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Transient nucleation of cavities under coupled lattice and boundary diffusion

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A diffusive process is proposed and examined for the nucleation of a cavity above half the melting point of a material and under low applied tensile stresses at which stress assisted diffusion occurs. An equation is developed for the diffusion of *N* atoms at a time into a bimaterial boundary to begin the nucleation. The stability of the solution of the equation is examined for a copper-sapphire interface, resulting in an activation energy for boundary diffusion that is in excellent agreement with a range of values previously recorded for metals. A calculation of the time taken for diffusion to create a small cavity is also obtained from the equation developed for the nucleation process. A mechanism for a supersaturation of vacancies that could result in final cavity formation is also developed, with the amount of calculated supersaturation in the range found in other studies. An incubation time before final stable cavitation is calculated and is also found to agree very well with experimental data.

1. Introduction

Since many materials fail by cavitation at elevated temperatures, it is of interest to develop models for the actual nucleation of the cavities. The goal is to determine atomic processes that cannot be seen directly due to their rapid onset and completion. Depending upon experimental conditions, the mechanism of cavitation and subsequent hole growth has been attributed to strain and grain boundary sliding [1] or to the clustering of vacancies [2, 3].

The work here focuses on an atomic process for nucleation under conditions of high temperatures and low applied stresses at which stress assisted boundary diffusion occurs. Complementing previous work that discussed a minimum threshold stress for nucleation [4], the model in this study centers around a range in stress and temperature at which the nucleation of cavities easily occurs. The work here also focuses on conditions in stress and temperature at which a metal-ceramic interface is crossing over to another state beyond cavitation. The state beyond cavitation is that at which fast fracture occurs at a planar metal-ceramic interface without subsequent evidence on the fracture surface that cavitation previously occurred [5].

The transition just mentioned between cavitation and fast fracture has been recorded experimentally at planar copper-sapphire interfaces [5]. In comparison with other works in which implanted gas bubbles [6] or previous irradiation [7] were present to help facilitate nucleation, the experiments on the copper-sapphire interfaces were performed on diffusion bonded specimens with no previous irradiation or implanted gas bubbles. Also in contrast with previous work that has analyzed the formation of voids at temperatures up to about 450°C for electronic interconnects [8–11], the study in this paper is based upon experiments performed near 700°C, which is close to 0.7 times the melting point of copper [5].

Nucleation has been recorded at stresses a few to a hundred times lower [5, 12] than the stresses that are predicted theoretically to be needed for nucleation by the aggregation of vacancies. Adding to those studies that have predicted possible stress concentrations from thermal cycling [13] and grain boundary particles [14] to facilitate cavitation at these lower recorded stresses, the study here proposes and investigates an atomic mechanism for cavitation that occurs readily at low stresses. The process is tested by the development of a simple differential equation to describe the time dependence of the movement of *N* atoms at a time into the boundary. The stability of the solution to the equation is examined and is found to be in excellent agreement with an accepted range for the activation energy for boundary diffusion. A mechanism for nucleation involving surface diffusion is also examined for its agreement with known experimental data.

It is also shown that by having several small nucleation events contribute to an excess of vacancies in a region where a final cavity is to form, estimates of both the amount of supersaturation of vacancies and an incubation time for nucleation agree very well with previous studies and experimental data. An estimate for the time needed to nucleate a single small cavity is also calculated.

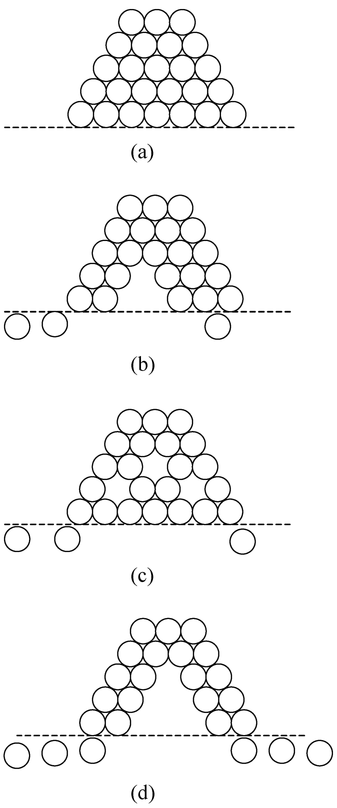

Figure 1 Nucleation of a cavity by diffusion near a bimaterial boundary (a). In part (b) N_0 atoms have diffused into the boundary to form a small cavity. In part (c) the small cavity in part (b) has collapsed due to its unstable size and has left vacancies behind in the lattice. A small cavity twice the size has formed in part (d) as N atoms have moved into the boundary.

