

MEASUREMENTS OF SOLID-VAPOR DIHEDRAL ANGLES FOR Cu AND Ni UNDER CONTROLLED OXYGEN PARTIAL PRESSURE

Toshikazu YOSHII*, Shigeta HARA**and Toshihiro TANAKA**

* Graduate school of Engineering , Osaka University, 2-1 Yamadaoka Suita 565-0871,

Now, THK Co. Ltd. Basic Research Laboratory, Osaka Japan

** Department of Materials Science and Processing, Faculty of Engineering, Osaka

University, 2-1 Yamadaoka Suita 565-0871, Japan,

ABSTRACT

Interferometry was applied to measure the solid-vapor dihedral angle of Cu at 1273K and Ni from 1473 to 1723K under controlled oxygen partial pressure by CO₂/H₂ mixed gases. Grain boundary free energy of copper is hardly affected by oxygen partial pressure in the gas phase. In contrast with Cu, that for Ni shows a remarkable decrease with increasing the oxygen partial pressure.

1. INTRODUCTION

Interfacial phenomena play an important role in many metallurgical processes, such as sintering, soldering, recrystallization and grain growth. In order to inspect these processes, values on the interfacial free energy are required, however, because of experimental difficulties, information on these quantities is limited especially for solids [1]. In this study, we applied the interferometry to measure the dihedral angle of Cu and Ni at grain boundary grooves formed at high temperature

2. EXPERIMENTAL

2.1 Preparation of Specimen

Copper samples are prepared by cold rolling of 7N grade pure copper rod to 1mm in thickness. They are polished mechanically by Emery papers and followed by electrolytic polishing in a 30% nitric acid and 70% ethanol solution at about 240K and rinse with pure ethanol. These Cu samples were annealed at 1273K for 2.6×10^5 sec. under a controlled oxygen partial pressure. Ni samples of 3N-grade sheet (1 mm in thickness) are polished mechanically by Emery paper and alumina powders with about

0.3 μ m diameter, and then annealed under various oxygen potentials at 1473K for 8.6×10^5 s, at 1573K for $1.7-4.3 \times 10^5$ s and at 1723K for 4.3×10^5 s. Surface structures of the samples after the cold rolling and annealing were examined by the analysis of electron channeling patterns (ECP) and showed typical recrystallized structures by the annealing.

2.2 Control of Oxygen Partial Pressure in Gas Phase

H₂-CO₂ or H₂-H₂O mixed gasses was used to control the oxygen partial pressure in the gas phase. The oxygen potentials were calculated on the assumption of the chemical equilibrium $\text{CO}_2 = \text{CO} + 1/2\text{O}_2$ or $\text{H}_2\text{O} = \text{H}_2 + 1/2\text{O}_2$ and also monitored directly by an oxygen concentration cell using a Ca-doped zirconia.

2.3 Dihedral angle

Figures 1a and 1b show a typical shape of grain boundary groove for well-annealed Ni sample, and the interferogram dihedral angles of the sample.

