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Cu GB Diffusion in Al. Effect of Alloying by Cu and Ce.

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Abstract. The diffusion of Cu in Al and Al based alloys was studied. It was shown the great scattering of triple product values, measured for different grain boundaries (GB) at the same samples. It was discussed in the terms of GB energy difference. It was also shown that GB triple product can be varied significantly by preliminary alloying of Al by 0.1% Cu. However, the alloying of Al by 0.5% Cu leads to disappearing of the effect of accelerated diffusion in GB in comparison with the bulk.

Introduction

Diffusion along grain boundary is one of the important processes, which occurred in polycrystalline materials. At relatively low temperature (less than 0.5 T_m, where T_m is a melting temperature of matrix) grain boundary diffusion is a dominating process in mass transport into polycrystalline materials. It becomes even more important because of wide application of nanostructured and ultra-fine grained materials, where the total area of GB is very high. Besides, the mobility of atoms at GB determines, according to different models, the GB mobility, phase growth in GB and adjacent region, and other processes.

Cu is the important alloying element for Al-based alloys. Alloying by Cu improve the mechanical properties of the alloys. However, the GB diffusion of Cu in Al was studied carefully only recently [1, 2]. To determine the triple product of Cu GBD in Al ($P=s\delta D_{gb}$; where s is enrichment coefficient, δ is GB width and D_{gb} is GB diffusion coefficient) two method were used. P-value was calculated for the set of individual GB at different temperatures by the treatment of Cu concentration profile in adjacent to GB area, obtained by X-ray microprobe analysis. The vertex angle of Cu iso-concentration profiles, which were visualized by etching of polished surface, was also measured. All experiments were made in "B" regime according to Harrison classification [3]. Fisher's model [4] of GB diffusion was used to extract P. Note, that for used regimes in measured concentration range the Fisher solution coincides with the Wipple solution [5].

In order to obtain new data about the segregation influence on GB diffusion the experiments were continued with preliminary alloyed by Cu and Ce samples. Ce being the elements of very small solubility in Al must be a strong segregant on Al GB according to Hondros and Seah [6]. Besides, we have a data on positive influence of Ce on corrosion stability of Al-Cu alloys.

Special attention in this paper is paid to the distribution of GBD triple product value for different grain boundaries.

Experimental

The alloys were prepared by dissolution of pure Cu and Al-10% Ce pieces in molten Al at the temperature 900 °C. The melt was kept for two hours at this temperature to ensure the dissolution and after that it was quenched to the cold iron plate. The samples were homogenized at the temperature 600 °C (just below the solidus line), and cut on the rectangular samples.

The Cu was electrochemically deposed on the polished surface of the samples according to the methods describes in [2]. The diffusion annealing was carried out with the samples put in quartz ampoules preliminary filled by Ar under the pressure of 10^{-2} Pa at the temperature 400 °C.

After diffusion annealing each sample was cut on two and the both cross-sections were carefully polished and etched.

The compositions of electrolytes were as follows:

- 10% HNO_3 for pure Al and Al-Ce alloys;
- 10% NaOH for Al-Cu alloys.

Such a procedure allowed to visualize the penetration of Cu in Al.

Results and discussion

The vortex angle was measured in the way as it is shown at Fig. 1 and triple product was calculated with the use of formula (1):

$$\mathrm{ctg}(\psi) = \pi^{-\frac{1}{4}} \beta^{\frac{1}{2}}, \qquad (1)$$

where $\beta = \dfrac{s\delta D_{gb}}{2D_v^{\frac{3}{2}} t^{\frac{1}{2}}}$ s is enrichment coefficient, δ is GB width, D_{gb} - GB diffusion coefficient, D_v is bulk diffusion coefficient and t is time

