Transactions of Materials Research Society of Japan, 25 (1), (2000)

Separation Mechanism of Compounds from Alloys with Arc Plasma Reactions

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The purpose of this study is to clarify the separation mechanism of compounds from Fe-Co-Ni and Fe-Co-Ni-Cr alloys with arc plasma reactions by thermodynamics, spectroanalysis, and chemical analysis. Alloy samples were melted with various kinds of gas arc plasmas under atmosphere pressure. Sample temperatures during plasma treatments were measured by radiation thermometry. Fumes generated by plasma reactions were caught with polyflon filters, and the concentrations of Fe, Co, Ni, and Cr were determined by ICP-AES after chemical separation pretreatments. Arc plasmas with Cl_2 resulted in the selective separation of Fe compounds from Fe-Co-Ni alloy, and Fe and Cr compounds from Fe-Co-Ni-Cr alloy. The concentration of each component in the fumes generated by the arc plasma treatments was correlated with Gibbs free energy changes of chlorination reactions.

Key words: arc plasma, separation, thermodynamics, Gibbs free energy change, melting

1. INTRODUCTION

Peculiar reactions result from the features of arc plasmas, high temperature and high chemical activity. However a few chemical reactions of arc plasmas have been known. Arc plasma reactions with hydrogen have been used to reduce metal oxides and to add heat to samples excessively [1-4], while there are very few thermodynamic data on hydrides which were concerned with the plasma reactions. We have investigated the arc plasma reactions with chlorine [5] 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 alloy, and iron and chromium component from Fe-Co-Ni-Cr alloy.

2. EXPERIMENTAL

Alloys based on Fe-Co-Ni (KOVAR; Fe=53, Co=17, Ni=29 (mass%) and Fe-Co-Ni-Cr (HASTELLOY; Fe=5.5, Co=2.5, Ni=57, Cr=15.5 (mass%)) were used for samples (10 x 10 x 5 mm, 4 g). They were set in the BN crucible, and melted with six kinds of gas arc plasmas; Ar, Ar-N_2, Ar-O_2, Ar-Cl_2, Ar-Cl_2-N_2 and Ar-Cl_2-O_2; under atmosphere pressure for 1 min. Fumes generated by the plasma reactions were caught with polyflon filters. The concentrations of Fe, Co, Ni and Cr in the fumes were determined by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry) and of Cl by ion chromatography after chemical separation pretreatments. Samples before and after plasma treatments were analyzed by EDX (Energy Dispersive X-ray Spectroscopy).

The arc plasma generator experimental apparatus is shown in Fig. 1. A dc non-transferred type plasma torch was used. The current was 185 A. The distance between the cathode and the anode was 3 mm, and the voltage was 16 V. The distance from the plasma torch and the sample was set at 40 mm. Plasma gas flow rates were 10 L/min for Ar, 0.25 L/min for Cl_2, 0.25 L/min for N_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 spec-

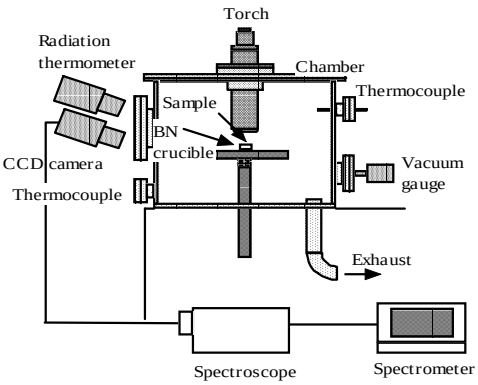

Fig. 1 Experimental system.

trometer (Japan spectrometry Co.) was used.

3. RESULTS

3.1 Sample temperature

Sample temperatures measured with the thermometer were about 1923 K during the plasma treatments, with an error of about 20 K depending on the surface condition of melting samples. The temperatures varied under the experimental conditions, while the variation was not so large. The temperature of 1923 K was used for calculations of Gibbs free energy changes.

