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Development of the Bubble Technique for the Measurement of the Surface Energy of Solids

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A method for the measurement of the surface energy of copper at 500° C is described. Argon or krypton gas is introduced into a thin surface layer of a specimen by an ion implantation process and subsequent annealing precipitates this gas. At equilibrium the gas pressure in the small bubbles formed is balanced by the surface tension forces and $\gamma = 1560 \pm 160$ erg cm^{-2} has been measured.

1. Introduction

There is a gap in the measurement of absolute surface energy of crystalline solids between the high-temperature zero creep method [1, 2] and the low-temperature brittle fracture methods [3, 4]. The purpose of this paper is to describe a method for the measurement of absolute surface energies at intermediate temperatures, which is applicable to a wide range of materials and which offers the possibility of making such measurements in a contamination-free environment. With measurements made over a wide temperature range an accurate value of the surface entropy may then be obtained.

This method is based on the well-established observation that insoluble inert gases are precipitated in a solid as bubbles when it is heated, thus leading to swelling and warping of fuels and fuel elements in nuclear reactors. The early work of Barnes [5] and of Barnes and Mazey [6], for example, established methods for examining the bubbles and they assumed a value of the surface energy in order to calculate the gas pressure within the bubbles. In the present experiment the gas pressure within the bubbles is found by a gas analysis procedure and the surface energy calculated. In order to facilitate the gas analysis and bubble measurement procedures the inert gas is introduced into specimens in a layer up to 400Å thick by high energy ion-implantation. Subsequently bubbles are formed and the gas pressure brought into equilibrium with the forces due to surface energy by annealing at the desired temperature.

There follows a description of the method for the measurement of the surface energy of copper at 500° C. The significance of the result, $\gamma = 1560 \pm 160$ erg cm^{-2}, is discussed and the limitations of the method are given.

2. Experimental

The pressure, P, in a gas-filled bubble of radius, r, in isothermal quasi-equilibrium with surface tension forces is given by

$$P = \frac{2\gamma}{r} . \qquad (1)$$

The mass of gas in n such bubbles is then

$$PV = \frac{8\pi}{3} \gamma n r^2$$

or more generally

$$PV = \frac{8\pi}{3} \gamma \sum n_i r_i^2 \qquad (2)$$

when the summation is taken over bubbles of all radii found in a typical annealed sample. Equation 2 assumes that the gas in the bubbles follows "ideal behaviour". A full discussion will be given later on the application of actual P–V–T data rather than the ideal gas law to equation 2. It further assumes that the surface "stress" and surface energy of a crystalline solid are identical at thermodynamic equilibrium, as is indeed the case for liquids. It has been shown by Shuttleworth [7] and by Herring [8] that this assumption does not necessarily hold. However Lidiard and Nelson [9] have shown for bubbles in isotropic crystalline solids under the conditions of this experiment that the only significant quantity in thermodynamic equilibrium with the gas pressure is the surface energy. Therefore γ will be referred to as the surface energy of the solid.

Although the detailed kinetics of the growth of bubbles does not concern us here since we are dealing with quasi-equilibrium conditions, it is the small size of the bubbles which enables equilibrium to take place quickly and thus allow the experiment to be extended to temperatures of the order of $T_m/2$, where T_m is the melting point of the solid in ° K. It is expected that, on annealing, all inert gas atoms will be precipitated into agglomerates containing random numbers of atoms from the supersaturated solution which exists after the implantation procedure. With the arrival of vacancies at the agglomerate sites [10] bubbles of different radius form and equilibrium is established. Assuming then that the sizes of the bubbles are randomly distributed about a mean radius, $\bar{r}$, the summation term in equation 2 may be written

$$\sum_i n_i r_i^2 = N(\sigma^2 + \bar{r}^2) \tag{3}$$

where σ is the standard deviation of the distribution and N is the number of bubbles counted in an area, A cm^2. Thus

$$PV = \frac{8\pi}{3} \gamma \frac{N}{A} (\sigma^2 + \bar{r}^2) \; . \tag{4}$$

It should be noted that $(\sigma^2+\bar{r}^2)N/A$ is dimensionless and hence the result is independent of the magnification used for the observation of the bubbles.

PV is found by gas analysis and the quantities on the right-hand side of equation 4 are found by examining electron micrographs of the bubbles.

