

Temptative to Elucidate the Effect of Copper on the Corrosion Resistance of Austenitic Stainless Steels

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Abstract

The effects of copper content on the pitting behaviour of SS304 austenitic stainless steels and austenitic grades with low nickel and high manganese contents in deaerated NaCl solution were investigated by potentiodynamic and electrochemical noise measurements. The results indicated that the addition of 3% copper decreased both pitting potential and repassivation potential of austenitic stainless steels. Moreover, electrochemical noise measurements showed that copper did not have any detrimental effect neither on pit initiation nor on pit propagation, but it had a detrimental effect on pit repassivation. It is proposed that when the potential at the pit wall is low enough for copper to remain metallic, this element does not dissolve, enriches at the surface, prevents the oxidation of iron and chromium and also delays the repassivation.

1. Introduction

This project is part of a research program which aims at producing new austenitic grades with low nickel contents for economic reasons. In these grades, nickel is replaced by manganese, nitrogen and copper. Hence, the propose of this work is to study the effect of copper on the pitting phenomena of this new grades and to suggest a mechanism for the actions of copper on the pitting phenomena.

Copper has shown different effects on the pitting resistance of steels; it can either improve or deteriorate pitting resistance [4-6]. Hence the understanding of the effect of copper on the pitting resistance of these steels is necessary to access the elaboration of grades which optimize corrosion resistance.

Electrochemical noise measurement has shown to be very powerful to investigate the early stages of pitting. Some precursor current fluctuations appear before the conventional pitting potential is reached. These are the signature of metastable pits and also call "pre-pitting noise". In this work this technique would be used to study the specific action on the different stages of pitting phenomena.

2. Experimental Works

2.1 Materials

Austenitic stainless steels used in this work are listed in Table 1. All specimens were discs with 1 mm thick and 15 mm diameter. These specimens were polished with SiC papers to No.1200 and polished with various sizes diamond pastes ie., 15 μ m, 6 μ m and 3 μ m respectively, then cleaned in acetone, rinsed with distilled water and dried with air spray.

2.2 Electrochemical Measurements

Two different techniques for characterizing

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Table 1 Chemical compositions of investigated steels. Analyzed by Ugine Ressearch Center

Alloys	Chemical composition (wt %)								
	C	Si	Mn	Ni	Cr	Cu	N	S (ppm.)	Ce+La (ppm.)
304	0.037	0.385	1.414	8.577	18.23	0.213	0.041	36	-
304+Cu	0.040	0.353	1.435	8.694	18.25	3.040	0.041	45	-
Low Ni+MnS	0.071	0.811	7.304	1.653	16.41	0.190	0.244	9	
Low Ni+MnS+Cu	0.058	0.740	7.510	1.620	16.36	3.040	0.216	6	-
Low Ni+CeS	0.090	0.854	7.300	1.677	16.20	0.182	0.210	20	200
Low Ni+CeS+Cu	0.069	0.828	7.380	1.681	16.31	3.030	0.192	17	200

pitting phenomena based on potentiodynamic measurements and pre-pitting noise analysis were used as follows.

2.2.1 Potentiodynamic Measurements

The polarization curves of the specimens were recorded by an anodic scan from -1V/SCE with a scan rate of 10 mV/min in 2M NaCl at pH 1.5, the corrosion rate and the critical current density were measured from the polarization curves. The pitting potential of each specimen was measured by anodic scan after 15 minutes at rest potential with scan rate of 100 mV/min in deaerated 0.02M NaCl at pH 6.6. The repassivation potential was evaluated by conducting cyclic polarization test in deaerated 0.02M NaCl at pH 6.6 with the scan rate of 100 mV/min.

2.2.2 Pre-pitting Noise Analysis

The current versus time signals under potentiostatic control were studied in deaerated 0.02M NaCl at pH 6.6. After 15 minutes at rest potential, the specimens were recorded. The potentiostatically pulsed to the desired passive potential and the current transients curve were quantified during 24 hours. Each current transient was considered to be associated with a number of transients would be signal of metastable pit. Lifetime, amplitude and charge of each transient were also determined.

