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FAILURE OF BRASS. 2.—EFFECT OF CORROSION ON THE DUCTILITY AND STRENGTH OF BRASS

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INTRODUCTION

Investigation¹ during the last few years has established the fact that brass will crack or fracture when exposed to the action of corroding agents, while at the same time under tensile stress, even when the value of this stress is much less than the ultimate strength or even the yield point of the material, as determined in the tensile test. It is well known that surface corrosion plays an important part, even a necessary one, in the "season cracking" of brass, and Jonson² has carried out a number of experiments, in which he has subjected brass test specimens to tensile stress in a testing machine, the specimens being at the same time immersed in a solution of concentrated ammonium hydroxide. He found that so long as the applied stress in these tests was not greater than the elastic limit of the material, the specimens did not fail, but when a stress was applied greater than this limit—e. g., from 20 000 to 40 000 pounds per square inch—cracks would appear after a few days, the specimen would yield continually and finally break.

The effect of corrosion, at least of that caused by the action of ammonium hydroxide, on brass under stress, be it initial or due to external load, is to decrease the strength and also the

¹ E. Heyn, Internal Stresses in Cold-Wrought Bars, and Some Troubles Caused Thereby, *J. Inst. Metals*, 12, 1914, p. 3; A. D. Flinn, Brass in Engineering Construction, *Engineering Record*, 68, 1913, p. 527; P. D. Merica and R. W. Woodward, The Failure of Structural Brass, *Trans. Amer. Inst. Metals*, 1915.

² E. Jonson, Failures of Forgible Brass Bars, *Trans. Amer. Inst. Metals*, 8, 1914, p. 135; The Fatigue of Copper Alloys, *Proc. Amer. Soc. Test. Materials*, 40, 1915, p. 101.

ductility of the material, for it is a striking feature of such brass failures as occur, due to combined stress and corrosion, that they occur with little elongation; the brass does not display its usual ductility. Parallel to his stress-corrosion tests, Jonson ran tensile tests on specimens of the same materials, subjecting them to the same loads, but not at the same time to the action of the ammonium hydroxide; such specimens did not fail after months of test. Furthermore, specimens were corroded with ammonium hydroxide and subsequently tested in tension, giving quite normal results, such that it must be considered that it is the simultaneous effect or action of tensile stress and corrosion (ammonium hydroxide) which produces failure in brass at stresses below its ultimate strength.

It may here be noted that Jonson used only ammonium hydroxide in his tests; he draws the conclusion, however, that any corroding agent, even water, will in time produce the same effect of cracking. The admissibility of this further conclusion seems probable, but is not to be regarded yet as proven.

The author wishes to advance an explanation for this rather striking phenomenon, of the combined action of tensile stress and corrosion on brass, indicating the actual manner or "mechanism" by which this effect is produced, in the hope that this explanation will contribute to progress in dealing with this important technologic problem.

The initial effect of corrosion on any metal, stressed or unstressed, is to roughen the surface, such that in section it appears with ridges or furrows. This nonuniform action of the corroding agent is due to slight variations of the electrolytic (solution) potential over the original (smooth) surface; in the case of a non-homogeneous alloy such as an alpha-beta brass—type, 60 per cent copper and 40 per cent zinc—a difference of potential would in general exist between the alpha and the beta constituents. If the corroded bar were under tensile stress, the value of the fiber stress at the surface would, theoretically at least for a very long bar, be the same at all points; this can no longer be true, however, of the roughened surface.

Leon³ has shown that the stress at the bottom of a semicircular notch, in a tensionally stressed bar, is twice that of the average stress for the section, and that for sharper notches the stress might, at least for hard rubber, be as much as five times the aver-

³ Leon, Über die Spannungsverteilung in einer halbkreisförmigen Kerbe, Österreichische Wochenschrift für den öffentlichen Baudienst, 29, p. 43; 1908.

age stress. The stress at the free edges of the notch is under such circumstances practically zero. The fiber stress along the roughened surface will therefore vary in value between zero, at the top of the small ridges, and a value, at the bottom of the furrows, much larger than that of the average stress.

Now the electrolytic potential of a metal or alloy is increased⁴—i. e., made more electropositive—by the application of a stress. The results of some measurements and further discussion of this effect of stress on the solution potential will be given below, under the next heading.

