VOID GROWTH MECHANISM IN BUBBLE STRENGTHENED TUNGSTEN

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SUMMARY

Bubble-strengthened tungsten lamp filaments must exhibit not only excellent high temperature creep strength but also poor susceptibility to cavitation. The paper presents a study on the mechanism of void formation in KSiAl-doped tungsten. It was concluded that even if no pre-existing bubbles of critical size are present in the initial bubble network, during lamp operation, as a result of bubble coarsening, bubbles can become large enough to act as nuclei for stress assisted void growth. In this case the void formation process can be separated into three regimes by two critical sizes. It was also suggested that the presence of very high potassium pressures in the smallest bubbles reduces the surface diffusion coefficient and, hence, the rate at which the bubbles can move and coalesce.
(Key words: doped tungsten, bubble coarsening, void growth)

INTRODUCTION

The production of high-quality, long life tungsten lamp filaments requires a strengthening mechanism which suppresses power-law creep, thereby ensuring a good form retention of the coils. This requirement can be successfully met by KSiAl-doping which introduces into tungsten wire a fine dispersion of potassium filled bubbles. The presence of these bubbles results in the development of highly elongated interlocked recrystallized grains that make grain boundary sliding difficult. On the other hand, the bubbles are effective hardening centers to impede dislocation motion and thus to prevent creep strain (1).

Although the aim of the doping is to produce a suitable bubble dispersion of high stability, this requirement cannot be perfectly fulfilled in practice. Several examinations have shown that at very high temperatures bubble coarsening and void formation may occur even in high quality lamp filaments (2-5). This paper presents a study on the mechanism of void growth in bubble-strengthened tungsten. It was concluded that even if no pre-existing bubbles of critical size are present in the filament at the beginning of lamp operation, later, as a result of bubble coarsening, bubbles can become large enough to act as nuclei for stress assisted void growth. In this case the void formation process can be separated into three regimes by two critical sizes.

EXPERIMENTAL RESULTS

In order to get an insight into the mechanism of void formation in bubble-strengthened tungsten wires, we intended to produce in the present work enhanced cavitation deliberately by applying drastic test conditions. Examinations were made on automobile lamp filaments that had been exposed to severe shocks and vibrations during their use and on 0.18 mm diameter straight wires that were creep tested at a temperature of T = 2800 K under an uniaxial stress of 10 MPa. As a control material, undoped (bubble-free) tungsten wire was also examined to compare its behaviour with that of the bubble-strengthened counterparts. Since the observation of the fracture surface of the samples by scanning electron microscopy afforded little information about the details of the void growth mechanism, the samples were examined mostly by conventional metallography. Although it is obvious that the small potassium bubbles, having diameters less than 0.01 μm, cannot be resolved by optical microscopy, their distribution in the neighbourhood of the large growing voids could be detected at higher magnifications on the over-etched surface of the longitudinally sectioned and electropolished wire. The results are summarized as follows.

a) In contrast to the undoped material, where only grain boundary cavitation could be observed, in doped wires void formation was detected not only on the grain boundaries but also within the grains as shown in Fig. 1.

b) Interrupted creep tests have shown that grain boundary cavitation in undoped tungsten begins immediately upon commencement of testing, and the number of voids (visible at a magnification of 1000 by optical microscopy) increases approximately linearly with time. In the case of doped wires, however, a relatively long incubation period was measured during which no visible

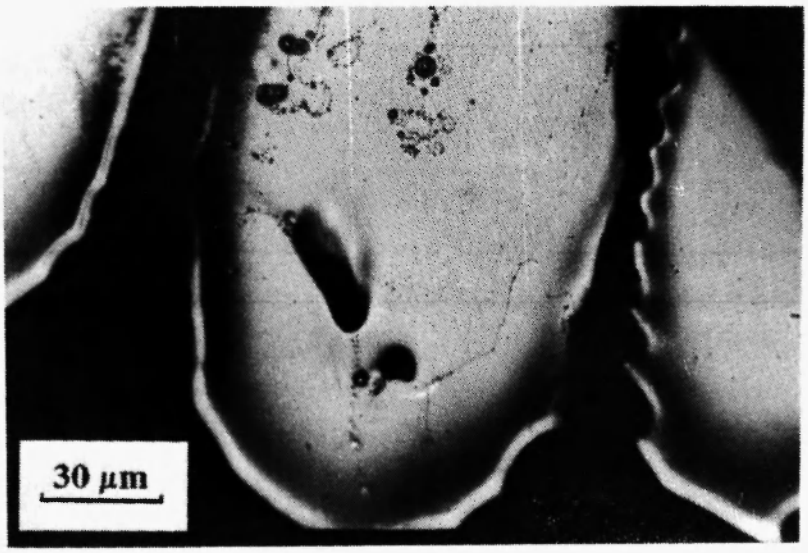

Fig.1. Light optical micrograph showing voids both on the grain boundary and within the grain in tungsten lamp filament

