THE VAPOR PHASE REACTIONS IN PLASMA JET AUGMENTED BY INDUCTIVE COUPLING OF RF POWER WITH DC ARC

K. Akashi, M. Nishimura and R. Ishizuka
Department of Metallurgy and Materials Science, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

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ABSTRACT

An rf plasma torch combined with a dc plasma torch was prepared to generate a stable and enlarged argon plasma and chemical reactions arised by introducing a mixture of $TiCl_4/H_2$ or $SiCl_4/NH_3$ into the argon plasma were examined. The reaction product deposited on the inner wall and a water cooled copper column or mold, and consisted of very fine powder. Most of the product were titanium subchlorides or silicon.

1. INTRODUCTION

The experiment to generate a large volume plasma by coupling of energy to dc plasma jet was carried out first by Vermeulen Ref.(1). But there have been no detailed reports concerning the application of such plasma to extraction metallurgy or synthesis of inorganic materials such as refractory compounds.

In this study, as a trial, an rf plasma torch combined with a dc plasma torch was prepared to generate a stable and enlarged Ar plasma, and chemical reactions arised by introducing a mixture of $TiCl_4/H_2$ or $SiCl_4/NH_3$ into the argon plasma were examined.

2. EXPERIMANTAL

Two types of combined plasma torches were used in our experiments. The first one is shown in Fig.1. The main part of dc plasma torch(OD: 44mm, L:170mm) is consisted of a tungsten rod cathode(OD:5mm, L:25mm) and a copper anode nozzle(ID:12mm, L:31mm). The dc plasma torch was set on the rf plasma torch consisted of a double walled tube of transparent quartz(OD:70mm,ID:58mm, L:380mm) in order to pass cooling water between the two walls.

An induction coil of copper pipe(OD:5 or 6mm), in which cooling water can be circulated, was used for supply of electric power to the dc plasma jet generated by the dc plasma torch. A water cooled copper column(OD: 30mm) was set at the lower part of the rf torch. The position of the upper end of copper column was adjusted and kept at a suitable level under the dc plasma torch. The copper column served as a condenser to deposit the reaction products. A cooling gas (Ar) was introduced horizontally at the highest part of the rf plasma torch to stabilize the plasma and protect the inner wall of the torch from the plasma. Three gas outlets were arranged with separation at angle of 120°,at the lowest part of the rf plasma torch. An annular quartz tube(ID:3mm) was set just under the dc plasma torch. Eight small holes(D;1.5mm) were made downward and obliquely at an angle of 45° in the wall of this tube. Gas reactants were introduced into the plasma through these holes.

Another type of the combined torch, as shown in Fig.2, is a modified one. In this torch, the inner and outer diameters of double walled quartz tube are smaller than those of the former one by about 15 mm. Therefore, the dc plasma torch was modified to accord with the quartz tube. The rf coil was covered with teflon tube for insulation and its dimension was also reduced.

The cooling gas was introduced horizontally from two opposite directions into the quartz tube. The reactant gases were injected into the plasma through three small copper pipes prepared at equal distances along the outside wall of the dc plasma torch. Six kinds of anode copper nozzles, in which each dimension is somewhat different, were used. At the lowest part of the double walled quartz tube, a water cooled copper mold was set for condensing the reaction products.

The maximum output powers of the dc and rf generators were 10KW respectively in the above mentioned both cases. The rf torch was operated at a frequency of 4-5 MHz.

At first, the experiment to generate a stable plasma was carried out by adjusting the amount of only Ar or Ar/H_2 flow without introduction of reactant gases and the distance between the top of dc plasma torch and the rf coil. The reactant gases were injected into such stabilized plasma. The condensed products collected from various parts of the inner wall of the quartz tube and the water cooled copper column of mold were examined with X-ray diffraction, chemical analysis, EPMA and thermal analysis.