2. Development of the transition in stability

The proposed mechanism for the cavitation is described by a sequence of events shown in Fig. 1. At time t in Fig. 1a and b, N atoms have moved into the boundary causing an energy change of $-N\sigma_n\Omega$, where σ_n is the local tensile stress in a direction normal to the bimaterial boundary [15]. The small cavity left behind shown in Fig. 1b is unstable, since it is not yet of a critical size at which the change in volume free energy balances the surface energy inside the cavity. The small cavity shown in Fig. 1b is therefore expected to collapse, as shown in Fig. 1c. Similar to the process depicted between Fig. 1a and b, more atoms move into the boundary again under the local applied tensile stress, as shown in Fig. 1d. The final cavity size in Fig. 1d is a little larger than the first unstable cavity shown in Fig. 1b.

In what follows a differential equation describing the number of atoms N moving into the bimaterial boundary shown in Fig. 1 is developed. The solution of the equation is examined and compared with known experimental data to provide insight into a possible pattern of atomic movement during the nucleation of a cavity.

The atomic flux J along an x axis along the boundary is given by [16, 17]

$$J = \frac{-D_b}{\Omega kT}\frac{\partial\mu}{\partial x} \qquad (1)$$

In the equation above, D_b is the boundary diffusion coefficient, which in the general sense here can be a grain, interphase or bimaterial boundary diffusion coefficient. In Equation 1, Ω is the atomic volume, k is Boltzmann's constant, T is the temperature in degrees Kelvin and μ is the chemical potential of the atoms diffusing into the boundary.

The flux of atoms given by Equation 1 was examined over a small volume becoming a cavity. The atoms individually moved in small time increments over distances d_A per time increment, where d_A is an approximate diameter of an atom. Since the flux of atoms is the number of atoms moving per unit cross sectional area A perpendicular to the direction of motion per unit time, the number of atoms per unit time moving in a particular direction was the flux of atoms multiplied by the cross sectional area.

In this analysis, the cross sectional area A was approximated as d_A^2 and the atomic volume Ω was approximated as d_A^3 for each atom. The change in chemical potential $\Delta\mu$ for each atom was $-\sigma_n\Omega$ for stress assisted boundary diffusion [15]. As each atom jumps into the boundary, the change in chemical potential of $-\sigma_n\Omega$ occurred over a distance Δx of d_A for atoms next to the boundary. Use of a small discrete form $\Delta\mu/\Delta x$ for these small atomic displacements for $\partial\mu/\partial x$ in Equation 1 gives $D_b\sigma_n/kTd_A$ for the flux J into the boundary. The number of atoms per unit time, given by J times A, was then $D_b\sigma_n d_A$/kT.

A few atoms moving into the bimaterial boundary are expected to form a small cavity that is energetically unstable, as shown in Fig. 1b and c. The decrease in energy from N atoms moving into the boundary is $-N\sigma_n\Omega$. There is an increase in energy, however, of $f(N)\gamma_s d_A^2$, where γ_s is the surface energy of the material undergoing cavitation and $f(N)$ is the number of atoms on the interior surface of the cavity.

The factor $f(N)$ was derived by considering the ratio of the number of atoms that move into the boundary to the number of atoms left on the surface of the cavity. If r is the radius of a hemispherically shaped cavity at, for example, a metal-ceramic interface, then N_V, the number of atoms that have left a volume of material to form the cavity, is $[(2/3)\pi r^3]/\Omega$. Similarly, N_S, the number of atoms left on the interior surface, is approximately $(2\pi r^2)/A$. If the atomic volume Ω and exposed surface area A per atom are again approximated by d_A^3 and d_A^2 respectively, then

$$\frac{N_V}{N_S} \approx \frac{r}{3d_A} \qquad (2)$$

Equation 2 shows that for a rapid nucleation process in which r begins to get large quickly, N_V can get large in comparison with N_s and the energy term $-N\sigma_n\Omega$ will begin to approach a surface energy term such as $f(N_V)\gamma_S A_S$.

