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Existing form and harmful effects of sodium in Al−4.5%Cu alloy

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Abstract: Plentiful sodium was introduced into the alloy using salt fluxes as medium, then the existing form and influence of sodium on the microstructure and tensile properties of Al−4.5%Cu (mass fraction) alloy were investigated. It is proved that the elemental sodium segregates at the grain boundaries of Al−4.5%Cu alloy and weakens the bond between the matrix and $CuAl_2$-phase. After T6 heat treatment, sodium results in micro-fracture and induces the residual of $CuAl_2$-phase in Al−4.5%Cu alloy. The tensile test results show that the sodium causes a transition from dimple fracture to intergranular fracture, which makes the mechanical performance of Al−4.5%Cu decrease dramatically.

Key words: Al−Cu alloy; sodium; grain boundaries; fracture; mechanical performance

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1 Introduction

Not only the primary aluminum produced by electrolysis from cryolite melts but also the aluminum purified by the salt fluxes with sodium which always are a mixture of molten salts to clean molten aluminum will contain sodium inevitably [1−3]. Sodium is an undesirable impurity in most aluminum alloys. Lots of studies and researches about this aspect have been reported, especially in the Al−Mg system alloys. In 1959, RANSLEY and TALBOT [4] found that the hot-working properties of Al−Mg alloys are severely impaired by sodium on the order of 0.001%. Until 1997, OKADA and KANNO [5] narrowed this number to 1×10^{-6}. The following researches still focused on the detriment of sodium in Al−Mg system alloys. They also found that Na is a harmful impurity and did some researches on how to eliminate the detriment, but they did not detect the Na at the grain boundaries or on the intergranular fracture surface either [6−9].

At the same time, the theoretical researches were done by some scientists. ZHANG et al [10−12] studied the thermodynamic modeling of the Al−Mg−Na system and gave the fundamental understanding of Na-induced high temperature embrittlement in Al−Mg alloys by means of the first-principles calculations. The detriment of sodium for other aluminum alloys has also been studied. In 1987, KOBAYASHI et al [13] proved the existence of sodium on grain boundary at room temperature through low energy Auger analysis in Al−Li system alloys. Meanwhile, they came to a conclusion that the low melting point metal phase probably causes liquid embrittlement at grain boundaries.

The Al−Cu system alloys are very common in the military areas, so the performance of these alloys has drawn too much attention. The existence of sodium is also inevitable in Al−Cu system alloys, but the existing form and the corresponding effect are rarely reported. This work does some researches on these neglected aspects.

2 Experimental

The Al−Cu alloy is Al−4.5%Cu in the experiments. To enlarge the detriment of sodium, we decide to introduce plentiful sodium in the Al−4.5%Cu alloy. The first considered question is that how to introduce the sodium into Al−4.5%Cu alloy. HORIKAWA et al [7] introduced the sodium into Al−Mg alloys with the alumina crucible of 99% purity containing Na_2O, Fe_2O_3, and SiO_2 as impurities. The method that is used to introduce plentiful sodium into the alloy is through the reaction between the salt fluxes and the molten aluminum. The salt fluxes chosen are given in Table 1.

The reasons why choosing these salt fluxes are as

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Table 1 Component of salt fluxes (mass fraction, %)

NaF	NaCl	Na_3AlF_6
60	25	15

follows: firstly, these salt fluxes have a low eutectic melting point, so they can adequately react with the molten aluminum; secondly, they can refine the molten aluminum to a certain degree because of the presence of Na_3AlF_6 [14]; thirdly, NaF will add traces of sodium to the Al−Cu alloy by means of the following reaction [14,15]:

$$3NaF+Al \longrightarrow AlF_3\uparrow+3Na$$

The Al−4.5%Cu alloy was prepared using high-purity Al and Cu with 99.999% purity by the high-frequency furnace. The salt fluxes in Table 1 whose mass is as 20% as that of the molten alloy were added into the alloy. The salt fluxes used are chemically pure. The alloy was kept holding for 8 min at 730 °C. Then, we got the Al−Cu−Na specimen. We also got the Al−Cu specimen at the same condition without salt fluxes.

