Contact-Potential Changes Produced on Metal Surfaces by Tensile Stresses*

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Contact-potential changes produced by applied tensile stresses on a number of metal surfaces have been measured. Except at very low tensile stresses, where the results are uncertain, it is found that in the elastic region of the metal, the contact potential becomes increasingly negative with increase of tensile stress. In the plastic region of the metal, the contact potential changes sign and increases in the positive direction until rupture occurs. The experiments were carried out in an atmosphere of nitrogen.

EXPERIMENTS have shown that small radial electrical potentials exist on the surfaces of rapidly spinning metal rotors.[1] The magnitude of these potentials was affected by a number of factors such as absorbed gases, oxide layers, etc., on the rotor surface. Nevertheless, it was possible to conclude that the periphery became positive with respect to the axis and that the radial potentials were roughly proportional to $\omega^2 r^2$, where r was the radius and ω was the angular speed of the rotor. In one of the experiments, the metal rotor was accidentially allowed to reach a speed where plastic flow took place and a comparatively large increase in potential was observed on the region of the rotor surface where the plastic flow had occurred. As long as the elastic limit of the rotor was not exceeded, the observed results were in general agreement with the theories of Davis,[2] Dressler, Michel, Rorschach, and Trammell[3], Herring[4], and Schiff and Barnhill[5] as modified by Barnhill[6] for the effect of a gravitational (or centrifugal) field on the electric surface potentials of a metal. It is found[3] that for a uniform gravitational field acting on a solid metal, the resultant electrical field E is directed upward and has the magnitude $E=\gamma(\mathrm{Mg})/e$, where M is the mass of the metallic ion, e is the electron charge, and γ is the ratio of the partial pressure of the electron gas to that of the ion lattice. Cottrell, Hunter, and Nabarro[7] have concluded that lattice distortions in a metal result in a charge separation and that regions of compression will acquire a net positive charge and regions of dilatation a net negative charge. They conclude that (except for an additive constant that measure the average dilatation of the sample) $\phi(\Delta)=-(4/15)E_F\Delta$, where $\phi(\Delta)$ is the change in potential energy of unit charge, E_F is the Fermi energy in the undistorted material, and Δ is the dilatation. Moore and Kuhlmann-Wilsdorf[8] have compared the above theories and find that they lead to approximately the same results. They have also calculated the charge separation in the earth due to hydrostatic pressure. Recently, Craig,[9] in an important experiment, has measured an increase in surface contact potential due to hydrostatic pressure on a number of different metals. The values found were in general agreement both in sign and magnitude with the above theories.[2–8] In view of the relevance of these theories not only to changes in the contact potential of rotor surfaces with angular speed, but also to many fundamental experiments where the contact potentials of stressed metal surfaces enter into the basic measurements, it was decided to study the change in contact potential when the metal is subjected to tensile stresses.

The experimental method is a modification of one originally devised by Kelvin and is shown in Fig. 1. The specimen B to be tested is mounted between insulating bakelite clamps E in such a way that the force F stresses it by a measured amount. The 1.5-cm^2-area 0.05-cm-thick gold-plated stainless-steel plate A, with its plane accurately parallel to that of B, is mounted on a Ling vibrator L in such a way that the distance between A and B is varied sinusoidally at a constant known frequency. The frequencies employed varied over the range from 20 to 100 Hz. A and B were en-

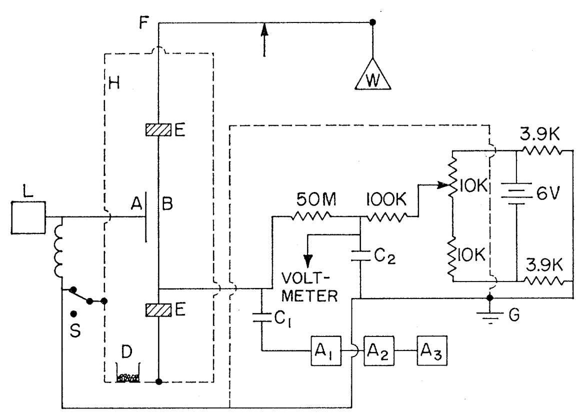

FIG. 1. Schematic diagram of the experimental method for measuring changes in contact potential produced by tensile stresses.