cavitation could be detected. Under the same test conditions the incubation period (roughly 10 hours) was usually longer than the lifetime of the undoped wires.

c) In the case of doped material, enhanced intragranular cavitation was observed near the cool end of the self resistant heated wires as shown in Fig.2. In this case the formation of large voids was a result of a combined effect of a temperature gradient, a uniaxial stress and the vibration of the wire sample associated with its heating by alternating current.

d) Void formation in doped wires was always accompanied by a disordering of the initial bubble arrangement. We found that in some regions the bubbles did not remain aligned parallel to the wire axis but they became chaotically distributed. Fig.3, taken from a coil of a projector lamp, shows that besides the initial bubble rows, randomly distributed enlarged bubbles are also present in the filament. In the course of such coarsening process; characteristic bubble-denuded zones extending several microns can develop around the growing voids in the initially very densely arranged bubble network as shown in Fig.4.

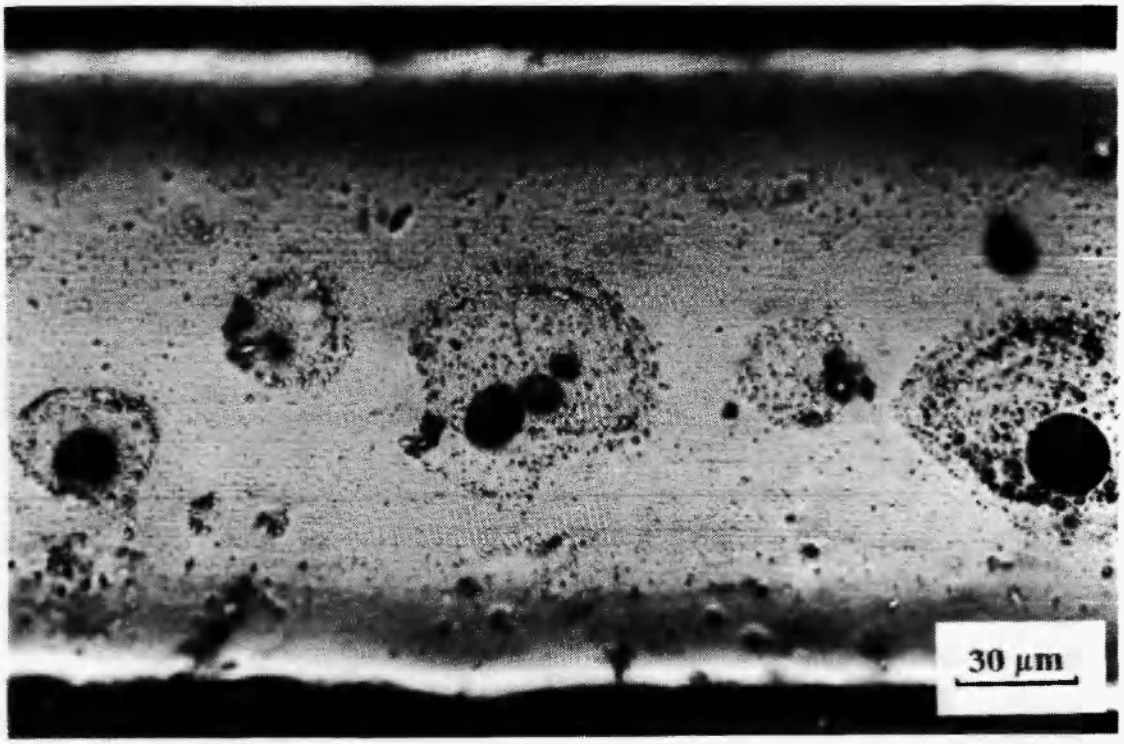

Fig.2. Optical micrograph showing enhanced intragranular cavitation in bubble-strengthened tungsten wire

