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NUCLEATION OF VOIDS IN METALS DURING
DIFFUSION AND CREEP

By
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May 24, 1956

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Bayside, New York

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TABLE OF CONTENTS

	<u>Page No.</u>
ABSTRACT.....	4
I. INTRODUCTION.....	5
II. DEGREE OF VACANCY SUPERSATURATION FOR THE NUCLEATION OF VOIDS IN ALPHA-BRASS.....	6
A. Method.....	6
B. Experimental Details.....	7
C. Results.....	7
III. EFFECT OF PURIFICATION ON VOID FORMATION...	11
IV. VOID FORMATION DURING CREEP.....	14
A. Experimental Details.....	15
B. Results.....	15
V. DISCUSSION.....	16
VI. CONCLUSIONS.....	18
REFERENCES.....	22

ABSTRACT

Experimental evidence is presented which proves that voids formed during diffusion in brass are heterogeneously nucleated. The nuclei appear to be oxide particles, probably ZnO. When these are removed by re-melting, voids practically do not form upon subsequent dezincification. Brass which had been freed of void nucleation catalysts exhibited a considerably reduced tendency for grain boundary cracking during creep, and increased stress-rupture life.

I. INTRODUCTION

Numerous experiments in the past few years have proven that void formation occurs quite generally in the diffusion zone of bi-metal specimens.⁽¹⁻⁴⁾ The phenomenon has been explained in terms of the generation of lattice vacancies by unequal diffusion and their eventual precipitation as holes.⁽⁵⁾ Attention has recently been directed to the fact that voids also form within homogeneous metals during high-temperature creep.⁽⁶⁾ The idea has been put forward that these voids form by the condensation of excess lattice vacancies generated by intersecting dislocations.^(6,7)

If the precipitation of lattice vacancies from solution is treated as a nucleation and growth process, the predicted vacancy concentration for homogeneous nucleation of voids at an observable rate is 100 to 1000 times the normal thermal equilibrium concentration. It appears that voids actually form during diffusion at vacancy supersaturations which are much lower than this.⁽⁸⁾ According to the calculations of Machlin,⁽⁷⁾ the same must be true for voids formed in homogeneous metals during creep, if these are considered to arise from the precipitation of lattice vacancies. Therefore it seems, if the vacancy mechanism is valid, that the holes which form in diffusion and creep specimens are heterogeneously nucleated by imperfections or impurities in the metal. Irregularities in the frequency and distribution of voids in diffusion couples bear out this explanation.^(5,8)

It is not known at the present time what the nuclei are on which vacancies condense. Various investigators have speculated that they could be certain dislocation configurations, already existing voids produced during solidification or working, gas pockets, or inclusions in the metal. Relatedly, the precise value of the degree of vacancy supersaturation for void nucleation is still uncertain. An initial attempt to estimate this value from diffusion data made by Balluffi,⁽⁸⁾ indicated that voids form in diffusion couples at vacancy concentrations which may be anywhere from 0.1 to 10% above the equilibrium concentration. He concluded that the excess concentration is most likely less than 1%.

The value of the excess vacancy concentration required to nucleate voids is of considerable significance, since it supplies a clue to the nature and size of the nuclei upon which voids form. For example, on the basis of the above estimate of 1% supersaturation, Machlin concluded that nucleation of voids probably does not occur at all, but the voids simply grow from pre-existing submicroscopic holes.⁽⁷⁾ This value is also important in the formal theory of diffusion, since the validity of Darken's analysis of the Kirkendall effect⁽⁹⁾ depends upon the existence of an equilibrium concentration of lattice defects at all times in the diffusion zone.⁽¹⁰⁾ The formation of voids indicates that there must actually be some deviation from equilibrium, at least that required to nucleate voids. Hence, it was considered worthwhile to attempt a more accurate estimate of the degree of vacancy supersaturation for the formation of voids during diffusion. Experiments were also performed to compare void formation during diffusion and creep in alpha-brass and to study the effect of purification upon void formation in this material.

