Diffusion mechanism of dezincification in double-phase brass exposed to seawater[①]

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Abstract: Zinc diffusion kinetics of double-phase brass as they were corroded in seawater was investigated by means of metallography microscope and mathematics regression analysis . The results showed that , the dezincification corrosion of β phase continuous H Mn58-2 brass is characterized by β phase volume diffusion , while that of α phase continuous HSn62-1 brass is controlled by α phase grain boundary diffusion . Apparent diffusion coefficients of zinc in both types alloys were calculated out by founding diffusion equation and boundary conditions . It was found that the value of theoretical calculation is close to that of experimentally measured , and it confirmed that Sn element inhibits dezincification of brass . The relativity between the dezincification depth and corrosion rate of different double-phase brasses immersed in seawater was revealed .

Key words: seawater corrosion ; brass ; dezincification ; boundary diffusion   **Document code: A**

1 INTRODUCTION

There are two kinds of mechanism of dezincification in brass[1] . One is dissolution-resedimentation and the other is preferential solution of zinc . Cooperation of both mechanisms is also reported . Pickering *et al*[2] pointed out that preferential dissolution of zinc in brass is achieved through volume diffusion of divacancy which is called " divacancy mechanism" . Qiu *et al*[3] . have studied defect structure in dezincification layer of brass by means of positron annihilation , which supports " divacancy mechanism" of dezincification of brass .

Sickanfus and Sans[4] indicated that trace alloy elements can change grain boundary structure , which contribute to get the coincidence boundary and special boundary , and intensify boundary , which restrains diffusion of zinc along grain boundary in brass . Qiu *et al*[5] indicated that arsenic forms " divacancy-impurity atom (As) pair" in brass , which slowers diffusion velocity of divacancy in vivo and restrains preferential solution of zinc . Having studied the casting Cu-35Zn alloy , Toivanen *et al*[6] considered that

boron can inhibit the vacancy produced by dezincification , which prevents zinc from migrating towards surface layer of the alloy and decreases the dezincification rate .

Wang *et al*[7] investigated diffusion kinetics of brass dezincification and verified that selective dissolution of brass is controlled by zinc diffusion in solid . They measured diffusion coefficient of different phase structure brass in different medium . It has not been reported that diffusion kinetics of brass exposed to seawater .

The present paper has investigated diffusion mechanism of brass in terms of dissolution of diffusion kinetics equation , searching for the relativity between dezincification depth and corrosion rate of brasses in seawater based on long term seawater corrosion experiment of the alloys .

2 EXPERIMENTAL

The sheet material samples were in size of 200 mm × 100 mm × 5 mm, the experiment methods were in accordance with national standard[8] . The compositions of materials are

shown in Table 1 .

Table 1　Chemical compositions of brasses (%)

Composition	Cu	Zn	Sn	Mn	Fe	Pb	P
HMn58-2	58.65	39.71	—	1.53	0.08	0.02	0.01
HSn62-1	61.40	37.63	1.01	—	<0.01	0.0062	0.05

The samples with corrosion product were retaked from seawater, then observed by metalloscpoe, and the dezincification depth was measured.

3　RESULTS

3.1　Establishment of diffusion equation

A coordinate system is founded in order to establish diffusion equation, which is shown in Fig.1 . The orientation of x-axis is opposite to the diffusion flux of zinc, y axis is interface between the corrosion products film and the matrix of the alloy. The corrosion products film will become thicker during the exposure period, that is, y axis will move forwards to the matrix at a certain velocity (v) so that an additional flux (Cv) is increased in fixed coordinate system. Then, the general flux is[9]

$$J_{Zn} = - D \frac{\partial C}{\partial x} + Cv \qquad (1)$$

where　D is the diffusion coefficient of zinc, and C is the concentration of zinc at a certain time and location.
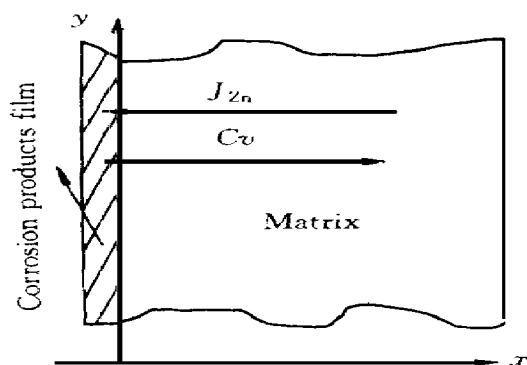
As a result of substance conservation,

