Separation Mechanism of Iron and Cobalt Components from Alloys by Arc Plasma Reactions with Cl_2 and O_2

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ABSTRACT: The arc plasma reactions with Ar, Ar-Cl_2 and Ar-Cl_2-O_2 arc plasmas were investigated. The amounts and the components of fumes produced by each gas plasma reaction were measured. Fe component was separated selectively from Fe-Co-Ni alloys with the plasmas with small concentration of O_2. Co component was separated with the plasmas with large concentration of O_2. The separation mechanisms of the plasma reactions were studied by ICP-AES, EDS, emission spectrometry and thermodynamic consideration.

I. INTRODUCTION

Arc plasmas have features of high temperature and high chemical activity. The chemical activity can be used for material syntheses and separations. We have investigated the arc plasma reactions with chlorine for separations of particular elements from alloys [1-3] since chlorine atom reacts with particular elements to form chlorides which have high vapor pressure and are separated from alloys peculiarly. There are also many available thermodynamic data on chlorides. Arc plasmas with oxygen react with metal to produce solid oxides that have low vapor pressure. The purpose of this study is to investigate the separation mechanism of Fe and Co components from Fe-Co-Ni alloys with Ar-Cl_2-O_2 arc plasma reactions.

II. EXPERIMENTAL

KOVAR alloy (Fe=53, Co=17, Ni=29(mass%), 10 x 10 x 5 mm, 4 g) was used for samples. It was set in the BN crucible, and melted with arc plasmas under atmosphere pressure for 1 min. Ar, Ar-Cl_2, and Ar-Cl_2-O_2 were used for plasma gases. Fumes produced by the

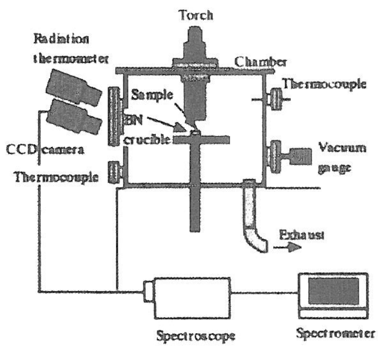

Fig. 1 Experimental system.

plasma reactions were collected with polyflon filters, and determined for Fe, Co, and Ni by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry). Samples before and after the plasma treatments were analyzed with SEM (Scanning Electron Microscope) and EDS (Energy Dispersive X-ray Spectrometer).

The arc plasma generator apparatus is shown in Fig. 1. The plasma torch was a DC non-transferred type. The adequate condition was determined at current of 185 A. The distance from the plasma torch and the sample was 40 mm. Plasma gas flow rates are summarized in Table 1. The plasma gas flow rate condition was written as follow in this study; Ar-Cl_2-O_2 (0.25) when O_2 flow rate was 0.25 L/min.

Table 1 Plasma gas conditions.

(L/min)

Ar	Cl_2	O_2
10	-	-
10	0.25	-
10	0.25	0.25
10	0.25	1.0
10	0.25	2.5

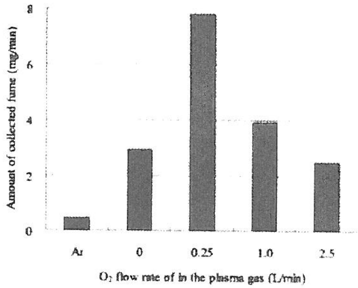

Fig. 2 Fume weights by various gas plasma treatments of KOVAR.

III. RESULTS

1. SAMPLE TEMPERATURE

Sample temperatures measured with the thermometer were about 1900 K during the plasma treatments. The temperatures varied about 20 K depending on the surface condition of the melting alloys. The variation was not large, therefore the temperature of 1900 K is used for the presentative value.

2. FUME WEIGHTS

The weights of the the fumes produced by the plasma treatments of the alloys are shown in Fig. 2. The collected fume weight is small with Ar plasmas. The fume weights increase with Ar-Cl_2 and Ar-Cl_2-O_2 (0.25) plasmas. The fume weights decrease with much increase in the O_2 flow rates over 1.0 L/min.