II. DEGREE OF VACANCY SUPERSATURATION FOR THE NUCLEATION OF VOIDS IN ALPHA-BRASS

A. Method

The instantaneous excess vacancy concentration at any point in the diffusion zone is determined by a balance between the rate of generation of vacancies due to unequal diffusion, and the rate of disappearance at various sinks. Assuming a vacancy diffusion mechanism, the rate of generation of vacancies can be computed from the concentration-distance curve, and a knowledge of the intrinsic diffusion coefficients.⁽⁸⁾ The rate of disappearance is obtained by estimating an appropriate distribution of vacancy sinks. With the above information, it is possible to associate an excess vacancy concentration with each point of the diffusion curve or each plane in the diffusion zone. The excess vacancy concentration at that plane at which voids are just observed is taken as the critical excess for nucleation.

In applying the above method, in order to compute the rate of generation of vacancies, Balluffi⁽⁸⁾ used a

variety of photomicrographs of diffusion zones from various sources and superimposed upon these estimated concentration-penetration curves. In no instance was the concentration-penetration curve available for the actual specimen in which the voids occurred. Hence, there is some uncertainty about the precision of correlation between the diffusion curve and the boundaries of the porous zone. In order to obtain a more accurate estimate of the critical generation rate and degree of supersaturation of vacancies, an experiment was carried out in which the concentration-penetration curve was measured directly in the porous specimen, and the relationship between the diffusion curve and the zone of void formation accurately determined.

B. Experimental Details

The diffusion experiments were carried out with a commercial high-purity brass containing 95% Cu and 5% Zn, the analysis of which is given in Table I. This material was of the same quality as that used for many similar experiments in our laboratory but of lower Zn content, which was preferable for the contemplated experiment. Discs two inches in diameter by 1/4" thick were prepared with accurately flat surfaces. These were heat treated in a continuously evacuated furnace at several temperatures and for various times. During heat treatment, zinc was evaporated from the specimen surface with the formation of voids in the interior. The use of specimens of this type in diffusion experiments has been described in the past.⁽⁴⁾

Following heat treatment, the specimens were sectioned, polished, and the cross-section examined to ascertain the depth of the porous zone. This depth was measured using a filar micrometer, many measurements being taken in order to obtain a good average value. Layers were next machined from the face perpendicular to the diffusion direction and chemically analyzed to obtain the concentration vs. distance curve.

C. Results

Microscopic examination of cross-sections after heat-treatment revealed the expected formation of voids just below the specimen surface (Fig. 1). Diffusion times and

temperatures had been chosen so that the diffusion zone did not extend far into the specimen. Distances from the surface to the inner edge of the porous layer, indicated by the dashed line in Fig. 1, are given in Table II. These distances were measured near the disc center, where diffusion was essentially unidirectional. It must be noted that it was difficult to locate the inner edge of the porous zone precisely, which is taken as the advancing front of void precipitation, because of a slight pitting over the entire polished surface. That distance was selected beyond which the pitting seemed to be uniform.

Superimposed upon the photomicrograph of Fig. 1 is the concentration-penetration curve determined by slicing and chemical analysis. Values of the overall or chemical diffusion coefficient computed from these curves by the Boltzmann-Matano method varied within 50 percent from those published by Horne and Mehl,⁽¹¹⁾ who used sandwich couples, and by Resnick and Balluffi,⁽¹²⁾ who used vapor-solid couples. Therefore, the value of the diffusion coefficient was apparently not greatly affected by the presence of voids in the brass, nor by zinc being diffused out instead of in.

The concentration-penetration curves were used to estimate the excess vacancy concentration at the boundary of the porous region by the method discussed previously. It is assumed that vacancies are pumped into each region of the specimen tending to lose mass because of the unequal diffusion of zinc and copper. Presumably, these excess vacancies are eliminated mainly by absorption at dislocations within this region. If a steady state is reached with respect to the vacancy concentration at each point in the diffusion zone, an assumption which seems reasonable in view of the much more rapid diffusion of vacancies than zinc or copper atoms, then the relative excess concentration of vacancies, $R = \frac{N_v}{N_{v0}} - 1$, is

$$R = -\left(\frac{N\tau}{N_{v0}}\right) \cdot \frac{\partial}{\partial x} \left[(D_{Zn} - D_{Cu}) \frac{\partial X_{Zn}}{\partial x} \right] \quad (1)$$