Fig.1　Diffusion flux for fixed
coordinate system

according to principle of continuity : $\frac{\partial C}{\partial t} = - \frac{\partial J}{\partial x}$

we get

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left[D \frac{\partial C}{\partial x} - Cv \right] \qquad (2)$$

In general, the dezincification depth in one unit time is far greater than corrosion depth, then, the additional flux (Cv) is negligible. If the diffusion coefficient (D) is thought to be independent of concentration as well as location, Eqn.(2) can be simplified as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \qquad (3)$$

Assume that the concentration at the interface between the corrosion products film and the matrix does not change with the time, the boundary conditions of Eqn.(3) are as follows :

$C = C_0$ 　($t = 0$, $x > 0$)
$C = C_s$ 　($x = 0$, $t > 0$)

The solution of Eqn.(3) satisfied with conditions mentioned above is[9]

$$C = C_0 + (C_s - C_0)\left[1 - erf\left[\frac{x}{2 \sqrt{Dt}} \right] \right] \qquad (4)$$

where　C_0 is the nominal composition of zinc in brass, C_s is the concentration of zinc at the interface, t is the time for seawater exposure, erf (x) is the error function.

3.2　Calculation of volume diffusion coefficient of HMn58-2 brass

HMn58-2 is a β phase continuous double-phase brass. Its dezincification begins from β phase first, and then gradually develops towards depth. After β phase corroded, α phase grain turns into " solitary island" in dezincified area, then α phase will subject to de-alloy corrosion[10]. Due to no characteristics of priority corrosion of grain-boundary shown in Fig.2, we can think that the zinc diffusion along β phase grain-boundary and in α phase grain contributes little to dezincification rate so that the apparent diffusion coefficient (D_{app}) is close to α phase volume diffusion coefficient (D_l).

Fig.2 is the cross-section metallograph of HMn58-2 brass exposed to seawater for 4 years. The dezincification depth shown in Fig.2 is about 1 000 μm, the volume diffusion coefficient
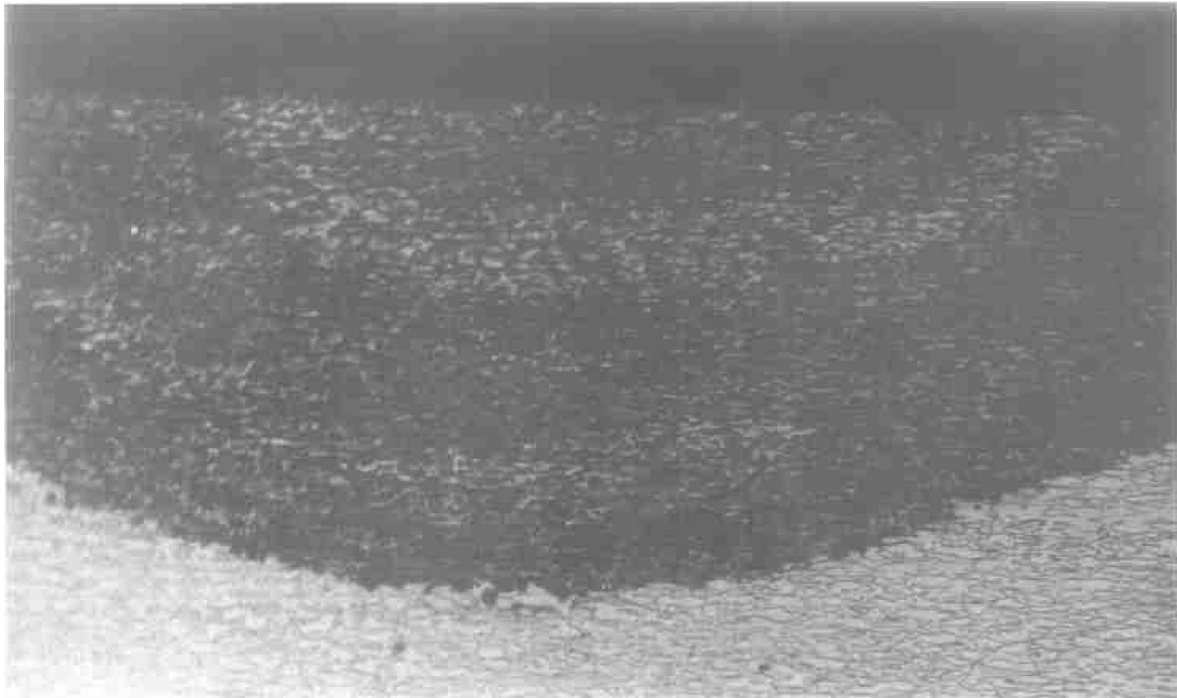
Fig .2   Polarizing metallograph of H Mn58-2 brass (× 60)