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[1] J. W. Beams, Phys. Rev. Letters **21**, 1093 (1968).
[2] H. M. Davis (private communication).
[3] A. J. Dessler, F. C. Michel, H. E. Rorschach, Jr., and G. T. Trammell, Phys. Rev. **168**, 737 (1968).
[4] C. Herring, Phys. Rev. **171**, 1361 (1968).
[5] L. I. Schiff and M. V. Barnhill, Phys. Rev. **151**, 1067 (1966).
[6] M. V. Barnhill, Phys. Letters **27A**, 461 (1968).
[7] A. H. Cottrell, S. C. Hunter, and F. R. N. Nabarro, Phil. Mag. **44**, 1064 (1953).
[8] J. T. Moore and D. Kuhlmann-Wilsdorf, Mater. Sci. Eng. **3**, 183 (1968).
[9] P. P. Craig, Phys. Rev. Letters **22**, 700 (1969).

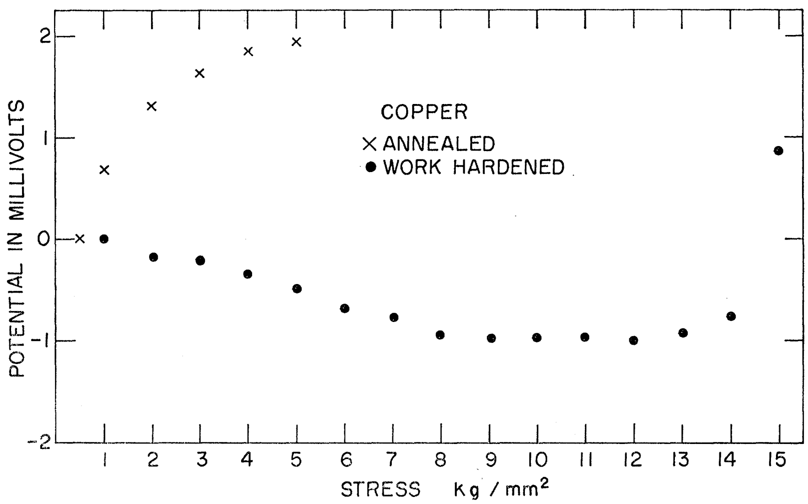

FIG. 2. Surface potential changes of 0.025-cm copper sheet as a function of applied stress. Circles are for work-hardened copper and crosses are for carefully annealed copper.

closed by a heavy metal chamber H which in a few of the experiments was evacuated but in most of the experiments contained pure nitrogen or carbon dioxide at atmospheric pressure. The gas was slowly passed through the chamber. D is a metal cup filled with Drierite to absorb water vapor leaving the surfaces. The metal chamber H could be connected to a source of potential at S. It will be noted that if an electrical potential exists between B and A, the vibration of A will generate an ac signal which is amplified by the preamplifier A_1, the lock-in amplifier A_2, and the linear amplifier A_3. If A and the case H are grounded and the potential of B is varied by the arrangement shown in Fig. 1, the magnitude of the signal will pass through a minimum when the average potential of B in the region opposite A is the same as that of A. If while the signal is at a minimum, a stress is applied to B, any change in the potential on the surface opposite A requires a change in the potential of B in order to again produce a signal minimum. The change in potential is measured by a digital voltmeter which could be read to 1 μV. The distances of A and B from the metal walls of H were many times that from A to B in order to avoid stray fields due to possible variable contact potentials on H. Also experiments were carried out with the specimen B and the chamber H grounded. All grounds were connected to the same point. Both methods gave essentially the same results. The plate B was much wider near the clamps E, and was tapered in such a way that the stress in B opposite A was roughly constant and much greater than that near the clamps. Before measurements, the specimens B, which were different polycrystalline metals, were carefully cleaned with soap and water, methyl alcohol, and acetone and left over night in the chamber in order for them to reach temperature equilibrium. The potential of the unstrained specimens remained constant when the temperature and circuit conditions reached equilibrium.

