Separation of iron component from alloys with arc plasma reaction

Akihiro Takeuchi[1], Kazushi Tanaka[1], Naoki Tanahashi[1] and Takayuki Watanabe[2]

[1]Electrotechnology Applications R&D Center, Chubu Electric Power Co., Inc.,
Nagoya 459-8522, Japan
[2]Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology,
Tokyo 152-8550, Japan
E-mail : Takeuchi.Akihiro@chuden.co.jp

ABSTRACT: Arc plasma reactions are effective to separate peculiar components from mixtures and alloys. We investigated the arc plasma reactions with Ar, Ar-O_2, Ar-Cl_2, and Ar-Cl_2-O_2 arc plasmas, and compared both the amounts and the components of fumes generated by each gas plasma reaction. We found that, using Ar-Cl_2 and Ar-Cl_2-O_2 arc plasmas, iron component could be separated from Fe-Co-Ni alloys. By chemical analysis, ICP-AES, ion-chromatography, EDS, spectrometric analysis, and thermodynamic consideration, the theoretical separation mechanisms of the plasma reactions are studied.

I. INTRODUCTION

Peculiar reactions result from the features of arc plasmas, high temperature and high chemical activity, according to reactive circumstances. However few chemical reactions of arc plasmas have been unknown. Arc plasma reactions with hydrogen have been used to reduce metal oxides and to add heat to samples excessively [1]-[3], while there are very few thermodynamic data on hydrides which cause the plasma reactions. We have investigated the arc plasma reactions with chlorine because it reacts with metal to form chlorides which have high vapor pressure to be separated peculiarly. Besides there are many available thermodynamic data on chlorides to study the reaction mechanism theoretically. The purpose of this study is to clarify the separation mechanism of iron component from Fe-Co-Ni alloys.

II. EXPERIMENTAL

Alloys based on Fe, Co, and Ni (KOVAR; Fe=53, Co=17, Ni=29(mass%), HASTELLOY; Fe=5.5,Co=2.5,Ni=57(mass%), 10 x 10 x 5 mm, 4 g) were used for samples. They were set in the BN crucible, and melted with various arc plasmas under atmosphere pressure for 1 min. Ar, Ar-O_2, Ar-Cl_2, and Ar-Cl_2-O_2 were used for plasma gases. Fumes generated by the plasma reactions were

caught with PTFE filters, and determined for Fe, Co, and Ni by ICP-AES and for Cl by ion chromatography after chemical separation pre-treatments. Samples before and after plasma treatments were analyzed by EDS.

Fig. 1 shows the arc plasma generator experimental apparatus. DC non-transferred type plasma torch was used. The adequate condition was determined at current of 185 A and the distance from the plasma torch and the sample of 26 mm. Plasma gas flow rates were 10 L/min for Ar, 0.25 L/min for Cl_2, and 0.25 L/min for O_2.

Sample temperatures during plasma treatments were measured with a radiation thermometer (VF-2100S type made by Optex Co.).

Spectroanalysis was carried out to identify the chemical species in the arc plasmas. MD-250 type spectrometer (Japan spectrometry Co.) was used. Table 1 shows the analytical conditions.
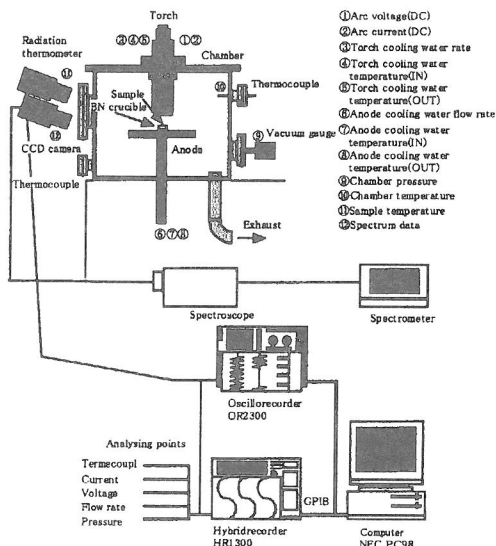

①Arc voltage(DC)
②Arc current(DC)
③Torch cooling water rate
④Torch cooling water temperature(IN)
⑤Torch cooling water temperature(OUT)
⑥Anode cooling water flow rate
⑦Anode cooling water temperature(IN)
⑧Anode cooling water temperature(OUT)
⑨Chamber pressure
⑩Chamber temperature
⑪Sample temperature
⑫Spectrum data

Fig. 1 Experiment system and analyzing points.