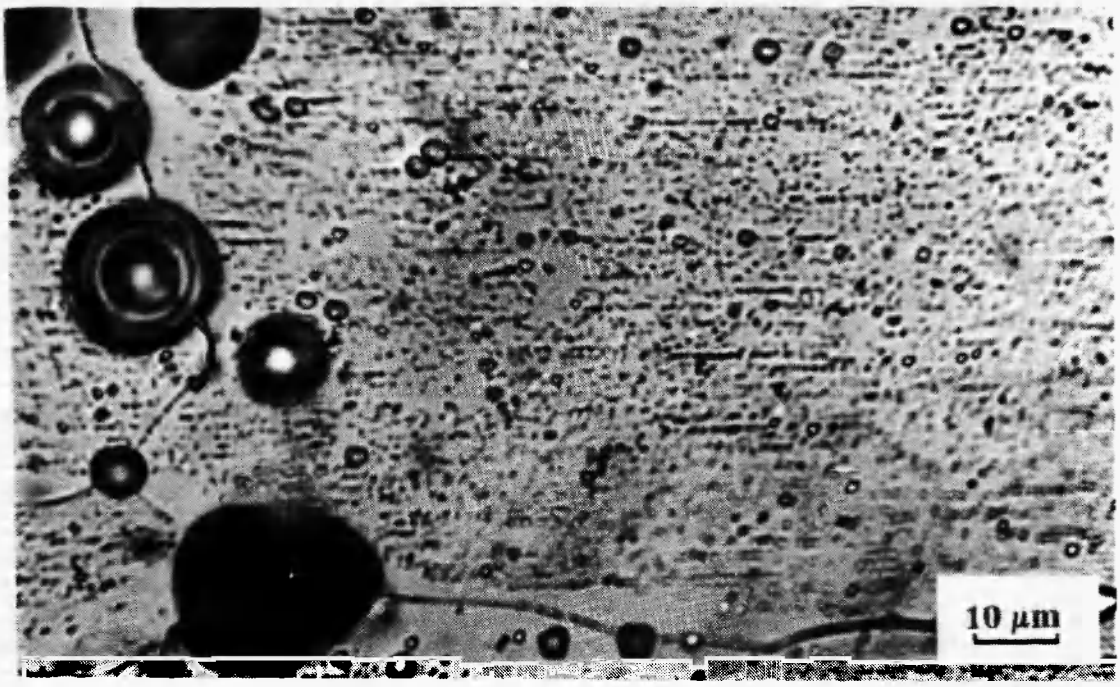

Fig.3. Optical micrograph showing coarsened bubble structure in tungsten lamp filament

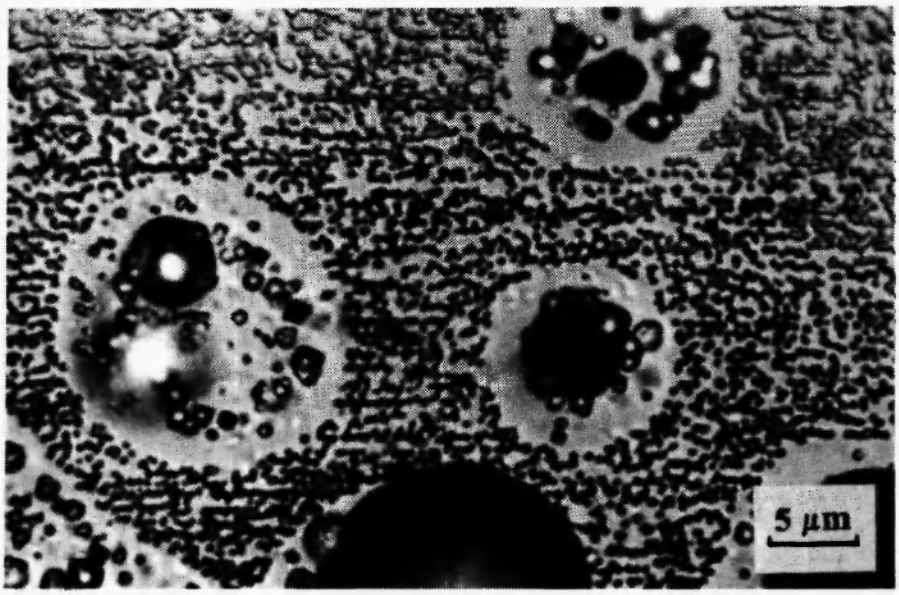

Fig.4. Coarsened bubble structure and bubble-denuded zones in bubble-strengthened tungsten wire