where N is the number of atoms per unit volume, N_v is the steady state vacancy number, N_{v0} the number of vacancies in thermal equilibrium with the lattice, τ the vacancy lifetime, D_{Zn} , D_{Cu} the intrinsic diffusion coefficients of zinc and copper, and X the mol fraction. Assuming that the ratio of the intrinsic diffusion coefficients, $K = \frac{D_{Cu}}{D_{Zn}}$ is independent

of concentration, the expression used by Balluffi(8) is obtained,

$$R = \left(\frac{N\tau}{N_{vo}} \right) \cdot \left[\frac{K-1}{X_{cu} + KX_{zn}} \right] \left[D \frac{\partial X_{zn}}{\partial x} + \left(\frac{\partial X_{zn}}{\partial x} \right)^2 \left(\frac{\partial D}{\partial X_{zn}} + \frac{D(1-K)}{X_{cu} + KX_{zn}} \right) \right] \quad (2)$$

where $D = (X_{cu} D_{zn} + X_{zn} D_{cu})$ is the chemical diffusion coefficient.

A simpler expression may be derived if it is assumed that the difference of the intrinsic diffusion coefficients, rather than the ratio, is independent of composition:

$$R = - \frac{N\tau}{N_{vo}} \cdot (D_{zn} - D_{cu}) \frac{\partial X_{zn}}{\partial x} \quad (3)$$

Since D is almost constant in the range 0 - 5% Zn we may closely approximate the diffusion curve by the Van Ostrand-Dewey equation, and R may therefore be expressed as follows:

$$R = \frac{N\tau}{N_{vo}} \cdot [D_{zn} - D_{cu}] \left[\frac{X X_{zn}^1}{2\sqrt{\pi}(Dt)^{3/2}} \exp. \left(- \frac{x^2}{4Dt} \right) \right] \quad (4)$$

In this equation, X_{zn}^1 is the initial concentration of Zn in the brass. Both equations (2) and (4) have been used to calculate R and yield values which differ by less than ten percent.

Recognizing that $\frac{N_{vo}}{\tau}$ is the rate of disappearance of vacancies at equilibrium, which is also the rate of generation at equilibrium, it can be seen that R is equal to the ratio of the rate at which vacancies are pumped into a given region by diffusion to the rate at which they are spontaneously generated by thermal fluctuations.

Table II presents values of the rate of generation of vacancies at the void precipitation front calculated from the diffusion data for a number of 5% Zn brass samples. It will be observed that the value for the critical rate decreases with increasing time of diffusion. This may be due to the longer time available for growth of voids in the long-time specimens permitting a more accurate location of the nucleation front in these. If appreciable growth is necessary for a freshly nucleated hole to become visible, the observed front of the porous zone will tend to lag behind the nucleation front. For

this reason the measured depths probably tend to fall on the low side. The critical generation rates given in Table II are lower, on the average, than those estimated by Balluffi, but not greatly different.

To proceed with calculation of the critical supersturation ratio, R_c , it is necessary to obtain a value for the quantity $\frac{N\tau}{N_{vo}}$. Substitutions may be made as follows:

$$\tau = \frac{n_j}{\nu} \exp\left(\frac{F_j}{kT}\right) \quad (5)$$

$$N_{vo} = N \exp\left(-\frac{F_f}{kT}\right) \quad (6)$$

where n_j = lifetime number of vacancy jumps, ν is the lattice vibrational frequency, F_j is the free energy of activation for the vacancy jump, and F_f is the work of formation of a vacancy.

$$\frac{N\tau}{N_{vo}} = \frac{Nn_j}{N\nu \exp\left(-\frac{F_f+F_j}{kT}\right)} = \frac{n_j}{\nu \exp\left(-\frac{F_D}{kT}\right)} \quad (7)$$

where F_D is the free energy of activation for diffusion in the solution. Assuming that in this dilute solution the chemical diffusion coefficient, D , can be expressed as

$$D = a^2 \nu \exp\left(-\frac{F_D}{kT}\right) \quad (8)$$

then

$$\frac{N\tau}{N_{vo}} = \frac{n_j a^2}{D} \quad (9)$$

In the above expression, a is the atomic spacing. In grain interiors ahead of the porous zone, it may be assumed that vacancies are absorbed only at dislocations. Two values of n_j are possible, depending upon whether a vacancy is or is not trapped at a dislocation (7).