2.1. Specimen Preparation

Sheets, 6 × 3 cm, consisting of ASARCO copper (99.999 % pure) were prepared by cold-rolling to 125 μm thick, care being taken to avoid contamination from the rolls. After thorough surface cleaning the specimens were electrolytically polished using Disapol D2 solution. The specimens were then annealed in dried hydrogen at 900° C for 48 h and thereafter stored under vacuum until required, particularly after ion-implantation. This treatment is important as one of the surfaces must be preserved throughout the experiment finally to be viewed through using an electron microscope.

The specimen sheets were implanted with 50 keV argon or krypton ions by the AERE, Harwell, Electromagnetic Separation Group. The dose was 5.10^{15} ions cm^{-2} and was given at a rate such that the temperature of the specimen sheet and its holder was less than 200° C. It was estimated that the depth of penetration of the ions was 160 and 400 Å respectively for krypton and argon using the equation developed by Nielson [11].

Working specimens of about 1 cm square were cut from the implanted sheet and annealed at 500° C in 0.2 torr of dried hydrogen for 2 h. For this purpose the specimens were placed with their implanted face uppermost in a vitreous carbon boat which was fitted with a close fitting lid of ASARCO copper sheet. After annealing, a 1 mm wide strip was cut from the periphery of the specimen for gas analysis and the central portion retained for electrolytic back-thinning. The specimen was thinned from the non-implanted side using the "window" method [12]. The implanted surface was protected by a layer of alcohol-insoluble varnish which was removed after thinning by washing with analar grade acetone. Thinned specimens could be stored under redistilled alcohol until they were examined in the electron microscope. It was found that high thinning rates gave best results. With Disapol D2 solution 125 μm thick specimens reached "breakthrough" in no more than 5 min.

2.2. Bubble Analysis

Up to six specimens were taken from widely spaced areas from each thinned square and examined in detail by a 100 keV electron microscope at magnifications up to × 60000. As many micrographs were taken as was possible from each specimen, again at widely spaced intervals, care being taken to avoid photographing areas near thinned edges or holes. Random areas on each print were marked out so as to enclose up to fifty bubbles and the latter measured. The size distribution of the bubbles was plotted on arithmetic probability paper in order to find $\bar{r}$ and σ, and to check that the distribution was random. The other quantities in equation 4, N and A, are the total number of bubbles examined and the total area which was marked out on the prints.

2.3. Gas Analysis

A gas chromatographic technique, described elsewhere [13], was used. It was modified for this

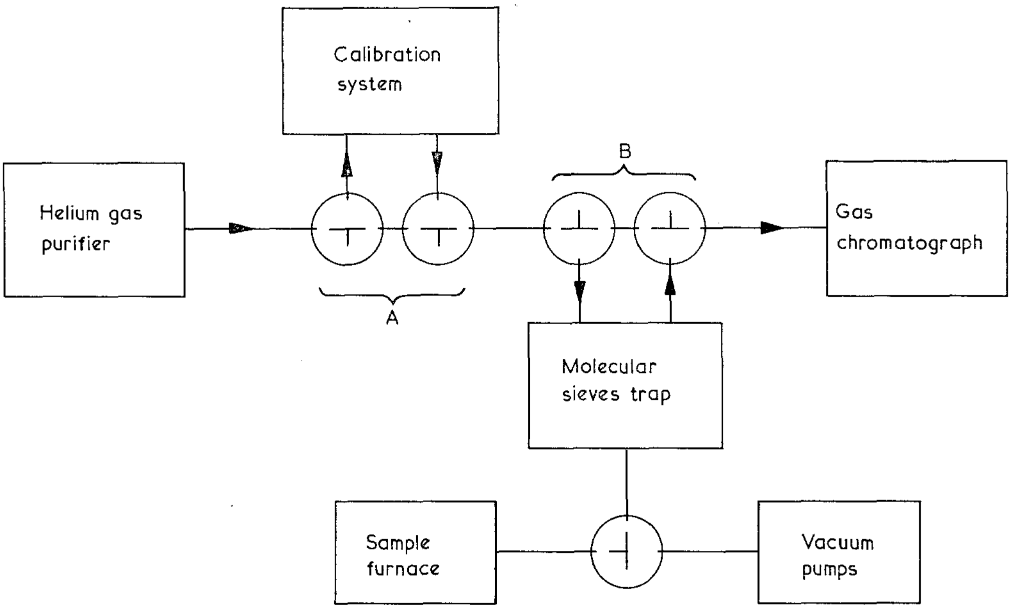

Figure 1 Schematic diagram of the gas analysis system. By manipulating taps A or B the carrier gas stream can be diverted through the calibration system or the trap as desired. In the condition shown, the carrier gas is passing directly from the purifier to the gas chromatograph.