Part of the Al−Cu and Al−Cu−Na specimens were subjected to T6 heat treatment, which were named as the Al−Cu-T6 and Al−Cu−Na-T6, respectively. These specimens were solution treated at (538±5) °C for 15 h, subsequently quenched in water, and then subjected to artificial aging at (175±5) °C for 4 h. A two-stage heat treatment suggested by SOKOLOWSKI et al [16] can give rise to better homogenization prior to aging, and improve the mechanical properties of the 319 alloys. JANG et al [17] made some researches on the T6 heat treatment in the Al−Cu alloy. In industry, the Al−Cu system alloys are used after heat treatment. Therefore, the detriment after T6 heat treatment will be studied in this work. At the same time, the tensile test bars of the Al−Cu-T6 and Al−Cu−Na-T6 alloys were obtained and machined to dog-bone type specimens.

3 Results

3.1 Existence of elemental sodium

Figures 1(a) and (b) show the SEM micrographs of Al−Cu and Al−Cu−Na, respectively. In both micrographs, the bright white zones are $CuAl_2$-phase. However, it should be noted that there are some black zones in the SEM micrograph of Al−Cu−Na specimen (Fig. 1(b)). The distributions of the bright white and black zones have the same regularities, and the composition of the black zone is close to that of the α(Al) matrix by the energy dispersive spectrometry analysis (Fig. 2). So, it is speculated that the black zones are pits and the phase of the black zones is the same as that of the bright white zones. During the fabrication of Al−Cu−Na specimen, some regions of $CuAl_2$-phase were detached from the specimen because of the existence of some components which reduced the bond between the matrix and $CuAl_2$-phase at the grain boundaries.

The $CuAl_2$-phase was divided into two types as shown in Fig. 1(c). Obviously, Phase *B* is combined with the matrix closely. There is a black gap between phase *A* and the matrix. So phase *A* is an easily-detached phase, while Phase *B* is a hard-detached phase. We can assume that if the $CuAl_2$-phases existed in the black zones are not detached from the matrix, the rear of the $CuAl_2$-phase would be like phase *A*.

To study why some of the $CuAl_2$-phases are easily detached in the Al−Cu−Na specimen, the specimen is investigated by electron probe micro-analyzer (EPMA). Referring to the bright white and black zones of the back-scattered electron image (BEI in Fig. 3(b)), we compare the contents of Al, Cu and Na in the corresponding zones of the other micrographs of Figs. 3(a), (c) and (d), and it is shown that the bright white zones are the $CuAl_2$-phase and the content of sodium in the black zones is higher than that in other areas. It is speculated that elemental sodium or some compounds containing sodium exist at the grain boundaries. It is also shown that there is plentiful sodium in the detected area, which is larger than that of other researches, and this will lead to the enlargement of the detriment after T6 heat treatment.

Further studies are performed in the Al−Cu−Na specimen by high resolution transmission electron microscope (HRTEM). It is interesting to find that the lattice fringe images cannot be obtained owing to the amorphous thin film on the specimen. The micrographs in Fig. 4 are obtained one by one in 10 s. From the comparison of the four images, it is found that the frontier which is pointed out by black arrow in Fig. 4(a) expands 10 nm in 10 s. So, the amorphous thin film grows when the images are obtained. We speculate that the amorphous thin film is a liquid thin film, which grows because some components are melted by the energy of electron beam. The energy of electron beam can heat the specimen and increase the temperature of the specimen by at most 100 °C. We compare the melting points of the elementary substance and compounds that probably exist, such as, Na, α(Al), $CuAl_2$, AlCu, Al_4Cu_9, Al_2Cu_3, $AlCu_3$, Na_3HAl_4, $NaAlH_4$, where the reason why the compounds contain hydrogen is that aluminum is so active that it easily reacts with gaseous H_2O in the melting operation [14]. So sodium is the elementary substance melted, the melting point of which is 97.82 °C. Combined with the above result of EPMA that the sodium element is detected at grain boundaries, it can be concluded that there will be elemental sodium at grain boundaries. According to the report by TALBOT and GRANGER [18], sodium is a layer with several atoms thickness.