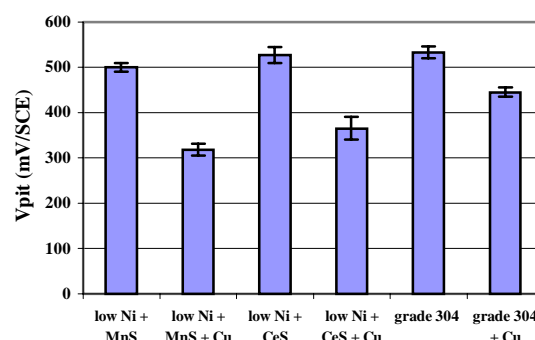


Figure 1 Pitting potential on SS304 and low Ni grades in 0.02M NaCl at pH 6.6.

3. Results and Discussions

3.1 Effect of Copper and Sulfide Inclusions on the Pitting Potential

Figure 1 shows the pitting potential of SS304 and low Ni grades. The results indicated that the addition of 3% Cu decreased the pitting potential of every grade.

However, pitting potential is thought to depend on the steel resistance to pit initiation, propagation and on the repassivation tendency of the stainless steel. The specific actions on the different stages of pitting phenomena will be considered in more details in the next sections.

3.2 Effect of Copper and Sulfide Inclusion on Pit Initiation

Figure 2 shows the number of type 1 transients during 24 hours divided by the number of sulfide

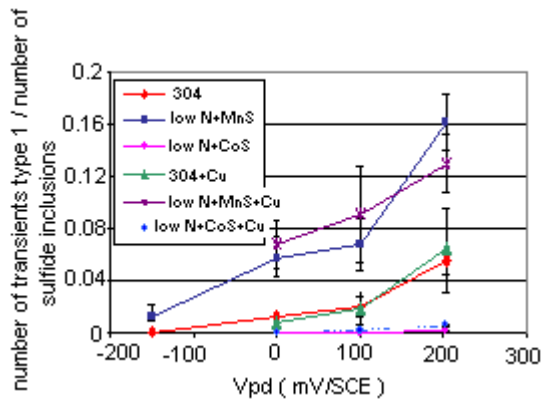


Figure 2 Number of type 1 transients during 24 hours in 0.02M NaCl at pH 6.6 on SS304 and low Ni grades.

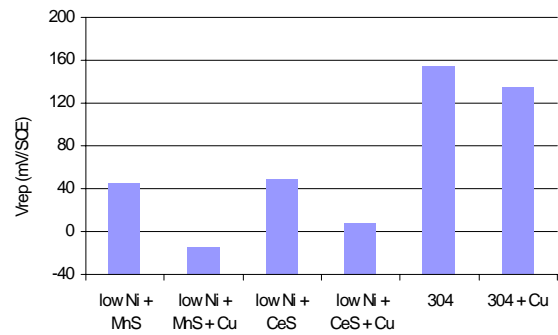
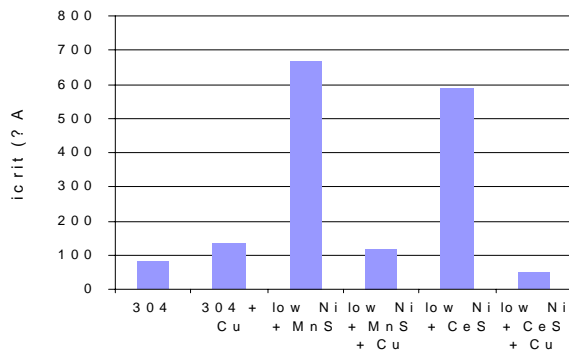
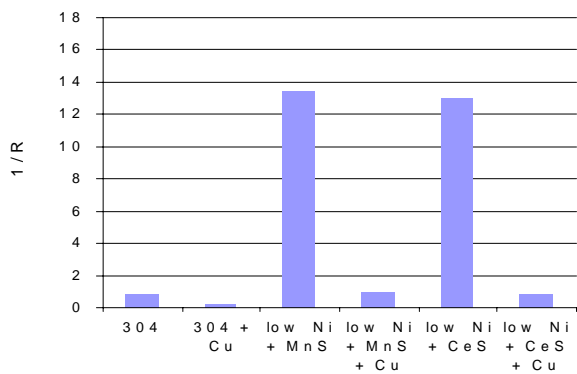


Figure 4 Repassivation potential on SS304 and low des in 0.02M NaCl at pH 6.6.