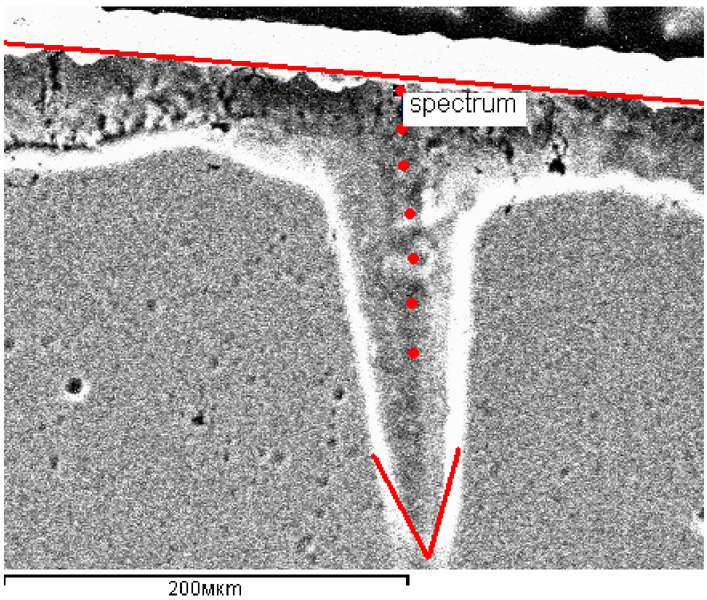


Figure 1 The iso-concentration profiles obtained by etching of the samples alloyed by Ce after Cu diffusion. Points indicate the places of X-ray microprobe analysis.

The mean values of P for the Al -0.1% Cu and Al-0.1% Ce are equal to 1.8×10^{-18} m^3/s and 5.6×10^{-19} m^3/s consequently (P_{Al}= 6.2×10^{-19} m^3/s [2]). On Fig.2 the Arrhenius plot for Cu GB diffusion in pure Al and obtained values for the alloys are presented. One can see that in the case the pre-alloying by Cu the P value changes in 3 times approximately, then in the case of addition of Ce there is no visible changes.

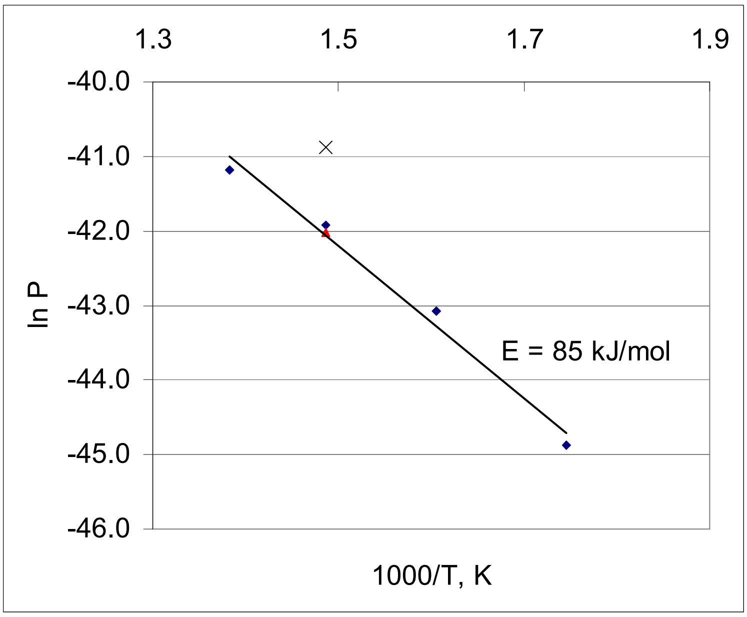
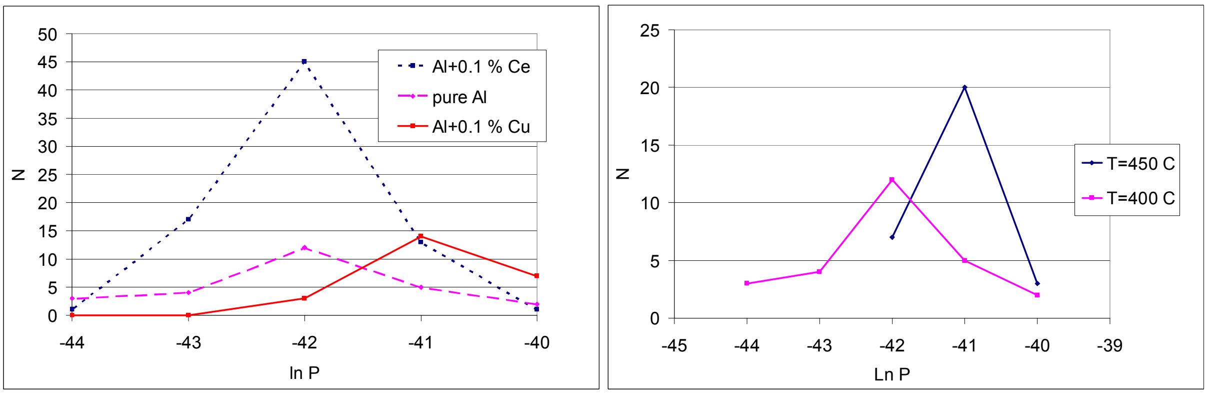