Table 1 Spectrometer condition.

Focus distance (mm)	250
Diffraction grating (mm^{-1})	1200
Wave length range (nm)	200-1100
Analysing time (s)	2
Resolving power (nm)	$\Delta\lambda=0.25$

III. RESULTS

1. SAMPLE TEMPERATURE

Sample temperatures measured with the thermometer were about 1973 K during Ar plasma treatments. The temperatures were depressed to about 1773 K after Cl_2 and O_2 plasma gases were flown, with an error of about 20 K depending on the surface condition of melting samples. This depression of temperature about 200 K was considered that the thermal energy of arc plasmas were used to dissociate molecular Cl_2 and O_2 into atomic Cl and O.

2. FUME WEIGHT AND COMPONENT

Table 2 shows the components and the amounts of the fumes from KOVAR generated by plasma treatments. At the case of Ar and Ar-O_2 plasmas, the components of the fumes were almost the same of untreated KOVAR alloy. With Ar-Cl_2 and Ar-Cl_2-O_2 plasmas, Fe was concentrated about 90 %. Ni concentrations were 7.0 % at Ar-Cl_2 plasmas, and 5.1 % at Ar-Cl_2-O_2 plasmas. Co concentrations were 6.1 % at Ar-Cl_2 plasmas, and 4.7 % at Ar-Cl_2-O_2 plasmas. This result

1916

Table 2 Concentration of elements in fumes and fume weigh using various gas plasma treatments.

Plasma gas	Concentration of elements in fumes (mass %)			Collected fume weight (mg)
	Ni	Co	Fe	
Ar	29.4	15.7	54.9	0.8
Ar-O_2	29.5	17.3	53.2	1.8
Ar-Cl_2	7.0	6.1	86.9	2.2
Ar-Cl_2-O_2	5.1	4.7	90.2	22.4
KOVAR	29	17	53	

showed that Fe could be separated selectively, with high concentration, from KOVAR alloy which contained the elements with very similar properties; Fe, Co, and Ni. Each of them was analyzed to form chlorides by the chemical analysis.

Table 2 also shows the fume weights generated by plasma treatments. The collected fume weight was 0.8 mg by using Ar plasmas. Collected fume weights by Ar-O_2 and Ar-Cl_2 plasma treatments were larger than that of Ar plasma treatment, 1.8 mg and 2.2 mg. At the case of Ar-Cl_2-O_2 plasmas, the collected fume weight was over 10 times larger than those of the others, 22.4 mg.

3. SPECTROANALYSIS

The chemical states of chlorine gas in the arc plasmas were seemed to have a large influence on the plasma reactions. Fig.2 shows the spectrum around 489 nm at which atomic Cl spectrum could be measured [4]. With Ar-Cl_2-O_2 plasmas, a Cl spectrum could be measured at 489.68 nm besides a spectrum at 487.99 nm measured with Ar plasma treatment. This result showed that Cl_2 gas dissociated into Cl in the plasmas.
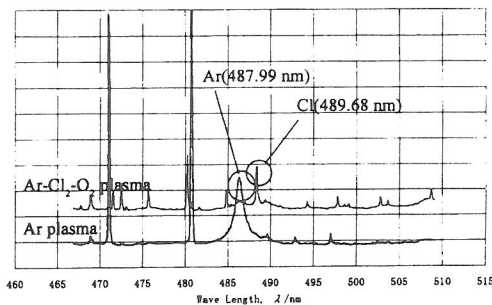

Fig. 2 Cl spectrum analyzed by a spectrometer.