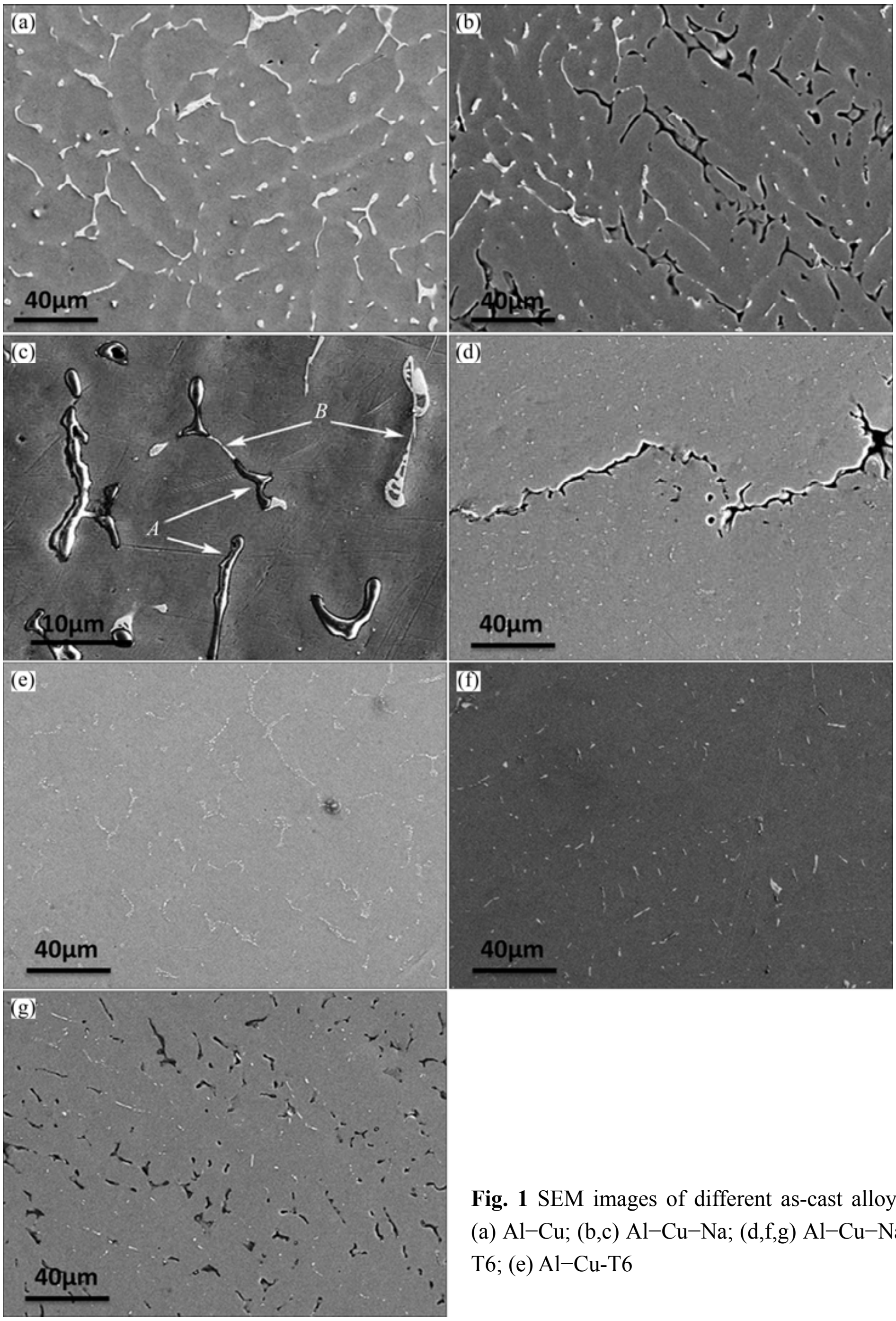
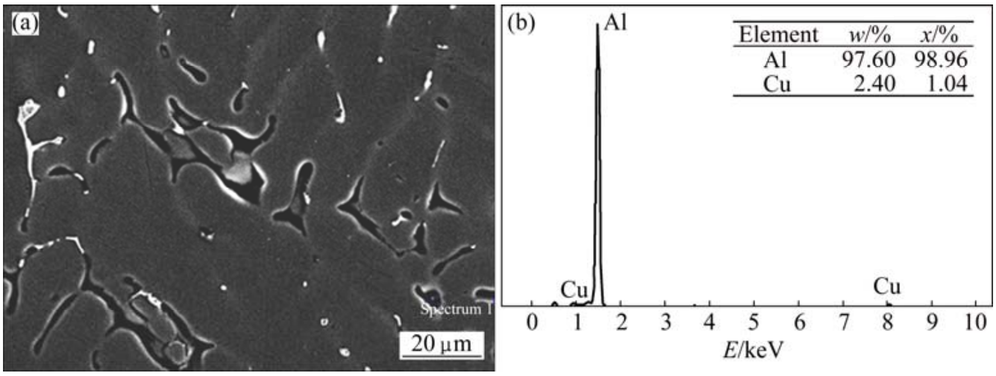


