Mn DEPLETION IN THE SURFACE LAYER OF STAINLESS STEEL 304 LN AT THE TEMPERATURE 1200 K

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ABSTRACT

The Mn component of stainless steel 304 LN has been found to be severely depleted in the surface layer during heating at the temperature 1200 K. The surface concentrations of Mn were reduced by about 2- 3 orders of magnitude in comparison with the bulk value, as was revealed by a secondary ion mass spectroscopy (SIMS) system. And the Mn concentration gradient in the surface layer was examined, too, by SIMS. Massive preferential losses of Mn have been determined by using the catcher technique and proton induced X- ray emission (PIXE). A theoretical model has been proposed for calculating the surface concentration changes for a component in an alloy under heating. A comparison shows a good agreement between the calculation and experimental results from SIMS and catcher technique.

Keywords: Preferential evaporation　Surface depletion　Ion beam analysis

I . INTRODUCTION

Stainless steel is commonly used for the first wall in fusion experiments, and its erosion properties have attracted much attention[1-4]. The released wall atoms, which enter the central plasma as impurities, will cool down and contaminate the plasma, and the wall modifications will limit the lifetime of the vessel wall. It has been found that the composition of the eroded wall material redeposited on probes at the first wall in plasma experiments deviated from the bulk composition of the wall material[5], and that the Mn component was almost completely lost in the melted area on the surface of the limiter made of stainless steel[6]. It has been confirmed in previous work[7] that the preferential losses of Mn at high temperature are dominated by evaporation instead of sputtering which is the main process causing erosion for other components (Fe, Cr and Ni) of stainless steel. In this work, theoretical descriptions of the phenomena are given and ion beam techniques have been used to investigate the dramatic depletion of the Mn component in the surface layer of SS 304 LN, caused by preferential evaporation of Mn at the high temperature.

II . THEORETICAL MODEL

The steady state evaporation rate, $n_i(T)$, for component i in a clean alloy surface at a temperature T can be calculated by following functions, if we assume that the surface binding for the component of the alloy is the same as that of its pure metal:

$$n_i(T) = K_i^s \, \dot{n}_i \, (T) \qquad \text{(atoms/cm}^2\text{s)} \qquad (1)$$

$$\dot{n}_i \, (T) = (\alpha \ 2.6 \times 10^{20}) \, P \, (T) \text{ (Pa) } /[M_i T \text{ (K)}]^{1/2} \qquad (2)$$

where K_i^s is the relative concentration of the component i in the surface of the alloy.

$\dot{n}_i(T)$ is the evaporation rate for pure metal of the component. α (about 1) is the sticking probability of metal atoms impinging on the surface. M_i is the atomic weight of the element i and $P(T)$ is the vapour pressure which can be found in literatures[8].

As a result of the surface evaporation, the target atoms are diffused from bulk to the surface. Fig.1 shows a diffusion model with an assumption that the concentration gradient is a constant. The diffusion flux, φ_i, from bulk to the surface for the component i in the alloy can be represented by

$$\varphi_i = D(C_i^b - C_i)/x =$$

$$D[C_o(K_i^b - K_i)]/x \quad \text{(atoms/cm}^2\text{s)} \quad (3)$$

where C_i^b and C_i are the bulk and surface concentrations of the component i in atoms/cm^3·K_i^b is the relative concentration of the component i in bulk.C_o, the atom density of the alloy, is assumed to be homogeneous. D is the diffusion coefficient of the component in the alloy and is expressed according to an Arrhenius law[9],

Fig.1 Sketch of the concentration gradient caused by surface evaporation and diffusion from bulk to the surface at high temperature

$$D = D_o \exp(-Q/kT) \quad (4)$$

where D_o is the frequency factor, in the same dimension as D. Q is the activation energy. Both are tabulated for various systems[10]. k is the Boltzmann constant.

