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TIME DEPENDENCE OF COPPER AND TIN COATED COPPER CORROSION UNDER STEAM ACTION

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Lucrarea prezintă studiul dependenței coroziunii de timpul de expunere pentru următoarelor materiale metalice: cupru, cupru sudat cu alamă, cupru acoperit cu staniu complet şi ½ şi respectiv cupru sudat acoperit cu staniu pe o față supuse acțiunii aburului in regim ciclic alternant. In toate cazurile, coroziunea materialelor metalice studiate se supune legii parabolice generale, dar în parametri diferiți. Curbele coroziune-timp, calculate şi experimentale prezintă o bună concordanță.

The work presents time corrosion dependence of the following metallic materials: copper, brass welded copper, complete and half tin coated copper and tin half coated welded copper subjected to cyclic/alternating steam action In all cases, the corrosion obeys to the general parabolic law, but with different parameters. The calculated and experimental corrosion-time curves show a good agreement.

Keywords: copper, welded copper, tin coating, corrosion, steam, parabolic law.

Introduction

Copper and copper alloys are used in hot- and cold water circuits and heating and cooling systems in hospitals and hotels. Copper itself has a fair corrosion resistance but traces of copper salts are often troublesome and a tin coating offer a convenient means of preventing their formation.

In the literature there are many studies concerning to the copper corrosion, especially in aqueous medium at room temperature or in air at high temperatures. The numerous works of polarisation and corrosion potential data has been available in the literature with respect to the copper corrosion in chloride media, and a comprehensive review was made recently by Kear, Barker and Walsh [1]. They concluded that the copper corrosion in aqueous chloride media is complicated by the formation of surface films, which generally act to reduce the rate of both anodic and cathodic charge transfer processes.

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In situ electrochemical scanning tunneling microscopy investigations of the anodic Cu(I)/Cu(II) duplex passive layers grown on Cu(111) and Cu(001) in 0.1 M NaOH are reported by Julia Kunze and co-authors [2].

The corrosive damage is not constant, showing changes in time. The corrosion products can accumulate on the metal surface and brake corrosion. The corrosion-time or corrosion rate-time curves have generally a complex character. Therefore, in certain cases the experimental data may be processed in empirical equations, $y = f(\tau)$, which are useful for practical purpose.

Fig. 1 shows typical curves [3-5] for the time dependence of the mass change (Δg) and corrosion rate, r_{cor}, respectively.

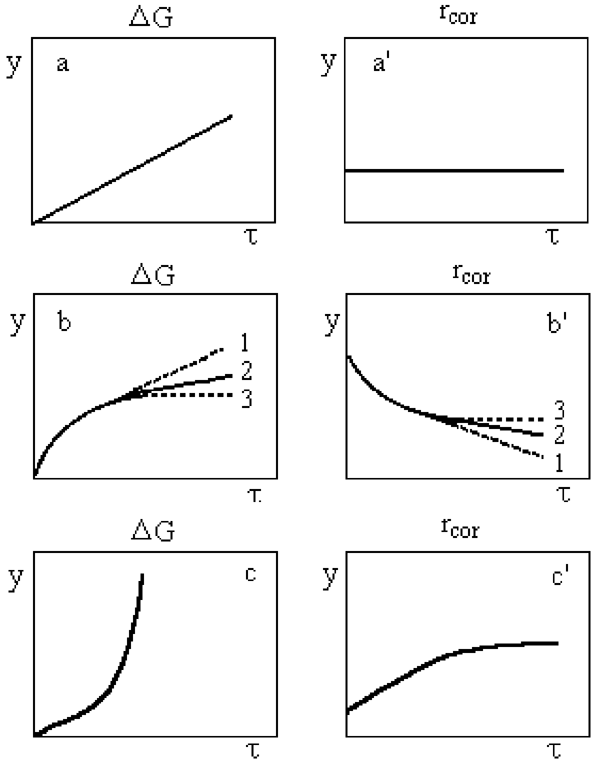

Fig. 1. Typical curves for time dependence of the mass change, Δg, and of the corrosion rate, r_{cor}.

The case shown in Fig. 1a, a’, in which the time dependence of the mass change, Δg, and corrosion rate, r_{cor}, are straight line, the corrosion process obeys a linear law, according to the equation:

$$y = k_1\tau \qquad (1)$$

where k_1 is the slope.

These systems corrode at a constant rate, equal to the direct chemical reaction between metal and oxidant agent, the corrosion product do not influence the corrosion process. However, in most of the cases, thin films of the corrosion products may have weak protection action and the corrosion time dependence correspond to the curves 1 from Fig. 1b, b’.

In case of protecting corrosion product films, the time dependence of the mass change and corrosion rate have the shapes of the curves 2 from Fig. 1b, b’, and corrosion process obeys a parabolic law, given by the general equation:

$$y^n = k_2\tau \qquad (2)$$

The graphic $\lg y = f(\lg \tau)$ must be a straight line, with the slope $1/n$.