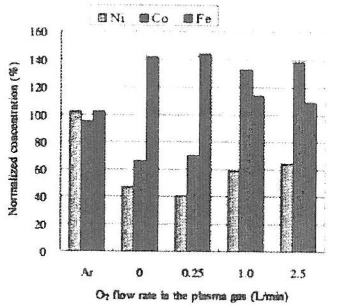

Fig. 3 Concentration of elements in fumes by various gas plasma treatments of KOVAR.

3. FUME COMPONENTS

The components of the fumes produced by the plasma treatments are shown in Fig. 3. The concentrations of the elements in the fumes are normalized as follows.

$$\text{Normalized concentration (\%)} = \frac{\text{Element concentration in fume (mass\%)}}{\text{Element concentration in initial alloy (mass\%)}} \times 100\ (\%) \qquad (1)$$

The components of the fumes are almost the same as the initial KOVAR alloy with Ar plasmas. The concentrations of Fe in the fumes are more than twice as those of Co and Ni with Ar-Cl_2 and Ar-Cl_2-O_2 (0.25) plasmas. The concentration of Co are larger than those of Fe and Ni with Ar-Cl_2-O_2 (1.0 and 2.5) plasmas. The concentrations of Ni are small with Ar-Cl_2 and Ar-Cl_2-O_2 plasmas since Ni compounds are not vaporized.

4. DISTRIBUTION OF THE COMPONENTS OF ALLOY

Photographs of SEM and the results of line analysis with EDS near the surface area of the alloys after Ar-Cl_2-O_2 (0.25 and 1.0) plasma treatments are shown in Fig. 4. The surface areas of each sample were divided to two layer; oxide layer (Area 1) and metal layer (Area 2). Concentrations of Fe, Ni, Co and O of each area are summarized in Table 2. Normalized concentrations without O concentration are designed in parentheses.

The oxide layer of porous solid structure contains large amount of Fe with Ar-Cl_2-O_2 (0.25) plasmas. The metal layer with Ar-Cl_2-O_2 (0.25) plasmas consists of the same composition as the initial KOVAR alloy. On the other hand, the compositions both in the oxide and metal layers with Ar-Cl_2-O_2 (1.0) plasmas are the same as the initial KOVAR alloy. Intermediate layer was observed between the oxide and the metal layers with Ar-Cl_2-O_2 (0.25) plasmas. The concentration of Fe in the intermediate layer is slightly smaller than that of metal layer. The mechanism of generation of the area is not clarified.

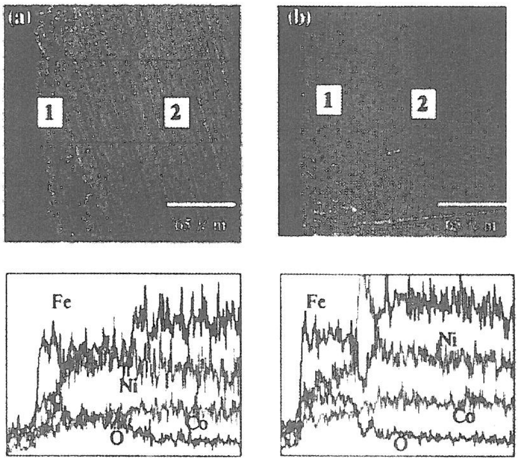

Fig. 4 SEM of the surface of KOVAR alloy after plasma reactions of (a)Ar-Cl_2-O_2 (0.25 L/min), (b)Ar-Cl_2-O_2 (1.0 L/min).

Table 2 Concentration of elements in each area of the alloy after various kinds of plasma treatments.