IV. DISCUSSIONS
1. EQUILIBRIUM CALCULATIONS OF CHLORINE AND OXYGEN

Fig. 3 shows the relationship between the states of chlorine and temperature by thermodynamic equilibrium calculations. A thermodynamic calculation software CHEMSAGE (GTT Co.) was used. Fig. 3 pointed out that atomic Cl was as stable as molecular Cl_2 at the temperature about 2000 K. Almost all the Cl_2 were dissociated at the temperature beyond 3000 K. This result was compatible with the result that Cl spectrum was observed by spectroanalysis in the plasmas.

Fig. 3 also shows the states of oxygen. Only molecular O_2 was stable and atomic O did not exist in an equilibrium state at the temperature of 1773 K because atomic O was appeared only at

the temperature over 2500 K.

2. FUME AND PLASMA GASES

Vapor pressures of most metal oxides are lower than those of metals. Therefore the reactions with melting metals and atomic O would be difficult to generate fumes. Atomic O was not stable at the temperature of 1773 K, therefore reaction heats would be generated when it recombined. This recom-

Fig. 3 Thermal equilibrium for Cl_2 and O_2 under 1.01×10^5 Pa.

bination energy would heat elements of the melting alloys to be vaporized effectively. This could be the reason with Ar-O_2 plasma the amount of generated fume was increased compared with that of Ar plasma treatment.

Fig.3 shows that the atomic Cl was as stable as molecular Cl_2 at the temperature of 1773 K. On the contrary of the reaction of atomic O, Cl could react with elements of melting alloy to be chlorinated easily to be vaporized. This chlorination reaction would cause the increase of amount of fume generated by Ar-Cl_2 plasma reaction compared with that of Ar plasma reaction. Besides selective separations would be appeared because chlorination reaction seemed to affect the vaporization of the components of the melting alloy.

The selective separation of Fe was appeared at the case of Ar-Cl_2 and Ar-Cl_2-O_2 plasma treatments. Using Ar-Cl_2-O_2 plasma treatment, both Fe selective separation and much generation of fume were appeared. These results would be attributed to both effects of the reaction heats of atomic O recombination and of the chlorination reaction of atomic Cl with Fe of the melting alloy.

3. FUME COMPONENTS AND GIBBS FREE ENERGY CHANGES

Fe, Co, and Ni were the elements in the VIII group in the same period, therefore their chemical properties were very similar. The reason that Fe component was separated selectively with Ar-Cl_2 and Ar-Cl_2-O_2 plasma treatments did not result from the difference of their chemical properties as melting points and boiling points. The chlorination reactions would be correlated with the generation of fumes.

Each chloride vaporization reaction was considered with thermodynamic calculations. Cl_2 was dissociated into Cl atom in the plasmas therefore considered reactions were decided on the eight equations below.
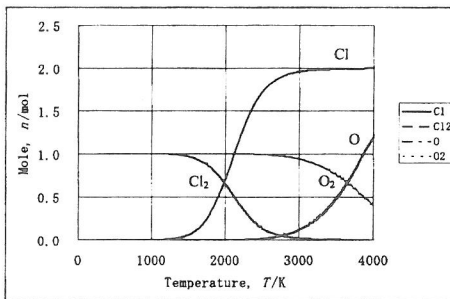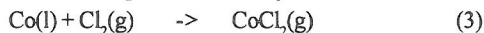
$$Fe(l) + Cl_2(g) \quad \rightarrow \quad FeCl_2(g) \qquad (1)$$
$$Fe(l) + 3/2 Cl_2(g) \rightarrow \quad FeCl_3(g) \qquad (2)$$
$$Co(l) + Cl_2(g) \quad \rightarrow \quad CoCl_2(g) \qquad (3)$$
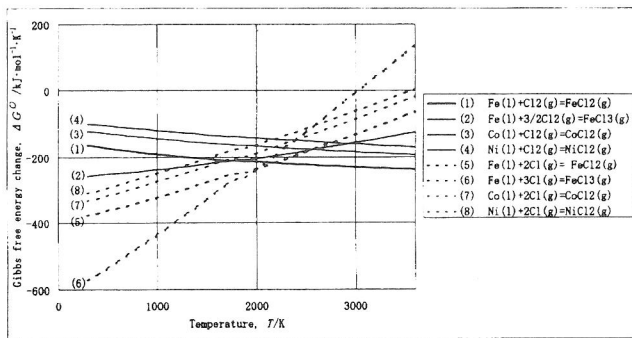
Fig. 4 Relationship between temperature and Gibbs free energy changes.