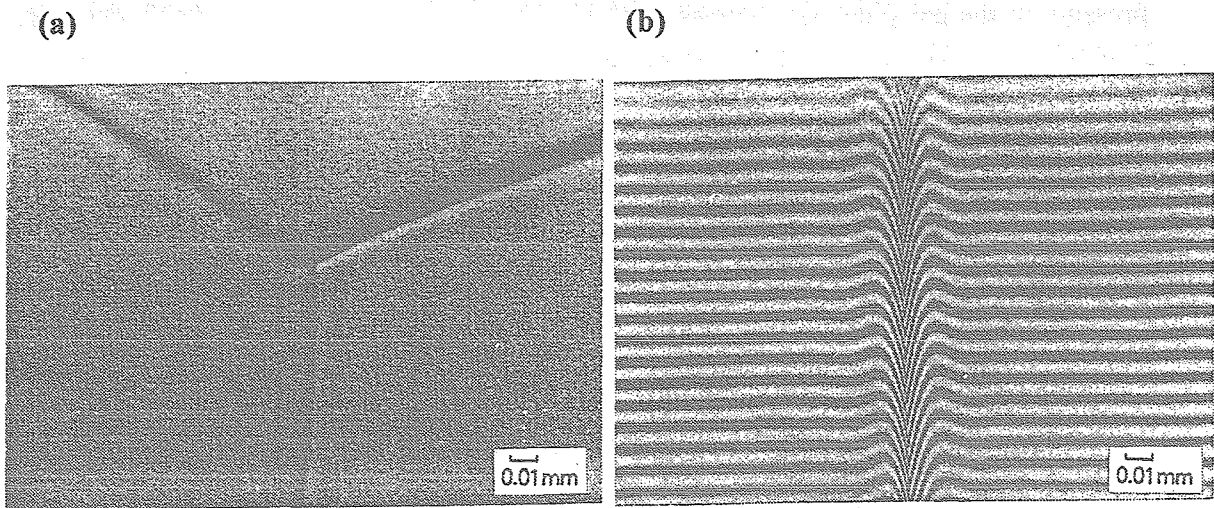


Fig.1 Typical shape of grain boundary (a) and the interferogram (b) for Ni annealed under a controlled oxygen potential.

Figure 2a shows a schematics of a dihedral angle $\Phi (= \alpha + \alpha')$ for a sample sectioned perpendicularly to its surface and Fig.2b corresponds to the perpendicular fringe pattern of the interferogram. If the angles, η and η' and distance, bm_{xy} were measured, the real angles, α and α' can be calculated by the following equations,

$$\tan \alpha = (2L)/(m_{xy} \lambda) \cdot \tan \eta \quad \tan \alpha' = (2L)/(m_{xy} \lambda) \cdot \tan \eta'$$

in which m_{xy} and m_z are magnification of the photograph (on x-y surface), and that of z-

direction perpendicularly to the x-y surface, λ is the wave length of the light used (546nm) and L is an interval of the fringes. The measured values for the L were corrected by 10% reduction in accordance with Tolmon and Wood's study [2].

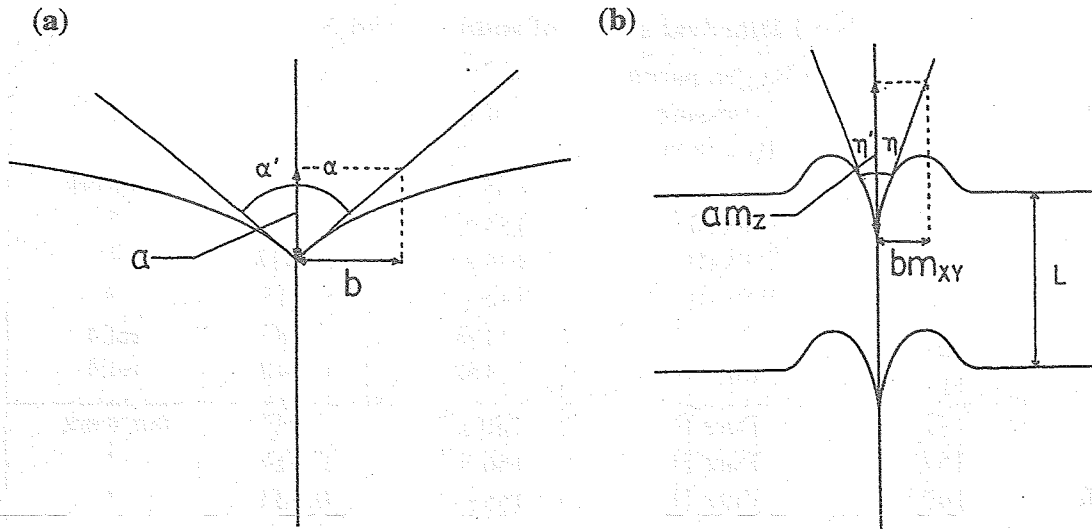


Fig.2 Schematics of dihedral angle (a) and the perpendicular fringe pattern of the interferogram (b).

