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

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

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]:

$$3NaF + Al \longrightarrow AlF_3 \uparrow + 3Na$$
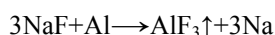
The Al−4.5%Cu alloy was prepared using high-purity Al and Cu with 99.999% purity by the high-frequency furnace. The salt fluxes in Table 1 whose mass is as 20% as that of the molten alloy were added into the alloy. The salt fluxes used are chemically pure. The alloy was kept holding for 8 min at 730 °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.