(D_l) of β phase can be figured out according to Eqn .(4) : $D_l = 3 .7 \times 10^{-11} cm^2/s$.

3 .3   Calculation of apparent diffusion coefficient of HSn62-1 brass

HSn62-1 brass is an α phase continuous double-phase copper alloy . During its seawater exposure , the dezincification corrosion occurs at β phase which is exposed to surface of substrate . α phase emerged after β phase has been dezincified[11] . Compared to β phase , α phase is not liable to be corroded , while α phase grain boundary is the preference to be corroded , and develops to a corrosion passage of β phase . Then , the course of dezincification corrosion is restrained .

Fig .3 is the cross-section metallograph of HSn62-1 brass exposed to seawater for 4 years . The dezincification depth is about 80 μm . The apparent diffusion coefficient is calculated to be $D_{app} = 2 .38 \times 10^{-13} cm^2/s$.

It is obvious that the β phase volume diffusion coefficient D_l is two orders larger than the apparent diffusion coefficient D_{app} of HSn62-1 . It is reasonable to be thought that the dezincifi-

cation corrosion of HSn62-1 is controlled by α phase grain boundary diffusion , which is congruent to the results analyzed above . We can get α phase grain boundary diffusion coefficient D_{gb} according to Eqn .(5) :

$$\frac{V_\alpha}{D_{gb}} + \frac{V_\beta}{D_l} = \frac{V}{D_{app}} \qquad (5)$$

where V , V_α , V_β are the volume of HSn62-1 , α phase and β phase in HSn62-1 brass respectively . They are shown in Table 2 .

D_{gb} is calculated to be $2 .02 \times 10^{-13} cm^2/s$.