An expression for the radius r in Equation 2 can be obtained from the volume from the hemispherical cavity given by $N_V/\rho = (2/3)\pi r^3$, where ρ is an atomic density expressed as a number of atoms per unit volume. Eliminating r from Equation 2, solving for N_S in terms of N_V, and equating N with N_V and $f(N)$ with

N_S gives

$$f(N) = (18\pi\rho)^{1/3} d_A N^{2/3} \tag{3}$$

Equation 3 shows that as N increases, $f(N)$ increases more slowly and the energy release of $-N\sigma_n\Omega$ will eventually approach $f(N)\gamma_S d_A^2$.

It is the purpose of this paper to propose a mechanism that does not rely on a condition that σ_n be very large to make up for the difference between the energy terms $N\sigma_n\Omega$ and $f(N)\gamma_S A_S$ in the early stages of nucleation. For copper at 700°C, for example, γ_s is 1.91 J/m^2 [18] and an applied tensile stress under which the copper side of a planar copper-sapphire interface is seen to form cavities is about 2.00 MPa [5]. The atomic volume Ω is about 1.18×10^{-29} m^3 and d_A can be approximated as about 2.28 Å by taking the cube root of Ω. With these values, $\gamma_s d_A^2$ is about 0.620 eV, whereas $\sigma_n\Omega$ is only about 0.000147 eV.

With the values of surface energy and applied stress just used at 700°C, use of Equation 3 shows that the total surface energy $f(N)\gamma_s d_A^2$ of a cavity formed by having N atoms move into the boundary does not equal the decrease in energy $N\sigma_n\Omega$ until N is about 4.16×10^{12} atoms. This value of N, when it is combined with an atomic density ρ of 8.45×10^{28} atoms/m^3, gives a hemispherically shaped cavity in the copper side of the copper-sapphire interface that is stable when its size reaches a radius r of 2.86 μm.

A much smaller cavity that forms as a result of just a few atoms moving into the boundary will therefore be unstable and will be expected to collapse. The collapse of such a cavity is expected to leave vacancies behind in the material lattice as atoms move forward to fill the cavity, as shown in Fig. 1c. The energy absorbed per vacancy formed as each vacancy moves backward into the lattice is ΔH_v when the entropy of mixing of the vacancies is put aside in the analysis [17].

The flux J from Equation 1 of atoms moving forward by lattice diffusion to fill the cavity, using the method discussed previously to approximate $\partial\mu/\partial x$, is then $(-D_\ell/\Omega kT)(\Delta H_v/d_A)$, where D_ℓ is the lattice diffusivity. Here a negative sign arises from an absorption rather than a release of energy ΔH_v during the diffusion process. As atoms move forward to fill the cavity through a cross sectional area d_A^2, the number of atoms moving per unit time, given again by the flux J times d_A^2, is then $(-D_\ell d_A \Delta H_v/\Omega kT)$.

The total nucleation process can take into account both the movement into the boundary itself and the subsequent movement of atoms to fill an unstable cavity. The total number of atoms per unit time moving into the boundary when a small cluster of N atoms moves simultaneously is then

$$\frac{\mathrm{d}N}{\mathrm{d}t} = \frac{N d_A}{kT}\left[D_b\sigma_n - \frac{D_\ell \Delta H_v}{\Omega}\right] \tag{4}$$

Equation 4 above has the general solution $N = N_0 e^{\alpha t}$, where N_0 is a small number of atoms entering the boundary at time $t = 0$ and α is a stability parameter [19]. For this study, the stability parameter α became $(d_A/kT)[D_b\sigma_n - (D_\ell \Delta H_v/\Omega)]$, which was examined in detail.

The transition in stability that was used to model a cavity nucleation process was that of cavitation at a planar copper-sapphire interface [5]. In the range of temperatures between 500 and 800°C, the interface exhibits cavitation that does not lead to fracture at the interface for several days under low applied tensile stresses of 1 to 2 MPa. When the applied stress is held constant and the temperature is increased, there exists a threshold temperature at which the stable cavitation disappears and the interface fractures rapidly without cavitation along the copper-sapphire interface boundary [5]. Various atomic processes were modeled in the study here for the actual sudden, stable, but unseen cavitation process until one process exhibited a change in stability at the experimental temperatures and stresses recorded for the transition to fast fracture.

