM and with EPM using a SETARAM thermal analysis tester.

3 Results and discussion

Figure 2(a) shows the structure factor (SF) curve of liquid Al−5%Cu alloy as a function of wave vector Q at different elevated temperatures and the SF curve shown in Fig. 2(b) relates to the EP modification.

One can see that their common features are a symmetrical principal peak and a similar broadened and blunted trend with increasing temperature. As for the unmodified one, it is noted in Fig. 3 that the neighbor distance r_1 changes from 0.290 nm to 0.295 nm during the 700−1000 °C temperature zone, which is dissimilar

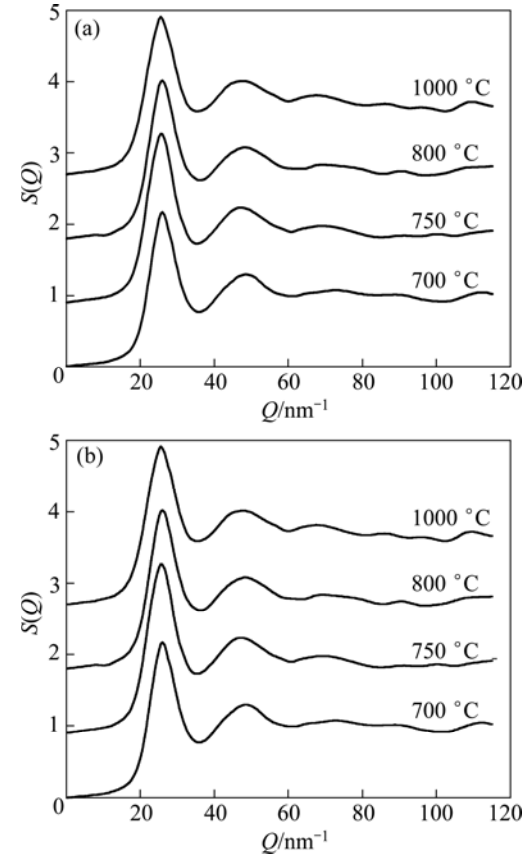

Fig. 2 Structure factor curves of liquid Al−5%Cu alloy at different temperatures: (a) Unmodified; (b) EP-modified

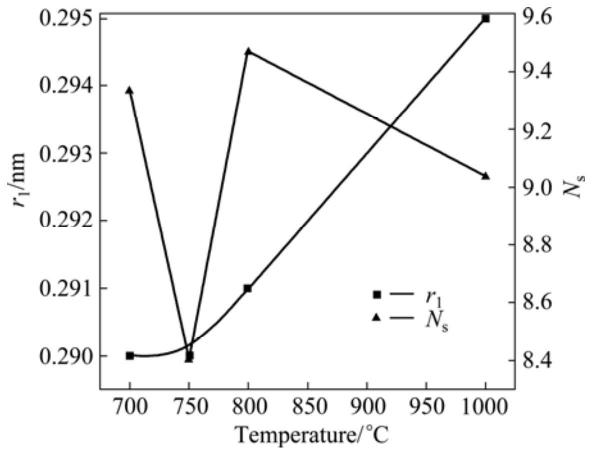

Fig. 3 Changes of r_1 and N_s in liquid Al−5%Cu alloy at various temperatures

with the thermal contraction phenomenon of atomic cluster in liquid pure aluminum. On the other hand, the value of coordinating number N_s exhibits a fluctuant variation tendency; furthermore, the minimum value of N_s appears at the EP treatment temperature of 750 °C, which could be ascribed to the abnormal changes of short range order (SRO) at this temperature. At 800 °C, N_s reaches its maximum value of 9.469, then N_s declines, indicating the leading role of thermal motion at an elevated temperature.