(a)



(b)

Figure 3 (a) Critical current densities and (b) corrosion rates of SS304 and the low Ni Grades in 2M NaCl at pH 1.5.

inclusions on the sample surface. The results revealed that the addition of 3% Cu did not increase the number of type 1 transients noticeably and it could be suggested that Cu did not have any pronounced effect on pit initiation.

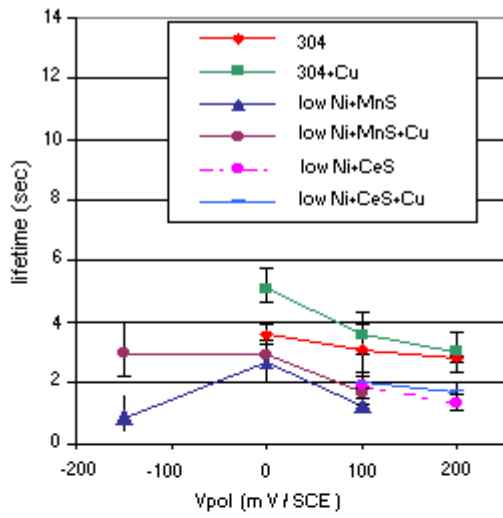
3.3 Effect of Copper and Sulfide Inclusions on Pit Propagation

Figure 3 (a) and (b) show the critical current densities and the corrosion rates of SS304 and the low Ni grades in 2M NaCl at pH 1.5, respectively. Both results indicated that the addition of 3% Cu sharply decreased the critical current densities and the corrosion rates on the low Ni grades, but slightly decreased for the SS304. According to the literature [2], the addition of 0.4-3.0% Cu decreases the corrosion rate by enrichment of metallic Cu on the surface which may act as a protective diffusion barrier for the steels.

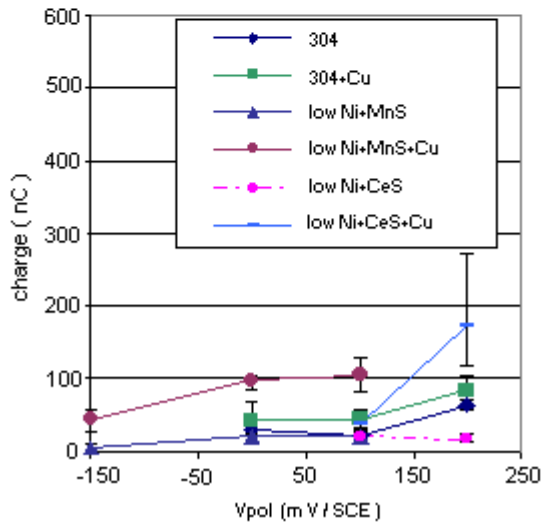
3.4 Effect of Copper and Sulfide Inclusions on Pit Repassivation

Figure 4 shows the repassivation potential of SS304 and the low Ni grades in 0.02M NaCl at pH 6.6. The results revealed that the addition of 3% Cu decreased the repassivation potential on every grade.

Figure 5 (a) and (b) show the values of the average lifetime and charge of type 1 transients observed on SS304 and the low Ni grades in 0.02M NaCl at pH 6.6, respectively. Both results agreed well with those found previously on repassivation potential: on every grade the addition of 3% Cu increases the lifetime and charge of type 1 transients. According to the results that were mentioned before, copper decreases the pitting



(a)



(b)

Figure 5 (a) the average value of lifetime and (b) charge of type 1 transients on SS304 and the low Ni grades in 0.02M NaCl at pH 6.6.

resistance. If the specific action of copper on the different stages of pitting phenomena is considered, the results indicate that copper does not have any pronounced detrimental effect on pit initiation nor propagation, but it retards pit repassivation. Hence, the following section will aim at proposing the repassivation process mechanism by copper.

3.5 Mechanism of Pit Repassivation by Copper

It is proposed that copper has a detrimental effect on pit repassivation due to the fact that it

may form a metallic copper film on the pit wall which inhibits the repassivation process.

Figure 6 shows the polarization curve of copper in 2M NaCl at pH 1.5. By referring to Pourbaix diagram for Cu-Cl-H₂O equilibria at 25°C in 1M NaCl as shown in Figure 7, it can be observed that at low pH and low potential. Copper is stable as metallic copper.

