

Repassivation Kinetics of Fe-20Cr-xNi Alloys (x = 0 ~ 80 wt%) and its Relation to Stress Corrosion Susceptibility

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Repassivation kinetics of rapidly scratched scars on the surface of Fe-20Cr-xNi alloys (x=0~80 wt%) in a chloride solution was examined using an ampero-chronometric method, and its relationship to stress corrosion cracking (SCC) susceptibility was explored. During the repassivation, passive film initially (0~10 ms) nucleated and grew according to the place exchange model, and then grew according to the high field ion conduction model. Based on the high field ion conduction model, a new parameter was proposed as a quantitative measure of repassivation rate and hence SCC resistance. Influences of Ni on the repassivation kinetics of Fe-20Cr-xNi (x=0~80 %) alloys were evaluated in terms of the new parameter, and the results were in good agreement with the influence of Ni on the SCC resistance of the alloys measured in a hot chloride solution.

Keywords : repassivation kinetics, Fe-Cr-Ni alloy, ampero-chronometric method, stress corrosion cracking susceptibility

1. Introduction

SCC of austenitic stainless steels has been well explained by the film rupture and slip dissolution model.¹⁾ According to the model, cracks initiated and propagate by repetitive processes of slip induced film rupture/dissolution/repassivation. The repassivation is a film reforming process on the film broken surface, and its kinetics have been considered to be a critical factor in determining the SCC susceptibility of stainless steels.^{2,3)} For a stainless steel/environment system subjected to deforming at a constant strain rate or to a constant loading condition, the inherent repassivation rate of the alloy measured without application of stress is presumed to determine the SCC susceptibility.

Repassivation kinetics on a scratched surface is generally analyzed by the relationship between anodic current density ($i(t)$) flowing from the scratch and charge density ($q(t)$) that has flowed from the scratch. Growth of passive film during the repassivation on a scratched surface of austenitic stainless steels in a chloride solution was found to follow the high field ion conduction model in which $\log i(t)$ is linearly proportional to $1/q(t)$ with a slope of cBV , where c is a constant for the alloy, B is a constant related to the activation energy barrier for ion movement

through the film, and V is the potential difference across the passive film.^{4,5)} Kwon et al.⁴⁾ demonstrated that the value of cBV is very effective as a measure of both repassivation rate and protective quality of reformed film, and hence can be used as a quantitative measure of the SCC susceptibility (or resistance). Specifically, the lower the value of cBV for a given alloy/environment system, the faster repassivated is the alloy with formation of thinner and more protective film, and thereby exhibiting less susceptibility to SCC.⁴⁾

Nickel (Ni), as an austenite stabilizing element in iron base alloys, is added to stainless steel primarily for determining its structure. Depending on the Ni content, stainless steels can be classified into ferritic, duplex stainless, and austenitic stainless steels. In addition to the structure determining role, Ni is known to have a significant effect on the resistance to Stress Corrosion Cracking of stainless steels as well as nickel base alloys.⁶⁻⁸⁾ It was reported that small amounts of Ni cause otherwise immune ferritic stainless steels to be susceptible to SCC in hot chloride solution.⁹⁾ For example, an 18% Cr-2% Mo-1% Ni ferritic stainless steels exhibited SCC in boiling 42% MgCl₂.⁹⁾ According to the well known Copson diagram,⁶⁾ Fe-20 wt.% Cr-x wt.% Ni alloys exhibited the maximum susceptibility to SCC in boiling MgCl₂ at 154

°C when they contain about 10 wt.% Ni, or the resistance to SCC of the alloys increased when the Ni content of the alloys decreased or increased from 10 wt.%. The reason why Ni affects SCC of Fe-20Cr-xNi (x=0 to 80%) is not yet clearly elucidated. However, nickel may have a significant influence on the repassivation kinetics of the alloys and hence on the SCC susceptibility. The research objective of present work is to analyze the influence of Ni on the repassivation kinetics of Fe-20Cr-xNi alloys (x=0-80 wt.%) in terms of the cBV value, and then to clarify the reason why Ni affects the SCC susceptibility of the alloys.