work in order to increase the sensitivity of detection and to separate argon from oxygen efficiently. Traces of the latter gas were sometimes present in the gas mixture extracted from the specimens and, if not separated from argon, could lead to erroneous results. Fig. 1 is a schematic diagram of the sytem. In essence, helium carrier gas transports the gas mixture extracted from the specimen through an analytical column packed with a powdered absorbant. By essentially a multiple distillation process the components of the mixture are separated in time and thus leave the column successively. They are then carried to a sensitive ionisation detector. The 5 m long analytical column was packed with 5 A molecular sieves and used at room temperature. With the helium carrier gas flow rates used, namely 60 cm^3 min^{-1}, the retention times for argon, oxygen, krypton and nitrogen were 300, 315, 720 and 900 sec. The internal calibration system enabled known amounts of any gas to be injected into the carrier gas stream. Normally, calibration was carried out before and after a gas analysis. This was found to be necessary because of the high detector voltage used, which greatly increased sensitivity but made the system susceptible to slight drift. For a detector voltage of 850 V the detection level was 5.10^{-9} cm^3 at NTP for both argon and krypton, but was substantially less for oxygen and nitrogen being only 1.10^{-7} cm^3 at NTP.

Gas analysis specimens of about 2 mm^2 area were cut from the previously prepared strips and melted *in vacuo*. The evolved gas was pumped from the furnace tube into a small molecular sieve-filled trap by the action of the trap itself when at liquid nitrogen temperature. Later the trap was isolated and heated to 200° C, and the

TABLE I Surface energy values for copper annealed at 500° C for 2 h.

$\bar{r} \times 10^{-6}$, cm	$PV \times 10^{-6}$, cm^3 at NTP	γ, erg cm^{-2}	z	$\gamma_{\text{corrected}}$, erg cm^{-2}
0.96	50	922	1.85	1706
0.84	50	591	1.76	1040
1.13	85	953	1.79	1706
1.03	50	1054	1.87	1971
0.88	50	771	1.81	1396
	mean value	856		1560

helium stream diverted through it, thus injecting the gas collected from the sample into the chromatograph. Typical amounts of argon or krypton collected varied upwards from 1.10^{-6} cm^3 at NTP, and together with the known area of the specimens, gave PV at that point. A mean value of the gas analyses of the strip was taken to be representative of the gas trapped in the bubbles of the inner square used in the electron microscope examination.

3. Results and Discussion

Table I gives values of γ. The error in such measurements has been estimated to be 9% being due to a 5% error in the gas analysis and a 4% error in the measurement of $\bar{r}$ and A. We conclude that the surface energy for copper at 500° C is $\gamma = 860 \pm 80$ erg cm^{-2}. However the ideal gas law cannot apply under these conditions, for substitution of $\bar{r}$ into equation 1 enables the pressure to be found in a bubble of that radius and it must be in the region of 1500 atm. If the Van der Waals equation is used, negative pressures are found. Recourse was therefore made to actual P–V–T data. These data can be expressed as a series of reduced parameter curves by plotting z as a function of P_R and T_R as in fig. 2. Here z is the compressibility factor of a real gas, its departure from unity being the measure of departure from real behaviour. That is to say, $(PV)_{\text{real gas}} = z(PV)_{\text{ideal gas}}$. $P_R = P/P_C$ and $T_R = T/T_C$ are the reduced pressure and temperature parameters, where P_C and T_C are the critical pressure and temperatures of gas used. The use of P_R and T_R is helpful because the data for krypton and argon form one set of curves since the law of corresponding states applies particularly well to these two gases.

