Annuaire de l'Université de Sofia "St. Kliment Ohridski", Faculté de Physique, 96, 2003

DETERMINATION OF THE HYDROGEN DIFFUSIVITY IN Al_9Si_3CuTi ALLOYS

JORDAN GEORGIEV*, STOYKO GYUROV*, NIKOLA STANEV

Department of Solid State Physics and Microelectronics
**Institute of Metal Science, Bulgarian Academy of Sciences*

Йордан Георгиев, Стоико Гюров, Никола Станев ОПРЕДЕЛЯНЕ КОЕФИЦИЕНТА НА ДИФУЗИЯ НА ВОДОРОДА В Al_9Si_3CuTi СПЛАВИ

Водородният пренос в сплави $Al_9Si_3Cu(0{,}2–4{,}1)Ti$ със съдържание на титан (0,2; 1,02; 2,3 и 4,1 wt.%) е изследван с използване на метод на проникване на водород през тънка пластина. Измерваният поток водород е получен в резултат на взаимодействието между мембраната (като катод) и йоните от водороден тлеещ разряд с плътност на тока 12 mA/cm^2, напрежение 500 V, постоянно налягане на водорода 1330 Pa и разстояние между електродите 24 mm при температури 640–780 K. За определяне коефициента на дифузия на водорода в изследваните сплави е използвано решение на II закон на Фик при едномерна дифузия през тънка пластина (мембрана). Решението описва случай, когато скоростта на повърхностните процеси е сравнима с тази на обемната дифузия. Стойностите на коефициента на дифузия D са представени в арениусови координати, обработени са по метода на най-малките квадрати и са получени предекспоненциалните множители и активиращите енергии.

Jordan Georgiev, Stoyko Gyurov, Nikola Stanev. DETERMINATION OF THE HYDROGEN DIFFUSIVITY IN Al_9Si_3CuTi ALLOYS

The hydrogen transport in the $Al_9Si_3Cu(0.2–4.1)Ti$ alloys with different content of Ti (0.2; 1.02; 2.3 and 4.1 wt.%) is studied by using of permeation method. The measured flux is obtained as a result of interaction between the specimen (as a cathode) and hydrogen glow discharge with current density 12 mA/cm^2, voltage 500 V, constant hydrogen pressure 1330 Pa, distance between electrodes 24 mm in 640–780 K temperature range. Solution of the second Fick's equation in case of uni-dimensional diffusion problem describing the diffusion through a thin plate (membrane) is used to determine the hydrogen diffusivity in studied alloys. The solution describes case when the rate of surface processes is comparable to the diffusion. Values of diffusivity D were presented in Arrhenius plot and worked out by the least-squares method and both preexponential factors and activation energies were obtained.

Keywords: diffusion, hydrogen, glow discharge, aluminium alloy
PACS number: 66.30J

INTRODUCTION

The aluminum alloy welding products are used increasingly for cars, wagons and high-pressure vessels production because of their mechanical and corrosion properties, great reduction of weight and easier recycling in comparison with the same steels products as well. The aluminum alloys are welded much difficult as compared to steels since its melts solved hydrogen intensively which produces porosity during the crystallization process and reduces mechanical properties of welded parts. The removal of porosity in the aluminum alloy welded parts is a one of the most important scientific task for welding specialists. It is impossible this task to be solved without a knowledge of the solubility, diffusivity and hydrogen permeation in aluminum alloys. A data for alloys to be investigated are not available in spite of it's importance which defines the aim of this work: obtaining of reliable data for hydrogen diffusivity in Al9Si3Cu(0.2–4.1)Ti alloys up to 780 K.

EXPERIMENTAL AND THEORETICAL APPROACH

Experimental method. The chemical composition of the alloys investigated is Al9Si3Cu(0.2–4.1)Ti. The specimens in the form of thin plates with exactly known surface area (3.14×10^{-4} m^2) and thickness (1×10^{-3} m) were cut from cylindrical bars, which had been cast in graphite mould. The diffusion cell consists of inlet and outlet chambers separated by the studied specimen, which is mounted vacuum tight between the cell flanges (Fig. 1).