In the case of EP modification, the almost same changes for principal peak in SF curves are found. It is also shown in Fig. 4 that N_{at} (average atom number per cluster) and r_c values of the EP-modified one are both lower than those of the unmodified one at the corresponding temperature. N_{at} is defined as

$$N_{at} = A\frac{4\pi\rho r_c^3}{3M} \tag{1}$$

where A is Avogadro constant, M is the relative atom mass of aluminum, ρ and r_c are density of liquid Al−5%Cu alloy and its correlation radius, respectively, r_c is commonly used for characterizing the statistical average size of the predominant atomic cluster at a certain temperature in the liquid phase. Since radius of Cu atom is smaller than that of Al atom (r_{Cu}=0.118 nm, r_{Al}=0.124 nm), when Cu as a foreign atom enters into Al−Al clusters, it has been calculated to lead to approximate 5% volume contraction [15]. As shown in Fig. 4, r_c at 750 °C changes from 0.92 nm down to 0.905 nm after EPM. This reduction just causes volume contraction value according to the calculation of Eq. (1). The result indicates that the Cu-containing Al clusters increase in EP-modified Al−5%Cu melt. At the same time, r_c value at 800 °C is equivalent to that at 750 °C, which suggests that this EP-induced cluster structure could possess some kind of stability. In addition, from the point of changing tendency, the size of SRO characterized by N_{at} value in EP-modified Al−5%Cu melt approximately linearly reduces as the temperature rises; however, the decline rate is bigger than that of the unmodified one.

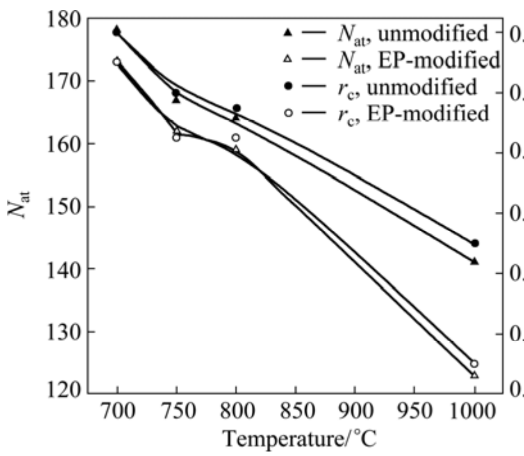

Fig. 4 Changes of N_{at} and r_c with increasing temperature in EP-modified Al−5%Cu melt

It is especially significant for the investigation of EP-modified liquid Al−5%Cu alloy structure at 750 °C, since at this temperature, the liquid Al−5%Cu alloy was EP-modified and the optimal grain refining effect was obtained. For a more careful comparison, the SF curves of the EP-modified liquid Al−5%Cu alloy at 750 °C coupled with those of the unmodified ones are shown in Fig. 5.

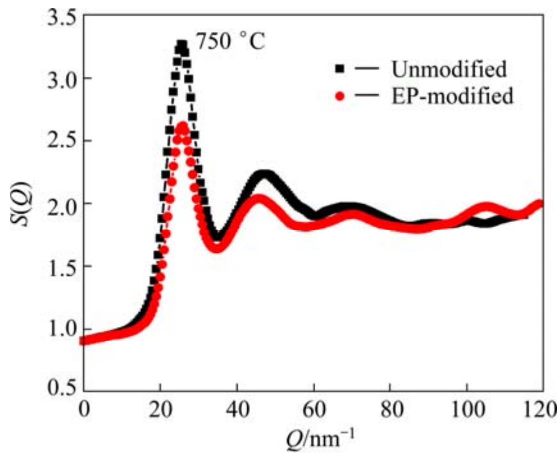

Fig. 5 SF curves of unmodified and EP-modified liquid Al−5%Cu alloy at 750 °C

As can be seen from Fig. 5, the first peak of SF curve is remarkably weakened for the EP-modified one, which clearly indicates its changes of SRO in this melt. On this point, it exhibits a significant discrepancy with that of EP-modified liquid aluminum reported in Ref. [9]. Obviously, it should be ascribed to the existence of the above-mentioned Cu-containing Al cluster. Therefore, the effects of this kind of liquid structure on the final solidification structure could be interpreted schematically in Fig. 6.