2. Experimental

Alloys fabricated for the study were high-purity laboratory heats of Fe-20Cr-xNi (x = 0, 5, 10, 15, 20, 40 wt.%) and Fe-25Cr-2Mo-xNi (x = 0, 2 wt.%) alloys in order to examine the effects of Ni on the repassivation kinetics of the designed alloys. Chemical compositions of the alloys are given in Table 1.

High purity alloying elements were vacuum-arc-melted to obtain extremely low interstitial grades, and cast in the form of button. The casts were homogenized for 100 min at 1200 °C and then hot rolled into 3 mm thick plates. The hot rolled plates were cold rolled into 1.5 mm thick sheets and then solution annealed for 20 minutes at 1050 °C, followed by water quenching.

A cell was devised to measure the repassivation current on the scratched surface of the alloys using the rapid scratching electrode technique. The cell consisted of a specimen as a working electrode, a platinum counter electrode, a saturated calomel electrode (SCE), and a scratcher with an alumina tip. The details in the cell were described elsewhere.^{4),5)} A scratch was made by pulling up the alumina tip loaded on a spring along the surface with a constant distance under a constant contact stress by an air pressure cylinder connected to a solenoid valve. The surface of the sample was scratched under a potentiostatic condition after a stable passive film had been formed. A scratch of about 0.6 mm length and about 35 μm width was formed on a #2000 grit polished specimen with an exposed area of 10 mm × 0.6 mm. Current flow from the scratch during and after the scratching was measured every millisecond and computer processed for further analysis. Anodic polarization responses of the alloys were measured at a scan rate of 0.5 mV/s using a conventional three electrode cell. All the tests were performed in 50 °C, 1 M MgCl₂ solution deaerated with nitrogen with polarization applied after a stabilized corrosion potential had been achieved. All the electrochemical potentials are

Table 1. Chemical compositions of the designed alloys used in this study (wt.%)

Alloy	Fe	Cr	Mo	Ni	Si	Nb
Fe-20Cr	Bal.	20.67	-	-	0.22	0.15
Fe-20Cr-5Ni	Bal.	20.85	-	4.91	0.25	0.16
Fe-20Cr-10Ni	Bal.	20.65	-	9.83	0.20	0.15
Fe-20Cr-20Ni	Bal.	20.59	-	20.29	0.17	0.17
Fe-20Cr-40Ni	Bal.	20.55	-	38.97	0.19	0.10
20Cr-80Ni	Bal.	20.88	-	Bal.	0.24	0.13
Fe-25Cr-2Mo	Bal.	26.22	2.02	-	0.23	0.14
Fe-25Cr-2Mo-2Ni	Bal.	25.79	2.03	1.86	0.18	0.14

referred to the SCE.

3. Theory

Growth of passive film on stainless steels during repassivation is usually described by the models based on the pioneering works of Sato and Cohen¹⁰⁾ and Cabrera and Mott.¹¹⁾ According to the place exchange model proposed by Sato and Cohen,¹⁰⁾ a layer of oxygen is adsorbed onto the surface and then exchanges places (possibly by rotation) with underlying metal atoms. A second layer of oxygen is adsorbed and the two M-O pairs rotate simultaneously. This process is repeated, and results in the formation of oxide film. Based on this model, it was induced that logarithms of anodic current density ($i(t)$) are linearly proportional to charge density ($q(t)$) that has flowed from the scratch during repassivation;

$$\log i(t) = \log k' + \beta V - \frac{q(t)}{K} \quad (1)$$

where β and k' are constants, V is the applied potential and $q(t)$ is experimentally determined by integration of the current density with time during the repassivation. The value of $1/K$ determined from the slope in the $\log i(t)$ vs. $q(t)$ plot is a constant directly proportional to the activation energy for the place exchange of a M-O pair. On the other hand, according to the high field ion conduction model,¹¹⁾ the passive film grows by the transport of metal ions across the film toward the film/electrolyte interface under high electric fields of a few MV/cm. Based on the model, logarithms of anodic current density ($i(t)$) are inversely proportional to charge density ($q(t)$);^{4),5),12)}

$$\log i(t) = \log A + \frac{cBV}{q(t)} \quad (2)$$

where A, B and c is constant, V is the potential drop across the film. Kwon et al.⁴⁾ demonstrated that the cBV , the slope in the $\log i(t)$ vs. $1/q(t)$ plot, can be used as a quantitative measure of repassivation rate of a stainless steel, and hence closely associated with susceptibility to SCC of stainless steels in a chloride solution.