$$n_j = \frac{1}{N_d a^2} \quad (10a)$$

$$n_j = \frac{1}{N_d j a^3} \quad (10b)$$

where N_d = dislocation density, j = frequency of jogs on dislocations. Correspondingly

$$\frac{N\tau}{N_{vo}} = \frac{1}{D N_d} \quad (11a)$$

$$\frac{N\tau}{N_{vo}} = \frac{1}{a j N_d D} \quad (11b)$$

Since D and a are measured quantities, it is necessary to guess only the dislocation density and frequency of jogs in order to obtain a value for R_c . It is not too easy to arrive at reasonable values for these quantities. Considerable subgrain formation is known to occur in the diffusion zone.⁽¹³⁾ Dislocation movements such as climb and slip under the action of the shrinkage stresses must occur steadily throughout the process. Therefore the dislocation density and configuration are probably far from static. Nevertheless, in the lack of any better number, it was decided to use Machlin's value for the dislocation density in an annealed silver crystal $N_d = 3 \times 10^6$ per cm^2 , and to assume $j = 1000$ per cm. Numerical values of $\frac{N\tau}{N_{vo}}$ computed on this basis from equations 11(a) and (b) are given in Table II and the corresponding values of R_c , the critical degree of vacancy supersaturation for void nucleation in this alloy.

At the elevated temperature under consideration, it appears reasonable to assume that vacancies will not be trapped at dislocations, and the estimate based upon equation 11(b) the favored one. In agreement with previous work, it is apparent that the degree of supersaturation is far below that for homogeneous nucleation. Our estimate of R_c is somewhat higher than that of Balluffi, suggesting a vacancy concentration at least 5% in excess of normal for void nucleation in these particular specimens.

III. EFFECT OF PURIFICATION ON VOID FORMATION

Since the low values of R_c obtained above confirmed the hypothesis that voids are heterogeneously nucleated, an experiment was undertaken to see if the unknown nuclei could be removed by zone purification. The material investigated was initially the same commercial high-purity 30% Zn alpha-brass used in previous experiments at this

laboratory. (4,8) Instead of actually being zone-melted, some of the brass was sealed in a Vycor capsule under argon, melted, and directionally solidified in a Bridgman single crystal furnace. It was expected that directional solidification would effect some purification of the solid by partition across the liquid-solid interface. Sections 1/16" thick were cut from the single crystal ingot produced in this manner, and dezincified in vacuum at 900°C. A section of the original material was also dezincified at 900°C.

Figs. 2 and 3 are photomicrographs of cross-sections through these specimens. It is evident that melting and directional solidification have drastically affected the number of voids formed upon dezincification. Practically no voids have formed in the interior of the re-melted specimen, although, as indicated by the weight loss, essentially all of the zinc has been removed. The pattern of void formation in the as-received brass is similar to that reported previously. In order to prove that the observed effect was not due to a lack of grain boundaries, a specimen from the re-melted single crystal ingot was reduced 90% by cold rolling and then dezincified at 900°C. As shown in Fig. 4, except for the immediate surface, this specimen was also quite free of voids.

An attempt was made to prepare brass of extremely high purity by zone refining an ingot of spectroscopic grade copper in a graphite boat in argon. Sections from this ingot were sealed in evacuated Vycor capsules with 30% Zn brass turnings and annealed at 900°C until an appreciable amount of zinc had distilled into the copper. The brass specimens so produced were then dezincified in vacuum at 900°C. Cross-sections of the dezincified specimens (Figs 5(a) and 6) show some void formation, but again a considerable decrease in numbers below the commercial brass, as received. More voids appeared in the section taken from the end of the zoned ingot than from the middle, as would be expected if void formation were catalyzed by impurities in the metal. Formation of voids was also followed by determining the density of the specimens as a function of the amount of zinc removed. Percentage of voids was calculated from the density measurements. The results in Fig. 6 indicate that at early times voids are formed with almost equal rapidity in both pure and impure brass, but later, void formation ceases in the pure brass, and possibly some sintering occurs. This result is in accord with the photomicrographs which show an initial porosity formation at the pure specimen surface, but the interior practically free of voids.