(mass%)

	Ar-Cl_2-O_2 (0.25)						Ar-Cl_2-O_2 (1.0)						KOVAR
	Area 1		Area 2		Area 3		Area 1		Area 2		Area 3		
Fe	26.3	(76.7)	25.5	(48.4)	48.2	(55.5)	22.7	(56.5)	39.4	(54.5)	49.1	(55.1)	53
Co	3.8	(11.2)	8.3	(15.8)	13.9	(16.0)	6.2	(15.5)	11.9	(16.5)	14.2	(15.9)	17
Ni	4.1	(12.1)	18.9	(35.9)	24.8	(28.5)	11.3	(28.0)	21.1	(29.1)	25.8	(29.0)	29
O	65.8	—	47.3	—	13.1	—	59.8	—	27.6	—	10.9	—	

IV. DISCUSSIONS

1. FUME WEIGHTS AND PLASMA GASES

The amounts of produced fumes with Ar-Cl_2-O_2 (0.25 and 1.0) plasmas are larger than that with Ar-Cl_2 plasmas. The large amounts of the fumes are attributed to three effects : (1) chlorination leading to the large amounts of the fumes generated by Ar-Cl_2 plasma treatments, (2) the reaction heat generated by Fe and O atom, (3) the recombination heat of O atoms [2, 4].

The amounts of produced fumes with Ar-Cl_2-O_2 (1.0 and 2.5) plasmas are smaller than that with Ar-Cl_2-O_2 (0.25) plasmas. More oxidation depresses vaporization of the fumes since oxides with low vapor pressure are produced under the conditions with large amounts of O atoms with Ar-Cl_2-O_2 (1.0 and 2.5) plasmas.

2. EQUILIBRIUM CALCULATION OF DISSOCIATION OF CHLORINE AND OXYGEN

The degrees of dissociation of Cl_2 and O_2 in the arc plasmas have large effects on the plasma reactions. Thermal equilibrium for Cl_2 and O_2 under $1.01x10^5$ Pa are shown in Fig. 5. A thermodynamic calculation software CHEMSAGE (GTT Co.) was used in this study. Cl_2 is dissociated at the temperature about 2000 K. This result agrees with the result that Cl spectrum was observed by spectroanalysis in the plasmas [5]. O_2 is dissociated at the temperature about 4000 K.

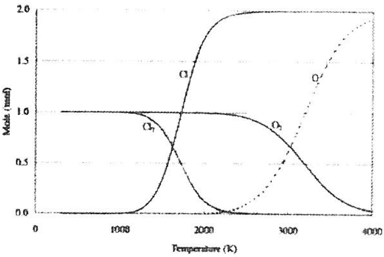

Fig. 5 Thermodynamic equilibrium for Cl_2 and O_2 under $1.01x10^5$ Pa. (Cl_2=1, O_2=1, Ar=40 (mol))

3. EQUILIBRIUM CALCULATION OF FUME COMPONENTS

Thermodynamic equilibrium calculation results are shown in Fig. 6. The result with the condition of small amount of O_2 is shown in Fig. 6 (a). That of large amount of O_2 is shown in Fig. 6 (b). $FeCl_2$(g) is produced more than 10 times of $CoCl_2$(g) and $NiCl_2$(g) at the temperature of 1900 K in Fig. 6(a). $CoCl_2$(g) is produced more than $FeCl_2$(g) and $NiCl_2$(g) with large amount of O_2 at the temperature of 1900 K in Fig. 6(b). These results indicate that concentration of Fe in the fume is large with Cl_2 and small amount of O_2, and that concentration of Co in the fume is large with Cl_2 and large amount of O_2.

4. ALLOY AND FUME COMPONENTS

The elements of Fe, Co, and Ni, in the VIII group in the same period, have very similar physical properties. The differences of their physical properties such as melting points and boiling points have

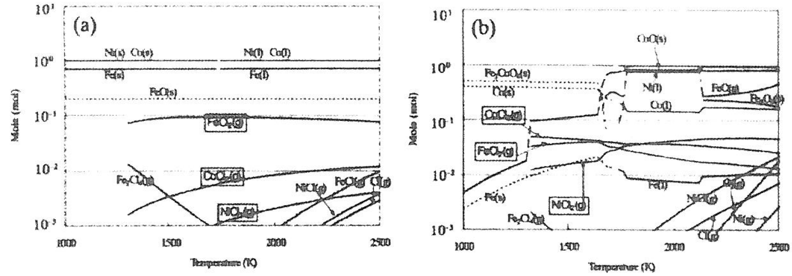

Fig. 6 Thermodynamic equilibrium calculation results. (a) Fe=1, Co=1, Cl_2=0.1, O_2=0.1 (mol), (b) Fe=1, Co=1, Cl_2=0.1, O_2=1 (mol)

little effects on the separation. Therefore reactivities of the components of the alloy with the reactive plasma gases are important to separate particular components from the alloy.