4. Results and discussion

4.1 Repassivation kinetics

Fig. 1(a) shows a typical current transient curve for Fe-20Cr alloy when a scratch was made on the surface of the alloy polarized to a passive potential, -300 mV in a deaerated 1 M MgCl₂ solution at 50 °C. Once the passive film is broken by a scratch, the anodic current flowing from the scratch increases abruptly to a peak due to an anodic oxidation reaction, and thereafter decreases as repassivation proceeds. Based on the data in Fig. 1(a), the $\log i(t)$ vs. $q(t)$ and the $\log i(t)$ vs. $1/q(t)$ plots were drawn respectively according to Eq. 1¹⁾ and 2²⁾ and presented in Fig. 1(b) and 1(c). Evidently, the repassivation of the alloy occurred in consecutive processes with different kinetics: passive film initially nucleated and grew for about 8 ~ 14 ms according to the place exchange model, in which $\log i(t)$ was linearly proportional to $q(t)$, and thereafter grew according to the high field ion conduction model from 8 to 100 ms, in which $\log i(t)$ was linearly proportional to $1/q(t)$. After 100 milliseconds, the anodic current density, $i(t)$, scattered over a small range of current density with a little increase in the charge density, $q(t)$, probably due to reaching a steady-state. All the alloys examined in this study exhibited repassivation behaviors similar to that described above. The transition of film growth mechanism from the place exchange model to the high field ion conduction model appears to occur because the activation energy for the place exchange process of M-O pairs increases as the film grows, and then reaches to the value beyond which the place exchange process of M-O pairs cannot occur.

4.2 Effects of Ni on repassivation kinetics of ferritic stainless steels

Fig. 2(a) shows the current transient curves for Fe-25Cr-2Mo- x Ni ($x = 0, 2$) ferritic stainless steels measured by scratching the surface of the alloys polarized to -300 mV in a deaerated 1 M MgCl₂ solution at 50 °C. The applied potential, -300 mV, was selected as that at which the two alloys formed stable passive films in the solution tested. The applied potential was marked in the anodic polarization curves of the alloys, which were shown in Fig. 2(a). It is evident from Fig. 2(a) that the peak

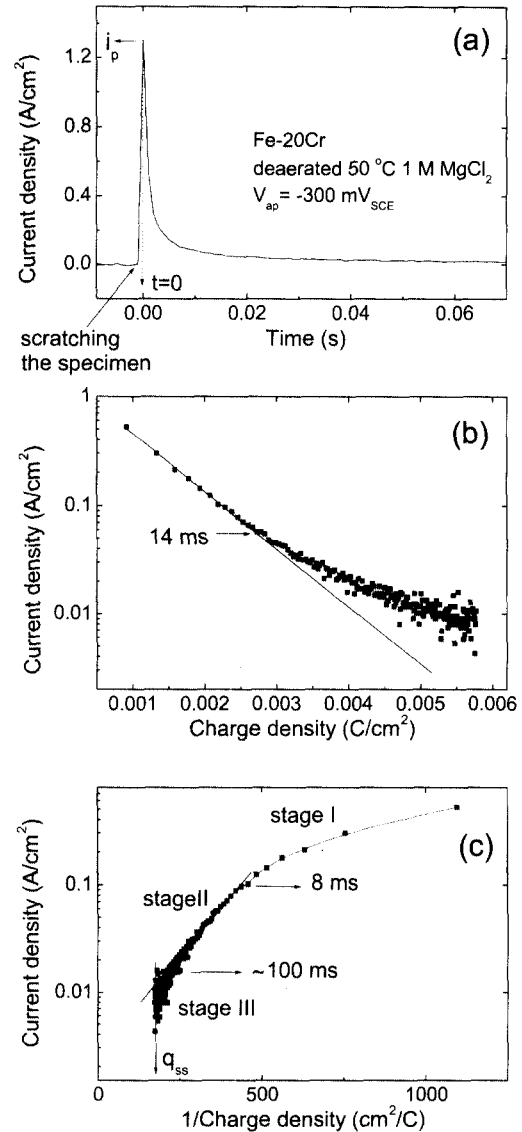


Fig. 1. (a) Current transient curve; (b) $\log i(t)$ vs. $q(t)$; and (c) $\log i(t)$ vs. $1/q(t)$ plot for Fe-20Cr alloy in deaerated 50 °C 1 M MgCl₂ solution at 300 mV_{SCE}.

current density of the current transient curve for Fe-25Cr-2Mo-2Ni is much higher than that for Fe-25Cr-2Mo, demonstrating that the anodic oxidation current density of bare metal significantly increased by the addition of 2 wt% Ni to Fe-25Cr-2Mo alloy.