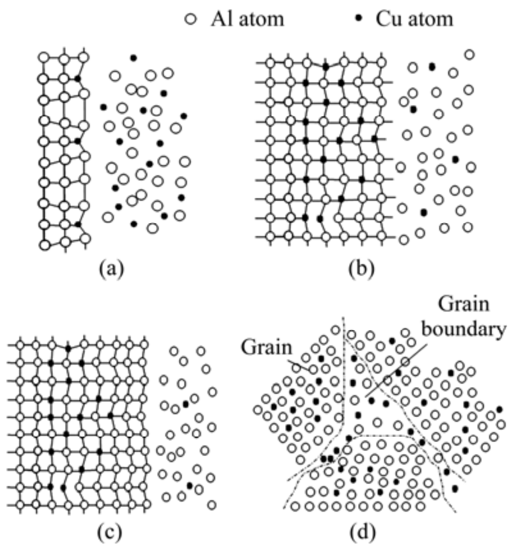

Fig. 6 Solidification procedure of EP-modified Al−5%Cu melt: (a) Before solidification; (b) Early stage of solidification; (c) Later stage of solidification; (d) Solidification structure

EPM results in the increase of Cu-containing Al cluster in the melt, and the addition of Cu atom certainly leads to so-called "lattice deformation" of Al−Al cluster, as shown in Fig. 6(a). At the early stage of solidification, this "lattice deformation" of Al−Al cluster facilitates the Cu atom deposition in the corresponding position, thus, the enough Cu atoms exist. This procedure goes on, and this crystal nucleus grows, as shown in Fig. 6(b). Furthermore, due to the Cu content of Al−5%Cu melt, namely the amount of Cu atom is far less than that of Al atom, at the later stage of solidification, the growth of Cu-containing Al cluster only depends on the deposition of Al atoms, then the Cu-containing α(Al) solution forms finally, as shown in Fig. 6(c). It is because of the formation of this kind of solution that the less Cu atoms participate in the subsequent eutectic reaction, leading to a reduction of eutectic structure and a more homogeneous Cu atom distribution, as shown in Fig. 6(d). From this point, EPM technique is a novel method to reduce the element segregation of alloy solidification structure. The solidification structure changes are given in Fig. 7.

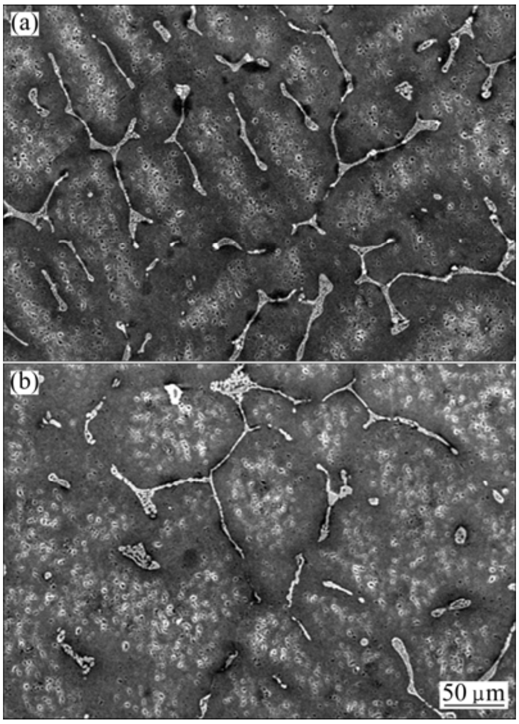

Fig. 7 Solidification structure of Al−5%Cu alloy: (a) Unmodified; (b) EP-modified

One can see that the unmodified one has large amount of binary eutectic structure (α(Al)+$CuAl_2$), and exhibits a reticular distribution. However, in the case of EP modification, the amount of binary eutectic structure obviously decreases. The increasing micro hardness of this alloy matrix could verify this conclusion, i.e., the solution strength effect of Cu atom contributes this improvement. The results are given in Table 1.