From Fig.1, n'_i, the atoms escaped from target in a unit of time could be expressed as

$$n'_i = \frac{d}{dt}[(C_i^b - C_i)x/2] = \frac{d}{dt}[C_o(K_i^b - K_i)x/2] \quad \text{(atoms/cm}^2\text{s)} \quad (5)$$

It is obvious that

$$n_i = \varphi_i = n'_i \quad (6)$$

i.e.

$$K_i \dot{n}_i(T) = DC_o(K_i^b - K_i)/x \quad (7)$$

$$K_i \dot{n}_i(T) = \frac{d}{dt}[C_o(K_i^b - K_i)x/2] \quad (8)$$

Solving equations (7) and (8) and with the critical conditions that $K_i = K_i^b$ and $x = 0$ at the heating time $t = 0$, the following relations of the relative surface concentration K_i and the depletion depth x to the heating time t could be derived respectively,

$$\ln K_i + (K_i^b)^2/2(K_i)^2 = 2t[\dot{n}_i(T)]^2/D(C_o)^2 + \ln k_i^b + 1/2 \quad (9)$$

$$[\dot{n}_i(T)/2DC_o]x^2 + x - [DC_o/\dot{n}_i(T)]\ln[1 + (\dot{n}_i(T)/DC_o)x] = [2\dot{n}_i(T)/C_o]t \quad (10)$$

III. EXPERIMENTAL

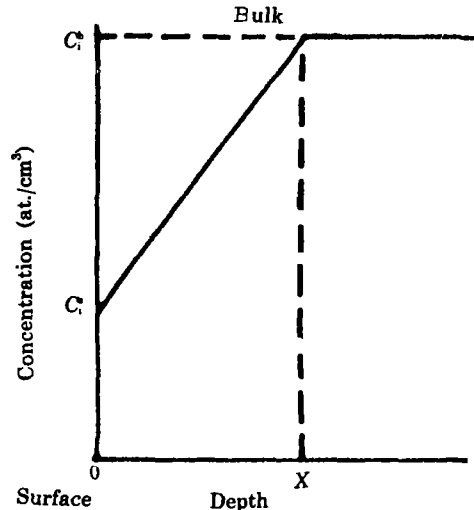SS 304 LN containing 2 at% Mn was used for these investigation. The targets were

cut from an SS 304 LN sheet and heated at 1200 K, which is about 0.7 times of the melting temperature of SS 304 LN. The Mn concentration changes in the surface have been measured by ion beam techniques.

1. SIMS measurements

Targets were heated by direct Ω heating for 600 and 1800 s, respectively, in a chamber with a base vacuum of better than 1.3×10^{-3} Pa at Shanghai Institute of Nuclear Research. The target temperature was adjusted at 1200 K as measured with a Pt– $Pt_{0.87}Rh_{0.13}$ thermocouple, which was mounted in good contact with the target surface. After heating the target was moved to a SIMS system for depth profile measurements. 5.5 keV O_2^+ ions at the incidence angle of $45°$ were used as primary ions. All data were taken at a flux density of about 3×10^{14} O_2^+/cm^2s.

2.Catcher technique and PIXE analysis

The experiments were carried out at Max– Planck– Institute of Plasma Physics in Munich. The targets were heated at 1200 K for 0.25×10^4, 0.75×10^4, 1.75×10^4 and 6.80×10^4s respectively. The eroded flux due to evaporation was condensed on the surface of clean Si slices mounted around the target in a cylindrical cup. The experimental set– up has been described elsewhere[7]. The angular distributions of the evaporated flux and the concentrations of the material condensed on the Si collectors were measured by 1.5 MeV proton induced X– ray emission (PIXE). The total amount of evaporated materials from SS target were determined in situ by a vacuum microbalance.
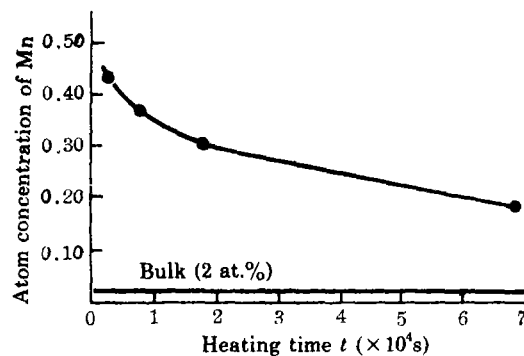
IV. RESULTS AND DISCUSSION
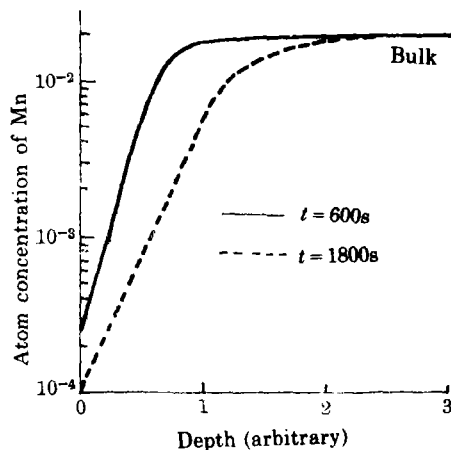
Fig.2　Concentration gradient of Mn in the surface layer of SS 304 LN caused by evaporation and diffusion at 1200 K

