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NUCLEATION OF SODIUM BOILING FROM SURFACE CAVITIES CONTAINING GAS

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Abstract—An analytical expression is derived for the increase in vapour pressure required to nucleate boiling of sodium due to diffusion of inert gas out of surface cavities. This results in an increase of superheat with heating time. The main result of the theory is confirmed quantitatively by the experimental work described.

NOMENCLATURE

A,	surface cavity meniscus area, πr^2;
c,	concentration;
D,	diffusion coefficient;
h,	Henry's Law constant;
M,	molecular weight;
m,	mass;
P,	pressure;
P_v,	vapour pressure;
P'_g,	initial gas pressure;
P_g,	partial pressure of gas;
R,	universal gas constant;
r,	cavity radius;
S,	saturation solubility;
T,	temperature [°K];
T',	initial temperature [°K];
T_0,	temperature of nucleation when heated infinitely quickly from T' to T_n so no gas is lost [°K];
T_n,	temperature of nucleation [°K];
t,	time [s];
V_c	cavity volume;
y,	distance from meniscus;
α,	$\dfrac{ART}{h(T)MV_c}$;
σ,	surface tension;
τ,	time constant [s];
μ,	viscosity.

1. INTRODUCTION

THIS paper is concerned with the nucleation of sodium boiling at surface cavities and the effect of the diffusion of inert gas out of the cavities during heating. In previous work in the field [1] a numerical solution was obtained to the exact equations of heat conduction and gas diffusion applied to an ideal cylindrical cavity assuming plane diffusion through one end. In the present work, an analytical solution is obtained by considering diffusion at constant temperature. The predictions have been tested experimentally and the results are described in section 5.

The vapour pressure necessary to nucleate boiling is given by,

$$P_v = P - P_g + \frac{2\sigma}{r}. \qquad (1)$$

We assume r is constant for given preboiling conditions e.g. [2].

2. GAS DIFFUSION OUT OF CAVITIES

P_g depends on the initial partial pressure of gas in the cavity P'_g. Neither P'_g nor P_g can be measured. However, the equilibrium state of a stagnant sodium system with a cover-gas is when the partial pressure of the gas is everywhere the same and equal to the cover-gas pressure. Then P'_g is known, but the length of time required to reach equilibrium depends on the rate at which the gas diffuses through the liquid, in an unstirred system this may take many days.

Inert gases are used to cover liquid sodium and the solubilities of inert gases in sodium increase exponentially with temperature. If the temperature is increased, the gas will dissolve and diffuse away from the surface cavities thus reducing P_g. The rate of losing gas depends on the solubility and diffusion coefficient, both of which increase with temperature. In the theory developed here it is assumed that all the gas is dissolved at a constant temperature T. This corresponds to an ideal experiment in which the sodium is heated infinitely quickly from its initial temperature T' to T, held at T for time t and then heated infinitely quickly to nucleation at T_n. This ideal procedure leads to equations which can be solved analytically and to the useful idea of a time constant for gas loss which depends on the temperature and gas.

Assuming that the cavity volume V_c remains constant and starting with the known initial gas pressure P'_g at T', the pressure will have risen, by Charles' Law, to $P'_g T/T'$ when diffusion starts. It is likely that the sodium–gas interface is near the bottom of a surface pit (Fig. 1) and prevented from entering further by a non-wetted impurity (perhaps a non-metallic inclusion). Because the main barrier to diffusion is then between the meniscus and the cavity mouth, the plane diffusion equation is used. This is an idealization of a complex and unknown geometry but is thought to be better than the simple alternative assumption of spherical diffusion.

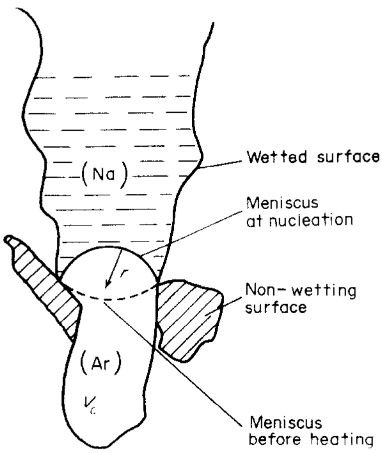

FIG. 1. A surface cavity with non-wetting advancing meniscus and wetting receding meniscus.

