JOURNAL DE PHYSIQUE
Colloque C6, supplément au n°11, Tome 48, novembre 1987

STABLE NECKS ON METAL TIPS

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ABSTRACT : On a metal tip (W, Ni, Au, Cu) heated in an electron microscope (SEM) a formation of stable necks is observed. As this does not agree with the theory, experiments are made for clarification. In situ electron microscopy (TEM, STEM, EELS) shows the existence of graphitized surface layers, which surprisingly remain stable up to near the melting point. These layers hinder a complete separation of a solid metal drop from the tip end. On the basis of this result spectacular tip and neck shape changes are explainable as an Ostwald ripening.

1. INTRODUCTION

When a nearly cylindrical metal tip is heated in the vacuum of an electron microscope, spectacular relatively stable necks are formed /1//2/. As this phenomenon is not understood, which hinders the use of tips for surface and materials science studies, we have now studied the stable neck phenomenon in some detail and describe the result in this paper.

2. DESCRIPTION OF THE PHENOMENON

2.1. Theoretical basis.

Which is the morphological evolution of a heated solid metal in vacuum ? An answer is given on the basis of the NERNST-EINSTEIN equation of matter transport in the case of metal tips by the calculated results of NICHOLS and MULLINS /1/. Depending on the tip cone angle α two domains of tip evolution exist : (1) for cone angles $\alpha > 3°$ the tip end radius r increases continuously and a measurement of r as a function of time has been often used to determine surface self-diffusion coefficients of metals /2/. (2) For smaller cone angles ($\alpha < 3°$) the calculation predicts a formation of a tip neck of decreasing diameter until a solid drop is separated from the tip end. An example of such an evolution is shown in fig. 1. This second evolution is the basis of the phenomenon described in this paper.

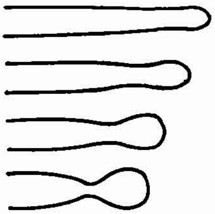

Fig. 1 - Calculated shape evolution of a heated tip by capillarity induced surface self-diffusion transport /1//3/. Tip cone angle 2°.

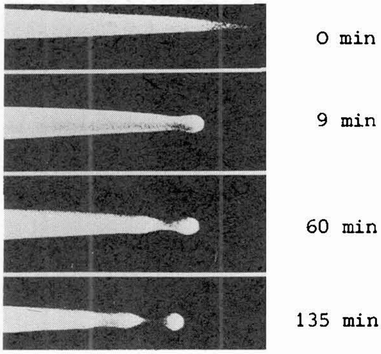

Fig. 2 - Shape evolution of a single crystal tungsten tip visualized by a scanning electron microscope /3/. $T = 2300$ K ; $\alpha \sim 3°$.

2.2. Stable neck on a single crystal tip.

The experimental evolution of a single crystal tip is shown in fig. 2. At first view calculated and experimental evolutions seems to agree. However there is an important discrepancy in the time dependence of this evolution. The calculation predicts that the time of the existence of a small neck is small compared to the time of the formation of the neck but this is opposite to the experimental result. So the fundamental problem exist : why are thin necks so stable ?

2.3. Stable necks on a polycristalline tip.

The necks on polycrystalline tips are somewhat different to those on single crystal tips. A typical experimental result is schematized in fig. 3. (see also fig. 10). Firstly the usual system of irregular grain boundaries is transformed by boundary migrations in a system of "bamboo" boundaries (fig. 3 a and b). Boundary grooves and necks are formed at these boundaries (fig. 3 b and c) /4/.

Fig. 3d illustrates again the main problem studied in this paper : While the calculation predicts a grain or solid drop separation from the tip, the experiment shows in nearly all cases an appearence of a stable neck. What is the reason for this discrepancy ?