Use of known and estimated data for copper [17] shows that as the temperature rises from about 550 to 700°C and the stress σ_n is held fixed under conditions for which stable cavitation occurs, the term $(d_A/kT)[D_b\sigma_n - (D_\ell \Delta H_v/\Omega)]$, which was defined earlier as the parameter α, is at first positive, but eventually equals zero and becomes negative. The point at which the term is zero is modeled here as the transition at which the specimen fractures rapidly at the copper-sapphire interface without evidence of cavitation in the copper beforehand. Having the term α positive can thus be interpreted as allowing N to diffuse into the boundary to nucleate a cavity.

A transition then exists when α equals zero or

$$D_b = \frac{D_\ell \Delta H_v}{\sigma_n\Omega} \tag{5}$$

For the planar copper-sapphire interface under tension, the transition of α equal to zero was confirmed with experimental data to see if values for the activation energy for boundary diffusion Q_b agreed with the range of other data for grain boundary diffusion in other metals.

3. Comparison with experimental data

Both D_ℓ and D_b in Equation 5 can be written in a form $D_o e^{-Q/RT}$, where D_o is a preexponential factor of about 1.6×10^{-5} m^2/s [17], Q is an activation energy for the type of diffusion involved, R is Boltzmann's constant for a mole of atoms and T is the temperature in degrees Kelvin. At 700°C, the transition between stable cavitation and fracture for a planar copper-sapphire interface occurs under a tensile stress of about 2.64 MPa [5]. Use of known data for copper of 1.17 eV for ΔH_v [17], 1.18×10^{-29} m^3 for Ω, a preexponential factor D_0 of about 1.6×10^{-5} m^2/s for both D_ℓ and D_b, and an activation energy of 197 kJ/mole for D_ℓ [17] gives a value of 4.24×10^{-16} m^2/s for D$_\ell$ and 2.55×10^{-12} m^2/s for D_b from Equation 5. From this value of D_b, the activation energy Q_b for the boundary diffusion in the cavity nucleation is approximately 127 kJ/mole. The value is about two thirds of the activation energy Q_ℓ of 197 kJ/mole for lattice diffusion and is in excellent agreement with the range for Q_{b} experimentally determined for grain boundary diffusion for other metals [17].

Other data at 600, 750 and 800°C used in the same preceding analysis yield activation energies Q_{b} for boundary diffusion of 137, 123 and 116 kJ/mole respectively. That the data produces values Q_b more easily in the range of one half to two thirds of Q_ℓ as the temperature rises suggests that at higher temperatures, lattice diffusion occurs more easily and the preceding mechanism requiring both lattice and boundary diffusion is more likely to be occurring. Any excess backstress from atoms moving quickly into the boundary [20] during nucleation would be expected to be alleviated by atoms moving further along the boundary through both lattice and boundary diffusion to regions where little or no backstress is occurring.

Mechanisms other than the alternating movement of atoms in the boundary and the subsequent collapse of an unstable cavity do not yield an activation energy for boundary diffusion that is in an estimated and accepted range. Having the atoms move by surface diffusion after a group of N atoms moves in the boundary, for example, gives by the preceding analysis a rate $\mathrm{d}N/\mathrm{d}t$ during nucleation of $(d_{\mathrm{A}}/kT)[D_{\mathrm{b}}\sigma_{\mathrm{n}} - (D_{\mathrm{s}}\gamma_{\mathrm{s}}d_{\mathrm{A}}^2/\Omega)]$, where D_{s} is the surface diffusion coefficient. Setting the parameter α equal to zero again at 700°C with known data for the surface diffusion coefficient D_{s} [17] yields an activation energy Q_{b} for boundary diffusion ranging from 44.9 to 48.6 kJ/mole. These values for Q_{b}, in contrast, are much lower than those in the range of one half to two thirds of Q_λ that are often measured or estimated for boundary diffusion [17]. Other experimental data for 600 to 800°C yield values for Q_{b} ranging from 36.9 to 64.1 kJ/mole, all of which are lower than expected. It is therefore concluded that the mechanism described earlier involving both boundary and lattice diffusion together is more likely occurring in the initial nucleation process.