The model is thus a cavity of constant volume which loses gas by plane diffusion through area A.

The plane diffusion equation is

$$\frac{\partial^2 c}{\partial y^2} - \frac{1}{D}\frac{\partial c}{\partial t} = 0 \tag{2}$$

where $c(y, t)$ is the concentration at time t, at a distance y from the interface. The two boundary conditions are as follows, at $t > 0$ and $y = 0$

(i) the interface concentration is equal to the solubility.

$$c(0, t) = S = P_g/h(T) \tag{3}$$

(ii)

$$\frac{dS}{dt} - \frac{ARTD}{h(T)MV_c}\frac{\partial c}{\partial y} = 0. \tag{4}$$

This boundary condition arises in the following ways, assuming the gas behaves ideally

$$AD\frac{\partial c}{\partial y} = \frac{dm}{dt} = \frac{V_c M}{RT}\frac{dP_g}{dt} \tag{5}$$

and using (3) gives (4).

The solution to this problem [3] is, when $c(y > 0, 0)$ is negligible which it is if $T \gg T'$ since the solubility increases so rapidly with temperature

$$c(0, t) = c(0, 0)e^{\alpha^2 Dt}\,\mathrm{erfc}\,[\alpha\sqrt{(Dt)}]$$

where

$$\alpha = \frac{ART}{h(T)MV_c}.$$

Therefore at nucleation

$$P_g = P'_g\frac{T_n}{T'}e^{\alpha^2 Dt}\,\mathrm{erfc}\,[\alpha\sqrt{(Dt)}] \tag{6}$$

and equation (1) may be written

$$P_v - P = \frac{2\sigma}{r} - P'_g \frac{T_0}{T'} e^{\alpha^2 Dt} \operatorname{erfc}[\alpha\sqrt{(Dt)}]. \qquad (7)$$

From this difference in pressure, the superheat is found from vapour pressure tables.

To see how the rate of loss of gas varies with temperature a "typical" cavity volume is postulated to have a radius of 1 μm and be a cone 5 μm deep. A time constant τ is then defined as the time to drop to $S = 0{\cdot}5\ S_0$ and these are tabulated below (using solubilities and D from [4]).

Table 1. *Time scales for loss of gas*

T(°C)	τ, argon (s)	τ, helium (s)
500	200,000	300
600	6000	30
700	400	4
800	40	0·7
900	6	0·1
1000	1	0·02

Two predictions from the theory are:—

(i) The timescale required for the diffusion process is of order τ from Table 1.

(ii) The difference in superheats between zero and long heating times is given in pressure terms by

$$P'_g \frac{T_0}{T'}$$

with a small correction for surface tension changes with temperature.

3. APPARATUS

The apparatus (described in detail in [4]) is a stainless steel tube 7 mm bore, heated by high frequency induction heating over about 40 mm. The temperature was measured in the centre of the tube by a 0·5 mm stainless steel sheathed chromel–alumel thermocouple.

4. PROCEDURE

The apparatus was left at 1 atm ($1{\cdot}01 \times 10^5$ N/m^2) for 14 days with trace heating giving a value of T' of 390°C. 14 days was long enough for argon to diffuse down to the test region.

The main series of experiments was performed at 1 atm by heating quickly from 390°C to 800°C, then holding at 800 ± 25°C by switching the heater on and off manually for the period of time shown on the abscissa, and finally heating rapidly until nucleation occurred. The results are plotted on Fig. 2.