It is reported that the diffusion coefficients of brass in different media are in the range of $10^{-15} \sim 10^{-13}$ orders[7] , Zhou and North[12] considered that the influence of grain boundary on the diffusion depends on the grain size and the D_{gb}/ D_l ratio . At low temperature ($T < (0 .5 \sim 0 .75) T_m$, where T_m is the equilibrium melting temperature of the material in K) , the D_{gb}/ D_l ratio is 10^5 or higher . So that the predicted D_{gb} should be in the range of $10^{-10} \sim 10^{-8}$ orders , but the calculated one is 10^{-13} order . It is because that the additional alloy element Sn has
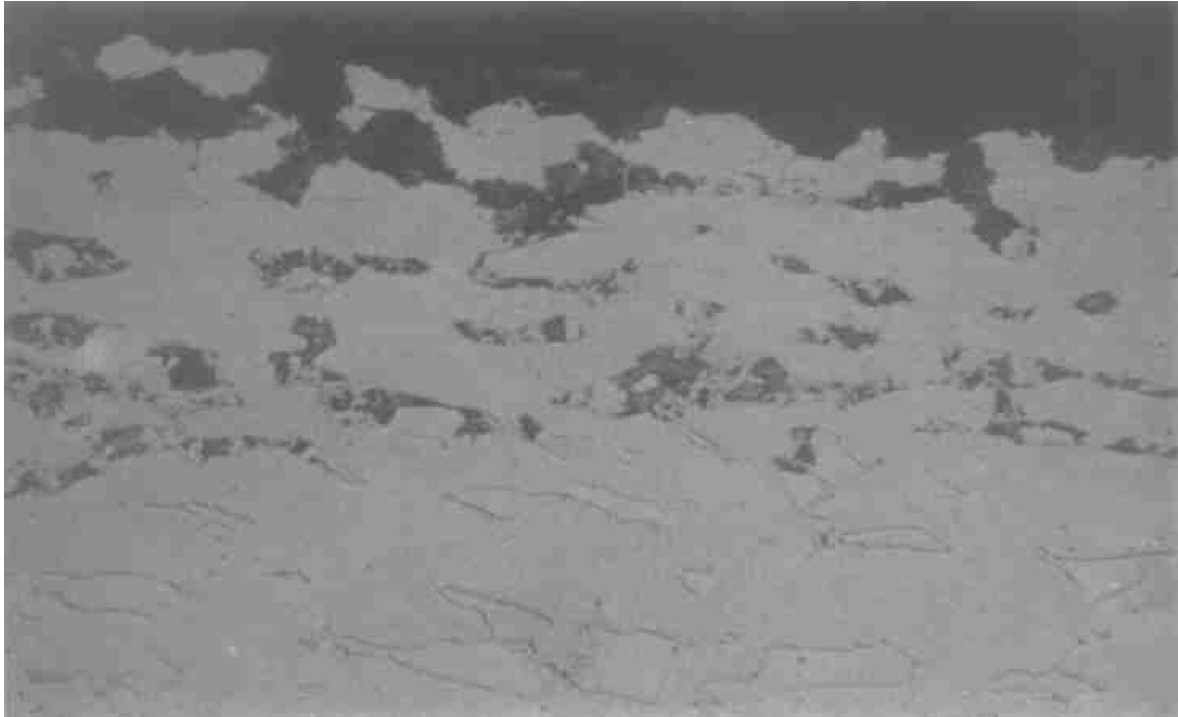
Fig .3   Polarizing metallograph of HSn62-1 brass (× 750)

Table 2   Chemical compositions and volume of two phases in HSn62-1   (%)

	Cu	Zn	Sn	V_i/V
HSn62-1	61 .40	37 .63	1 .01	1 .00
α phase	62 .70	36 .70	0 .38	0 .85
β phase	53 .80	44 .50	1 .70	0 .15

stronger trend to enrich at phase boundary and grain boundary than at surface film during the course of dezincification corrosion[13] . As a result , the zinc diffusion in α phase grain boundary cannot be restrained , which makes the grain boundary diffusion coefficient diminish .

However , for double-phase brass with continuous α phase , the β phase dezincification corrosion is connected through α phase grain boundary (as shown in Fig .3) . Thus , the zinc diffusion along α phase grain boundary becomes the controlling process of dezincification corrosion of HSn62-1 brass .

It is very reasonable for the control process that zinc diffuses along phase grain boundaries .

And the magnitude of the apparent diffusion coefficient is the same to that of the diffusion coefficient of α phase grain boundary .

3 .4   Distribution curves of zinc and dezincification depth

When the boundary conditions are $x = 0$, $C_s = 0$, we can run distribution curves of zinc in H Mn58-2 and HSn62-1 brass at 1 ,2 ,4 ,8 ,16 years based on the results got above . The theoretical curves calculated are shown in Fig .4 .