3.2 Fume weights

The weights of the fumes generated by plasma treatments of KOVAR are shown in Table I. The collected fume weight was 0.95 mg with Ar plasmas. The collected fume weight with Ar-O_2 plasmas was slightly smaller than that with Ar plasma treatment. The fume weights of both Ar-N_2 and Ar-Cl_2 plasma treatments were larger than that with Ar plasma treatment. The collected fume weight with Ar-Cl_2-N_2 plasmas was 23 mg, and that with Ar-Cl_2-O_2 plasmas was 22 mg. Both of them were over about 10 times larger than those with other plasma gases.

The weights of the fumes generated by plasma treatments of HASTELLOY are shown in Table II. The fume weights from HASTELLOY were very small with Ar, Ar-N_2 and Ar-O_2 plasmas. The amounts of generated fumes with Ar-Cl_2, Ar-Cl_2-N_2, and Ar-Cl_2-O_2 plasmas were much larger than those with Ar, Ar-N_2 and Ar-O_2 plasmas. The fume weight with Ar-Cl_2 plasmas was 3.1 mg. That with Ar-Cl_2-O_2 plasmas was larger, 8.0 mg, and that with Ar-Cl_2-N_2 plasmas was much larger, 21.1 mg.

3.3 Fume components

The components of the fumes generated by plasma treatments of KOVAR are also shown in Table I. The components of the fumes were almost the same as initial KOVAR alloy with Ar, Ar-O_2 and Ar-N_2 plasmas. The concentrations of Fe in the fumes were about 80 mass%, and the concentrations of Co and Ni were about 10 mass% with Ar-Cl_2 and Ar-Cl_2-N_2 plasmas. The concentration of Fe was 91.3 mass% with Ar-Cl_2-O_2 plasmas, and larger than those with Ar-Cl_2 and Ar-Cl_2-N_2 plasmas. The concentrations of Ni and Co were smaller than those by any other gas plasma treatments. This result shows that Fe can be separated selectively, with high concentration, from KOVAR alloy which contained the elements with very similar properties; Fe, Co and Ni.

The components of the fumes from HASTELLOY by plasma treatments are shown in Table II. The fume amounts from HASTELLOY with Ar, Ar-N_2 and Ar-O_2 plasmas were very small, and the concentrations of components of fumes could not be measured by ICP-AES. The concentrations of Ni and Co were less than initial HASTELLOY concentrations by Ar-Cl_2, Ar-Cl_2-N_2 and Ar-Cl_2-O_2 plasma treatments. The concentrations of Fe and Cr were more than twice as large as those of initial HASTELLOY by Ar-Cl_2, Ar-Cl_2-N_2 and Ar-Cl_2-O_2 plasma treatments.

3.4 Spectroanalysis

The degree of dissociation of Cl_2 in the arc plasmas has large effects on the plasma reactions. An atomic Cl spectrum was measured at 489.68 nm [6] with Ar-Cl_2-O_2 plasmas. This result shows that Cl_2 gas dissociated into Cl

Table I Concentration of elements in fumes and fume weight with various gas plasma treatments of KOVAR.

Plasma gas	Concentration of elements in fumes (mass %)			Weight (mg/min)
	Ni	Co	Fe	
Ar	30.2	16.4	53.4	0.95
Ar-N_2	30.0	16.7	53.4	2.5
Ar-O_2	29.8	16.5	53.7	0.54
Ar-Cl_2	11.4	7.9	80.7	2.1
Ar-Cl_2-N_2	11.8	9.4	78.8	23
Ar-Cl_2-O_2	4.2	4.5	91.3	22
KOVAR	29	17	53	

Table II Concentration of elements in fumes and fume weight with various gas plasma treatments of HASTELLOY.

Plasma gas	Concentration of elements in fumes (mass %)				Weight (mg/min)
	Ni	Co	Fe	Cr	
Ar	-	-	-	-	0.00
Ar-N_2	-	-	-	-	0.05
Ar-O_2	-	-	-	-	0.01
Ar-Cl_2	24.2	2.0	12.7	61.1	3.1
Ar-Cl_2-N_2	45.8	1.4	11.4	41.4	21.1
Ar-Cl_2-O_2	41.7	1.2	10.7	46.4	8.0
HASTELLOY	57	2.5	5.5	15.5	

in the plasmas.