It is known that the measured values on dihedral angle scatter around the true one due to the effect of the sectioning directions. To determine the true value, more than 100 fringe patterns were taken for samples prepared under the same experimental conditions

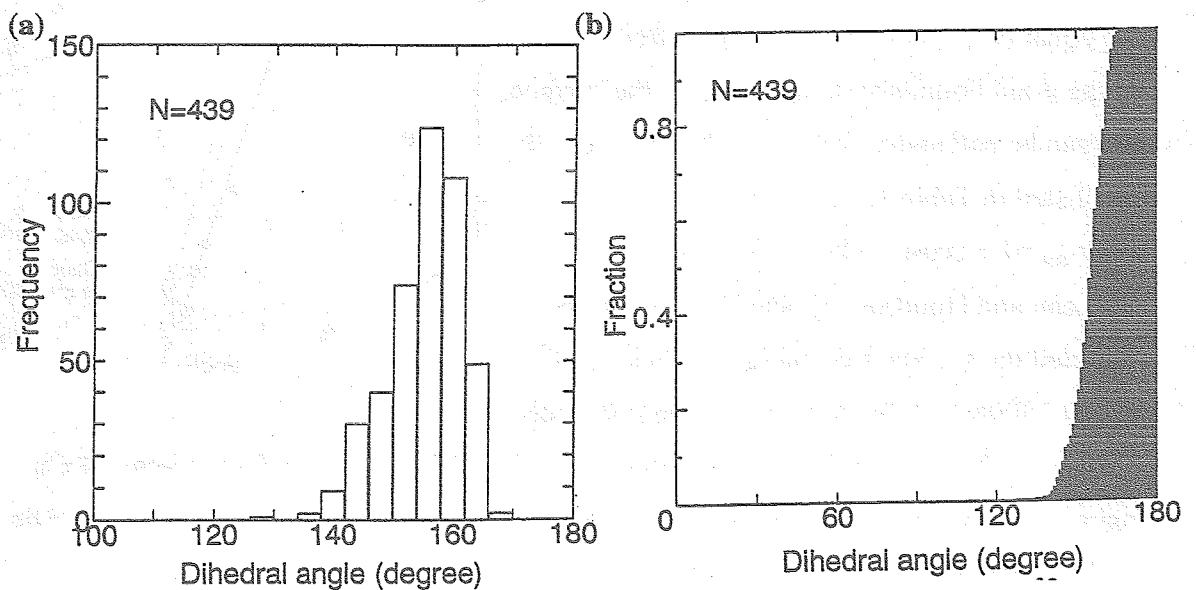


Fig.3 Histogram of distribution of measured dihedral angles (a) and the cumulative curve (b) for Ni annealed at 1573K under pure hydrogen.

as shown in Fig.3a and 3b. From the cumulative curve, the true contact angle is determined as the angle at 50% point of the curve [3].

Table 1 Dihedral angles of solid Cu and Ni.

Metal	Temperature (T/K)	Oxygen partial pressure P_{O_2} (atm)	Dihedral angle (deg.)	$\frac{\gamma_{GB}}{\gamma_s}$	Remarks
Cu	1273	Pure H_2	158 ± 2	0.382	this work
	"	3.8×10^{-20}	153 ± 2	0.467	"
	"	2.9×10^{-19}	150 ± 2	0.518	"
	"	2.9×10^{-18}	150 ± 2	0.518	"
	1073	Pure H_2	158	0.382	ref.4
	1173	Pure H_2	160	0.347	ref.4
Ni	1723	Pure H_2	160 ± 2	0.347	this work
	1573	Pure H_2	156 ± 2	0.416	"
	1473	Pure H_2	155 ± 2	0.433	"
	1573	3.8×10^{-20}	157 ± 2	0.399	"
	1573	2.9×10^{-19}	157 ± 2	0.399	"
	1573	2.9×10^{-18}	157 ± 2	0.399	"

3. RESULTS

The dihedral angles for Cu and Ni obtained in this work are summarized in Table 1 in comparison with reported ones. Assuming that the equation (2) is valid, the ratio of free energy of the grain boundary, γ_{GB} on that of the surface, γ_s can be calculated from the dihedral angle, Φ and listed in Table 1.

$$\gamma_{GB} = 2 \gamma_s \cos(\Phi / 2) \quad (2)$$

McLean and Hondros [5], and Bauer et. al [6] reported the surface free energy of Cu at 1200K and at 1300K as a function of oxygen potentials of the gas phase. Using thermo-chemical data, the oxygen potentials for each run can be converted to the corresponding CO_2/H_2 gas ratios.