Table 1 Microhardness of alloy

Status	Microhardness (HV)	Average
Unmodified	55.21, 54.89, 56.70, 55.62, 55.83	55.65
EP-modified	77.25, 76.92, 78.46, 79.01, 77.63	77.85

On the other hand, based on the heredity of melt, differential scanning calorimetry (DSC) test results are shown in Fig. 8. It could provide more information on the changes of melt structure under various treating conditions, and then confirm the consistency and rationality of the above analysis.

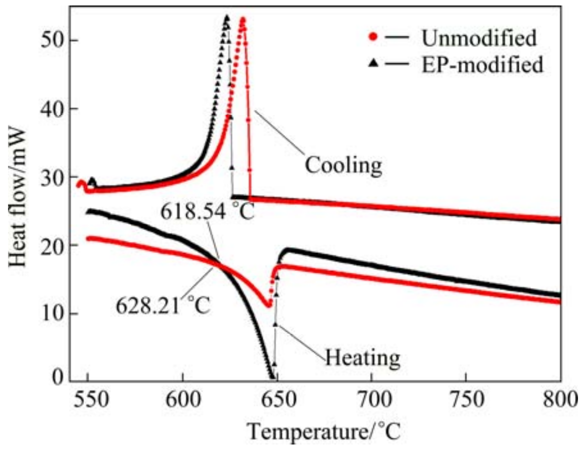

Fig. 8 DSC results of specimens under various treating conditions

As shown in Fig. 8, the EP-modified specimen exhibits its discrepancies with the unmodified one whether it is heated or cooled. During melting, the phase transformation temperatures are 618.54 °C (the unmodified) and 628.21 °C (EP-modified), respectively, and almost no change occurs. However, the latent heat of melting of the EP-modified one is 95.58 J/g, which is 44% less than that of the unmodified one. It is well known that the long range order (LRO) is cut off when an alloy is melted. Obviously, the sharp increase of Cu-containing Al clusters induced by EP contributes to that cutting-off process, and results in the above heat absorption reduction. It should be noted that the Cu-containing Al cluster here is assumed to be constant during remelting, just like a genetic carrier. During cooling, one can see that the latent heat of crystallization and the solidification temperature for the EP-modified are both dissimilar with those of the unmodified one. On the aspect of solidification, the increase of super cooling degree is beneficial for grain refinement of solidification structure. As previously mentioned, the contraction of Cu-containing Al cluster is bound to the increase of super cooling degree. Actually, the EP-modified one has a super cooling degree of 24.54 ºC, which is 2.36 times that of the unmodified one. These facts verify the above results on changes of EP-modified melt structure. At the same time, the effects of this melt structure on the final solidification structure are clarified.

4 Conclusions

1) EPM on liquid Al−5%Cu results in the increase of Cu-containing Al cluster, and this kind of cluster exhibits size contraction to a certain extent and shows a relative stability at various temperatures.

2) As crystal embryos, these EP-induced Cu-containing Al clusters are apt to form a more homogeneous Cu-rich phase distribution in the final solidification structure. This melt structure transformation leads to the changes of binary eutectic structure, micro hardness of alloy matrix and solidification behaviors of this alloy.

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电脉冲孕育处理对 Al−5%Cu 合金液态结构的影响

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摘 要：利用高温 X 射线衍射仪对经电脉冲孕育处理的 Al−5%Cu 合金液态结构进行表征。结果表明：在经电脉冲孕育处理的熔体中，含 Cu 的铝团簇数量明显增加，由于相关原子半径和配位数的减小而使这些团簇呈现某种热收缩状态。这种液相结构将使最终的凝固组织中富 Cu 相更趋于均匀分布。DSC 测试表明，经电脉冲孕育处理的液相在结晶过程中，其过冷度是未处理液相的 2.36 倍。可以确定，电脉冲处理后的 Al−5%Cu 熔体中原子团簇的变化与先前提出的纯金属电脉冲孕育处理机理模型存在明显差异。

关键词：电脉冲孕育处理；Al−Cu 熔体；原子团簇；液态结构

(Edited by Hua YANG)