It was found that the measured absolute values of the contact potentials varied from metal to metal and from one specimen of the same metal to another depending upon the work hardening, surface condition, thermojunctions, and contact potentials in the circuit, etc. In general, although not in all cases, when a small tensile stress is first applied to the metal specimen, the change in contact potential is erratic. On the other hand, with increasing tensile stress the contact potential becomes increasingly negative and has a magnitude approximately proportional to the applied stress. However, as the stress is further increased, a point is finally reached where the contact potential changes sign and increases rapidly in the positive direction before rupture occurs. Examination of the metal specimens showed that the stress where the contact potential reversed sign and began increasing in the positive direction coincided with the onset of plastic flow, i.e., in the elastic region an increase in tensile stress produces a negative change in contact potential while in the plastic region it produces a positive change in contact potential. Figure 2 shows typical curves of tensile stress versus contact potential for carefully annealed and for work-hardened copper. If the annealed specimen of copper is first stressed beyond the elastic limit several times without rupture the lower curve is finally obtained. On the other hand, once the specimen is thoroughly work-hardened, the curve is repeated over the elastic range as long as the elastic limit of the copper is not exceeded. In Fig. 2 the curve for the work-hardened copper is arbitarily adjusted to zero for a stress of 1 kg/mm². This was done because of the uncertain nature of the curve below stresses of 1 kg/mm². It will be noted that in the elastic region the change in the contact potential with increasing applied stress is in the negative direction and is approximately proportional to the applied stress. As the elastic limit is approached, the curve flattens out and finally bends upward when plastic flow begins. The straight part of the curve is lengthened as the elastic region is increased by work-hardening. The potentials were determined to better than 0.005 mV and the stresses were applied by standard laboratory weights, but the actual stresses were only known to about 2%. However, the theoretically important quantity is the slope of the straight part of the curve over the elastic region. An analysis of a number of curves for work-hardened copper gave 0.12 ± 0.04 mV per kg/mm^2 in the negative direction. Curves similar to the lower curve in Fig. 2 were obtained with work-hardened silver, nickel, steel, and gold-copper alloy. By averaging the negative slopes of a number of curves over the elastic range in the case of each metal, the following values were obtained: 0.15 ± 0.03, 0.20 ± 0.04, 0.10 ± 0.04, and 0.20 ± 0.06 mV per kg/mm^2 for silver, nickel, steel, and gold-silver alloy, respectively. In the case of gold, the elastic range was so small that a reliable quantative value for the slope could not be obtained. On the other hand, the data definitely showed that the contact potential increased in the negative direction with increasing applied stress. The observed data indicated a slope which was significantly larger than in the case of the gold-silver alloy. Also the curve flattened out and actually turned slightly upward in the plastic range. In the plastic region the contact potential changed in the positive direction with increasing stress in all of the measurements taken with copper, silver, and nickel. However, the actual values obtained could not be systematically repeated. In all cases the metals were of commercial grade, not of highest purity. Because of the importance of the region from zero stress to 1 kg/mm^2 in several basic experiments (such as those of Witteborn and Fairbanks[10] and Tolman and Stewart[11]), a special effort was made to obtain consistent repeatable measurements in that region. Unfortunately, we were unable to get reliably consistent values there in the important cases of copper, silver, and nickel. Actually, in some cases the initial observed change was zero or slightly positive for small stresses, but changed sign before reaching stresses of 1 kg/mm^2. On the other hand, with specimens of 0.025-cm-thick shimstock steel and of 0.008-cm-thick alloy containing equal parts of gold and silver, the slopes of the curves were negative from zero stress to near the elastic limit, within experimental error. The experimental error in the region from zero stress to about 1 kg/mm^2 was in all cases much larger than in the region of higher stresses. It is hoped that more reliable experimental values can be obtained with improved apparatus especially designed to study this region of small applied stresses, both tensile and compressive, with metals free of surface layers.

Except in the cases of the pure gold and gold-silver alloy specimens which are thought to be almost free of oxide layers, the contact potential measurements were made on the oxide and other layers which cover the surface of the metal rather than on the metal itself. This fact complicates the theoretical interpretation of the results because this oxide layer also is subjected to stresses produced by the strain in the metal. Furthermore, the experimental method measures an average value of the contact potential over an area of 1.5 cm^2 rather than at a point on the surface. Consequently, the theories which are for a pure metal in the elastic region might not be expected to apply strictly to the measurements. Nevertheless, over the elastic range the slopes of the curves are of the same order of magnitude as those calculated from theory.[3–8] On the other hand, theory[7,8] predicts that the magnitude of the negative slope of the curves in work-hardened copper should be slightly less than in silver, and that nickel would have the smallest negative slope of the three. The fact that the observed magnitude of the negative slope in nickel is greater than in copper may be due to the influence of the oxide layer, or to variation in the unknown value of the constant in the equation; this constant depends upon the average dilatation of the sample. The value obtained for work-hardened copper, 0.12 ± 0.04 mV per kg/mm^2, is the same order of magnitude although smaller than that observed by Craig (0.3–0.7 mV per kg/mm^2) for the compression of copper. The differences may possibly be due to differences in the oxide layers which were under tension in one case and compression in the other. In view of the differences in the conditions of the two experiments they may be considered to be in rough general accord. The values obtained in Fig. 2 are in good agreement with those found by the rapidly spinning rotor experiment.[1]