Fig. 1 SEM images of different as-cast alloys: (a) Al−Cu; (b,c) Al−Cu−Na; (d,f,g) Al−Cu−Na-T6; (e) Al−Cu-T6



Element	w/%	x/%
Al	97.60	98.96
Cu	2.40	1.04

Fig. 2 SEM image (a) and energy dispersive spectrometry of Spectrum 1 (b) in Al−Cu−Na specimen

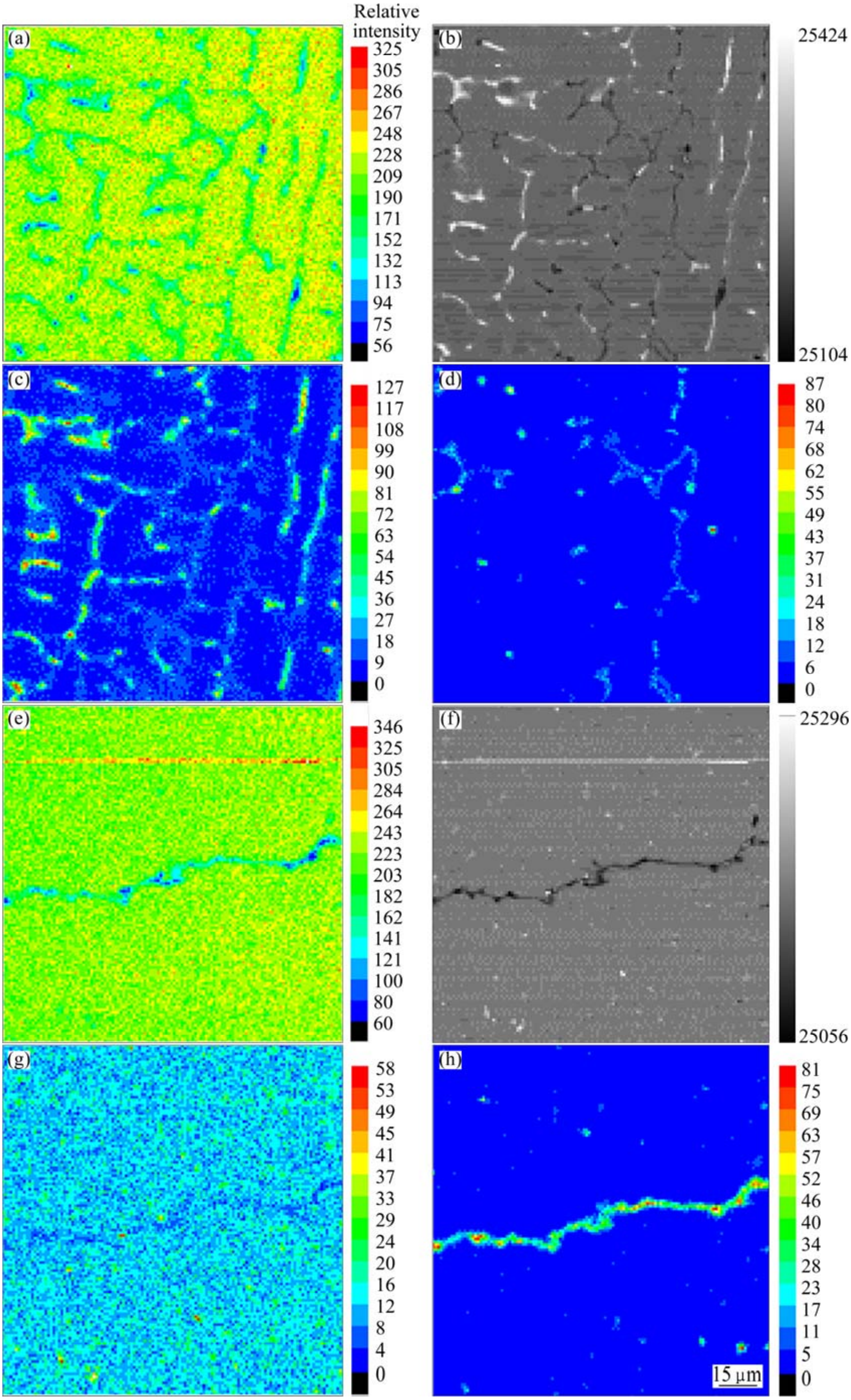


Fig. 3 EPMA micrographs of Al−Cu−Na (a−d) and Al−Cu−Na-T6 (e−h): (a, e) Al K_{α}; (b, f) BEI images; (c, g) Cu K_{α}; (d, h) Na K_{α}