If 70 % of C_0 is defined as the dezincification state , we can get the dezincification depth of H Mn58-2 brass exposed to seawater for 1 ,2 , 4 ,8 ,16 years according to Fig .4(a) . They are 500 , 700 , 1 000 , 1 410 ,1 990 μm respectively . The former four data are very close to the measured values . It turned out that the model established and corresponding supposition is reasonable and the diffusion equation we used above is reliable in general .

We can also get the dezincification depth of HSn62-1 brass according to Fig .4(b) . They are

Fig .4　The oretical distribution curves of Zn in brass
(a) —H Mn58-2 (Boundary conditions :　$x = 0$, $C_s = 0$, $D_1 = 3 .7 \times 10^{-11}$ c m^2/ s) ;
(b) —HSn62-1 (Boundary conditions :　$x = 0$, $C_s = 0$, $D_{app} = 2 .38 \times 10^{-13}$ c m^2/ s)
1 —1 year ; 2 —2 years ; 3 —4 years ; 4 —8 years ; 5 —16 years

40 , 56 .5 , 80 , 113 , 160 μ m respectively . Our calculation is based on the sa mple exposed to seawater for 4 years . Since the dezincification process of α phase continuous double-phase HSn62-1 brass proceeds in β phase grain and along α phase grain boundary respectively , in the strict sense , the mathe matics treat ment should be considered on subsection . The present paper determines that the diffusion of α phase grain boundary is the control process of dezincification , then we si mplify the process in mathe matics , but we can not eli minate the error generated by the si mplification . In addition , the selective boundary conditions of diffusion equation is not completely congruent to practical situation , it should also be considered the influence of interface move ment

on the accuracy . All of these need further study .

3 .5　Relativity bet ween dezincification depth and corrosion rate of brass

According to the dezincification depth of H Mn58-2 and HSn62-1 brass exposed to seawater for different time , we get the regression curves and functions which are shown in Fig .5 . The regression curves and functions of annual average corrosion rate are shown in Fig .6 .

In the figures , x is exposure time($x \neq 0$) , y is annual average corrosion rate(dezincification depth) , r is relativity coefficient .

If we define the ratio bet ween annual average dezincification depth and corrosion rate as the relativity coefficient (n) , we can get it

Fig .5　Regression curves for annual average dezincification depth of brass
(a) —H Mn58-2 ; (b) —HSn62-1

according to the respective function :

H Mn58-2 : $n_1 = 13.88\ x^{-0.0771} \cong 13.88$

HSn62-1 : $n_2 = 2.038\ x^{-0.034} \cong 2.038$

Fig .6　Regression curves for annual average
corrosion rate of brass
1 — H Mn58-2 ; 2 — HSn62-1

It is obvious that there is very good relativity between the dezincification depth and the corrosion rate of these two brasses , so that the dezincification depth can be forecasted according to the corrosion rate and relativity coefficient .

It is proved that the dezincification depth predicted is very close to that measured , and shown that the relativity coefficient is reliable . However, it should be validated by the data measured in other periods .

4　CONCLUSIONS

(1)　The dezincification corrosion of H Mn58-2 brass is characterized by β phase volume diffusion during exposure to seawater , while the diffusion of β phase grain boundary and α phase grain contribute little to dezincification. Based on the measured dezincification depth of sample exposed to seawater for 4 years and the diffusion equation established , we can figure out β phase volume diffusion coefficient $D_{gb} = 3.70 \times 10^{-11}$ cm^2/s .

(2) The dezincification corrosion of HSn62-1 brass is controlled by α phase grain boundary diffusion, the apparent diffusion coefficient of HSn62-1 brass and α phase grain boundary are 2.38×10^{-13} and 1.53×10^{-13} cm^2/s respectively .

(3)　There is good relativity between the dezincification depth and the corrosion rate of these two brasses . The relativity coefficients are about 13.88 for β phase continuous H Mn58-2 , and 2.038 for α phase continuous HSn62-1 . The dezincification depth can be anticipated according to the annual average corrosion rate by using the relativity coefficient data .

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