$$Ni(l) + Cl_2(g) \quad -> \quad NiCl_2(g) \qquad (4)$$
$$Fe(l) + 2Cl(g) \quad -> \quad FeCl_2(g) \qquad (5)$$
$$Fe(l) + 3Cl(g) \quad -> \quad FeCl_3(g) \qquad (6)$$
$$Co(l) + 2Cl(g) \quad -> \quad CoCl_2(g) \qquad (7)$$
$$Ni(l) + 2Cl(g) \quad -> \quad NiCl_2(g) \qquad (8)$$
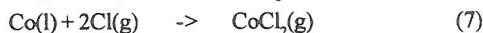
l : liquid, g : gaseous

Fig. 4 shows that the Gibbs energy changes [5] with each element of the melting alloy and atomic Cl were smaller than those with Cl_2 at the temperature of 1773 K. Each element reacted with atomic Cl more easily than with molecular Cl_2. Besides atomic hydrogen dissociated from molecular H_2 had much influence to the Ar-H_2 plasma reactions with melting metals [1]. These lead that the reactions with each element of the melting alloys and atomic Cl to occur at the equations (5) to (8). The reaction with Fe and Cl would occur more easily than with Co or Ni and Cl.

The generated fume amounts from KOVAR and HASTELLOY by plasma treatments were discussed from Gibbs free energy changes of these chlorinating equations. Table 3 shows the amount of chlorides generated by the plasma treatments of alloy samples. The generated amounts were normalized by the equation (9).

$$\text{Generated amount(mg)} = \frac{\text{Element amount in fume(mg)}}{\text{Element concentration in alloy(\%)}} \qquad (9)$$

The relationship between the amount of chloride and Gibbs free energy changes of each chloride at the temperature of 1773 K are shown at Fig. 5. Table 3 revealed that generated amounts had a tendency to increase in order of Ni, Co, and Fe at both cases of KOVAR and HASTELLOY. Fig. 5 pointed out that the order

Table 3 Generated amount of elements in fumes of KOVAR and HASTELLOY after plasma treatments.

	Ni	Co	Fe	(mg)
KOVAR	17. 6	27. 5	170. 2	
HASTELLOY	55. 9	134. 9	264. 6	

of the elements had a relationship with Gibbs free energy changes of chlorination reactions. The larger Gibbs free energy changes of the reaction with chlorine atom resulted in the more amounts of chemical compounds generated by the plasma treatments.
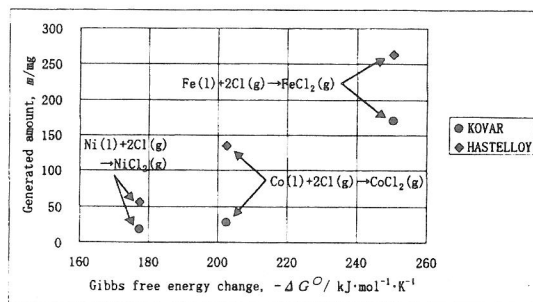

Fig. 5 Relationship between Gibbs free energy change and generated amount.

V. SUMMARY

A selective separation and generated amounts of components were discussed with arc plasma reactions of various kinds of plasma gases. Especially using chlorine for plasma reactions, iron components were separated selectively from Fe-Co-Ni alloys. The separation mechanism was discussed by thermodynamic considerations.

(1) Molecular Cl_2 in the plasmas were found to be dissociated into atomic Cl with the results of the spectroanalysis,

(2) The amounts of fumes generated by using $Ar-O_2$ and $Ar-Cl_2$ plasmas were larger than that of using Ar plasmas. Using $Ar-Cl_2-O_2$ plasmas, the amount of fume was over 10 times larger than any other amounts of fumes.

(3) Using arc plasmas with chlorine, iron components could be separated selectively from Fe-Co-Ni alloys of both KOVAR and HASTELLOY.

(4) The amount of metal chlorides from alloys generated by the arc plasma treatments could be correlated with Gibbs free energy changes of reactions with each component and chlorine atom.

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