When the potential increases and reaches the dissolution potential, copper tends to dissolve and form the CuCl₂⁻ which is soluble in water via equation (1) :

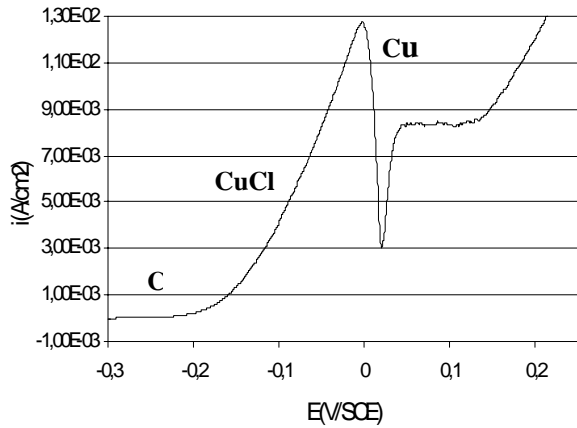


Figure 6 Polarization curve of a sheet of 99.99% copper in 2M NaCl, pH 1.5 at 23°C and at scan rate 10mV/min.

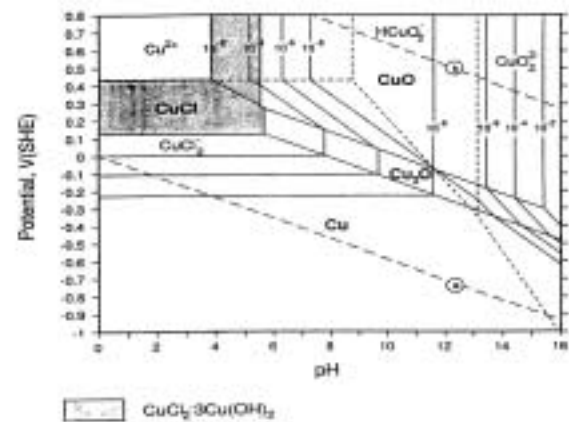


Figure 7 Potential-pH (Pourbaix) diagram for Cu-Cl-H₂O equilibria in 1M NaCl at 25°C.

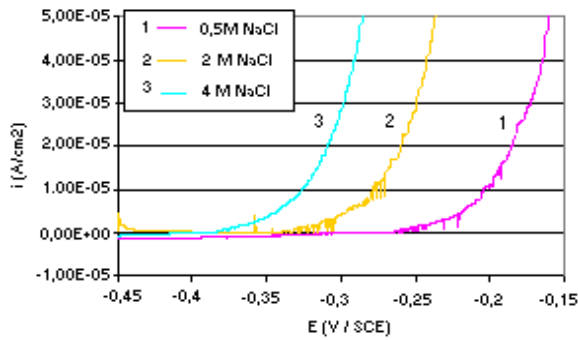


Figure 8 Polarisation curves of a sheet of 99.99% pure Copper with scan rate 10mV/min in 0.5, 2, 4M NaCl respectively, at pH 1.5, 23°C.

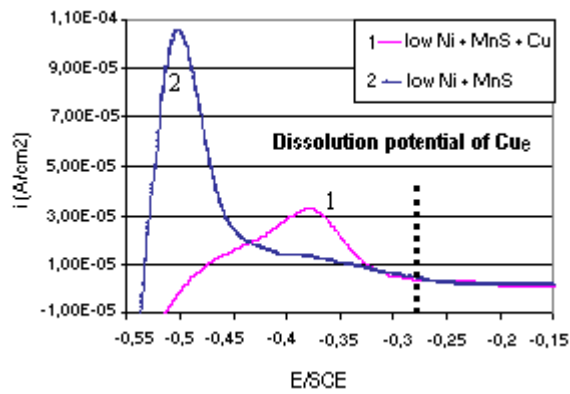


Figure 9 Polarisation curves of the low Ni + MnS and low Ni + MnS + Cu grades at with scan rate 10 mV/min in 0.5M NaCl at pH 1.5

When the potential is raised up to 0.001 V/SCE, the critical current density decreases due to the precipitation of CuCl which is governed by the chemical equilibrium between CuCl_2 and Cl^- species as shown in equation (2):



This is illustrated by Figure 6 which represents the polarization curve of a 99.99% pure copper sheet in 2M NaCl at pH 1.5, 23°C and at scan rate of 10 mV/min.