Solid line: heated for 600 s,

dotted line: heated for 1800 s

Fig.3　Relative concentrations of the evaporated Mn on Si collectors

The bulk value (2 at%) is given for comparison

Fig.2 shows Mn depth profiles measured by SIMS on SS 304 LN targets. The Mn concentrations have been found to be 2.5×10^{-4} and 1.1×10^{-4} at the surface of samples heated for 600 and 1800 s, respectively. They increased with depth until reaching the bulk value of 2 at %. This can be explained by the fact that the evaporation would cause a quick depletion of Mn in the surface at first and the process slowed down because of Mn diffusion from bulk to the surface. It is also clear in Fig.2 that the longer the heating time, the lower is the surface concentration and the larger is the depth where the Mn concentration reaches its bulk value.

Fig.3 shows the heating time dependence of PIXE– examined Mn condensation on Si collectors. A drastic preferential evaporation occurs at first, then the Mn evaporation decreases from 43% to 18% in the period from 0.25×10^4 s to 6.80×10^4 s due to the gradual depletion of Mn in the surface layer. These values are much higher than its bulk concentration, 2 at%, which is shown in Fig.3 for comparison.

In all the cases of our experiments the concentrations of the materials condensed on collectors are independent of the escape angle of the evaporated atoms and agree well with the concentrations obtained by integrating over all emission angles in a hemisphere. The results suggest that it is reasonable to take the concentration measured from collectors as that for total losses from the target.

Assuming the surface binding of Mn in stainless steel is not very different from that of pure Mn metal, the surface concentration of Mn in SS 304 LN can be calculated from $\dot{n}(T)$, the evaporation rate of pure Mn metal and N_{Mn}, the amount of the Mn component evaporated from a surface area S of an SS target during heating time t at temperature T:

$$K^S_{Mn} = N_{Mn}/\dot{n}(T)\ St \qquad (11)$$

$$N_{Mn} = K_c\ N \qquad (12)$$

where N is the total evaporated atoms of an SS target, which was measured by weight loss. K_c is the relative concentration of Mn on collectors, which was shown in Fig.3. Equations(11) and (12) give the way to determine sample surface concentrations

Table 1

Surface concentration of Mn in SS 304 LN calculated from N_{Mn} and N'_{Mn}, the amount of Mn evaporated from SS target and from pure Mn metal, respectively

Heating time t (s)	0.25×10^4	0.75×10^4	1.75×10^4	6.80×10^4
N^*_{Mn} (atoms)	6.75×10^{17}	1.35×10^{18}	2.42×10^{18}	4.61×10^{18}
$N'_{Mn} = \dot{n}(T)St^{**}$ (atoms)	6.58×10^{21}	1.97×10^{22}	4.61×10^{22}	1.79×10^{22}
Surface concentration	1.0×10^{-4}	6.8×10^{-5}	5.2×10^{-5}	2.6×10^{-5}
$K^*_{Mn} = N_{Mn}/N'_{Mn}$				

* $N_{Mn} = K_c N$, atoms measured by weight loss and catcher technique.

* * N'_{Mn} = Mn atoms calculated for pure Mn metal with $S = 1.86$ cm^2 at 1200 K.

   by collector measurements. Table 1 shows the results at 1200 K. It can be seen that

the surface concentrations of Mn are 2– 3 orders of magnitude lower than the bulk value in the evaporation time from 0.25×10^4 to 6.80×10^4 s.