The above results confirm beyond any reasonable doubt that voids formed during diffusion are heterogeneously nucleated. A clue to the nature of the nuclei was obtained by vacuum fusion analysis (Table II) which showed that the as-received brass contained 0.284 wt. % oxygen. A single re-melt in argon and directional solidification reduced the oxygen content to 0.072%. Therefore, it appears likely that the nuclei were oxide particles, presumably ZnO. In order to check this conclusion one of the purified ingots was re-melted and cast in air. A specimen from this material was dezincified in vacuum at 900°C with the formation of many voids, as shown in Fig. 7. The voids appear to fall in a dendritic pattern, which suggests again that the nuclei are non-metallic particles present in the melt. Photomicrographs (Figs. 8-10) show also that the inclusion count was changed by the melting treatment. The gray inclusions present appear to be ZnO. Although the nuclei are seemingly oxide particles in the commercial brass, the same cannot be stated for the high-purity material, since no appreciable oxygen could be found in this by vacuum fusion analysis (Table I). Nevertheless there was extensive void formation in samples taken from the end of the zoned ingot. At present we do not know what the nuclei are in this material.

In the photomicrographs in Figs. 3-5, it is clear that even in the re-melted and purified specimens a shallow layer of voids occurs just below the surface. This is not unexpected, since in the early stages of dezincification rapid changes in concentration occur near the specimen surface, and the divergence of the vacancy flux is correspondingly high. Therefore, by the analysis given in the preceding section, the degree of vacancy supersaturation must initially be relatively high near the surface and the probability of void nucleation a maximum. As the diffusion zone spreads into the specimen, the concentration gradients become flatter, the number of excess vacancies smaller, and the tendency to nucleate voids diminished. We may visualize a wave of excess vacancies which moves into the specimen with the diffusion zone. Initially, the wave is very high with a narrow base but becomes shallower with a broader base as it moves inward. If we consider the vacancy concentration at a specific depth within the specimen, this is initially the equilibrium concentration, rises to a maximum as the wave passes by and then decreases. Under the steady-state assumption made previously, this maximum occurs when $\frac{\partial}{\partial x} \left[(D_{Zn} - D_{Cu}) \frac{\partial X_{Cu}}{\partial x} \right]$ is a maximum at the given position.

If we again assume for convenience that the chemical diffusion coefficient, D , and the quantity $(D_{Zn} - D_{Cu})$ are independent of composition, making use of the Van-Ostrand-Dewey solution, we may write

$$\frac{\partial \tilde{x}_{Zn}}{\partial x^v} = - \frac{\chi x_{Zn}^1}{2\sqrt{\pi} (Dt)^{3/2}} \exp. - \left(\frac{\chi^2}{4 Dt} \right) \quad (12)$$

The condition for the maximum is

$$\frac{\partial}{\partial t} \left[(D_{Zn} - D_{Cu}) \frac{\partial \tilde{x}_{Zn}}{\partial x^v} \right] = 0 \quad (13)$$

By differentiating and solving the resulting equation we obtain $t_m = \frac{\chi^2}{6D}$, where t_m is the time at which the vacancy concentration is a maximum at the depth, χ . Setting $t = t_m$ in eq. (4), we obtain the following expression for the maximum relative excess vacancy concentration which is developed at any depth, x

$$R_{max} = \left[\frac{N_T}{N_{Vo}} \right] \cdot \left[\frac{(D_{Zn} - D_{Cu}) x_{Zn}^1}{1.09 \chi^v} \right] \quad (14)$$

This expression enables us to evaluate the critical vacancy supersaturation ratio for void formation in the purified brass, by letting χ equal the depth of the shallow porous layer in the extensively dezincified samples. Values of R_c so computed are presented in Table II, and it may be seen that the degree of vacancy supersaturation required for the nucleation of voids in the purified specimen is a few orders of magnitude greater than in the impure specimen. Because it is difficult to precisely locate the boundary of the porous region, and R_{max} varies sharply with distance at the specimen surface, these values could be an order of magnitude in error. Many of the pores in Figs. (3) and (4) are connected with the surface, and in many areas void nucleation may have occurred only very close to the surface, the pores then growing inward to some extent.