The reaction mechanism is considered with Gibbs free energy changes. Chlorination and oxidation of Fe, Co and Ni are considered as follows. These are the reactions with the lowest values of Gibbs free energy changes with each element.

$$Fe(l) + 2Cl(g) \rightarrow FeCl_2 \quad (2)$$

$$Co(l) + 2Cl(g) \rightarrow CoCl_2 \quad (3)$$

$$Ni(l) + 2Cl(g) \rightarrow NiCl_2 \quad (4)$$

$$Fe(l) + 3/2O(g) \rightarrow 1/2Fe_2O_3 \quad (5)$$

$$Co(l) + O(g) \rightarrow CoO \quad (6)$$

$$Ni(l) + O(g) \rightarrow NiO \quad (7)$$

l : liquid, g : gaseous

The relationship between temperature and Gibbs free energy changes of Fe, Co and Ni with Cl and O are shown in Fig. 7. The amounts of Cl and O atoms flowing to the alloys are smaller than Fe content in the alloy. O atoms react with Fe selectively since Gibbs free energy changes of Fe with O atom are lower than the other reactions. Cl atoms also react with Fe selectively since Gibbs free energy changes of Cl atom with Fe are lower than with Co or Ni. These reactions result in the large concentrations of Fe both in the fume and in the oxide layer of the alloy after the treatment.

O atoms react with Fe, Co and Ni since the amount of O atoms are large with Ar-Cl_2-O_2(1.0 and 2.5) plasmas. All the components in the alloys are oxidized. The oxidation results in the compositions of the oxide layers are similar to that of initial KOVAR alloy. O atoms react with Fe more easily than with Co and Ni in the melting alloys. Cl atoms react with Co more easily than with Fe since Co reacts less O than Fe does. The normalized concentrations of Co in the fumes are consequently larger than those of Fe with Ar-Cl_2-O_2(1.0 and 2.5) plasmas.

V. SUMMARY

Selective separations of the Fe and Co from Fe-Co-Ni alloy (KOVAR) were studied by arc plasma treatments by changing flow rates of O_2 with Ar-Cl_2 plasma gases. The amounts and the components of produced fumes and the concentrations of the elements in the alloys were discussed.

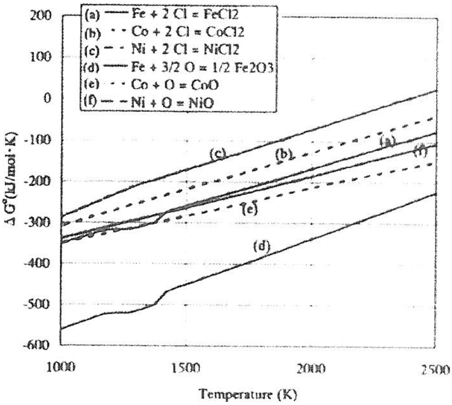

Fig. 7 Relationship between temperature and Gibbs free energy changes.

(1) Fe component was separated selectively from the alloy with Ar-Cl_2 and small flow rate of O_2 (0.25 L/min) with Ar-Cl_2 plasma gases. The separation of Fe components resulted from selective chlorination of Fe. Fe concentration in the oxide layer of the alloy was larger than that in the initial alloy. The large concentration of Fe results from selective oxidation of Fe.

(2) Co component was separated with Ar-Cl_2 with large flow rates of O_2 (1.0 and 2.5 L/min) plasma gases. The large concentration of Co results from both effects of chlorination of Co and oxidation of Fe.

(3) The amount of the fume with Ar-Cl_2-O_2(0.25) plasmas was the largest because of the effects of chlorination, the reaction heat generated by Fe and O atoms, and the heat of recombination of O atoms in the melting alloy. The amount of the fumes decreased with over 1.0 L/min of O_2 flow rates because of production of oxides.

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