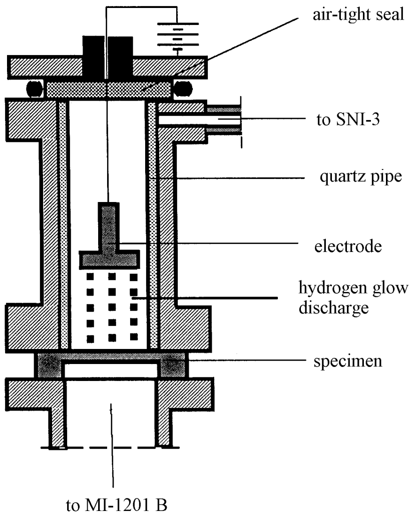

Fig. 1. Principle scheme of the diffusion cell

A high vacuum of 10^{-6}–10^{-7} Pa is reached in both cell chambers with the aid of high vacuum pumping sets of mass-spectrometer MI-1201B and SNI-3 (system for introduction of isotopes) apparatus. After pumping the diffusion cell heating unit is switched on and when the desired working temperature is reached high purity hydrogen from hydride container is introduced into the inlet chamber. Both literature data and our previous experiments show that the permeated hydrogen flux through the samples is low and it may be measured with precision only at higher working temperatures. A suitable experimental equipment and test procedure was developed to overcome this very serious restriction. The measured flux in 640–780 K temperature range is obtained as a result of interaction between the specimen (as cathode) and ions of hydrogen glow discharge with current density 12 mA/cm^2, voltage 500 V, constant hydrogen pressure 1330 Pa, distance between electrodes 24 mm.

Theoretical approach. Solution of the Fick's equation in case of unidimentional diffusion problem describing the diffusion through a thin plate (membrane) was used to determine the hydrogen diffusivity in the alloys studied:

$$
\begin{aligned}
J(t) = -D\frac{\partial C(x,t)}{\partial x}\bigg|_{x=1} &= \frac{C(0,\infty)D}{1}\left\{1-\frac{Al\exp(-kt)}{\sin\left[\left(\frac{k}{D}\right)^{1/2}1\right]}\left(\frac{k}{D}\right)^{1/2}\right. \\
&\left.+2\sum_{n=1}^{\infty}(-1)^n\left[\frac{An^2}{n^2-\frac{kl^2}{D\pi^2}}-1\right]\exp\left(-\frac{n^2\pi^2Dt}{l^2}\right)\right\}.
\end{aligned}
\tag{1}
$$

Here $C(0,t)\ :\ t=0,\ C(0,t)=C(0,0)$, and $t\to\infty,\ C(0,t)=C(0,\infty)$; $A=\left[1-\dfrac{C(0,0)}{C(0,\infty)}\right]$, k—the kinetic rate constant, and l—the thickness sample.

This equation describes the case when the rate of surface process is comparable to the diffusion [1]. The diffusion coefficient of hydrogen D in the alloys studied is calculated using equation (1) with data from experimentally obtained curves $J_H = J(t)$ showing the permeated gas flux.

EXPERIMENTAL RESULTS AND DISCUSSION

Typical experimental curves $J_H = J(t)$ of gas penetration through Al9Si3Cu(0.2–4.1)Ti alloys (with different Ti content) membranes are shown in (Fig. 2–5). All experimental curves $J_H = J(t)$ obtained at different temperatures were analyzed by non-linear regression using Eq. (1). Figures 2 to 5 show the experimental generalized penetration curves of hydrogen through Al9Si3Cu(0.2–4.1)Ti alloys as well as their best fit and the confidential intervals.

The values of the calculated correlation coefficient r^2 are between 0.98 and 0.995. Values of diffusivity D for all studied temperatures derived from Eq. (1) are presented in Arrhenius plot in (Fig. 6). The same values for D worked out by

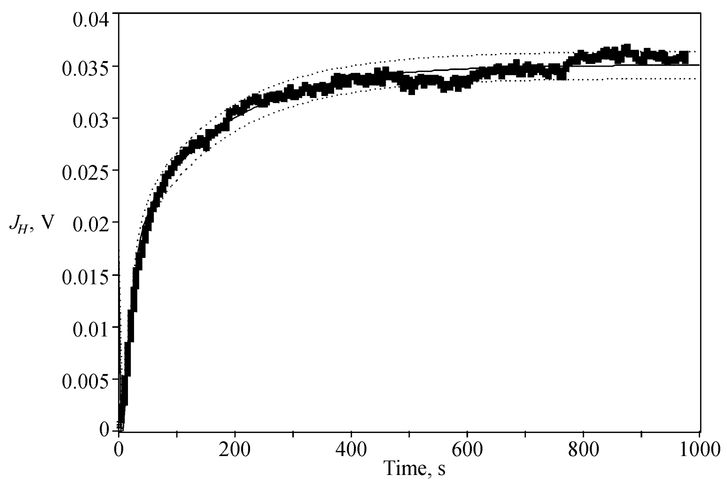

Fig. 2. A generalized penetration curve of hydrogen through $Al_9Si_3Cu_{0.2}Ti$ alloy specimen obtained by a non-linear regresion of experimental data at 736 K, using Eq. (1)