The two experimental methods, SIMS and catcher technique, supplement each other for the measurements of surface concentrations in different heating periods. The catcher technique was used for long time evaporation (0.25×10^4– 6.80×10^4 s) in order to collect enough evaporated atoms for PIXE measurements. On the other hand, the target surface suffering from long heating seemed too rough for SIMS detection. It is the reason why SIMS was exploited only for the measurement after short time heating of samples.

In Fig.4 the theoretical curve based on Eq.(9) shows the heating time dependence of the Mn concentration in the surface of SS 304 LN at 1200 K. The Mn concentration decreases with the heating time, and a sharp loss occurs in the beginning of evaporation. It can be seen from the curve that the Mn concentration drops from its bulk value to 0.1 at% in only about 30 s. It also can be seen that the loss rate of Mn decreases with the heating time, which suggests that the preferential evaporation gradually subsides along with the depletion of Mn in the surface layer. The curve is compared with the experimental results derived from SIMS and PIXE measurements, which are shown in crosses and circles respectively in Fig.4. The experimental data show the same tendency as the curve.
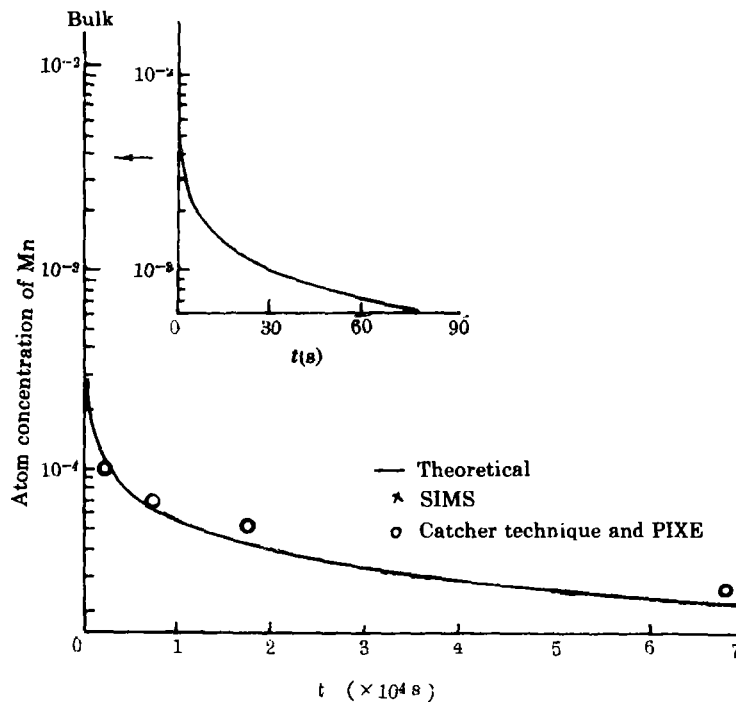

Fig.4 Comparison between the theoretical curve calculated with Eq.(9) and the experimental

results from SIMS ($\times$) and PIXE (o)

Inserted is the first portion of the curve in magnification

Eq.(10) shows a reasonable result that the depletion depth increases with heating time. We have not proved the theoretical calculation by experiments in this work because the catcher technique could not give the depth information and SIMS system has not been calibrated in depth. An improved measurement will be performed to get a further experimental investigation.

V. CONCLUSION

The preferential evaporation of Mn occurs in the surface of SS 304 LN at 1200 K. The concentrations of evaporated Mn are about $9-20$ times as high as its bulk value (2 at%). As a result, Mn depletions take place quickly in a surface layer of considerable depth. The depletion eases gradually with depth because the Mn atoms of inner depth diffuse towards the surface.

The Mn component decreases sharply at the target surface in initial heating, and the loss rate slows down with heating time due to the drastic depletion of Mn in the surface layer.

The surface concentrations of Mn in SS 304 LN decrease by $2-3$ orders of magnitude during heating at 1200 K. The experimental results from SIMS and catcher technique agree well with a theoretical calculation proposed in this paper.

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