IV. VOID FORMATION DURING CREEP

In a recently published article, Greenwood and co-workers⁽⁶⁾ draw attention to the occurrence of minute voids in the

grain boundaries of metals strained in tension at elevated temperatures. Such voids may initiate intercrystalline cracking and ultimate rupture. The authors suggest that these voids could be formed by the migration of vacant lattice sites existing in the metal or created during deformation. Machlin⁽⁷⁾ has shown that this mechanism is theoretically reasonable if essentially no work is required to nucleate a void, and vacancies merely condense on existing nuclei of unknown nature. The foregoing diffusion experiments suggest that Machlin's condition is essentially satisfied in the as-received alpha-brass, but probably not in the purified brass. It was of interest, therefore, to compare the behavior of these materials in a stress-rupture test.

A. Experimental Details

The experiments were performed on 30% Zn alpha-brass specimens of the same stock as before. The as-received and directionally solidified bars were cold rolled approximately 80%, and stress-rupture specimens 0.125" thick, 0.155" wide, with a 1.0" gauge length machined from the cold-rolled stock. The test specimens were annealed in evacuated Vycor capsules at 800°C for three hours in order to stabilize the grain structure.

Stress-rupture tests were conducted at 400°C and an elongation rate of 40% per hour, using a conventional tensile testing machine. The heated specimens were surrounded in the furnace by brass chips of similar composition, to prevent the distillation of Zn from the test samples. Later examinations revealed no evidence of Zn loss from the stress-rupture specimens, specifically, no void formation due to dezincification. Elongations were measured between gauge marks inscribed on the surfaces.

B. Results

The first specimens tested were pulled to failure. The as-received brass fractured intergranularly after 6.0% elongation. The directionally solidified brass fractured intergranularly after 14.5% elongation. Since the strain rates were equal, the stress-rupture life of the treated brass was almost 2 1/2 times that

of the as-received brass. These tests were repeated a few times and the above result confirmed.

Microstructures of the as-received and directionally solidified specimens after test are shown in Figs. 11-13. For comparison, the structure of a specimen of purified brass strained 6.5% under similar conditions is also shown. It is obvious that the frequency of occurrence of voids at grain boundaries is much higher in the as-received than in the purified brass. There is a correlation, therefore, between the frequency of void formation upon dezincification and the frequency of grain boundary cracking in brass stretched at an elevated temperature. The removal of the nuclei which catalyze void formation during diffusion also decreases the tendency toward void formation at grain boundaries in creep, and thereby significantly improves the stress-rupture life of the material.

V. DISCUSSION

The experiments described above make it evident that the nucleation of voids during diffusion and creep in metals is catalyzed by the presence of impurities. Inclusions of substances which tend not to be wet by the metal are theoretically effective nuclei. According to Kingery and others⁽¹⁴⁻¹⁶⁾ the contact angles between liquid metals and solid oxides are frequently high. In the presence of a trace of sulphur, the contact angle between liquid copper and silica reaches a value of 172°.⁽¹⁶⁾ One may suspect, therefore, that oxide inclusions furnish a common site for vacancy condensation.

This supposition is borne out by calculation of the degree of supersaturation theoretically required to produce the observed nucleation frequency in the presence of a nucleation catalyst. Assuming that embryos on the surface of the catalyst are in equilibrium with lattice vacancies in the matrix, the number of nuclei per unit area of surface, N_s^* , is following the Volmer-Weber theory⁽¹⁷⁾

$$N_s^* = N_v \exp. \left(- \frac{\Delta F_s^*}{kT} \right) \quad (15)$$

For nuclei in the form of spherical caps on a plane surface

$$\Delta F_s^* = \frac{16\pi\gamma^3}{3(\Delta F_v)} f(\theta) \quad (16)$$

where γ is the surface energy of the metal, ΔF_v the bulk free energy change upon formation of a void, θ the contact angle, and $f(\theta) = (2 + \cos \theta)(1 - \cos \theta)^2/4$. The rate of nucleation, I_s , is, following Volmer-Weber,

$$I_s = Z_s N_s^* \quad (17)$$

where Z_s is the net rate of arrival of vacancies to the nucleus. A value of Z_s may be obtained from Machlin's calculation of void growth rates,⁽⁷⁾ assuming his estimate of the radial growth rate, and noting that the free surface of the nucleus is equal to $\frac{8\pi\gamma^2(1 - \cos\theta)}{(\Delta F_v)^2}$

$$Z_s = \frac{8\pi\gamma^2(1 - \cos\theta)}{(\Delta F_v)^2} R_g \sqrt{D_v \tau} \quad (18)$$

in which D_v is the vacancy diffusion coefficient, τ the vacancy lifetime, and R_g the rate of generation of excess vacancies in the matrix. Therefore

$$I_s = \frac{8\pi\gamma^2(1 - \cos\theta)}{(\Delta F_v)^2} N_v R_g \sqrt{D_v \tau} \exp\left(-\frac{\Delta F_s^*}{kT}\right) \quad (19)$$