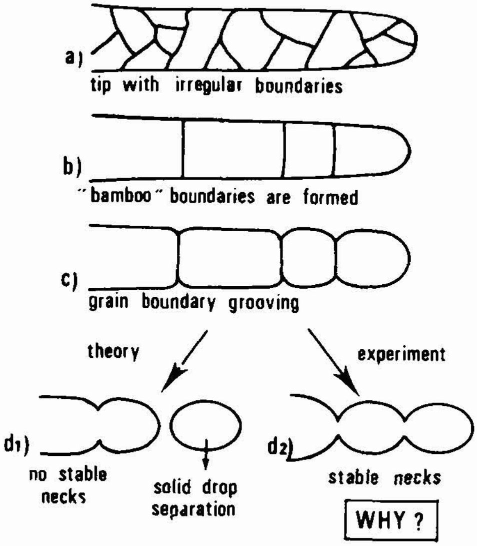

Fig. 3 - Scheme of the formation of stable necks on a polycrystalline tip (tip radius increase is neglected).

2.4. Cylindrical necks.

A special type of (relatively) stable necks are cylindrical necks. An example is shown in fig. 4. The diameter of the neck is about 400 Å. It is surprising that a neck with such a great surface to volume ratio is formed.

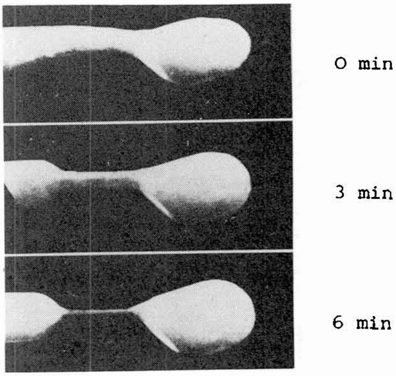

Fig. 4 - Formation of a cylindrical stable neck on a Ni tip /3/ heated (1250 K) in the absence of electron impact.

3. THE FINDING THAT STABLE NECKS MUST BE RELATED TO SURFACE LAYERS

In order to obtain better information on stable necks we started to study the problem by transmission (instead of scanning) electron microscopy. Used was a 100 kV TEM (Philips) with a heating chamber up to 1500 K /5/ and the 3 MV microscope of Toulouse with a heating chamber up to 1000 K. In situ video registration was used in both cases. The advantages of using a TEM are : (1) The much better resolution (~ 5 Å). (2) The visualization of surface layers /6/ (fig. 8). (3) The possibility to obtain information on impurities by dark field diffraction imaging. Impurities can originate from the residual gas in the microscope of ~ 10^{-6} Torr (typically H_2O, O_2, N_2, H_2, hydrocarbons as CH_4, ...). In fact the dark field study indicates and localizes an impurity (fig. 5 and 6). The surprising result is that the neck region is sometimes completely metal (Cu) free (fig. 5 and 6). Bright field imaging show that the whole tip surface is often covered with a surface layer (fig. 8) /6/. The measured layer thickness is in the range between zero and ~300 Å /6/. A correct layer substance analysis was made by STEM electron energy loss spectroscopy (with the help of Mr. Fourmeaux, Toulouse). The generalized result is that the substance of the layers is graphitized carbon. This is surprising because the well known graphitized layers in TEM and SEM microscopy are known to be detached from the specimen surface at temperatures in the order of 300 C (also confirmed by our observations) while other layers were stable up to about 1000 C and some probably up to 2000°C. A general conclusion of these results is that graphitized layers of very different stability exist. If a layer is more or less stable seems to depend (1) on the layer preparation and (2) on the specimen geometry (plane film, tip, supported particles).

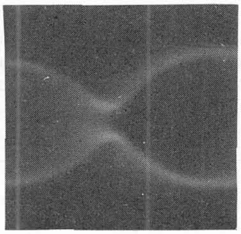

Fig. 5 - Stable neck on a Cu tip during in situ heating (1200 K) and video registration. TEM dark field image. The bright lines indicate a non-copper surface layer. Neck diameter ~ 400 Å.

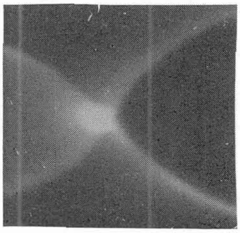

Fig. 6 - Stable neck as in fig. 5. The neck appears bright that is free of copper.