If, in the corrosion product film, the braking supplementary elements appear, as worsened of the electronic and ionic conduction of these, the time dependence of the mass charge and corrosion rate have the shape to the curves 3 from Fig. 1b,b’. In this case the corrosion process obeys a logarithmic law, given by equation:

$$y = k_3 \ln \tau \qquad (3)$$

In this case the graphic, $y - \lg\tau$, is a straight line with the slope $2.303k_3$.

The case shown in Fig. 1c, c’ corresponds to the corrosion process, that obeys an exponential law, given by the equation:

$$y = k_4 e^{-k_5/\tau} \qquad (4)$$

Plotting in the co-ordinates $\lg y - f(1/\tau)$ leads to a straight line, where: lg. k_4 = lg y at $1/\tau = 0$ and $k_5/2{,}303$ represents the line slope.

In many practical cases, the time corrosion-dependence curves of the metallic materials may be more complex and thus, difficult to include in the above laws. In function of temperature, nature and concentration of the corrosive agent and the expose time, the same metal may behave after different laws.

At high temperature, the oxidation and scaling of copper take place. The volume ratio between cuprous oxide and copper is 1.7, so an initial protective film is to be expected. Such a film must grow by a diffusion process and should obeys a parabolic law. This has been found for copper in many conditions, but other relationships have been noticed [5].

Evans [6] has shown how internal stresses in growing films may have various effects that can lead to any of the first three growth laws referred above.

In the case of copper alloys containing usual alloying metals, as brass, the alloying element will appear as an oxide in the scale, often in greater concentration than in the alloy itself, and sometimes leads to the exclusion of copper oxides.

The oxidation of tin in dry air is a slow process; the metal remains bright and interference colors are not developed below about 180^{o}C. On a tin surface heated in air [7] the thickness of the oxide grew according to a logarithmic law at temperatures up to about 160^{o}C and according to a parabolic law at higher temperatures, for which the oxide was identified as SnO.

The aim of this paper is to study the time corrosion dependence for copper and welded copper as well as for tin-coated copper and tin coated welded copper subjected to the steam action in the cyclic/alternating conditions.

Experimental

Metallic materials corrosion samples were: copper of electrolytic purity, welded copper with brass, tin full coated copper (Cu/Sn 1/1), ½ tin half coated copper (Cu/Sn ½) and tin half coated welded copper (welded Cu/Sn ½). The first four specimen sizes were 50x30x2 mm and the 5th were 60x50x2 mm.

The chemical composition of the welded brass was 59-61% Cu, 0.2-0.3% Si, 0.8-1.2% Sn, maximum 0.5% impurities (Pb, Fe, Sb, Ni) and Zn.

The surface preparation of the copper and welded copper specimens was carried out by mechanical polishing with 1200 emery paper, followed by accurate rinsing with distilled water and degreasing with acetone. The total or partial tin coating was made with molten tin by dipping or wiping.

The specimens were exposed at cyclic-alternating steam action in an autoclave [8] for sterilizing metallic medical instruments. The Fig. 1 shows the diagram of a sterilizing cycle. Ten successive cycles were applied in 24 hours. The steam parameters are 2.0 - 2.2 bar pressure and 180-200^{o}C temperature.

The exposing time varied between one day and 59 days. The corrosion products were removed by wiping with cotton wool dipped in 5% sulphuric acid solution. The mass change was reported to the specimen area, Δg (g/m^2) and plotted as function of corrosion time, τ. Each point represents the average of three specimens.

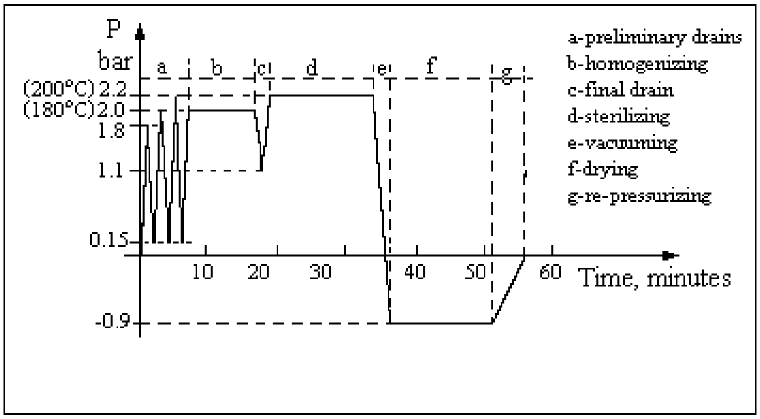

Fig. 2. Scheme of the cyclic alternating steam action in a cycle

Results and discussion

The experimental curves representing the mass change of the studied metallic materials, Δg (g/m^2), with corrosion time, τ, show a parabolic dependence (the dot lines from Figs. 2-6) for all studied materials.