Also the dissolution potential of copper depends on the chloride concentration. Figure 8 shows the polarization curves of a copper sheet in different chloride concentrations at pH 1.5 and the dissolution

potentials can be deduced from these curves.

Figures 9 and 10 show the polarization curves of the low Ni + MnS and low Ni + MnS + Cu with scan rate 10 mV/min in 0.5M and 2M NaCl at pH 1.5, respectively. These tests show the potentials to be chosen for studying the repassivation kinetics since they have to be located in the passive domain of the steel. To analyze the effect of metallic copper on repassivation kinetics, the values of the chosen potentials should be both lower and higher than the potential of the dissolution of copper. To characterize the repassivation kinetics, the repassivation time (τ 0.1 and τ 0.01) was measured when the current density decreased at a factor of 10 and 100, respectively, from the passivation curves as shown in Figure 11.

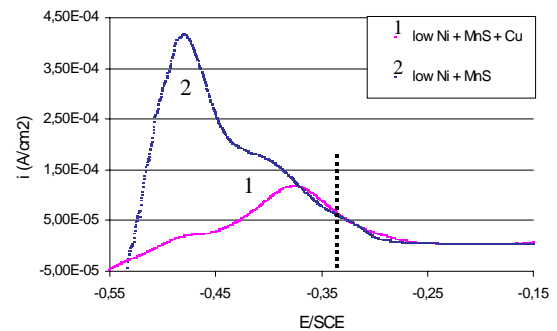


Figure 10 Polarisation curves of the low Ni + MnS and the low Ni + MnS + Cu with scan rate 10 mV/min in 2M NaCl at pH 1.5.

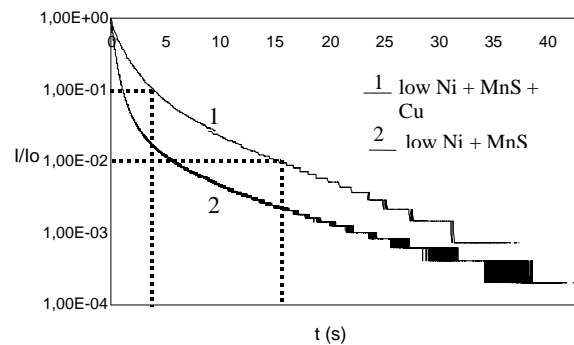
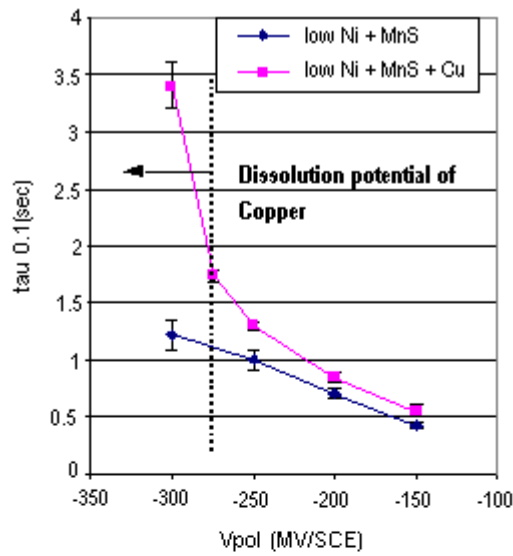
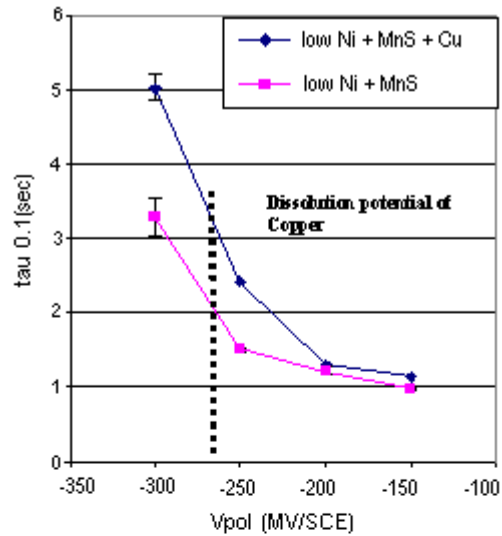