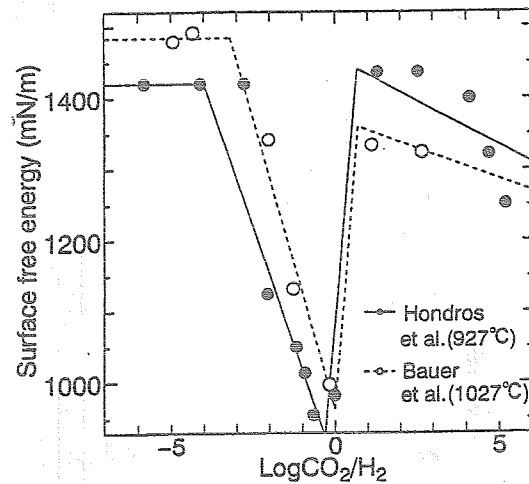


Fig.4 Surface free energy of Cu as a function of the CO_2/H_2 ratio in the gas.

Figure 4 shows the surface free energy of Cu as a function of the CO_2/H_2 ratio. It is seen that the change in surface free energy with this ratio is very similar whatever the temperature. On the other hand, only one study by Stickle et. al [7] is available for the surface free energy of Ni as a function of oxygen partial pressure of gas. In combination with these values, the grain boundary energies of Cu at 1273K and Ni at 1573K were estimated by the equation (2). They are shown in Fig. 5a for Cu and 5b for Ni as a function of the oxygen partial pressure of the gas. In contrast with Cu, the grain boundary free energy of Ni shows a remarkable decrease with increasing the oxygen partial pressure.

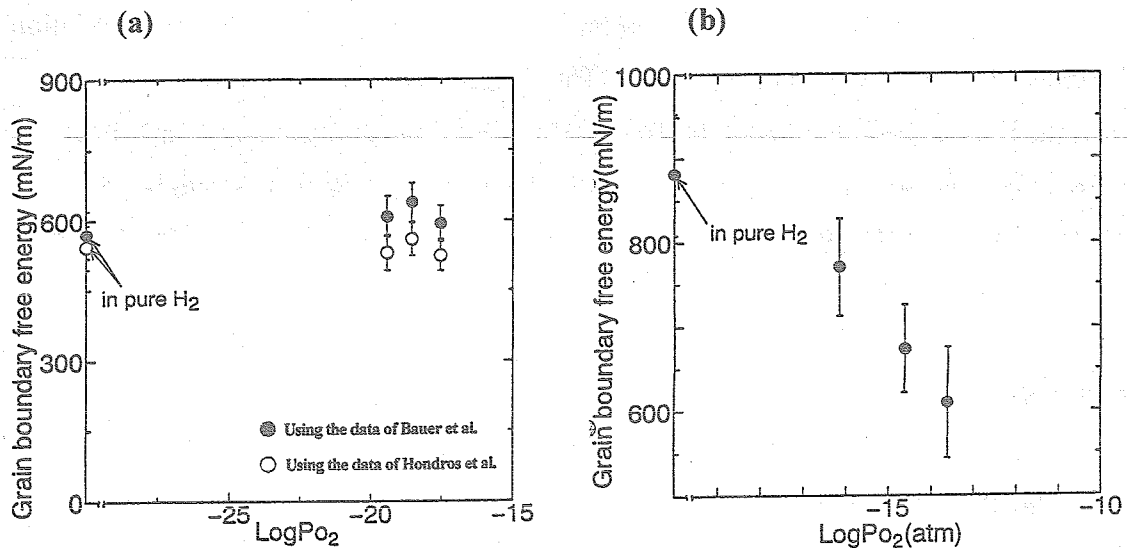


Fig. 5 Grain boundary free energy of (a) Cu at 1273K and (b) Ni at 1573K as a function of the Oxygen Partial Pressure in the gas, $\log P_{\text{O}_2}$.