It is therefore evident that after the formation of the furrowed or roughened surface on the brass specimen under tension, the emf will be greater at the bottom of the small nicks or notches than on the side of these notches immediately adjacent. Corrosion will therefore, other things being equal, be more severe at the bottom of these notches than elsewhere, and the notches will grow inward, becoming sharper and sharper, quite in contrast to their behavior when uncorroded, since in a ductile material such notches tend to flatten or smooth out under tension, thus reducing the local fiber stresses at these points.

In fact, Heyn⁵ finds that the behavior of a notch in a bar under tensional stress distinguishes brittle from ductile material. The notch in a ductile material tends to smooth out, whereas in the brittle material it becomes sharper and narrower under tension, finally causing fracture. Thus, the effect of corrosion under stress is to favor the growth and narrowing down of cracks and to cause an apparent brittleness of the brass.

MEASUREMENT OF THE ELECTROLYTIC POTENTIAL OF BRASS UNDER STRESS

The increase of electrolytic emf of a simple metal to a solution (containing ions of the same metal) due to the application of a stress may be calculated⁶ from the consideration that the increase of emf of a system is proportional to the increase of free energy, and that for isothermal, reversible processes the increase of free energy of a system is equal to the amount of work done on it. The application of stress of values below the true elastic limit is a reversible process and can be carried out isothermally. Consid-

⁴ C. Hambuechen, *The Corrosion of Iron*, Bull. Univ. Wisconsin, No. 8, 1900; T. Richards and Behr, *The EMF of Iron Under Various Conditions*, Publ. Carnegie Inst., No. 61, 1906.

⁵ E. Heyn, *Materialienkunde*, p. 376.

⁶ Walker and Dill, *The Effect of Stress on the EMF of Soft Iron*, Trans. Amer. Electrochem. Soc., 7, p. 153; 1907.

ering, for the purpose of simple and approximate calculation, that brass is a simple metal of equivalent weight equal to

$$\frac{63+65}{2 \times 2} = 32,$$

a stress of 25 000 pounds per square inch, applied isothermally to a brass rod, having a modulus of elasticity of 15×10^6 pounds per square inch, and a density of 8, should produce an increase of emf equal to

$$\begin{aligned} & \frac{\text{work (in ergs)}}{\text{density}} \times \frac{\text{equivalent weight} \times 10^{-7}}{96\,500} \\ &= \frac{25\,000}{2} \times \frac{25\,000}{15\,000\,000} \times \frac{1000 \times 980}{14.2} \times \frac{32 \times 10^{-7}}{96\,500 \times 8} \\ &= 0.000006 \text{ volt;} \end{aligned}$$

with greater stresses and after plastic yielding had commenced, an increase of 2 millivolts might be obtained, assuming that one-half of the energy of deformation is potentialized.

Some measurements have been made of these quantities, with, however, contradictory results. Hambuechen (*loc. cit.*) finds for brass—composition of the brass and of the electrolyte not stated—an increase of 0.3 millivolt at the elastic limit, and an increase of about 4 millivolts at the point of rupture. For iron and steel he finds much larger values. Both Walker and Dill and Richards and Behr, on the other hand (*loc. cit.*), come to the conclusion that, although there is an increase in the emf of iron (they did not work with other metals) caused by application of stress up to and beyond the elastic limit, it is so small as to defy measurement; they explain Hambuechen's results on iron as having been due to the hydrolysis of the ferric salt, which he used as electrolyte.

In the measurements made by the author use was made of two electrodes of the same material, and in the same condition; one of these could be stressed, the other served as a comparison electrode, measurement being made in each case of the difference of potential between the two. These were immersed side by side, in a solution contained in a large glass tube, with stopper at the bottom, the solution being contained between a layer of paraffin below (to which was sometimes added a slight amount of carbon tetrachloride) and a layer of a transformer oil above; these precautions were taken to prevent oxygen from the air from affecting the emf.

The arrangement is shown in the sketch, Fig. 1; the potential measurements were made by a potentiometer. It was found necessary to protect the electrodes from light during measurements, by wrapping black cloth around the container.