4. EXPLANATION OF THE STABLE NECK PHENOMENON

The stable neck model which agrees best with the experimental results is schematized in fig. 7. Fig. 7a shows a low angle tip after some surface self-diffusion. At ~ 10^{-6} Torr and elevated temperature a graphitized surface layer of increasing thickness is formed. In detail, the hydrocarbons of the gas are adsorbed and desorbed on the tip surface, where a submonolayer of adsorbed hydrocarbons is formed. These are cracked by the high temperature, by the impinging electrons (100 kV) or by both. The hydrogen desorbs while the carbon effects the growth of the graphitized layer. The experience show that the presence of the graphitized layer has often (surprisingly) little influence on the Cu surface diffusion transport along the Cu surface. In former interpretation of stable neck micrographs (as in fig. 10) it was assumed that the solid metal drop is not separated from the tip shank. This interpretation must be revised. The drop is mostly separated from the tip metal but still hold by the non-metallic layer (fig. 7c, fig. 6 and 8).

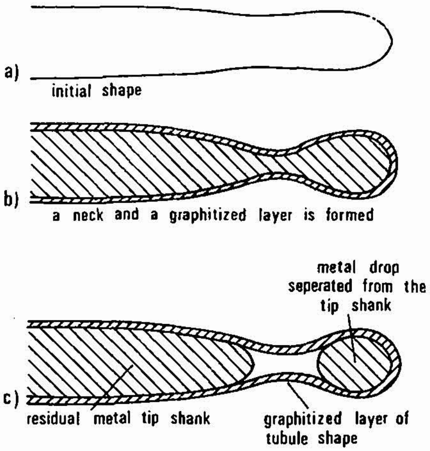

Fig. 7 - Explanation of the formation of a stable neck on a single crystal tip (see text).

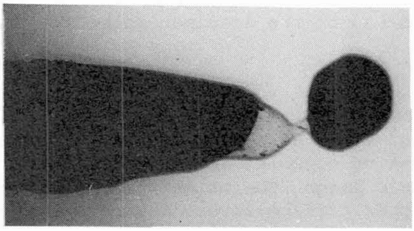

Fig. 8 - TEM ($3x10^6$ V) micrograph of a Cu tip after heating during observation (~ 800 C for ~ 20 min). The solid Cu drop (~ 1,5 μm) is separated from the metal shank and is only hold by the layer (~ 10^3 A thick) which has a tubule shape at the neck. STEM-EELS analysis has shown that the bright appearing layer is graphitized carbon. The few small dark point in the layer are isolated very small Cu crystallites.

5. A MODEL FOR THE FORMATION OF CYLINDRICAL NECKS

Why stable necks evolute sometimes to filiform necks (fig. 3) must be explained too. When the metal inside a neck (fig. 9a) is transported to the metal drop or the tip shank a special vacuum space is formed (fig. 9b). The residual layer has a shape similar to a hollow double cone. Such a cone seems to be submitted to a driving force which tends to reduce the cone diameters (reduction of the surface area). The hypothesis is that this cone can not resist to this force because (1) experiments show that such layers are very flexible (adaptation to support shape changes) and (2) the tiny lamellas of a graphitized layer should be easily displacable at high temperatures in lamella directions. Consequently the cone diameters should decrease, the lamellas may become more slightly curved and the layer thickness may increase somewhat. But this process must be limited because the increasing curvature causes an increasing counter force. The state of minimum free energy formed should be a tubule of a limit diameter.

6. UNSTABILITIES OF STABLE NECKS

Stable necks are only relatively stable. In fact necks and tips show slow but spectacular shape variations. An example /3/ is shown in fig. 10. Formerly it was supposed that such shape changes are perhaps caused by thermo-diffusion. Though thermo-diffusion may play a role, it seems not be a dominant role. The finding of the existence of the graphitized layers opens a new way to explain the mysterious unstabilities.

The new hypothesis is that the disappearence of stable necks is a special type of Ostwald ripening. The ripening of spherical metal crystals is schematized in fig. 11a and b. Surface diffusion effects a transport of metal atoms from the small to the greater crystal; which reduces the total metal surface area and the total free energy of the system. In the case of a tip with a stable neck (fig. 11 c and d) the metal atoms migrate also to surface regions of greater surface radii so that the free energy of the system is reduced (the surface free energy of the graphitized layer is very small and can be neglected in the energy balance for simplification).