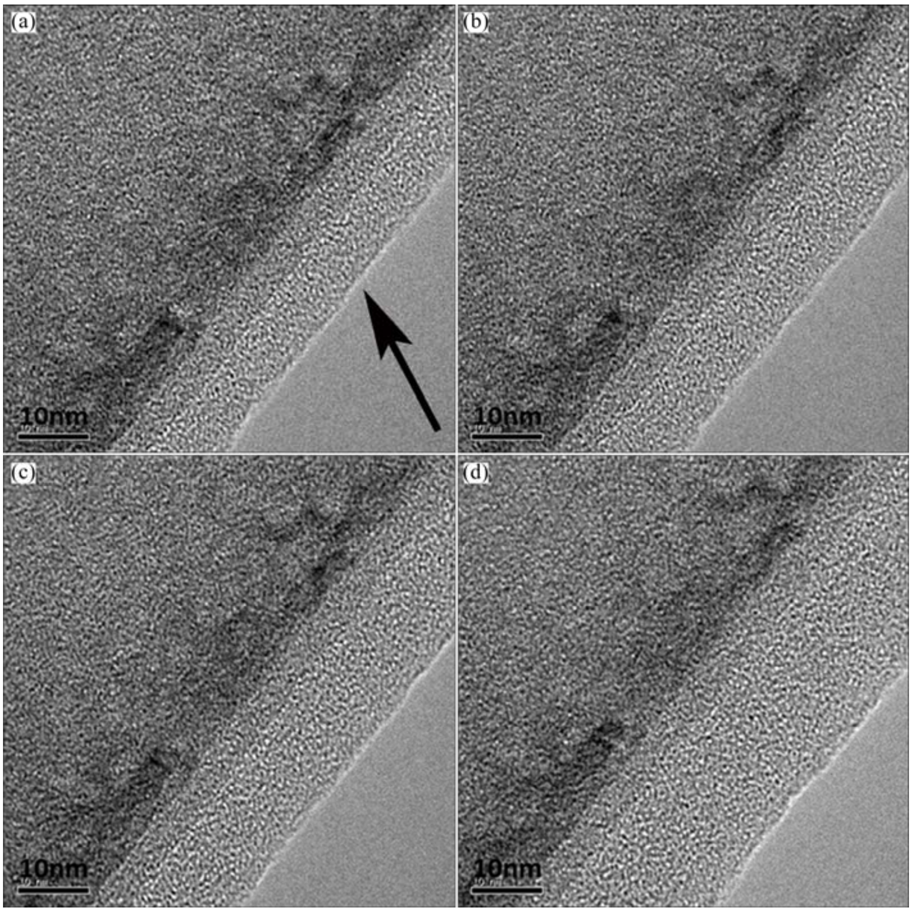


Fig. 4 Continuous HRTEM micrographs of Al−Cu−Na (The frontier is pointed out by black arrow, images are obtained one by one in 10 s)

3.2 Harmful effects of elemental sodium

After T6 heat treatment, as shown in Fig. 1(d), the crack appears in the Al−Cu−Na-T6 specimen. According to the crack in the BEI shown in Fig. 3(f), it is found that the contents of Al and Cu in the crack are lower than that in other areas of Fig. 3(e) and Fig. 3(g). In contrast, sodium is enriched in the crack in Fig. 3(h). So, the formation of the crack has a direct relation with sodium. This is because that sodium segregates to grain boundaries and makes the boundaries easy to fracture [4]. The formation of intergranular liquid phase sodium at high temperature significantly weakens the strength of grain boundaries and leads to intergranular fracture at higher temperature [13]. When the micro-crack occurs, it begins to propagate and form the big crack in the process of heat treatment.

The reason why so big crack takes place has two parts. One is that plentiful sodium makes intergranular fracture easy. The other is that there is plenty of time at high temperature to make intergranular fracture propagate.