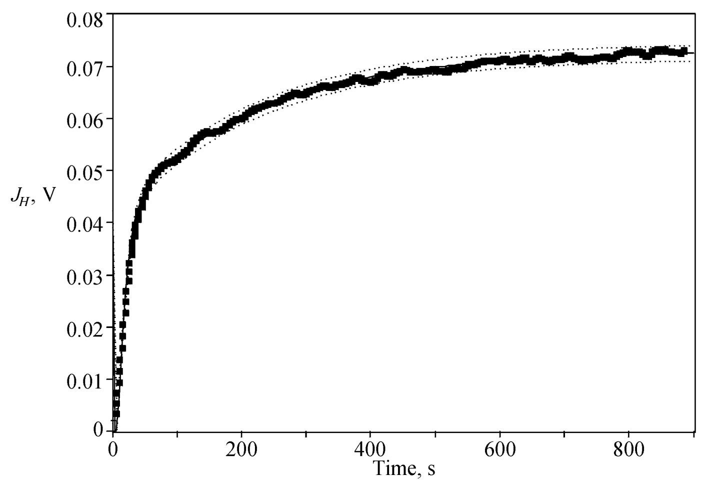

Fig. 3. A generalized penetration curve of hydrogen through $Al_9Si_3Cu_{1.2}Ti$ alloy specimen obtained by a non-linear regresion of experimental data at 734 K, using Eq. (1)

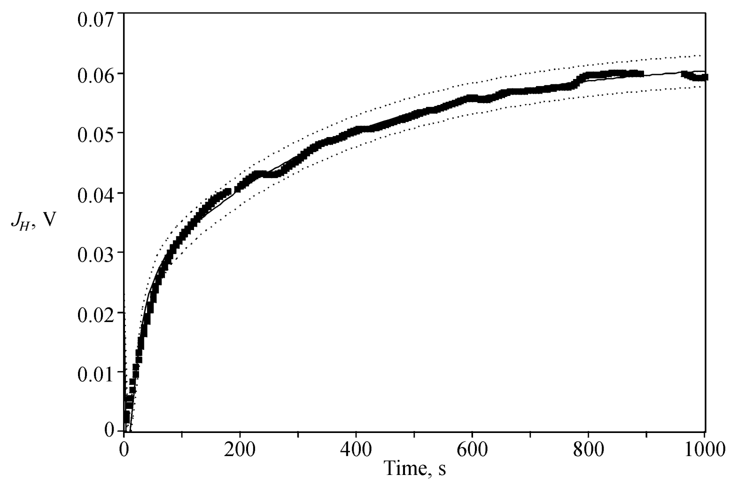

Fig. 4. A generalized penetration curve of hydrogen through $Al_9Si_3Cu_{2.3}Ti$ alloy specimen obtained by a non-linear regresion of experimental data at 722 K, using Eq. (1)

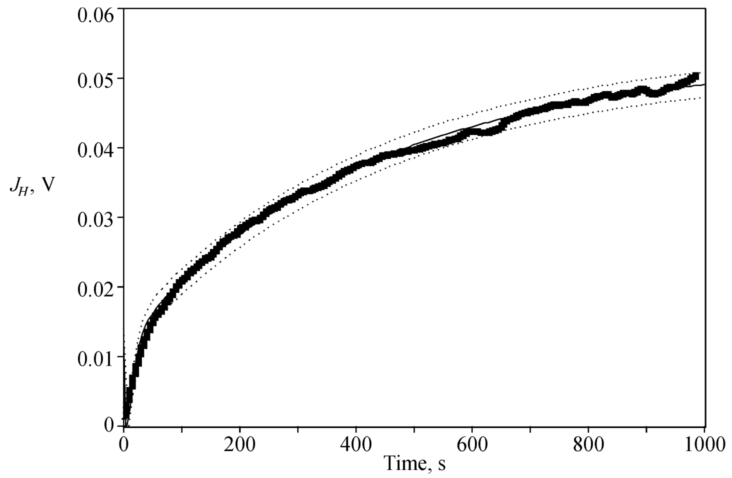

Fig. 5. A generalized penetration curve of hydrogen through $Al_9Si_3Cu_{4.1}Ti$ alloy specimen obtained by a non-linear regresion of experimental data at 700 K, using Eq. (1)