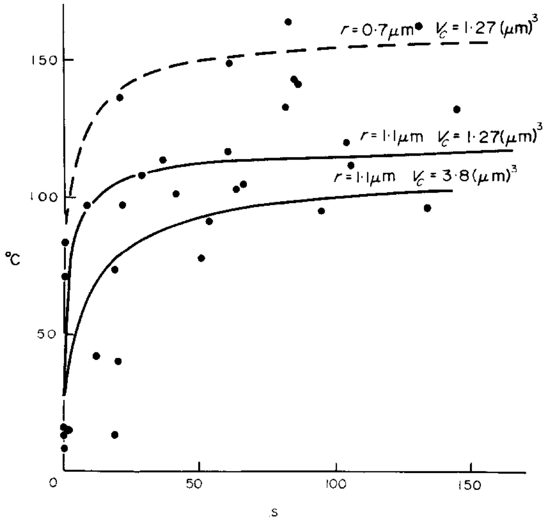

FIG. 2. Superheat against time at 800°C (argon cover-gas, $T_{\text{sat}} = 881$°C).

Following each run the system was left for some hours to regain equilibrium conditions with the cover-gas. Because such a small volume of sodium was heated, the net departure from equilibrium due to boiling was not very great. Sodium from the pool would mix with the re-entering sodium and the time to reach equilibrium runs would be of the order of the time taken to diffuse the tube radius, $t \sim x^2/D \sim h$.

Boiling with helium cover gas was done at a saturation temperature of 688°C (pressure

$1{\cdot}1 \times 10^4\ \mathrm{N/m^2}$) after being left to saturate with helium at 1 atmosphere for three days. A different heating procedure was used in which the power control on the heater was varied to give total heating times from 3 to 14 s with no hold time.

To see if argon was lost from cavities continuously during a series of fast-transient heating boiling experiments performed in rapid succession, the sodium was boiled eight times in succession at

(i) the same pressure as that at which it was saturated

(ii) a lower pressure ($1{\cdot}6 \times 10^4\ \mathrm{N/m^2}$).

5. RESULTS

5.1 *Argon diffusion at 800°C, followed by boiling at atmospheric pressure*

The superheat measurements obtained by keeping the liquid sodium for varying lengths of time at 800°C before heating to nucleation are plotted in Fig. 2. The main features of the results are exhibited by averaging into discrete time intervals.

Table 2.

Time interval (s)	Superheat (°C)
0–30	57 ± 12
31–60	108 ± 10
61–90	131 ± 12
91	120 ± 10

It appears that an asymptote of 125 ± 7°C is reached after a minute. This corresponds to a vapour pressure of $2{\cdot}85 \times 10^5\ \mathrm{N/m^2}$. Assuming this asymptote corresponds to $P_g = 0$ equation 1 gives:

$$P_v - P = \frac{2\sigma}{r} = 1{\cdot}84\,(\pm 0{\cdot}14) \times 10^5\ \mathrm{N/m^2}$$

$$\therefore \qquad r = 1{\cdot}1 \pm 0{\cdot}1\ \mu\mathrm{m}.$$

At zero hold times the superheats average to 34° ± 12° which correspond to a vapour pressure of $1{\cdot}36 \times 10^5\ \mathrm{N/m^2}$. Thus using equation (1), the gas pressure at 915°C (saturation temperature of 881° plus 34° of superheat) is $1{\cdot}67\ (\pm 0{\cdot}25) \times 10^5\ \mathrm{N/m^2}$.

The theoretical difference is

$$\frac{T_0}{T'} P'_g = 1{\cdot}8 \times 10^5\ \mathrm{N/m^2}.$$

Theoretical lines are drawn on the graph using equation (7).

The results of an earlier argon experiment with a different test section and a slightly different heating procedure are shown in Fig. 3. The rate of increase of superheat with hold times is less rapid, as predicted by the theory for a lower temperature.