4. Time needed to nucleate a cavity

An estimate of the time needed to nucleate a cavity can be obtained from integrating Equation 4. As discussed previously, Equation 4 can be separated with respect to the variables N and t and integrated to give a solution of the form $N = N_0 e^{\alpha t}$, where N_0 here is a small number of atoms diffusing into the interphase boundary at a time equal to zero to begin the nucleation process and α again is the parameter $(d_{\mathrm{A}}/kT)[D_{\mathrm{b}}\sigma_{\mathrm{n}} - (D_\lambda \Delta H_{\mathrm{v}}/\Omega)]$. For some number of atoms N greater than N_0, the time t for the small nucleation events in Fig. 1 can then be estimated from the equation $t = (1/\alpha)\ln(N/N_0)$.

Since the nucleation might be a process in which N and N_0 are kept small, a sample ratio of N/N_0 equal to 2 was used to estimate the time t. For the parameter α, a temperature of 650°C and the activation energies of 127 and 197 discussed in the last section for Q_{b} and Q_ℓ were used. With the atomic volume Ω equal to 1.18×10^{-29} m^3, d_{A} approximated as 2.28 Å, D_{b} equal to 1.04×10^{-12} m^2/s, σ_{n} taken as 2.00 MPa, D_ℓ equal to 1.14×10^{-16} m^2/s, ΔH_{v} equal to 1.17 eV and k equal to 1.381×10^{-23} J/K, α is $4.92 \times 10^3\mathrm{s}^{-1}$. For a ratio of N/N_0 equal to 2 occurring somewhere in the middle of the nucleation process, the time t from the expression $(1/\alpha)\ln(N/N_0)$ is about 0.141 ms.

5. Discussion

There is a variation in the mechanism of nucleation just discussed that agrees with both the experimental data just presented and previous models involving a supersaturation of vacancies leading to a cavity [22]. Instead of the collapsing event shown in Fig. 1c occurring repeatedly at a single point in the interface with the number of atoms N getting larger each time, it might be that N remains small at about two to five atoms. The events shown in Fig. 1b and c might occur many times in a region of the interface where a cavity more than a micron in radius will eventually exist.

The event of a small number of N atoms moving at once into the bimaterial boundary might repeatedly occur at points near each other, bonding the atoms in the boundary to take advantage of lowering energy by creating additional atomic bonds. Having the event in Fig. 1b occur at many points near each other would also help spread the new layer of atoms evenly in the boundary to reduce the possibility of backstress occurring [20]. Having N remain small would also eliminate the possibility of a large number of atoms moving by surface diffusion to enlarge or to collapse the cavity of unstable size. A mechanism requiring extensive surface diffusion during nucleation was shown in the last section not to agree with experimental data used to analyze Equation 4.

As vacancies accumulate in the material after the collapsing event shown in Fig. 1c, the total energy of formation of a large number of these vacancies will increase. The total energy of formation will eventually exceed the surface energy that would be left behind if an entire stable cavity formed and all the vacancies were annihilated. Similar to the notation used in Section 2, let N_{s} be the number of surface atoms creating the surface energy of the entirely formed cavity of stable size and N_{v} be the total number of atomic sites in the volume that will become the cavity. A value g_{v} can then be defined as the fraction of the N_{v} atomic sites that are vacancies. The energy balance as the vacancies accumulate can be written

$$g_{\mathrm{v}} N_{\mathrm{V}} \Delta H_{\mathrm{v}} = N_{\mathrm{S}} \gamma_{\mathrm{S}} d_{\mathrm{A}}^2 \tag{6}$$

In Equation 6 above, ΔH_{v}, γ_{S} and d_{A}^2 are again respectively the energy of formation of a vacancy, the surface energy, and the approximate surface area exposed per atom at the surface.

The fraction g_{v} can be estimated by rearranging Equation 6 and combining it with Equation 2 to give

$$g_{\mathrm{v}} \frac{N_{\mathrm{V}}}{N_{\mathrm{S}}} \approx g_{\mathrm{v}} \frac{r}{3d_{\mathrm{A}}} = \frac{\gamma_{\mathrm{S}} d_{\mathrm{A}}^2}{\Delta H_{\mathrm{v}}} \tag{7}$$