The *n* and k_2 parameter values calculated according to equation 2, and the parabolic empirical equation corresponding to corrosion of the studied materials are presented in the Table 1.

Table 1.

The parabolic dependence parameters and corresponding empirical equations

Metallic material	*n*	k_2	*Parabolic equation*
Copper	*1,62*	*0,22*	$\Delta g^{1,62} = 0,22\tau$
Welded copper	*10,38*	*39,48*	$\Delta g^{10,38} = 39,48\tau$
Cu/Sn 1/1	*4,83*	*0,0151*	$\Delta g^{4,83} = 0,0151\tau$
Cu/Sn ½	*6,67*	*0,0231*	$\Delta g^{6,67} = 0,0231\tau$
Welded Cu/Sn ½	*6,35*	*0,23*	$\Delta g^{6,35} = 0,23\tau$

The calculated and experimental curves show a very good agreement, as one can see in the Figs. 2-6.

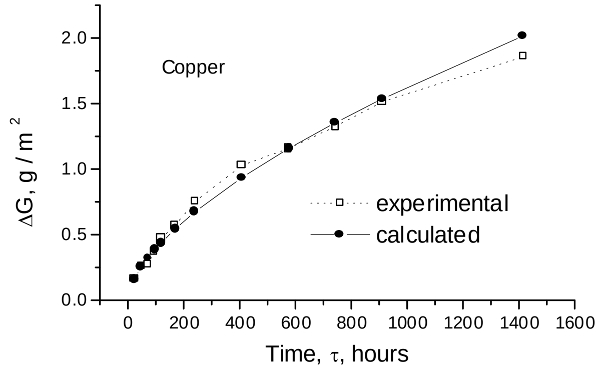

Fig.2. Experimental and calculated curves for copper under cyclic/alternating steam action

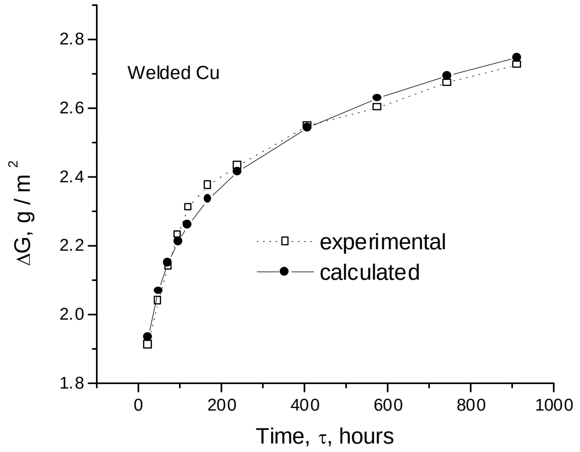

Fig. 3. Experimental and calculated curves for welded copper under cyclic/alternating steam action

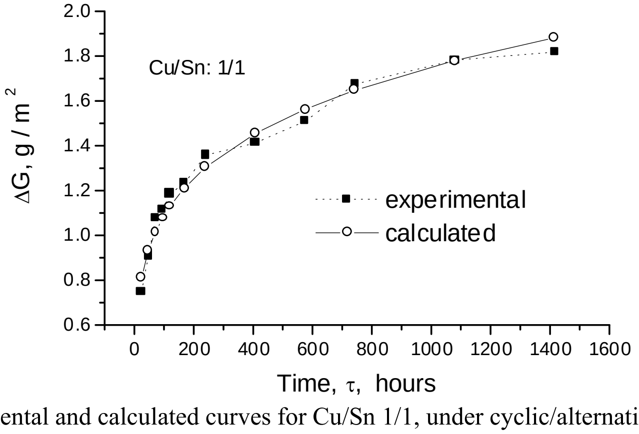

Fig. 4. Experimental and calculated curves for Cu/Sn 1/1, under cyclic/alternating steam action

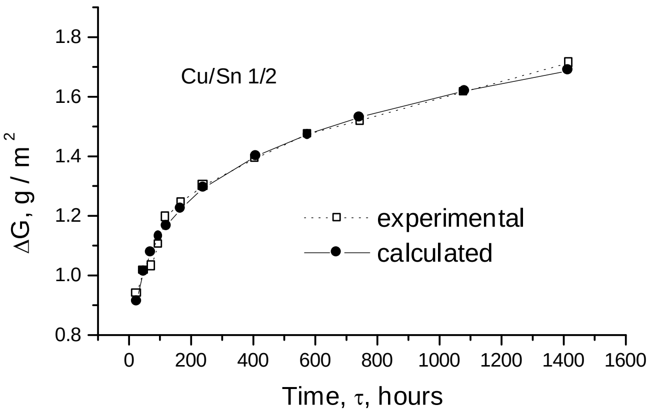

Fig. 5. Experimental and calculated curves for Cu/Sn 1/2, under cyclic/alternating steam action