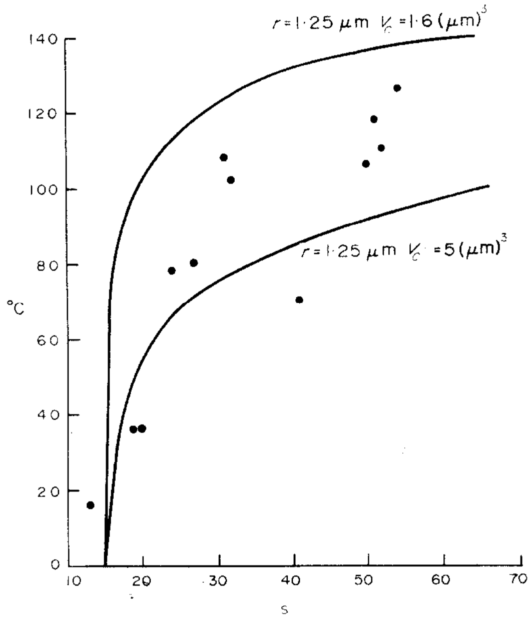

FIG. 3. Superheat against total heating time (argon cover-gas, $T_{\mathrm{sat}} = 805$°C $T = 750$°C).

5.2 *Helium experiments*

The helium results are shown on Fig. 4. The line drawn on the graph has a gradient of 10°C s^{-1}. Equation (7) is not valid because of the different procedure. The experiments were concluded by failure of the test section.

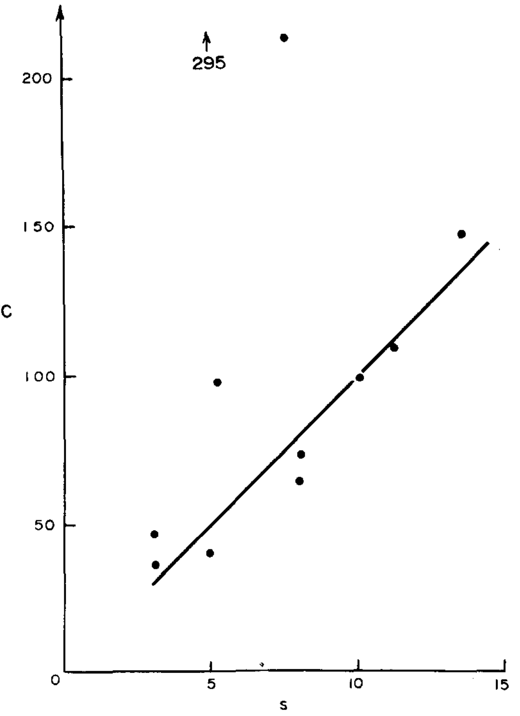

FIG. 4. Superheat against total heating time (helium cover-gas, $T_{sat} = 688°C$).

5.3 *Repeated boiling*

The results for boiling eight times in rapid succession are summarized below. At the start of each series the gas pressure in the cavities was one atmosphere.

Table 3.

Sat. pressure (10^5 N/m^2)	Sat. temp.	Mean of first 4 superheats (°C)	Mean of second 4 superheats (°C)
1·0	881	55 ± 14	54 ± 20
0·16	711	60 ± 17	104 ± 26

6. DISCUSSION

The results from two different test-sections in which sodium was boiled with an argon cover-gas, show an increase of superheat with heating time over a timescale consistent with the theory.

The results with helium cover-gas also show an increase of superheat with heating time although the results are not in quantitative agreement with the theory. From the expected timescale of 4 s for helium loss at 700°C one would expect a larger rate of increase of superheat than the observed 10°C s^{-1}. Also, with the 1·1 μm radius of the cavity calculated from the argon measurements on the same test section the minimum superheat predicted is 142°C, and when t is very long so that $P_g = 0$ the superheat is 277°C. Thus, most of the measurements, including all the ones which give the slope of 10°C s^{-1}, are less than the predicted minimum.

A possible explanation is that surface active impurities are present on the liquid–gas interface. These have two effects: (a) σ is reduced, a drop of 30 per cent would account for the helium results (such a reduction of surface tension due to saturation with oxygen has been reported [6]), (b) solution of gas is hindered; the rate of absorption of nitrogen by liquid iron is reduced to 5 per cent of its initial value by the addition of 0·02 per cent of oxygen to the iron [7]. It is also known [8] that surface activity decreases with temperature. Thus at higher temperatures surface activity may be unimportant.