DISCUSSION

Extensive studies on high temperature creep have shown that cavities grow in most materials (and also in undoped tungsten) only on the grain boundaries. This experimental fact can be explained by the difficulty of void nucleation within the grain interiors. According to the current models, void nucleation may occur as a result of grain boundary sliding at any site of the boundary where the stress is concentrated and local decohesion produces a microcrack. Therefore, the void embryo must grow rapidly to above the critical size, otherwise it will be sintered out instead of beginning to grow.

Doped tungsten wire is one of the rare materials in which voids can grow not only on the grain boundaries but also within the grains. This behaviour refers to the fact that void nucleation in doped tungsten does not occur by the usual microcrack mechanism which is characterisitic of most materials.

While the critical radius of an empty void for growth, r_c, is given by the expression

$$r_C = \frac{2\gamma}{\sigma}$$

where γ is the surface energy and σ is the stress arising from the externally applied stress, the

critical radius of a gas filled bubble, r_0, for its unlimited growth is given by the expression of Hyam and Sumner (6):

$$r_O = \frac{4\gamma}{3\sqrt{3}\sigma} \tag{1}$$

Calculating with γ = 2300 erg/cm^2, and assuming that the stress arising from the own weight of the lamp coils does not exceed σ = 10 MPa, one obtains r_0 = 0.18 μm. This simple estimation suggests at first sight that voids in lamp coils cannot form by a stress-assisted bubble growth mechanism because the size of the bubbles in lamp filaments having radii of the order of 0.01 μm is much below the critical.

In a recent study Briant and Walter (7) have shown that void growth is possible at preferred sites (at undulations) on the grain boundaries, where a stress concentration locally drops the critical radius to a value of the radii of the largest pre-existing bubbles. Equation (1) shows that a decrease in the surface energy by segregation of oxygen also results in the decrease of the critical radius. They concluded that the stress concentration and/or oxygen segregation may have a deleterious effect if relatively large bubbles (r > 40 nm) are present in the filament. The unfavourable role of oversize potassium bubbles was also demonstrated by Zilberstein and Kim (8). While the proposed mechanism can account for the formation of grain boundary voids, void formation within the grains (where no stress concentration can set up and oxygen segregation can not decrease the critical size by more than a factor of two) must occur by a different mechanism.

Fig.1 and Fig.2 show that void formation in doped tungsten is accompanied by a coarsening of the initial bubble network. Since potassium is insoluble in tungsten, the observed bubble coarsening cannot be explained by Ostwald ripening. Consequently, bodily migration of the bubbles and their coalescence seems to be the only mechanism by which the subcritical bubbles can become large enough to satisfy relation (1) and, hence, to act as nuclei for stress-assisted void growth. Since at the beginning of the life of a doped tungsten wire the potassium bubbles are everywhere very densely arranged (the interbubble spacing in the initial bubble network is less than 0.3 μm), the development of relatively large bubble-denuded zones shown in Fig.4, provides an indirect evidence for the assumed bubble migration (9,10). From the measured extent of the bubble-denuded zones and the burning time of the wire, we estimated for the rate of migration of the subcritical bubbles a value of about 10^{-5} μm/sec.

Thus, because of the presence and mobility of the bubbles, a special void nucleation mechanism may work in doped tungsten that differs in two respects from the usual nucleation mechanisms:

i) As a result of migration, collision and coalescence of the subcritical bubbles, void nuclei can form everywhere in the wire (both on the grain boundaries and within the grains). This nucleation process explains the observed intragranular cavitation in doped tungsten.
ii) The formation of the void nucleus occurs by a relatively slow diffusion controlled process. In contrast to the microcrack mechanism, no sintering tendency acts against the development of the void embryo and, hence, the void nucleation process may last for a long time.