After T6 heat treatment, sodium not only causes Al−4.5%Cu to fracture directly, but also produces other adverse effects indirectly. Compared Fig. 1(e) with Fig. 1(f), the residual $CuAl_2$-phase exists in the Al−Cu−Na-T6, which has the needle-like morphology; in the Al−Cu-T6, the primary $CuAl_2$-phase is dissolved in the α(Al) matrix in the process of solution treatment, then precipitates small and dispersive distributed θ-phase whose composition is still $CuAl_2$ at the stage of artificial aging, which tends to distribute at which $CuAl_2$-phase ever existed.

In Fig. 5, before heat treatment, the X-ray diffraction (XRD) results of Al−Cu and Al−Cu−Na are almost the same. Under the same condition of heat treatment, the $CuAl_2$-phase cannot be detected in the Al−Cu-T6, but some peaks of $CuAl_2$-phase which are pointed out by the red arrows in Fig. 5 still can be detected in the Al−Cu−Na-T6.

Figure 1(g) shows the SEM micrograph of the Al−Cu−Na-T6 in which the $CuAl_2$-phase is also detached from the matrix. The majority of the residual of primary $CuAl_2$-phase sheds, which is worse than the Al−Cu−Na specimen. This proves that the residual primary $CuAl_2$-phase has some direct relation with sodium. Generally speaking, the thin liquid film of sodium at the grain boundaries is poorly soluble in the α(Al) matrix and $CuAl_2$-phase, and this makes the

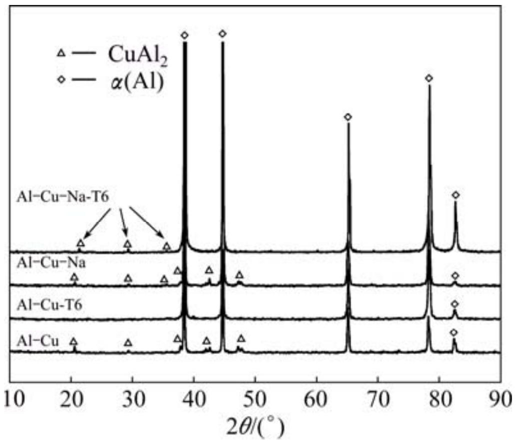


Fig. 5 XRD patterns of different Al−Cu alloys

$CuAl_2$-phase hardly dissolve with the matrix in the process of solution treatment. Finally, this leads to the increase of the residual $CuAl_2$-phase. There is an enrichment of sodium on the surface of the residual, thus the detachment amount of $CuAl_2$-phase in the Al−Cu−Na-T6 is more than that in the Al−Cu−Na. The primary $CuAl_2$-phase is easier to be detected than the small, poor orientative and dispersive distributed θ-phase. Hence, after the T6 heat treatment, the XRD patterns like Fig. 5 are obtained.

The residual of the needle-like $CuAl_2$-phase and the decrease of the effect of the precipitation strengthening make the performance of the Al−4.5%Cu poor. But the elemental sodium at grain boundaries plays a vital role in the decrease of the mechanical properties.

The mechanical properties of the Al−Cu-T6 and Al−Cu−Na-T6 are displayed in Table 2. It can be found that, without the sodium, the values of UTS (ultimate tensile strength) and δ of Al−4.5%Cu are 217 MPa and 11.0%, while with the addition of sodium, the UTS and δ are dramatically decreased to 128 MPa and 5.3%. Figure 6 shows the magnified images of fracture surface of Al−Cu-T6 and Al−Cu−Na-T6. The dimple fracture is observed in Al−Cu-T6, while the intergranular fracture is observed in Al−Cu−Na-T6. This is precisely because the intergranular fracture makes the mechanical properties of Al−4.5%Cu decrease dramatically. As mentioned above, EPMA and HRTEM analyses revealed that sodium segregates to the grain boundaries and thus weakens interatomic bonds and facilitates decohesion of grain boundaries, which is consistent with the above results.

4 Discussion

The solubility of sodium in the solid aluminum is extremely low. RANSLEY and NEUFELD [19] found that the maximum solubility of sodium in the solid aluminum is (0.0023±0.0005)% (mole fraction). In this study, the sodium introduced through salt fluxes at the high temperature segregates at grain boundaries owing to the low solubility of sodium. The existence of the sodium in the EPMA analysis and the amorphous film in HRTEM proves that the elemental sodium segregates at grain boundaries.