Apparently, phenomena occur in the plastic region which overshadow the effects predicted by theory for the elastic region, because the curve first flattens out and then bends upward before rupture occurs. Some of this change might be produced by the mechanical motion of the stretched specimen when it flows plastically, but the grounded shield H (Fig. 1) is so large that such effects should be much smaller than observed. It is well known that if an oxide layer on a metal surface such as copper or aluminum is abraided, the surface contact potential may change drastically. Since the oxide layer is disturbed when plastic flow takes place, it is reasonable to expect some change in the contact potential. A number of workers[12] have observed that in many metals electrons are emitted from the surface when plastic flow occurs. Most of the electrons have comparatively low energies; these have been called exoelectrons by Kramer.[12] The emission of these electrons from the stressed surface of B would leave any partially insulated

[10] F. C. Whitteborn and W. M. Fairbank, Phys. Rev. Letters **19**, 1049 (1967).

[11] R. C. Tolman and T. D. Stewart, Phys. Rev. **8**, 97 (1916); **9**, 164 (1917); R. C. Tolman and L. M. Mott-Smith, *ibid.* **28**, 794 (1926).

[12] For a review of this effect see L. Grun, Brit. J. Appl. Phys. **9**, 85 (1958); R. N. Claytor, J. E. Gragg, and F. R. Botzen, J. Appl. Phys. **37**, 149 (1966).

oxide layers with positive charges and consequently would account for the positive increase in contact potential when plastic deformation occurs. In order to investigate this possibility, negative potentials up to 18 V were placed on the case H (Fig. 1). Some of the low-energy exoelectrons should have been prevented from escaping from B. This should have reduced the contact potential. In the case of work-hardened copper, changes in the right direction were observed, but were not large enough to conclude that exoelectrons alone were producing the entire effect. Unfortunately, the design was such that some of the exoelectrons could escape from B and be collected on A which was grounded. In the case of the gold-silver alloy where very little or no oxide layer occurs, the plastic range was so small that no clear cut positive changes in contact potential could be observed, although the curves definitely flattened out before rupture. This also occurred in the case of gold. In view of the above results, it is believed that at any rate, not all the observed positive potential changes in the plastic range can be due to exoelectrons. Also, there is reason to believe that the same phenomena which produce the positive contact potential changes when plastic flow occurs, also produce the positive increase in contact potential observed when annealed copper is initially stressed. It may be interesting to note that specimens of the gold-silver alloy which were taken directly from the rolling machine and washed only once with acetone showed positive changes in contact potential with increasing tensile stresses even in the elastic range. It was only after careful heating to temperatures high enough to remove all of the moisture, oil, oil additives, etc., followed by careful cleaning with soap and water, acetone, and alcohol, that reproducible negative changes in contact potential with increasing tensile stresses were observed. In work-hardened copper, silver and nickel, it was usual to find a very small positive increase in contact potential with increasing tensile stresses well below 1 kg/mm^2 before the increase in the negative direction started. As pointed out above, this was not observed in the case of steel or the gold-silver alloy. The effect may be due to the adjustment of the oxide layer in certain regions where the metal has high internal stresses, to the adjustment of the stresses around the clamps, or the straightening of possible irregularies in the surface.

In conclusion, the results reported here show that oxide layers, moisture, impurities, etc., on the surface of a metal or alloy influence the measured contact potential changes produced by tensile stresses. The results are in general accord with what might be expected from the rapidly spinning rotor experiments and from the results of Craig[9] on the compression of metals. On the other hand, they do not give the necessary information desired when the metal is subjected to relatatively small applied tensile stresses in the important cases of copper and silver. The results obtained in the elastic region are in rough agreement with theory. The observed increase in contact potential when plastic flow occurs has not been completely explained, but there is little doubt that the disturbance of the oxide and other surface layers by the plastic deformation is a major factor.

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