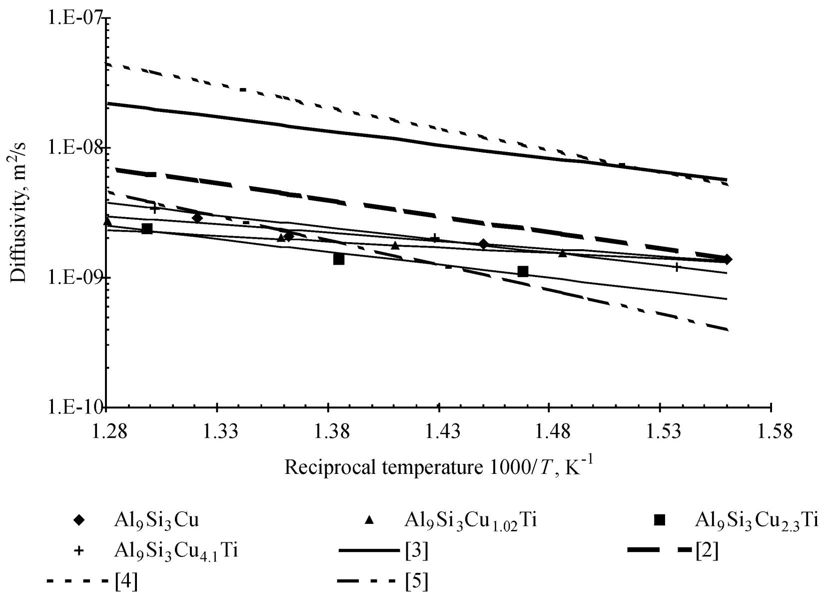

Fig. 6. Arrhenius plot of the diffusion coefficient D, for the AlSiCuTi allows in 644–780 K temperature range (solid square), compared with the literature data for Al [5–9]

Table. 1. Values of preexponential factors and activation energies for investigates alloys

Alloys	D_0, m^2/s	E_{diff}, kJ/mol
$Al_9Si_3Cu_{0.2}Ti$	1.13×10^{-7}	23.64
$Al_9Si_3Cu_{1.02}Ti$	3.39×10^{-8}	17.36
$Al_9Si_3Cu_{2.3}Ti$	9.08×10^{-7}	38.30
$Al_9Si_3Cu_{4.1}Ti$	1.09×10^{-6}	36.76

the least-squares method yield the following dependence, $D = D_0 \exp(-E_{\mathrm{dif}}/RT)$. The D_0 and E_{dif} values are presented in Table 1.

The hydrogen diffusivity data obtained for AlSiCuTi alloys are very similar to the same for AlSiMg [5]. Data obtained for hydrogen diffusivity—see Fig. 6, show that the adding of alloying elements (Si, Cu and Ti) in pure aluminum lead to decreasing of hydrogen diffusivity [2–4].

CONCLUSIONS

The difficulties related to diffusivity determination of AlSiCuTi alloys are overcome successfully by appropriate experimental equipment and test procedure.

The diffusion process in aluminium alloy can be quantitatively described with the aid of hydrogen glow discharge like hydrogen ion gun.

The diffusivity of hydrogen in AlSiCuTi alloys was determined.

Acknowledgement: The authors are grateful to the Bulgarian National Found Scientifics Research for financial support (contract TN–1101/01) of the present work.

REFERENCES

1. Georgiev, J. S., L. A. Anestiev. *J. of Nuclear Mater.*, **249**, 1997, 133.
2. Outlaw, R., D. Peterson, F. A. Schmidt. *Scripta metal.*, **16**, 1982, 287.
3. Eichenauer, W. et al. *Z. Metalkd.*, **52**, 10, 1961, 682.
4. Csanady, A., Papp K. *Mater. Sci. Engng.*, **48**, 1981, 35.
5. Georgiev, J. S., S. Gyurov. Proc. of 11th International Metallurgy and Materials Congress, 5-8 June, 2002, Istanbul, Turkey, 423.

Jordan Georgiev
Institute of Metal Sciences, Bulgarian Academy of Sciences
67 Shipchensky Prohod Str.
BG-1574 Sofia, Bulgaria
E-mail: j.georgiev@ims.bas.bg

Received April 2003