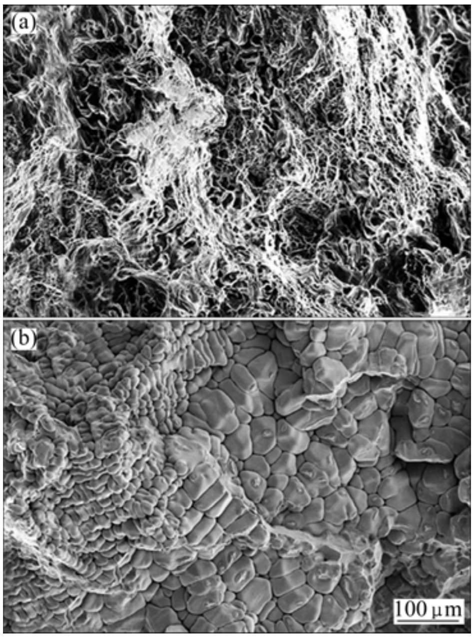


Fig. 6 Fracture images of different Al−Cu alloys: (a) Al−Cu-T6 (dimple fracture); (b) Al−Cu−Na-T6 (intergranular fracture)

Table 2 Mechanical properties of Al−Cu-T6 and Al−Cu−Na-T6

Alloy	UTS/MPa	δ/%
Al−Cu-T6	217	11.0
Al−Cu−Na-T6	128	5.3

*Each value of UTS and δ is an average of four measurements.

The existence of the sodium atom layer makes the bond between the matrix and $CuAl_2$-phase weaken so that the $CuAl_2$-phase is easy to detach from the matrix. The high temperature in solution process of T6 treatment will make the sodium atom layer melt to liquid film at the grain boundaries. This film is poorly soluble in the matrix and $CuAl_2$-phase and prevents the pass of atoms at both sides. So, this film obstructs the counter diffusion between matrix and the $CuAl_2$-phase at high temperature and makes the quenched structure inhomogenous. This is because the $CuAl_2$-phase cannot dissolve in the matrix sufficiently. Finally, the residual of the needle-like $CuAl_2$-phase exists after T6 treatment.

Meanwhile, in Al−Mg alloys, HORIKAWA et al [7] found that sodium brings about the high temperature embrittlement (HTE) based on intergranular fracture. And ZHANG et al [10−12] suggested that HTE is related to the formation of low melting point sodium-rich liquid phases that precipitates at grain boundaries by means of thermodynamic simulation. In this study, the crack forms without the tensile force because of the plenty of the sodium, content of which is about a few thousandths as shown in Fig. 3. It is found that the crack forms after T6 treatment. We believed that the crack also forms at high temperature in solution treatment and is easier to form in Al−Mg alloys owing to the amount of sodium. A large number of liquid films appear in the process of solution treatment and form a net of thin liquid film. The crack forms because of thermal stress and propagates quickly. As a result of cracks and the weak bond between grains, the mechanical performance of Al−4.5%Cu decreases dramatically. Sodium atom layer weakens the bond between the matrix and $CuAl_2$-phase and makes the boundaries easy to fracture. When the tensile tests start, the crack propagates along grain boundaries then test bars fracture. So, the magnified images of fracture surface show the transition from dimple fracture to intergranular fracture.

5 Conclusions

1) It is found that the elemental sodium segregates at the grain boundaries, which weakens the bond between the matrix and $CuAl_2$-phase.

2) After T6 heat treatment, cracks take place in the Al−4.5%Cu alloy containing sodium and the residual needle-like $CuAl_2$-phase exists.

3) The tensile test shows that the sodium results in the fracture mechanism changing from dimple fracture to intergranular fracture, which makes the mechanical performance of Al−4.5%Cu decrease dramatically.

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钠在 Al−4.5%Cu 合金中的存在形式及不利影响

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摘 要：通过熔盐向 Al−4.5%Cu 引入足量的钠，研究钠在 Al−Cu 合金中的存在形式以及对合金显微组织和抗拉性能的影响。结果表明：钠以单质形式存在于合金晶界中，这种钠降低了基体和 $CuAl_2$ 相之间的结合力。T6 时效处理后，钠导致了微观裂纹的产生和 $CuAl_2$ 相的残留。抗拉实验的结果显示钠使得合金的断裂方式由韧窝断裂向晶间断裂转变，这导致了合金性能的急剧降低。

关键词：Al−Cu 合金；钠；晶界；断裂；力学性能

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