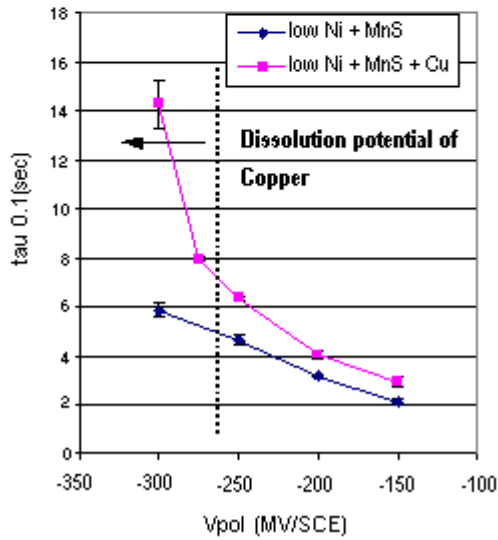
Figure 11 Current density versus time curves measured during potentiostatic measurement at -300mV/SCE in 2M NaCl at pH 1.5, 23°C.



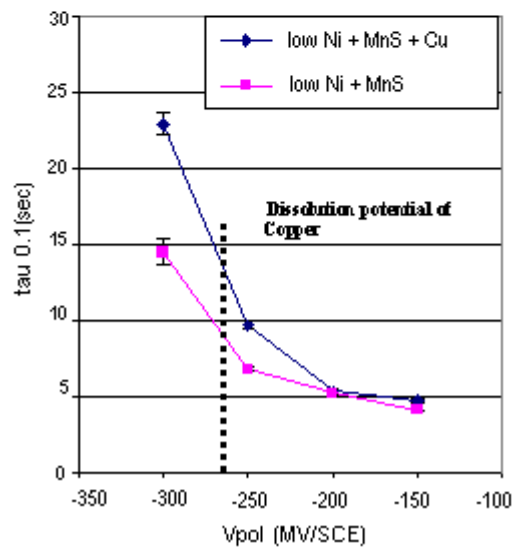
(a)



(a)



(b)



(b)

Figure 12 Evolution of (a) $\tau_{0.1}$ and (b) $\tau_{0.01}$ with polarisation potential on low Ni + MnS and low Ni + MnS + Cu grades in 2M NaCl at pH 1.5, 23°C.

Figure 12 (a) and (b) shows respectively the values of $\tau_{0.1}$ and $\tau_{0.01}$ measured for the low Ni + MnS and the low Ni + MnS + Cu grades polarised at different potentials in 2M NaCl at pH 1.5. Both results showed the same trend: when the steels were polarised at a high potential (higher than the potential of dissolution of copper), the τ value for the low Ni + MnS + Cu and the low Ni + MnS

Figure 13 Evolution of (a) $\tau_{0.1}$ and (b) $\tau_{0.01}$ with polarisation potential on low Ni + MnS and low Ni + MnS + Cu grades in 0.5M NaCl at pH 1.5, 23°C.

grades were close to each other, whereas the polarisation potential decreases towards the values of the potential of dissolution of copper. Tau values for the low Ni + MnS + Cu grade became higher than those or the low Ni + MnS grade, indicating that copper retards repassivation when it is metallic, and does not have any marked effect when it dissolved. The same trends were observed in 0.5M NaCl

solution (see Figure 13). It can be noted that the potential above which the effect of copper on repassivation become negligible is shifted to a more anodic value when compared the results tested in 2M NaCl and 0.5M NaCl solutions. These observations assert that copper retards the repassivation process mainly when it is metallic. It can be explained by the fact that metallic copper does not dissolve into solution so it is enriched at the surface and may prevent the oxidation of iron and chromium.

4. Conclusion

Copper decreased the pitting resistance of austenitic stainless steels and more pronounced on the low nickel grades than SS304 grades. Electrochemical noise measurements showed that copper did not have any detrimental effect on pit initiation neither on pit propagation, but it retarded pit repassivation. Potentiostatic tests in simulated pit solution were also shown that copper mainly acts on repassivation when it is metallic and that its influence is negligible when it dissolves as soluble copper chloride complexes. It is proposed that

metallic copper becomes enriched at the pit wall which inhibits the repassivation process.

5. Acknowledgements

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