The repassivation rate of an alloy can be compared by the repassivation time that has been passed from scratching to achieve the predetermined degree of repassivation represented by i_r in Fig. 2(a). The shorter the repassivation time, the faster will be the repassivation rate of an alloy. In Fig 2(a), it took longer time (t_{2Ni}) for Fe-25Cr-2Mo-2Ni alloy to be repassivated to the predetermined degree of repassivation represented by i_r than that (t_{0Ni}) for Fe-25Cr-

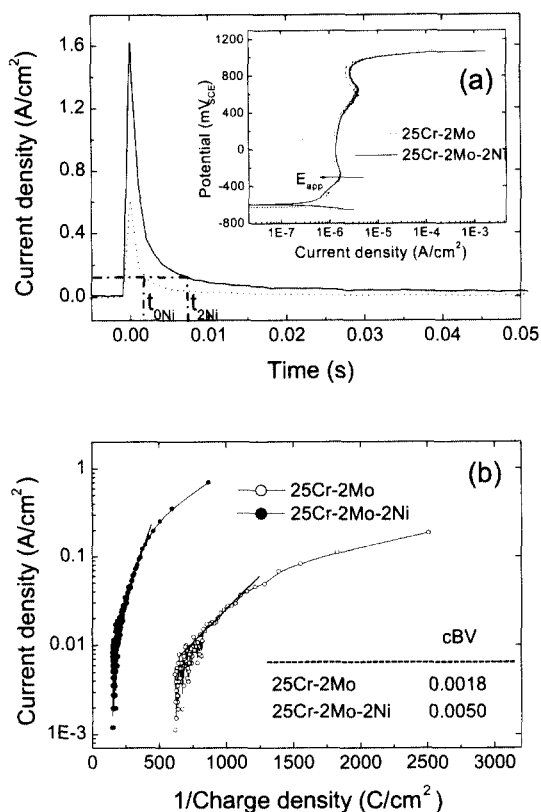


Fig. 2. (a) Current transient curve and (b) $\log i(t)$ vs. $1/q(t)$ plot of Fe-25Cr-2Mo-0 and 2Ni alloys.

2Mo. These results suggest that a small amount addition of Ni to Fe-25Cr-2Mo alloy reduces significantly the repassivation rate of the alloy.

The $\log i(t)$ vs. $1/q(t)$ plots were drawn based on the data of the current transient curves in Fig. 2(a) and shown in Fig. 2(b). By addition of 2 wt % Ni to Fe-25Cr-2Mo alloy, the value of cBV or the slope of the linear region in the $\log i(t)$ vs. $1/q(t)$ plots increased significantly. Thus Fe-25Cr-2Mo-2Ni alloy with lower repassivation rate exhibits higher value of cBV than Fe-25Cr-2Mo. According to the previous results reported by Kwon et al.,⁴⁾ the higher the value of cBV , the slower repassivated is the alloy, thereby exhibiting the more susceptibility to SCC. Based on these relationships between the change in cBV and the SCC susceptibility, we predict that the alloy with Ni will have higher SCC susceptibility than that without Ni. This prediction clearly corresponds to the results of U-bend tests previously reported by Bond and Dundas⁹⁾ for Fe-18Cr-2Mo and Fe-25Cr-3.5Mo alloys with or without Ni in boiling MgCl₂ solution at 140 °C; the Fe-18Cr-2Mo-1~2 % Ni and Fe-25Cr-3.5Mo- 1~2.5 Ni alloys failed within 22 hr whereas Fe-18Cr-2Mo-0.6Ni and Fe-25Cr-3.5 Mo alloys were immune to SCC.