Figure 2. GB diffusion triple product of Cu in Al and Al based alloys as a function of temperature.

To analyze the effect of alloying we studied carefully the difference of GB triple product obtained for the same sample. To do that the obtained (ln P)-values were separated on the groups with the step equal to 1, so that the values in region minus 41±0.5 were united in one group minus 42±0.5 to another, etc. Such a procedure was fulfilled for each alloy.

On Fig.3a the numbers of GB triple product values at the temperature 400 °C for the groups are shown. One can see that the maximum for Al+0.1 %Cu alloy is shifted to the right in comparison with pure Al and Al+0.1 %Ce alloy. For the last two cases the mean values are the same. On Fig. 3b we presented the same distribution for pure Al at different temperatures.



a b

Figure 3 Distribution of P-value for Cu GB diffusion in pure Al and Al-based alloys (a) and for Cu GB diffusion in pure Al at temperatures 450 and 400 °C(b).

The alloy, containing 0.1 % Ce is characterized by much smaller grain size (less than 100 μm) than for pure Al and Al-Cu alloy (about 500-1000 μm) and thus the number of P values measured for the samples are 5 times larger.

The experiment with alloying by copper was continued with the sample containing 0.25 and 0.5 % Cu. On fig. 4 the typical view of the etched sample pre-alloyed by 0.5 % Cu is presented. On the photo one can easily see the Cu layer, the zone of recrystallization, corresponding to bulk diffusion and GB. In the sample with 0.25 % Cu no trace of leading GB diffusion can be observed also but we have found two GB with observable GB diffusion. Measurements of concentration in different points of GB did not show any concentration increasing below of recrystallization zone.

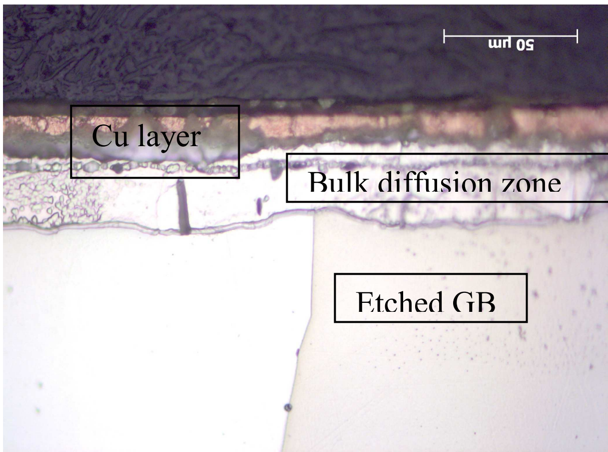


Figure 4. The cross-section of the samples with 0.5 % Cu after diffusion annealing and etching in NaOH.