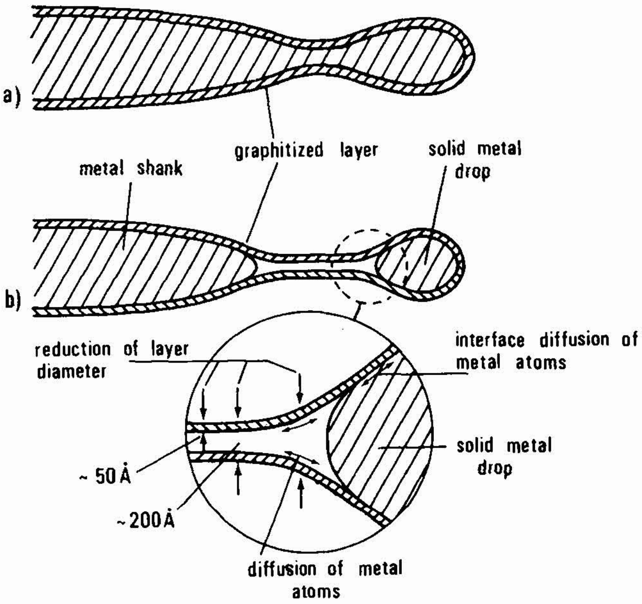

Fig. 9 – Explanation of the formation of a filiform neck.

An analysis of micrographs series as that of fig. 10 show that the total metal surface area is continuously decreasing with time in all cases studied so far. This is a strong argument to assume that the described Ostwald ripening hypothesis is correct. Residual parts of graphitized layer are not visible in the SEM micrographs of fig. 10, but found in analogous TEM experiments with Cu tips.

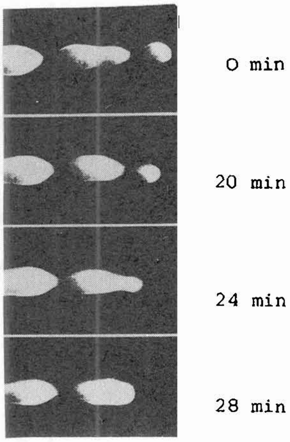

Fig. 10 – Disappearence of a solid drop with a stable neck (W, 2600 K).

7. DISCUSSION

The explanation of the stable neck phenomena presented here is preliminary and need to be confirmed. It may be also desirable to study the stable necks in more detail in a quantitative manner.

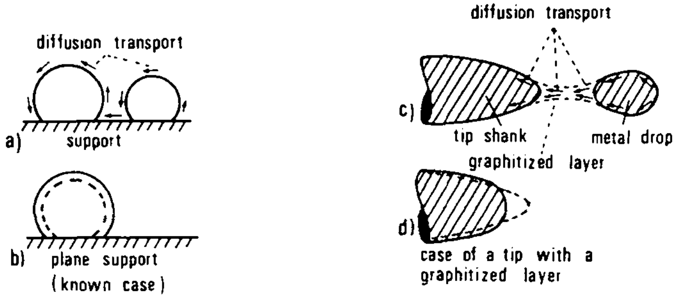

Fig. 11 - Scheme of the disappearence of a crystal by Ostwald ripening on a plane support (a and b) and on a tip with a graphitized layer (c and d). The arrows indicate the diffusion transport direction.

8. CONCLUSIONS

(1) The formation of stable necks on metal tips is a consequence of an existence of graphitized surface layers.
(2) Besides the known graphitized layers formed on electron microscope specimens (and detached above ~ 300°C) exist others which are stable up to ~ 2000°C).
(3) A stable neck is formed by a capillarity induced seperation of a solid metal drop from the tip but both remain hold together by the tubule graphitized layer.
(4) Metal atoms diffuse easily along (1) the interface metal-graphitized layer and (2) the inner side of the tubule layer.
(5) Solid drops and stable necks disappear on long term by Ostwald ripening.

ACKNOWLEDGEMENTS

The authors like to thank Mr. R. Fourmeaux, Toulouse, Laboratoire d'Optique Electronique du CNRS, for the analysis of the layer subtance.

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