Setting $D_v \tau = n_j a^2$, and utilizing eq. (10b) as the best value for n_j at high temperatures

$$I_s = \frac{8\pi\gamma^2(1 - \cos\theta)}{(\Delta F_v)^2} R_g N_v (N_d j a)^{1/2} \exp\left(-\frac{\Delta F_s^*}{kT}\right) \quad (20)$$

From the appearance of the microstructure (Fig. 1) it is estimated that the density of voids at the apparent precipitation front is about 10^5 per cm^3 . Assuming that all of the oxygen was present as one micron diameter spherical particles of ZnO, the total surface available for nucleation is about 500 cm^2 per cm^3 of metal, and the nucleation frequency of the order of 0.01 per sec per cm^2 of oxide surface (assuming a 10-hour nucleation period). Setting $\gamma = 1000 \text{ ergs/cm}^2$, $N_v \sim N_{v0} = 10^{19}$ per cm^3 at 900°C , $R_g = 10^9$ per cm^3 from the

diffusion data, and assuming the same values for N_d and j mentioned previously, the following values of $R_c = \frac{N_v}{N_{vo}} - 1$ are calculated from equation (19) corresponding to the tabulated values of contact angle between metal and oxide.

θ	$\frac{N_v}{N_{vo}} - 1$
180°	0
170°	.03
160°	.12
150°	.29

The calculated degrees of supersaturation are in the same range as those estimated from the experimental data (Table II).

The agreement of the theoretical calculations with the experimental results indicates that the oxide-metal interface is a sufficiently potent catalyst to produce the observed ease of void formation during diffusion. This interface may likewise catalyze the precipitation of lattice vacancies during creep and be an important agent in accelerating rupture at elevated temperatures. The retardation of grain boundary cracking by the elimination of oxides from the microstructure is support for the hypothesis that cracking is initiated by the condensation of lattice vacancies on heterogeneous nuclei in the metal. This observation also suggests an explanation for the phenomenal effect of vacuum melting on the stress-rupture life of some high-temperature alloys,⁽¹⁸⁾ i.e., vacuum melting frees the metal of impurities on which vacancies can condense.

VI. CONCLUSIONS

1. The relative critical supersaturation of vacancies required for void formation during diffusion in alpha-brass was found to be a strong function of the melting procedure used in preparing the material. Values of R_c ranged from 0.0461 for commercially air-melted material, to 141 for zone-purified brass.
2. This spread in R_c is due to the fact that the voids are nucleated by foreign particles; in the case of brass, oxide particles.

3. Evidence has been presented which indicates that grain boundary failure during creep may be initiated by a process analogous to pore formation during diffusion. Removal of the nuclei which catalyze void formation during diffusion also decreases the tendency for grain boundary void formation during creep, and thereby significantly improves the stress-rupture life of the material.

TABLE I
CHEMICAL ANALYSIS OF MATERIALS USED

<u>M A T E R I A L</u>	<u>Impurities Detected By Spectrographic Analysis</u>	<u>Wt. % O₂ Determined By Vacuum Fusion Analysis</u>
Commercial Brass	No impurities except a faint trace of lead	0.284
Remelted and Directionally Cooled Commercial Brass	-	0.072
Middle of Zone melted Cu ingot	Very faint trace of Mg	< 0.001
End of zone melted Cu ingot	Faint trace of Fe and Mg Strong trace of Si	< 0.001