The material used in the tests was a homogeneous alpha brass of the following composition:

	Per cent		Per cent
Copper.....	67.5	Lead.....	0.06
Zinc.....	32.5	Iron.....	0.02
Tin.....		Manganese.....	

This material was most kindly furnished by the American Brass Co., in the form of one-fourth inch rods. Before the tests, this material was annealed at 400° C for an hour in order to relieve any initial stress, and the surface thereupon prepared by light rubbing with fine emery paper, followed by etching with nitric acid, washing and drying.

The test procedure consisted in placing the specimens in position, with the electrode (a) under zero stress, noting from time to time the emf between (a) and (b), then applying a stress, in units of 10 000 pounds per square inch, again noting during a certain period of time the emf, removing the stress, noting the emf, re-applying the stress, etc. The results of these measurements are best studied in the form of a curve, giving the emf as a function of the time, a change of stress being noted on the curve. Two such curves showing typical results obtained are given in the Figs. 2 and 3.

It is seen that there is a small but unmistakable increase in the emf, due to the application of stress, and that this becomes relatively quite large, in Fig. 2, when the yield point of the brass is reached.

It is now to be noted that when a bar of metal is subjected to a tensile stress a lowering of temperature takes place, and this lowering of temperature itself produces a momentary change in

FIG. 1.—Disposition of electrodes

emf, which often masks the permanent one; this effect can be noticed in the curves, and it is for this reason that the author adopted the method of holding the specimen at a constant stress for some time, and noting the emf, instead of using Hambuechen's method of continually increasing the stress during the course of the measurements.

CONCLUSIONS

It is believed that an increase in emf of alpha brass to solutions

FIG. 2.—The emf of stressed to unstressed brass in a solution of $N/10 \text{ CuSO}_4 \cdot \text{ZnSO}_4$. The + sign indicates that the bar under stress is electropositive to the comparison electrode

containing zinc and copper ions, caused by the application of tensile stress, has been indicated and measured. This amounts to about 0.2 millivolt for 20 000 pounds per square inch (below the elastic limit) and to about 1 millivolt at the yield point of the material, 30 000 pounds per square inch. This value is apparently much greater than would be calculated for elastic stresses from

FIG. 3.—The emf of stressed to unstressed brass in a solution of $N \text{ ZnSO}_4$. The + indicates that the stressed bar is electropositive to the comparison electrode

thermodynamic considerations; it agrees well with values calculated for stresses above the elastic limit. The author does not wish at present to discuss this divergence otherwise than to point out that the emf measured may be that at some point of the surface, e. g., at the bottom of a small notch, where the fiber stress is much greater than the average; in that case these results could be brought into agreement with thermodynamic theory.

An explanation is given of the effect of corrosion on brass under stress, in decreasing the ductility and strength, and which is based upon this fact of the increased emf and therefore corrodibility of brass under stress. At the bottom of small furrows in the roughened surface the stress is greater than at ridges immediately adjacent; a galvanic couple is formed, and the bottom of the furrow only is corroded, forming in time a crack, which becomes narrower and sharper as it penetrates inward, finally so reducing the cross section that fracture occurs.

This conception of the cause of the embrittling effect of corroding agents on brass under stress is borne out by the examination of samples which have been subjected to Jonson's test. In such samples, not one but several fissures appear, narrowing down and becoming microscopically fine as they penetrate farther and farther into the interior of the specimen. It may be noted in this connection that these fissures appear to favor the beta constituent and to avoid the alpha in a brass, such as manganese bronze, containing both of these.

The question as to why brass should be so susceptible to this effect, and not also iron and steel (apparently, at least), can not at present be adequately answered, not indeed until further investigation has considerably increased our knowledge concerning the values of the stress-emf effect in these materials, the relative significance of this effect in comparison with other local emf's (due to oxide and slag inclusions, etc.), the effect of the covering of corrosion product formed, and other points.

Apparently the effect produced by corroding solution having a low conductivity will, other things being equal, be greater than that of one of high conductivity, since it allows greater prominence to those local stress emf's between portions of the material immediately adjacent. It is known, for example, that nitric acid does not produce cracking in initially overstressed brass in the manner in which ammonium hydroxide or mercurous nitrate or chloride does.

WASHINGTON, July 12, 1916.