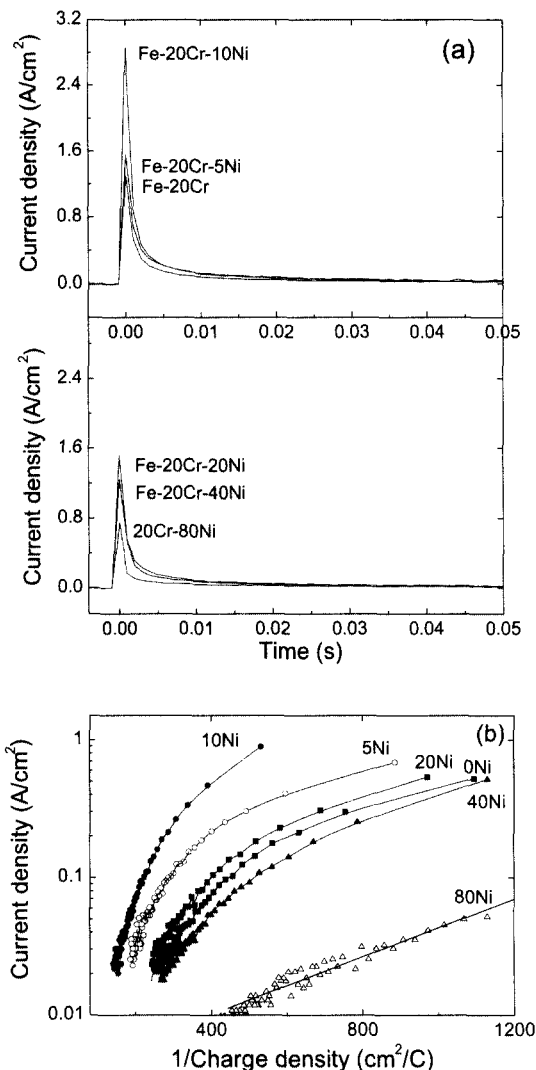


Fig. 3. Effects of Ni content (a) on the current transient on the scratched surface and (b) on the $\log i(t)$ vs. $1/q(t)$ plots for Fe-20Cr-xNi alloys ($x = 080$) polarized to 300 mV in deaerated 1 M MgCl₂ at 50 °C.

4.3 Effects of Ni on repassivation kinetics of Fe-20Cr-xNi alloys

In order to confirm the validity of the cBV as a parameter of repassivation rate and hence SCC resistance of an alloy, the effects of Ni on the repassivation kinetics of Fe-20Cr-0~80Ni alloys were also examined in terms of the cBV , and compared with the SCC susceptibility of the alloys measured under a constant loading condition in a boiling MgCl₂ solution. Fig. 3(a) shows the current transient curves of the Fe-20Cr-xNi ($x = 0, 5, 10, 20, 40, 80$) alloys when a scratch was made on the surface of the each alloy polarized to -300 mV in a deaerated 1 M MgCl₂ solution at 50 °C. The potential, -300 mV, is that at which all the tested alloys form a stable passive film

Table 2. *cBV* values determined from the $\log i(t)$ vs. $1/q(t)$ plots for Fe-20Cr-*x*Ni alloys polarized to 300 mV_{SCE} in 1 M MgCl₂ at 50 °C.

Chemical composition	<i>cBV</i> (mC/cm ²)
Fe-20Cr	3.8
Fe-20Cr-5Ni	4.4
Fe-20Cr-10Ni	8.4
Fe-20Cr-20Ni	3.9
Fe-20Cr-40Ni	3.1
20Cr-80Ni	1.0

on the surface. Fig. 3(a) demonstrates that the peak current density of Fe-20Cr-*x*Ni upon scratching alloy increases with Ni content up to 10 wt. %, and thereafter decreased as the Ni content increases above 10 %.

The values of *cBV* for the Fe-20Cr-*x*Ni alloys were determined from the slopes of $\log i(t)$ vs. $1/q(t)$ plots in Fig. 3(b) that were drawn using the data of the current transient curves in Fig. 3(a), and presented in Table 2. Fe-20Cr-10Ni alloy exhibited the highest value of *cBV* and hence the highest susceptibility to SCC. The *cBV* of Fe-20Cr-*x*Ni alloys decreased with either an increase or a decrease in Ni content from 10 wt %, suggesting that the SCC susceptibility of the alloys will be decreased with either an increase or a decrease in Ni content from 10 wt %.