21

TABLE II

Specimen	Wt.% Zn Before Diffusion	Type of Material	Dezincing Temp.	Dezincing Time	Depth of Porous Zone	Rate of Vacancy Generation	$\frac{a}{N_{vo}} = \frac{1}{D N_d}$		$\frac{b}{N_{vo}} = \frac{1}{a J N_d D}$		$R_C = \frac{N_v}{N_{vo}} - 1$	
							$\frac{a}{N_{vo}}$	$\frac{1}{D N_d}$	$\frac{b}{N_{vo}}$	$\frac{1}{a J N_d D}$	$\frac{a}{N_{vo}}$	$\frac{b}{N_{vo}}$
2 - 3	5%	Commercial	900°C	8 hrs.	0.01564cm.	1.03×10^{-7}	2.56×10^2		7.1×10^6		2.64×10^{-5}	.731
2 - 4	5%	Commercial	900°C	29.2 hrs.	0.02800cm.	5.9×10^{-8}	"		"		1.51×10^{-5}	.419
2 - 8	5%	Commercial	900°C	120 hrs.	0.07500cm.	6.5×10^{-9}	"		"		1.66×10^{-6}	.0461
S-C-2	30%	Purified by Directional Solidification	900°C	17 hrs.	0.0046 cm.	8.36×10^{-5}	6.05×10^1		1.68×10^6		5.06×10^{-3}	141.0
S-C-4	30%	"	900°C	65 hrs.	0.0065 cm.	4.14×10^{-5}	"		"		2.5×10^{-3}	69.5
S-C-3	30%	"	900°C	72 hrs.	0.0075 cm.	3.15×10^{-5}	"		"		1.91×10^{-3}	53
S-C-Z-2	30%	Zone Purified	900°C	16 hrs.	0.00667cm.	4.37×10^{-5}	"		"		2.65×10^{-3}	73.5
S-C-Z-1	30%	"	900°C	18.5 hrs.	0.0093 cm.	1.38×10^{-5}	"		"		8.35×10^{-4}	23.6

Diffusion coefficients used to calculate values
Listed above are taken from ref. (11, 12)

5% Zn alloy: $D = 1.3 \times 10^{-9}$ cm²/sec.
 $D_{Zn-D_{Cu}} = 1 \times 10^{-9}$ cm²/sec.

30% Zn alloy: $D = 5.5 \times 10^{-9}$
 $D_{Zn} - D_{Cu} = 6.4 \times 10^{-9}$

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Plate No. 13899

Mag. 75X

Fig. 1 - Void formation in the diffusion zone of 5% Zn alpha-brass. Heat treated at 900°C for 120 hours in vacuum.

Plate No. 14120

Mag. 75X

Fig. 2 - Commercial brass (30% Zn), as received.
Heat treated at 900°C for 22 hours in vacuum. Weight loss = 28.3%.

Plate No. 13703

Mag. 75X

Fig. 3 - Commercial brass (30% Zn), remelted and directionally solidified. Heat treated at 900°C for 72 hours in vacuum. Weight loss = 26%.

Plate No. 14968

Mag. 75X

Fig. 4 - Remelted brass single crystal, cold rolled 90%. Heat treated at 900°C for 67 hours in vacuum. Weight loss = 18.8%.

Plate No. 14367

Mag. 75X

Fig. 5a - High purity alpha-brass (middle of ingot).
Heat treated at 900°C for 128 hours in
vacuum. Weight loss = 17.4%.

Plate No. 14366

Mag. 75X

Fig. 5b - End of zoned ingot. Weight loss = 16.5%.

Fig. 6 - Formation of Porosity during the dezincification of alpha-brass.

% Volume Porosity

Plate No. 14188

Mag. 75X

Fig. 7 - Purified brass remelted and cast in air.
Heat treated at 900°C for 24 hours in
vacuum. Weight loss = 16.5%.

Plate No. 15623

Mag. 75X

Fig. 8 - Inclusions in commercial brass (30% Zn)
as received.

Plate No. 15626

Mag. 300X

Fig. 9 - Inclusions in remelted and directionally
solidified brass.

Plate No. 15633

Mag. 300X

Fig. 10 - Inclusions in purified brass, remelted and
cast in air.

Plate No. 15470

Mag. 14X

Fig. 11 - Commercial brass (30% Zn), as received.
Stress rupture tested at 400°C. Elongation = 6.0%. Fracture profile is at right.

Plate No. 15550-51

Mag. 14X

Fig. 12 - Commercial brass (30% Zn), remelted and directionally solidified. Elongated 6.5% at 400°C.

Plate No. 15552-53

Mag. 14X

Fig. 13 - Commercial brass (30% Zn), remelted and directionally solidified, stress rupture tested at 400°C. Elongation = 14.5%. Fracture profile is at right.

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