The data of Din [14] for argon and of Trappeniers *et al* [15] for krypton were used. Since these data did not fully cover the range required they were extrapolated using an equation of the form $z^2 + az + bP_R + c = 0$ for constant T_R. The constants a, b and c were fitted to the experimental data for $P_R > 9$. An interpolation was made from the low temperature curves ($T_R < 3.6$) which enabled the higher temperature curves to be drawn. Slightly lower values of z are obtained in this manner for $P_R > 30$ than those predicted by complex equations of state,

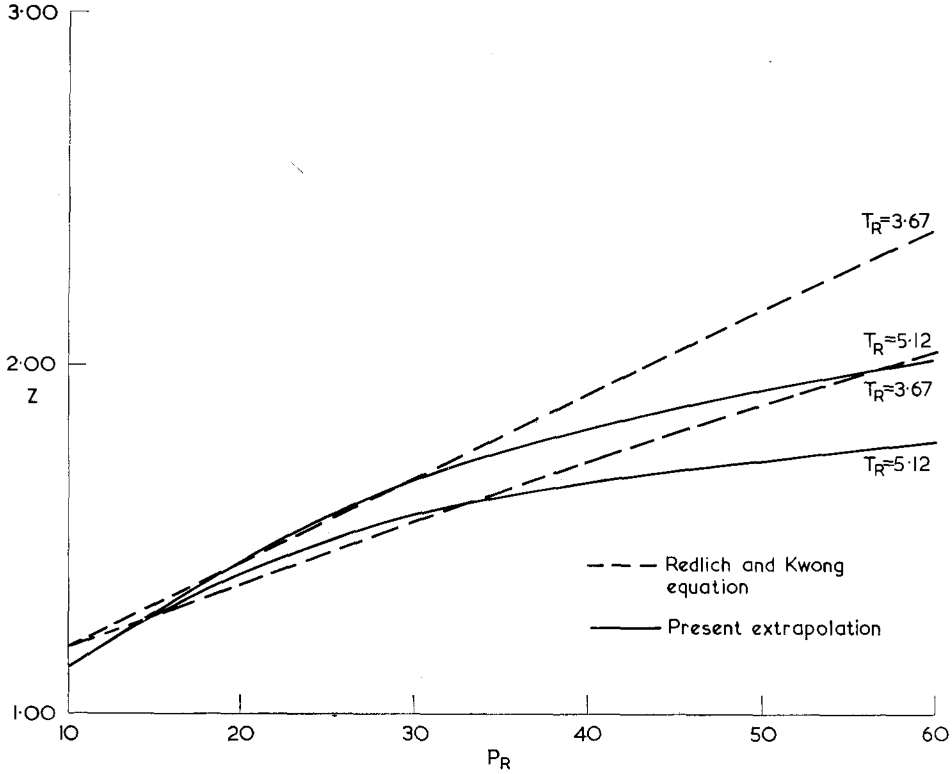

Figure 2 Reduced parameter curves for argon ($T_R = 5.12$) and krypton ($T_R = 3.67$).

such as the Redlich and Kwong [16] formula, which are given in fig. 2 for comparison.

The appropriate value of z was found from the curves using the experimental values of $\bar{r}$ and γ to calculate P_R. A reiterative process was carried out until z converged to a single value, an example of which is given in table II. In this manner the final two columns in table I were prepared. The curves of fig. 2 were preferred to the nearly straight line graphs predicted by the Redlich and Kwong equation as z did not converge to a single value when the latter were used, even after many iterations. Thus, assuming the curves to be exact, a corrected value of the surface energy of copper is $\gamma = 1560 \pm 160$ erg cm^{-2}.

TABLE II The gas-law correction of the surface energy values.

Number of iterations	z	$\gamma_{\text{corrected}}$
0	1.00	858
1	1.65	1416
2	1.78	1527
3	1.81	1553
4	1.81_5	1557

This value of γ for copper may be compared with the high temperature results summarised by Inman and Tipler [17] who give $\gamma = 1730$ erg cm^{-2} and that of Hondros and McLean [2] who give $\gamma = 1420 \pm 40$ erg cm^{-2} at 1200° K. The former results were obtained in conditions of unknown but low oxygen concentration at the surface of the specimen, whereas the measurement of Hondros and McLean was carried out in a known and carefully controlled environment. Nevertheless it is difficult to see why earlier measurements should give higher values because any effects due to oxygen must lower the value [18]. Using $\gamma_{1200°\text{K}} = 1420$ and $\gamma_{770°\text{K}} = 1560$ erg cm^{-2}, since the source of the copper specimens used was common to both measurements, $d\gamma/dT$, the surface entropy, is -0.3 erg cm^{-2} °C^{-1}. This result may be compared with that obtained by Hondros and Stuart [19] for oxygen-free 3% Si–Fe alloys, namely, -0.36 erg cm^{-2} ° C^{-1}. Moreover -0.3 erg cm^{-2} ° C^{-1}, corresponds to 2.6 cal mole^{-1} ° C^{-1} and is thus comparable with the entropy of fusion which, according to Richards' rule, is 2.2 cal mole^{-1} ° C^{-1}.