The observed long incubation period is in accordance with the results of our interrupted creep tests, reflecting the importance of bubble migration and coalescence in void nucleation. Once the critical size is attained, a stress-assisted void growth process begins, i.e., continuous vacancy flux will be directed to the growing void. Because of this vacancy flux, however, each bubble in the vicinity of the growing void experiences a force which tends to move the bubbles in the opposite direction. This reverse flow of the subcritical bubbles results in the development of a bubble-denuded zone around the growing void as shown in Fig.4.

When in the densely spaced bubble network the small subcritical bubbles move away from the growing void, they will necessarily collide and coalesce. In this way a ring of enlarged and, hence, practically immobile bubbles forms around the growing void. This stage of cavitation is shown in Fig.5. In order to better demonstrate that a vacancy absorbing void pushes away the small bubbles and, therefore, a ring of coalesced bubbles forms around the growing void, the micrograph was made deliberately in a slightly defocussed position.

As the void progressively grows, it overtakes and annexes the enlarged and thus immobile bubbles that are arranged around the void. This stage is shown in Fig.4. During further growth a new bubble-denuded zone and a new ring of coalesced immobile bubbles will develop around the void, which subsequently will also be occupied by the growing void. As this process repeatedly continues, more and more tungsten atoms diffuse away from the growing void, while the insoluble potassium cannot escape and, thus, it will be trapped in the void.

Therefore, the potassium content of a large void is identical to the amount of potassium present initially within that volume of the wire which was later occupied by the growing void.

Consequently, the amount of potassium within a growing void steadily increases. Because of this continuous supply of potassium, the internal pressure in a growing void cannot decrease below a threshold pressure level, p_0, which depends only on the potassium concentration and temperature of the wire (9):

$$p_O = \frac{\rho c R T}{A} \tag{2}$$

where $\rho = 19.35$ g/cm^3 is the density of tungsten, c is the potassium concentration in weight ppm, $R = 8.314$ Joule K^{-1}mole^{-1} is the gas constant, T is the temperature of the filament and $A = 39.1$ g/mole is the atomic weight of potassium.

Since during void growth the Laplace pressure, $2\gamma/r$, continuously decreases, but the potassium pressure inside the growing void cannot decrease below p_0, after a certain point the potassium pressure will necessarily be higher than the Laplace pressure. From this point unlimited void growth is possible even if no external stress is applied, i.e., a driving force for void growth arises from the potassium content of the wire itself. This regime begins when the growing void reaches the radius

$$R_O = \frac{2\gamma A}{\rho c R T} \tag{3}$$

This void size can be considered as a "second" critical size, because if $r > R_0$, the void is able to expand solely by its (non-decreasing) internal pressure. For example, in the case of a typical potassium concentration of $c = 70$ μg/g, and a filament temperature of $T = 3000$ K, we obtain from equation (2) for the threshold pressure: $p_0 = 0.9$ MPa and from equation (3) for the corresponding void radius: $R_0 = 5.3$ μm.

If at the beginning of the life of a lamp coil even the largest bubbles are unable to grow by a stress-assisted growth mechanism, then, the void formation process can be separated into three regimes. In the first regime bubble coalescence by migrating bubbles leads to the formation of a void nucleus with radius r_0 according to equation (1). When this "first" critical size is reached, the void begins to grow by absorbing vacancies under the action of the externally applied (gravitational) stress. During this second regime void growth would in principle stop if the externally applied stress would be decreased to zero. However, when the growing void reaches the second critical size, R_0, its further growth requires no longer any external stress: in this third regime the void may expand even solely due to its non-decreasing internal potassium pressure.