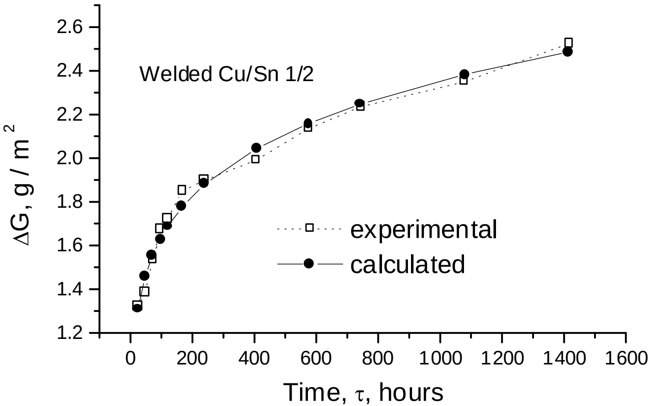

Fig. 6. Experimental and calculated curves for welded Cu/Sn 1/2, under cyclic/alternating steam action

For copper the parabolic index is $n<2$ (the square parabola index). This behaviour corresponds to the interrupted corrosion product film, fact observed experimentally. The corroded copper surface presented isles of corrosion product.

In the case of the welded copper, it was observed the covering of the brass welded inlet with a thick layer of black corrosion product. This layer is the result of a severe corrosion at the beginning of the process that had subsequently a good protection effect, which was confirmed by the large values of both k_2 constant and parabolic index, *n*.

The presence of a thin continuous corrosion product film on the tin-coated areas has protection effects on the corrosion of the copper and welded copper. The low values of the k_2 constant indicate a reduced corrosion rate of the tin as compared to copper and welded copper. The parabolic index is more than 2, which indicates the formation of corrosion product films with protective properties.

The results of this study could be regarded with precautions. Tin is more anodic than copper in the water supplies and in all solutions except those in which copper is dissolved as a complex. The corrosion of tin coating is, like that of tin, extremely localized, but once the copper substrate is reached it may spread slowly. This behaviour can, however, be considerably altered by the action of tin-copper compound layers in the coating. A hot-dipped or wiped coating will have from the outset a layer of Cu_6Sn_5 and and also a layer of Cu_3Sn nearer the copper [9]. These compounds are always more cathodic than tin. As long as some tin coating remains it will protect the copper, and a complete coating of compound is protective, but if all the coating is converted to compound and if there is a break which exposes the copper, than quite severe pitting can occur. Corrosion Testing Laboratories, Inc. [10] reported advanced pitting of the copper under tin coating.

Conclusions

Starting from the experimental data, it has been deduced empirical equations for corrosion calculation of the following materials: copper, brass welded copper, tin full and half coated copper and tin half coated welded copper subjected to cyclic/alternating steam action.

The corrosion process obeys a parabolic law in all cases, but having different parameters.

The experimental and calculated curves for time corrosion dependence shown a very good agreement.

The empirical equations obtained could be used to estimate the long time corrosion resistance of the studied materials in these experimental conditions.

REFERENCES

1. *G.Kear, B.D.Barker and F.C.Walsh*, Corr.Sci., 46, 109, 2004.
2. *J. Kunze, V.Maurice, L.H.Klein, H-H.Strehblow and Ph. Marcus,* Corr.Sci., 46, 245, 2004.
3. *T.Badea, G.Ciur and, A.Cojocaru*, "Coroziunea si controlul coroziun*i",* Ed. Matrixrom, Bucuresti, 2000, p 198.
4. *T.Badea, M.Popa and M.Nicola*, "Ştiința si ingineria coroziunii", Editura Academiei Române, Bucureşti, 2002, p 239.
5. *L. L. Shreir*, Corrosion, vol.I, Corrosion of metals and alloys, Newnes LMT, London, 1963, p 4.47.
6. *U.R.Evans,* Trans.Electrochem.Soc., 91, 547, 1947.
7. *S.C Britton and K.Bright,* Metallurgia, Mannchr., 56, 163, 1957.
8. *T. Badea*, "Comportarea la coroziune a cuprului şi a cuprului acoperit cu staniu în condițiile de funcționare a instalațiilor de sterlizare a materialelor tehnico-sanitare", Raport de cercetare la contractul CH104416, 2004.
9. L. L. Shreir, *Corrosion, vol.II, Corrosion Control*, Newnes LMT, London, 1963, p 14.55.
10. * * * "Under coating corrosion of tin coated copper", Corrosion Testing Laboratories, Inc. ctlweb@corrosionlab.com.