4. DISCUSSIONS

4.1 Fume weights and plasma gases

The reaction heat of recombination of atomic N was generated when atomic N reached the melting alloys. This recombination energy results in the vaporization of elements in the melting alloys [2]. This is the reason that the amounts of generated fumes with Ar-N_2 plasmas were larger than those with Ar plasma treatments.

The reaction heat of recombination of atomic O was also generated by Ar-O_2 plasma treatments. However oxidation occurred easily at the surface of melting alloys to generate solid metal oxides, and depressed the vaporization. The oxidation resulted in the small amounts of fumes with Ar-O_2 plasma treatments.

Atomic Cl reacted with the metals in the melting alloys, and the generated chlorides were easily vaporized. This chlorination leads to the large amounts of fumes generated by Ar-Cl_2 plasma reactions. The reaction heat of recombination of atomic Cl was also generated, however the heat would be small.

The amounts of generated fumes by Ar-Cl_2-N_2 and Ar-Cl_2-O_2 plasma treatments were larger than those by other kinds of gas plasma treatments. Following three effects were considered. First, the chlorination leads to metal chlorides with high vapor pressure. Second, the recombination energy of atomic N and O would transport heat to metals in the melting alloys and vaporize them effectively. Third, stable compounds such as metal chloride oxides, e.g., FeClO, would be generated. Ar-Cl_2-O_2 plasma treatments would generate stable metal chloride oxides, while Ar-Cl_2-N_2 plasma treatments would not generate stable metal chloride nitrides. This indicates that the large amounts of fumes by both Ar-Cl_2-N_2 and Ar-Cl_2-O_2 plasma treatments do not result from the third effect. Both effects of the chlorination of melting metals with atomic Cl and the reaction heats of atomic N or O recombination would be attributed to the large amounts of the fumes by Ar-Cl_2-N_2 and Ar-Cl_2-O_2 plasma treatments.

4.2 Fume components and Gibbs free energy changes

The elements of Fe, Co, and Ni, in the VIII group in the same period, have very similar physical properties. The reason that Fe component was separated selectively with Ar-Cl_2, Ar-Cl_2-N_2 and Ar-Cl_2-O_2 plasma treatments did not result from the difference of their physical properties such as melting points and boiling points. The chlorination reactions would be correlated with the generation of fumes.

Chloride vaporization reactions were considered with thermodynamic calculations. Chlorine was dissociated into Cl atom in the plasmas, therefore considered reactions were determined below.

$$Fe(l) + 2Cl(g) \rightarrow FeCl_2(g) \quad (1)$$
$$Co(l) + 2Cl(g) \rightarrow CoCl_2(g) \quad (2)$$
$$Ni(l) + 2Cl(g) \rightarrow NiCl_2(g) \quad (3)$$
$$Cr(l) + 3Cl(g) \rightarrow CrCl_3(g) \quad (4)$$

l : liquid, g : gaseous

The generated fume amounts from KOVAR and HASTELLOY by plasma treatments were considered with Gibbs free energy changes of these chlorination equations. Figure 2 shows that the Gibbs free energy changes of the reactions with each element in the melting alloy and atomic Cl.

The relationship between the concentrations of elements in the fumes and Gibbs free energy change of each chlorination reaction at the measured temperature of the melting alloys of 1923 K are shown in Fig. 3 in the case of KOVAR, and in Fig. 4 in the case of HASTELLOY. The concentrations of elements in the fumes were normalized by the equation (5).

$$\text{Normalized concentration (-)} = \frac{\text{Element concentration in fume (mass\%)}}{\text{Element concentration in initial alloy (mass\%)}} \quad (5)$$

Figures 3 and 4 reveal that the concentrations of the elements in the fumes correlate with Gibbs free energy

