

Influences the Nature of Aggressive Anions on Corrosion Copper Resistance in Bicarbonate Solutions Under Heat-Transfer and Elevated Temperatures

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Ion-activators are the main reasons for depassivation copper and its alloys in near-neutral solutions. They are due to the formation pit and pores on metal surface. Its characteristics are widely observed and local metal dissolution can lead to dangerous situation. The connections between the nature ion-activator, thermal conditions and anodic copper behavior are very interesting for accurate description the mechanism copper depassivation. This research continued the cycle investigations on influence these factors on copper local activation (LA) process in sodium bicarbonate solutions with different activators (F, Cl, Br, I, SO₄²⁻, NO₃⁻, ClO₄⁻).

The compared data were received on complex plant which design and using methods were presented in early papers [1 - 4].

Experimental results show that copper is remained in passive state up to potential of oxygen reduce in 0,1 M NaHCO₃. The reason of this fact is formation the complicated passive oxide-hydroxide film which structured by malachite [3].

Passive state is broken at aggressive anion presence at potential more positive than the steady-state potential. And stability of copper relative to LA is varied in range ΔE_{LA}=0,130 – 1,000 V in dependence from the nature of aggressive anions and thermal conditions (table1).

The influences of temperatures on behaviors of the thermal equilibrium electrode (TEE) and heat-transferring electrode (HTE) are opposite in solutions with halide-ions. Stability of passive state on TEE relative to LA is increased, stability on HTE is decreased. On the contrary, in systems with SO₄²⁻, NO₃⁻, ClO₄⁻ anions resistance copper to LA is decreased under rise temperature of HTE and TEE, and more effective in thermal equilibrium conditions. Corrosion resistance of copper in fixed thermal regime is determined by the nature of aggressive anions. It was decreased in the following line for halide-ions F⁻ → Cl⁻ → Br⁻ → I⁻ and oxygen-containing anions ClO₄⁻ → NO₃⁻ → SO₄²⁻. These results correlate with adsorption susceptibility of anions.

Identification corrosion products of copper in pure sodium hydro-carbonate solution and in solutions with oxygen-containing anions have shown that the passive states of metal are analogic. But in solutions with halide-ions the presence of solid phase (CuX) was fixed in composition of passive layer. The copper resistance to LA decreases under rising the quantity of CuX in a film and decreasing its solubility. At that time, in all electrolytes the temperature increase is accompanied by rising the film mass. More significant effect was observed on HTE with t_r=80°C in halide-ions presence and on TEE with t_r=80°C in electrolytes with ClO₄⁻, NO₃⁻, SO₄²⁻ - ions (t_r – temperature of metal surface). Correlation between decrease of corrosion copper stability to LA and rise of film mass was fixed in all thermal conditions.

The limit stages of LA process were determined. They are dependent from the nature of aggressive anions. In halide-ions presence the limit stage of pit initiation is the diffusion of metal cation from interface metal/film to film/solution interface with formation solid phase CuX. In solutions with ClO₄⁻, NO₃⁻, SO₄²⁻ - ions the LA is controlled by deliver of aggressive anions to film surface and cation vacancy migration from film/solution interface to metal/film interface, which cause the destabilization of passive state [2].

The dependence of stability passive copper state from adsorption susceptibility of aggressive anions and film mass make it possible to explain the mechanism of LA on the base of adsorption and penetration theories.

Table 1.

Electrochemical characteristic for copper anodic dissolution in solutions 0,1M NaHCO₃ + 0,01 M NaY at different thermal conditions

Solution NaHCO ₃ with additives	E _{GC} , V (NHE)			E _{LA} , V (NHE)			ΔE _{LA} , V		
	20°C	80°C	80°C	20°C	80°C	80°C	20°C	80°C	80°C
	TEE	TEE	HTE	TEE	TEE	HTE	TEE	TEE	HTE
NaF	0,070	-0,040	0,040	1,010	-	0,270	0,940	-	0,230

NaCl	0,060	-0,050	0,030	0,450	-
NaBr	0,030	-0,060	0,030	0,260	0,750
NaI	-0,070	-0,110	0,110	AD	0,110
NaNO ₃	0,070	-0,040	0,030	0,280	0,150
Na ₂ SO ₄	0,060	-0,030	0,040	0,270	0,120
NaClO ₄	0,060	-0,030	0,060	0,800	0,560

Some data are not present because of disappear pit on metal surface (the reason for local activation) (-) or active metal dissolution (AD).

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