In order to estimate the accuracy of experiments the sample of pure Al after Cu diffusion was carefully examined in order to study Cu distribution in etched zone. On Figure 5 the view of etched zone, the points of X-ray microprobe analysis and Cu concentration distribution are shown.

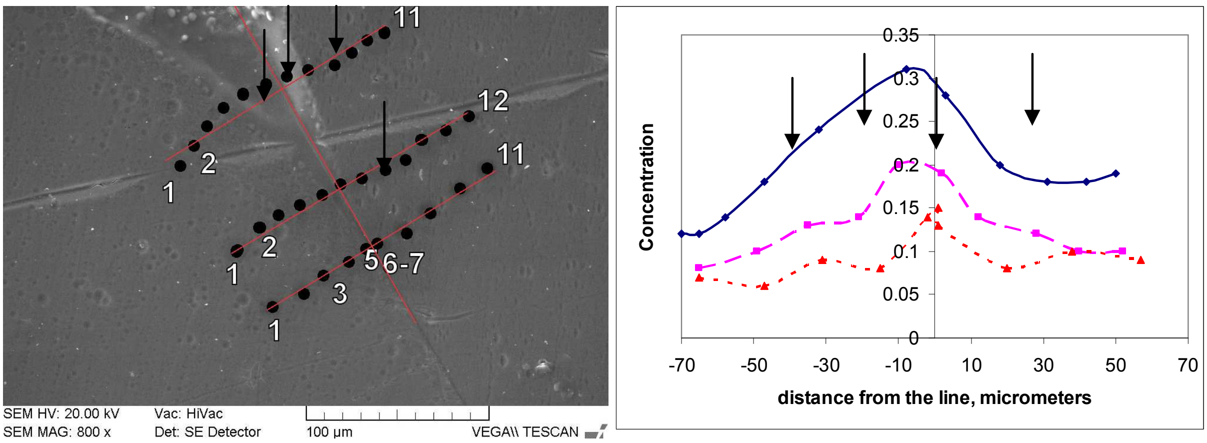


Figure 5. GB diffusion iso-concentration line, etched with HNO_3 water solution, (a) and the results of X-ray microprobe analysis in the points indicated on the photo (b).

Let's compare the concentration in points indicated by arrow on the upper and on the middle lines, which are corresponds approximately to the visible iso-concentration profile. It is easy to see that this profile corresponds to the concentration about 0.2% and the concentration in this range can be determined with sufficient accuracy.

Thus we have to discuss several unclear results:

- The different value of triple product for the same sample: is that the experimental error or different values corresponds to the different objects of investigation?
- Why pre-alloying by Cu increases the triple product at relatively small concentration and stop the GB diffusion at the higher one?
- Why pre-alloying by Ce does not change the results?

To discuss the first question let's look at the difference between the distribution of the P value for diffusion at the temperatures 723 and 673 K in the pure Al (Fig. 3b). Difference in mean values corresponds to the value of effective activation energy equal to 85 kJ/mol [2] (the ratio of P_{723}/P_{673}= 2.5). One can see that the distribution is quite wide and the ratio maximal to minimal P value is also about 2.5 at e.g. 723K. It can be described by not very high difference in GB energy (This idea was proposed by Prof. E. Glickman during the discussion). We do not know the value of GB energy, but let's assume that the difference in GB diffusion activation energy is determined by the GB energy difference. At the indicated temperature the variation of activation energy on 5 kJ/mol gives the change in P value approximately to 2.4 times. Thus we can conclude that the scattering of results described by the difference in GB even for the same samples rather than accuracy of measurements.