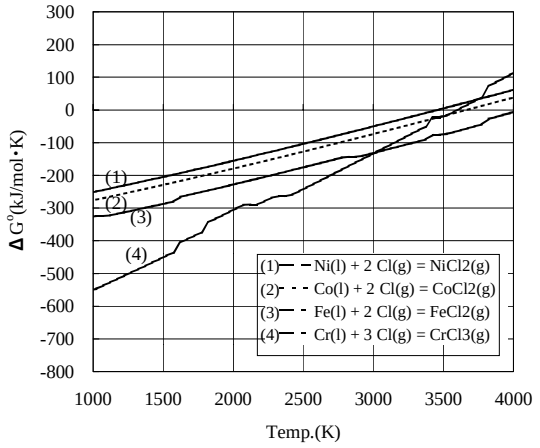

Fig. 2 Relationship between temperature and Gibbs free energy changes.

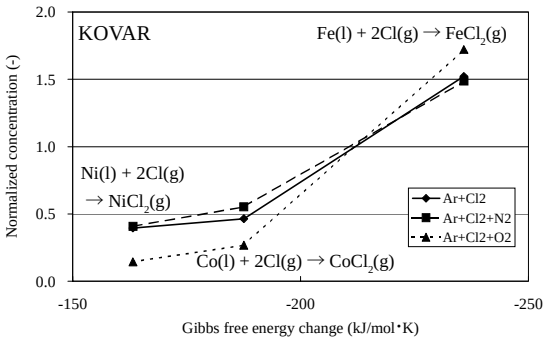

Fig. 3 Relationship between Gibbs free energy change at the temperature of 1923 K and normalized concentrations of fumes.

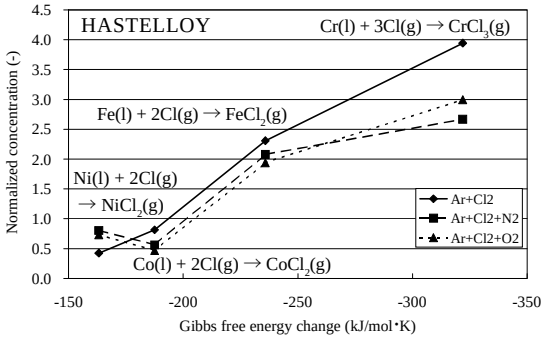

Fig. 4 Relationship between Gibbs free energy change at the temperature of 1923 K and normalized concentrations of fumes.

changes of chlorination of the metals in the melting alloys with atomic Cl in the both cases of KOVAR and HASTELLOY. The larger Gibbs free energy changes of the reactions with atomic Cl result in the larger concentrations of chemical compounds generated by the plasma treatments.

5. SUMMARY

Selective separation and generated amounts of components were considered with arc plasma reactions of various kinds of plasma gases. Especially Fe components were separated selectively from Fe-Co-Ni alloy, and Fe and Cr components were separated from Fe-Co-Ni-Cr alloy using Cl_2 for plasma reactions. The separation mechanism was considered by thermodynamics of chlorination of metals in the melting alloys with atomic Cl.

(1) The amounts of fumes generated from KOVAR with Ar-N_2 and Ar-Cl_2 plasmas were larger than that with Ar plasmas. The amounts of fumes with Ar-Cl_2-N_2 and Ar-Cl_2-O_2 plasmas were greatly larger than those with any other plasma gases in the both cases of KOVAR and HASTELLOY.

(2) The reason of the large amounts of fumes by Ar-Cl_2-N_2 and Ar-Cl_2-O_2 plasma treatments were attributed to both effects of the chlorination of metals in the melting alloys with atomic Cl and the heat of recombinations of atomic N and O .

(3) Iron components were separated selectively from KOVAR, and iron and chromium components were separated from HASTELLOY, using Ar-Cl_2, Ar-Cl_2-N_2, and Ar-Cl_2-O_2 plasma treatments.

(4) The amounts of metal chlorides from alloys generated by Ar-Cl_2, Ar-Cl_2-N_2, and Ar-Cl_2-O_2 arc plasma treatments were correlated with Gibbs free energy changes of reactions with each component and chlorine atom.

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