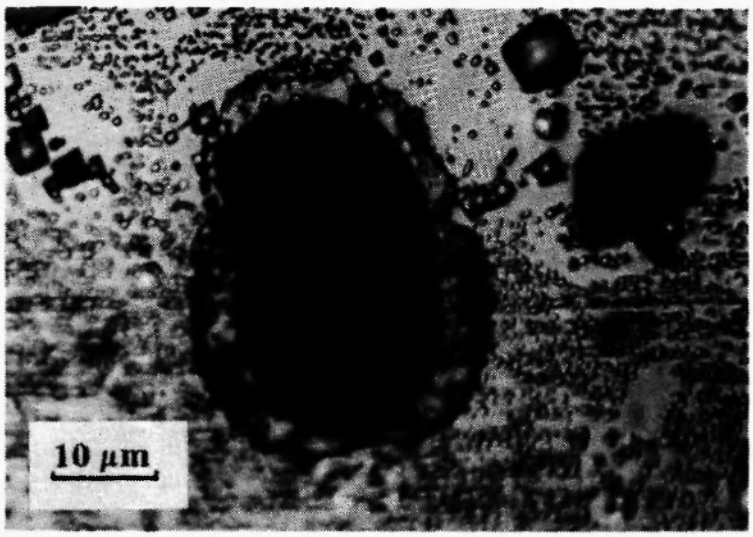

Fig.5. Large growing void surrounded by immobile coalesced bubbles

The time needed to produce coalesced bubble nuclei for the stress assisted void growth process depends on the features of the initial bubble network (e.g., number density of the bubbles) and the mobility of the bubbles. The motion of potassium bubbles requires the transport of tungsten atoms from the leading bubble surface to the trailing one. This material transfer may occur by volume diffusion, by surface diffusion or by transport through the bubble. Shewmon (11) showed that, in the case of a temperature gradient (vacancy flux), the velocity of the bubble migration varies as 1/r for surface-diffusion controlled migration, is independent of r for volume diffusion and varies as r if the rate is determined by vapour transport. This theory predicts that if the migration is controlled by surface diffusion, small bubbles migrate faster than large ones.

In the case of our experiments the coalesced and, hence, relatively large ($r \sim 1$ μm) potassium bubbles that were arranged in rings around the growing void (Fig.4,5) seemed to be virtually immobile. On the other hand, from the measured extents of the bubble-denuded zones and from the known burning time we obtained for the migration velocity values of the order of 10^{-5} μm/sec for the small ($r \sim 0.01$ μm) subcritical bubbles. These experimental results suggest that the migration velocity of the bubbles, v, in our experiments varied as 1/r corresponding to a surface-diffusion controlled process.

In the case of $v \propto 1/r$, it would be expected that the low wattage coils are most susceptible to bubble migration, and, hence, to void growth, since in these very fine filaments the bubbles are

extremely small. This suggestion is, however, not supported by the experimental observations: the very fine lamp filaments show practically no sign of bubble migration even if their temperature is increased to near the melting point. Thus, it seems that the $v \propto 1/r$ size dependence of the migration velocity of the potassium bubbles is valid only in a limited size range.

In variance with the previously generally accepted idea, recent studies carried out on other materials have showed that the mobility of very small bubbles ($r < 10$ nm) decreased with decreasing r, i.e., it was found that the large bubbles migrated faster than the small ones. This unexpected behaviour was explained by the effect of extremely high internal pressure which exists in the very small bubbles (12,13). In these bubbles, because of the dense gas phase, surface diffusion of the matrix atoms around the bubble wall is restricted, which results in a similar behaviour of solid inclusions of low mobility. Applying this theory to the behaviour of bubble-strengthened tungsten lamp filaments, it is reasonable to assume that the very high potassium pressure within the smallest bubbles slows down the diffusion of tungsten atoms around the bubble surface and, hence, the low wattage tungsten lamp filaments have little susceptibiliy to bubble coarsening and void growth.

Since the mobility of both the extremely small and the relatively large bubbles is very low, bubble migration and coalescence seems to be a significant void formation mechanism over a limited size range. Although the determination of this "dangerous" bubble size range and the clarification of other factors which influence bubble coarsening require further studies, we can conclude that the most effective way to prevent void formation is to reduce the mobility of the potassium bubbles. To satisfy this requirement, filament strengthening might be accomplish in principle either by very small or by fairly large bubbles. However, the latter method is obviously inapplicable, because it involves the risk of an instantaneous stress-assisted cavitation. Thus, it seems that the only way to suppress void formation is to decrease the size of the bubbles to radii as small as possible.

CONCLUSIONS

1) As a result of coalescence of migrating potassium-filled bubbles, high temperature cavitation may occur in doped tungsten wires not only on the grain boundaries, but also within the grains. Intragranular void formation was found, however, to be a much slower process than grain boundary cavitation.

2) If no pre-existing bubbles of critical size are present in the initial bubble structure of a lamp filament, later on, coalesced bubbles can become large enough to act as nuclei for stress-assisted void growth.

3) Once the growing void reaches a second critical size, a driving force for void growth arises from the potassium content of the doped wire itself. At this stage further growth of the void is possible even if the external stress is reduced to zero.

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