Letting the atomic volume Ω be approximately d_A^3 then gives

$$g_v = \frac{3\gamma_S \Omega}{\Delta H_v r} \tag{8}$$

In the experiments discussed in the last section, the average size of some initial cavities at a copper-sapphire interface measured after interrupted tests at 700°C was about 0.41 μm [21]. The value is smaller than the 2.86 μm calculated in the last section for the radius of a stable cavity. It is possible that stress concentrations making σ_n larger by a factor of three or four are existent to assist cavitation. The mechanism shown in Fig. 1 and that discussed here leading to a supersaturation of vacancies would provide an additional mechanism so that very large concentrations of stress are not needed for the cavitation. A substitution of the value of 0.41 μm for r in Equation 8 along with ΔH_v being again equal to 1.17 eV, Ω equal to 1.18×10^{-29} m^3 and γ_S equal to 1.91 J/m^2 at 700°C gives a value of 8.80×10^{-4} for g_v.

The fraction of vacant atomic sites at equilibrium is given by $\exp(-\Delta H_v/kT)$, where k is Boltzmann's constant and T the temperature in degrees Kelvin [16]. The fraction of atomic sites that are vacancies in copper at equilibrium at 700°C is then 8.75×10^{-7}. The fraction of vacant sites of 8.80×10^{-4} just calculated from Equation 8 is 1000 times this value at equilibrium. The amount of supersaturation of 1000 times its equilibrium value and the concentration of 8.80×10^{-4} itself is in the same range as that calculated previously for cavitation in stainless steel at about 0.4 times its melting point under applied stresses of 50 MPa [22].

The preceding analysis can also be used to derive an incubation time for the nucleation of the cavities. For a cavity modeled with a hemispherical shape 0.41 μm in diameter, the vacancy concentration 8.80×10^{-4} combined with an atomic density ρ of 8.45×10^{28} atoms/m^{-3} gives 10.7 million vacancies in the hemispherical volume when it is supersaturated with vacancies just before the final formation of the cavity. It might be assumed that the small collapsing events in Fig. 1c contain one to three atoms for N_0 and two to six atoms for N in a two step process, making N/N_0 a value of 2. It was also found in Section 4 of this work from the formula $(1/\alpha)\ln(N/N_0)$ that the time needed for such an event is about 0.141 ms.

Some of the small nucleation events shown in Fig. 1b might proceed simultaneously. Other nucleation events might take place sequentially. Taking into account both these possibilities, with a time of 0.141 ms elapsing for every 3 to 10 vacancies formed, gives 3 to 8 min as the time needed for all the vacancies to supersaturate in the hemispherical volume.

Such an incubation time was seen by the author when tests for the copper-sapphire interface were interrupted after times of 30 s and 5 min. Subsequent examination of the copper at the interface revealed that cavities were just beginning to form in a particular region of the interface after these time intervals. The process presented here consisting of small cavitation events of N atoms at a time without large stress concentrations is therefore in agreement with ranges modeled in previous studies or recorded by experiment for an activation energy for boundary diffusion, for the amount of supersaturation of vacancies and for an incubation time before cavitation occurs.

6. Conclusions

1. For individual atoms, the low values of energy release from movement into a boundary in comparison with the increase in surface energy during cavity nucleation can be resolved by considering the cavity nucleation to involve N atoms at a time. The subsequent collapse of a cavity of an unstable size can form excess vacancies in the lattice and can drive boundary diffusion further by providing more atoms at the interface that could diffuse into the boundary.
2. It is found from an equation describing the movement of atoms during nucleation that a transition from stable cavitation to rapid fracture at the copper-sapphire interface yields a value for the activation energy for boundary diffusion in the range of 116 to 137 kJ/mole. The range for the activation energy is in excellent agreement with the range of one half to two thirds of the activation energy for lattice diffusion found experimentally for other metals for grain boundary diffusion.
3. From the stability parameter α and a small cavitation event involving N atoms at a time, it is estimated that the diffusion of atoms into a material boundary occurs in a fraction of a millisecond to nucleate a single small cavity.
4. A series of small nucleation events allows for a supersaturation of vacancies of about 1000 times its equilibrium value in a region to become a cavity at a copper-sapphire interface. The result is within the ranges of supersaturation calculated for other materials in models in which cavitation occurs by a condensation of vacancies.
5. The accumulation of vacancies in the material lattice also predicts an incubation time of a few minutes before the final formation of a cavity, in very good agreement with direct experimental observations of the copper-sapphire interface at 650°C under a stress of 2 MPa.

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