The two very high results on Fig. 4 do agree with the gas loss theory. These two results occurred after the heater had already been on in error which led to what were considered to be negligible temperature increases (390–450°C) in the gas loss context, but could be significant in disturbing surface activity. Since these two results are near the maximum theoretical superheat in less than 8 s they are in agreement with Table 1 timescales.

The "ageing" results of Table 3 give an indication of how the gas in solution changes with repeated boiling. At atmospheric pressure, the superheat is not measurably affected. This is because the dissolved argon in the bulk sodium above the test section is in equilibrium with the cover-gas. At reduced pressure, however, argon leaves solution at the free surface and each boiling run will tend to bring sodium containing less argon down to the test section. P'_g decreases and so P_v must increase.

7. CONCLUSIONS

The importance of the gas partial pressure in the nucleating cavity on the superheat needed to initiate boiling of sodium has been clearly demonstrated.

In a fast reactor, the saturation temperature is over 1000°C. The timescale for argon loss is under a second. If surface cavities are the only nucleation sites available high superheats will result.

REFERENCES

1. R. M. Singer and R. E. Holtz, On the role of inert gas in incipient boiling liquid metal experiments, *Int. J. Heat Mass Transfer* **12**, 1045–1060 (1969).
2. R. E. Holtz, The effect of the pressure temperature history upon incipient boiling superheats in liquid metals, Argonne National Laboratory report 7184 (1966).
3. H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, 2nd ed., p. 306. Oxford University Press (1959).
4. P. K. Holland, CNAA Ph.D. Thesis (1972).
5. R. M. Singer and R. E. Holtz, A study of the incipient nucleation of sodium, Paper B.8.6. *Heat Transfer 1970* Vol. VI. Elsevier, Amsterdam (1970).
6. D. H. Bradhurst and A. S. Buchanan, Surface properties of liquid sodium and sodium–potassium alloys in contact with metal oxide surfaces, *Aust. J. Chem.* **14**, 397–408 (1961).
7. P. Kozakevitch, Surface activity in liquid metal solutions, S.C.I. monograph No. 28, p. 233, S.C. I. (1968).
8. K. D. Hondros, Energetics of solid–solid interfaces, *Proc. Interfaces Conf. Melbourne.* Butterworth, London (1969).

NUCLEATION DE SODIUM EN EBULLITION A PARTIR DE CAVITES SUPERFICIELLES CONTENANT DU GAZ

Résumé—On a obtenu une expression analytique pour l'augmentation de pression de vapeur nécessitée pour l'ébullition nucléée de sodium due à la diffusion d'un gaz inerte depuis des cavités superficielles. On en déduit une augmentation de surchauffe avec le temps d'échauffement. Le résultat principal de la théorie est confirmé quantitativement par le travail expérimental décrit.

DIE KEIMBILDUNG BEIM SIEDEN VON NATRIUM AN GASGEFÜLLTEN OBERFLÄCHENPOREN

Zusammenfassung—Für die Zunahme des Dampfdruckes, die notwendig ist, um Blasensieden von Natrium zu ermöglichen, wenn Inertgas aus den Oberflächenporen diffundiert, wird ein analytischer Ausdruck abgeleitet. Diese Zunahme bewirkt einen Anstieg der Überhitzung mit der Heizzeit.

Das wichtigste Ergebnis der Theorie wird quantitativ bestätigt durch die hier beschriebene experimentelle Arbeit.

ОБРАЗОВАНИЕ ПУЗЫРЕЙ ИЗ СОДЕРЖАЩИХ ГАЗ ПОЛОСТЕЙ ПРИ КИПЕНИИ НАТРИЯ

Аннотация—Дается аналитическое выражение процесса роста давления пара до величины, необходимой для возникновения пузырькового кипения натрия, вызываемого диффузией инертного газа из полостей на поверхности. В результате диффузии инертного газа величина перегрева увеличивается со временем. Основной теоретический вывод количественно подтверждается описываемыми экспериментами.