The prediction of the SCC resistance of Fe-20Cr-*x*Ni alloys in terms of the influence of Ni on the *cBV* was in a good agreement with the experimental results that

were provided by Copson (6). Fig. 4(a) shows the effects of Ni content on the time-to-failure of Fe-20Cr-*x*Ni (*x*= 0–80) alloys that were measured by a constant loading SCC test in boiling MgCl₂ solution at 154 °C. Evidently, the Fe-20Cr-10Ni alloy exhibited the lowest value of time-to-failure, thereby reflecting the highest SCC susceptibility. With an increase or decrease in Ni content from 10 wt %, the value of time-to-failure of the alloys increased. Fig. 4 (b) illustrates the effects of Ni content on the SCC susceptibility predicted from the value of *cBV*, by taking the y-axis as the decreasing direction of *cBV*. By comparing Fig. 4(a) with Fig. 4(b), we found a similarity in the SCC resistance as a function of Ni content between the actual SCC experimental data and those predicted from the *cBV* values obtained from the scratch tests. This confirms that the *cBV* determined from the slope of the $\log i(t)$ vs. $1/q(t)$ plot can be used as an effective parameter for the prediction of SCC susceptibility of an alloy.

5. Conclusions

Influences of Ni on the repassivation kinetics of ferritic stainless steels and Fe-20Cr-*x*Ni alloys were evaluated in terms of the *cBV* value, and compared with the SCC susceptibility of the alloys in a hot chloride solution. Conclusions drawn from this study are as follows:

1) Repassivation on the scratched surface of the alloys occurred in two kinetically different processes; passive film initially nucleated and grew according to the place

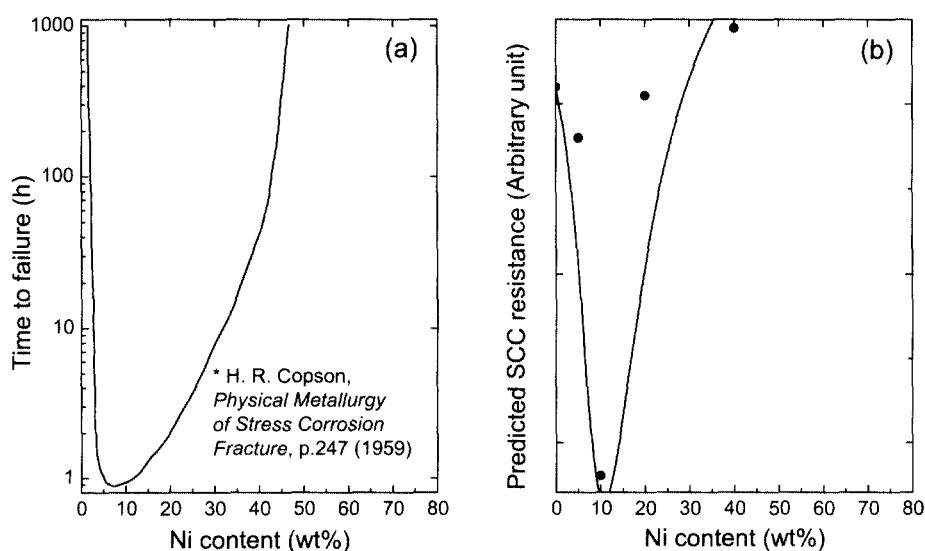


Fig. 4. Effect of Ni content (a) on the SCC of Fe-20Cr-*x*Ni alloys (*x* = 0–80) exposed to boiling (154 °C) 42 % MgCl₂ solutions and (b) on SCC resistance predicted from the value of *cBV*.

exchange model, and then grew according to the high field ion conduction.

2) The addition of 2 wt% Ni to Fe-25Cr-2Mo alloy decreased significantly the repassivation rate, when evaluated in terms of the change in the value of cBV . Thus the susceptibility of Fe-25Cr-2Mo-2Ni alloy to hot chloride SCC is due primarily to the decrease in repassivation rate induced by the addition of Ni.

3) For Fe-20Cr-xNi alloys ($x = 0, 5, 10, 20, 40, 80$), influences of Ni content on the SCC susceptibility predicted from the changes in cBV relatively are in good agreements with those measured using a constant loading SCC test, which confirmed the validity of cBV as a parameter of predicting the SCC susceptibility.

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