4. DISCUSSION

Assuming that the Gibbs' adsorption isotherm (3) is valid on the Cu and Ni surface, the excess of oxygen on the surface, Γ_{O} can be computed to be $6.1 \times 10^{-6} \text{ mol/m}^2$ for Cu at 1200K and $7.3 \times 10^{-6} \text{ mol/m}^2$ at 1300K, and $10.5 \times 10^{-6} \text{ mol/m}^2$ for Ni at 1573K.

$$d\gamma/d\ln P_{\text{O}_2} = -RT\Gamma_{\text{O}}/2 \quad (3)$$

where R is the gas constant (8.31J/mol.K).

The computed values for the grain boundary from the Figure 5a and 5b are negligibly small for Cu at 1273K and $4.2 \times 10^{-6} \text{ mol/m}^2$ for Ni at 1573K. For Ni, the Γ_{O} value is comparable with that on the surface. The difference of oxygen adsorption at the grain

boundary between Cu and Ni may be attributed to differences in the solubility limit of oxygen for Cu (0.03 at%) and Ni(0.9 at%).

Currently, scanning probe microscope (SPM) is applied to reveal the adsorption structure of oxygen on metals surface. From the atomic force microscope (AFM) observation for the initial stage of electrochemical oxidation on Cu(111) surface in an aqueous solution [8], we proposed the epitaxial relationship / (3x3)Cu₂O(111)//(7x7) Cu(111). This is also in good agreement with scanning tunneling microscope (STM) images of Cu(111) surface after oxidation at 673K obtained by Jensen et.al [9]. The above epitaxial relationship corresponds the the value $\Gamma_o = 5.4 \times 10^{-6} \text{ mol/m}^2$ which leads to $d\gamma/d\ln P_{O_2} = -64.3 \text{ mN/m}$ at 1250K in agreement with data from the high temperature measurement. On the other hand, Maurice et. al [10] proposed the relation of (6x6)NiO(111) //(7x7) Ni (111) by the STM images in an aqueous solution, from which the Γ_o can be computed to be $10.0 \times 10^{-6} \text{ mol/m}^2$ ($d\gamma/d\ln P_{O_2} = -150.3 \text{ mN/m}$ at 1573K in comparison with -158.2 mN/m by Stickle et al) . These facts strongly suggest that information on the adsorption of oxygen on metal surface obtained by the SPM at room temperature can be also used at high temperature.

REFERENCE

- [1] L. E. Murr , "Interfacial Phenomena in Metals and Alloys" , (1975), Addison-Wesley Publishing Co.
- [2] F. R. Tolman and J. G. Wood, J. Sci. Instrum. Vol.33 , p236 (1956)
- [3] S. Hara, M. Hanao, and K. Ogino, J. Japan Inst. Metals, Vol.57, p164 (1993)
- [4] G. L. Baily and H.C.Watkins, Proc. Phy. Soc. Ser. B, Vol.63, p350 (1950)
- [5] M. MacLean and E. D. Hondoros, J.Mat.Sci. Vol.8, p349 (1973)
- [6] C. E. Bauer, R. Speiser and J.P. Hirth, Met. Trans. Vol.7A ,p75 (1976)
- [7] D. R. Stickle, J. P. Hirth, G. Meyrick and R. Speiser, Met. Trans. Vol.7A, p71 (1976)
- [8] N. Ikemiya, T. Kubo and S.Hara, Surf. Sci. , Vol.232, p81 (1995)
- [9] F. Jensen, F. Besenbacher, E. Laegsgaard and I. Stensgaard, Surf. Sci. Letter, Vol.259 , L774 (1991)
- [10] V. Maurice, H.Talah and P.Marcus, Surf. Sci. Vol.304, p98 (1994)