The difference in P values for preliminary alloyed samples can be discussed in terms of segregation. Experimental results published earlier showed different tendency. In [7] it was shown that pre-alloying of Cu by Ag lead to decreasing of Ag GB diffusion triple product. The influence of purity of Cu [8] and Ni [9] on GB self-diffusion also showed the decreasing of P values with total impurity concentration. To describe the results it was supposed that the segregated atoms "poison" the neighbor places and by this way slow down the diffusion. On the other hand in [9, 10] in discussion of acceleration Fe GB diffusion in Al – 0.01 % Cu alloys in comparing with pure Al we proposed the idea that if the places on GB are different for segregation they are very different for diffusion. During sample preparation and recrystallization Cu atoms occupy "good" segregation places at GB but these places are not good for diffusion. Thus only places of "bad segregation" and "fast diffusion" are free for diffusion. Effective activation energy (measured in the experiment) in this case corresponds only to the minimal true activation energy, in opposite to the case of pure material, where it corresponds to some average value for all types of segregation and diffusion places. That can be some explication of faster diffusion in pre-alloyed samples in this case also.

Why it does not happen for Al-Ce alloy? According to Hondros and Seah rule the segregation of Ce has to be stronger than of Cu in Al because of lower solubility (less than 0.1 %). The possible reason is that for Cu and Fe there are common segregation places: the atomic radii are approximately equal (r_{Cu} =1,28 and r_{Fe} =1.26 Å); in both case they are sufficiently smaller than Al (r_{Al}=1.43 Å). As for Ce (r_{Ce}=1,81 Å) it can be forced to occupy other places, and does not change the preferential paths of Cu diffusion.

The last point in the discussion is absence of observable GB diffusion in alloyed samples with 0.25 and 0.5 % of Cu. It does not mean that atom mobility on GB became lower. It means only that we can not see the accelerated flux along GB. Such a case occurs if e.g. concentration gradient is very small. In [11] the segregation of Cu in alloys with 0.5 and 2 % of Cu was measured. It was observed that the segregation (concentration excess on GB) varies from almost 0 (for a few GB) up to 0.8 monolayer for the sample with 0.5 % Cu. If we assume that GB is almost saturated like according to Langmuir –McLean isotherm (see e.g. [12]), than GB concentration gradient is small, or more exactly, concentration gradient in bulk much more than the concentration gradient in GB.

Conclusion

Cupper GB diffusion in Al varies significantly (up to 2.5 times) even for the same sample. It can be connected with difference in GB energy. Pre-alloying of matrix can sufficiently change the triple product of GB diffusion. The important point is that GB diffusion in alloys can be faster than in pure Al, if the segregation places are the same. In saturated due to segregation GB the GB diffusion becomes impossible due to very small GB concentration gradient.

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Reference

[1] N. Dolgopolov, A. Rodin, A. Simanov, and I. Gontar’: Izvestiya vusov, Non-Ferrous metallurgy, (in Russian) Vol. 50 (2009), p. 133.
[2] N. Dolgopolov, A. Rodin, A. Simanov, and I. Gontar’: Mater. Lett. Vol. 62 (2008), p. 4477
[3] L. G. Harrison: Trans. Faraday Soc. Vol. 57 (1961), p. 1191.
[4] J. C. Fisher: J. Appl. Phys. Vol. 22 (1951), p. 74.
[5] R. T. P. Whipple: Phil. Mag. Vol. 45 (1954), p. 1225.
[6] E. D. Hondros and M. P. Seah: Int. Met. Rev. Vol. 22 (1997), p. 262.
[7] J. Bernardini, Zs. Tokei, and D. L. Beke: Phil. Mag. A Vol. 73, N 1 (1996), p. 237.
[8] T. Surholt and Chr.Herzig: Acta Mat., Vol. 45 (1997), p. 3817.
[9] M.Astahov, B.Bokstein, A.Rodin, and M.Sinyaev: Izvestiya vusov, Non−Ferrous metallurgy, № 4 (1998), p.4 (in Russian).
[10] B.S.Bokstein and A.O. Rodin: Proc. Int. Conf. "Mass and Charge Transport in Solids" (2000), p. 213.
[11] M.B. Small, D.A. Smith, and AJ. Garratt-Reed: Scr. Metal. Mater. Vol. 3D (1994), p.1531.
[12] B.S. Bokstein, V.E. Fradkov and D. L. Beke: Phil. Mag. A, Vol. 65 (1992), p. 277.

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