The lower practical limit for the measurement of surface energy by this method is near $T_m/2$ (400° C for copper) as the limiting step is volume diffusion. (Although surface diffusion is undoubtedly occurring this process may alter the shape of the bubbles and not their size.) This low temperature results from the small diffusion distances involved which enable equilibrium to be established quickly. In the zero creep experiment where the diffusion distances are $\sim 10^3$ times greater, the lower practical limit is near $3T_m/4$. If the bubble annealing times are extended to 300 h, a typical period for the zero creep experiment, it is possible that the bubble experiment may be viable at temperatures as low as 350° C for copper. (There is virtually no loss of implanted gas in copper when it is heated at 385° C for 100 h.) The upper limit of the bubble experiment in copper is 700° C owing to the high

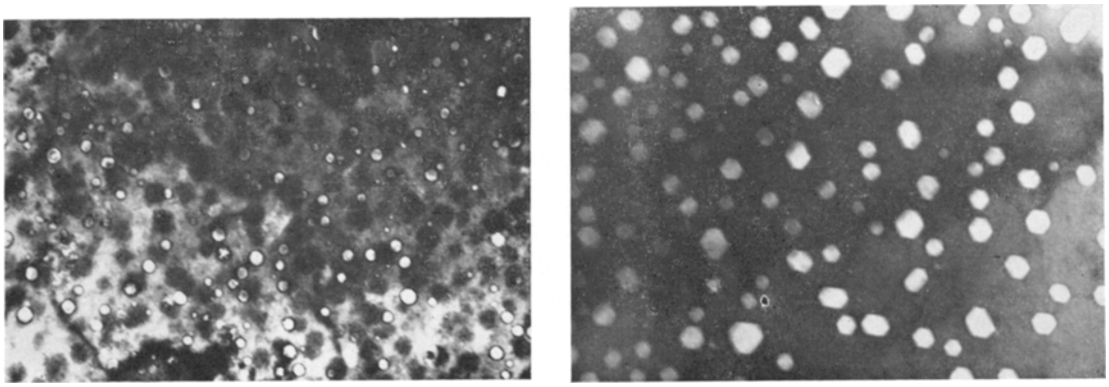
(a) (b)

Figure 3 (a) Argon bubbles in copper annealed in dried hydrogen for 2 h at 500° C. (b) Argon bubbles in copper annealed at 500° C for 2 h in a vacuum of 1 to 10^{-5} torr.

evaporation rate at this temperature. With possible surface loss at the rate of 40 Å h^{-1} the loss of implanted gas becomes important. For example, after a 2 h anneal there is less than 1% of the implanted gas remaining in a sample.

The implantation process itself can alter the effectiveness of the bubble experiment in an unexpected way. Although copper surfaces are not affected, aluminium surfaces become etched during implantation. This etched surface is retained throughout the experiment and these artefacts mask the bubbles which have been formed immediately underneath.

The bubble experiment can only give an average value of surface energy as anisotropic effects cannot be taken into account. These effects appear to be quite small as the bubbles are nearly spherical when the specimen is annealed in hydrogen. On the other hand, when the specimens were annealed in a vacuum of 5 to 10×10^{-6} torr the bubbles were faceted and the average value of the surface energy was found to be low, as can be seen in fig. 3. It is thought that oxygen had diffused to the bubble surfaces during annealing.

The main criticism of the experiment is that only a small sample of bubbles was taken and consequently this should be representative of all bubbles in the specimen. The scatter of the results in table I is thought to be due to this problem. It is possible to measure a larger number of bubbles instrumentally by using the "Quantimet" image analyser thus minimising this effect. This was attempted but the poor and variable contrast between the bubbles and the background on the photographic prints prevented the use of this instrument.

4. Conclusions

The surface energy of copper has been measured at 500° C by a new method and found to be $\gamma = 1560 \pm 160$ erg cm^{-2}. This result, and that of Hondros and McLean, together enable the surface entropy to be calculated as -0.3 erg cm^{-2} ° C^{-1}. It is believed that this technique could be refined so as to yield more precise values of surface energies. However, as all experimental steps have a critical effect on the final figure, the yield is low.

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