3. RESULTS AND DISCUSSIONS

In the preliminary experiments using the combined plasma torch shown in Fig.1., the stabilized and enlarged plasma was obtained by supplying the cooling gas (Ar:20-30l/min) and the plasma forming gas (Ar:7-8l/min) for dc plasma jet at a dc power of about 3 KW and a rf power of 5-10 KW. The plasma became more stable by connecting three gas outlets with a large bottle (gas reservoir), from which gas was ejected in the air through a washing bottle containing NaOH solution. When the water cooled copper column was brought closer to the dc plasma torch, the plasma became unstable.

The remarkable changes of volume,shape and length of the Ar plasma jet generated by using the dc plasma torch were observed with coupling of rf power, as shown in Fig.3.

$TiCl_4$ was introduced into the plasma with H_2 through small holes of the annular quartz tube. The flow rates of $TiCl_4$ and H_2 are 2-6x10^{-4}mol/min and 2.2-6.6x10^{-2}mol/min respectively. The consumed time for supply of $TiCl_4$ and H_2 was about 30 min in each run.

The reaction products deposited on the inner wall of the quartz tube and the copper column were consisted of very fine particles and had its own color such as black, blackish purple, dark blue or brown depending upon the position where the products were deposited. The product recovered from the inner wall of the quartz tube was nearly amorphous and showed spontaneous combustibility in the air. Titanium subchlorides such as $TiCl_3$ and $TiCl_2$ were contained in the amorphous product. For example, the chemical analysis of the blackish purple deposit recovered from the upper part of the quartz tube showed us that the contents of $TiCl_3$ and $TiCl_2$ were about 85% and 14% respectively. A few X-ray diffraction lines were observed in such deposit after its vacuum heating at temperatures between 250 and 800°C. From the analysis of these lines, the existence of anatase and rutile was recognized. It may be due to the oxidation or hydrolysis of subchlorides containined in the deposit after it was recovered in the air.

In a few cases, an alumina pipe or a tungsten rod was used in place of the copper column to deposit the reaction product. A very small amount of crystalline metallic deposit grew on the alumina tube, which was not water-cooled and heated just under the plasma. The existence of TiO or TiN were recognized in the brown product deposited on the top of tungsten rod heated under the same condition as the case of alumina tube. A black deposit obtained on the zirconia tube, which was used to cover the side wall of the tungsten rod, showed the weight increase by 25% in the gravimetric analysis (heating in the air), while the deposit recovered from the inner wall of the quartz tube showed the weight decrease by 10% in the same analysis. From this fact, it was estimated that the black deposit on the zirconia tube was not subchloride. Chlorine was not detected in the deposit recovered from the top of the tungsten rod by EPMA.

The thermodynamical consideration concerning the vapor phase equilibrium in the Ar-Ti-Cl-H system at high temperatures between 2000 and 6000K was done , according to the calculation of concentration (number of moles) of gaseous secies such as e^-, H, Cl, Ti. Cl, HCl, TiCl, $TiCl_2$, $TiCl_3$, $TiCl_4$, Ar^+, and Ar which were assumed to be present in this system at 6000K. Therefore the temperature corresponding to the starting point of this calculation was 6000K.

An example of the calculation was shown in Fig. 4. The molar ratios of Ar, Ti, Cl, and H in this system were determined on referring to the flow rates of Ar, $TiCl_4$ and H_2 in the experiment. The dotted line in Fig. 4 was obtained on using the vapor pressure values of Ti in the presence of condensed Ti phase. From such result, it is estimated that condensed Ti phase may be obtained only by quenching of Ti vapor to about 2000K

In the above mentioned experiment, $TiCl_4$, H_2 and Ar of commercial grade were used, while, in the experiment using the combined plasma torch, shown in Fig. 2., NH_3 of commercial grade and $SiCl_4$ of very high purity were introduced into the Ar plasma generated in the water cooled double walled quartz tube. Ar was used as the plasma forming gas and the cooling gas. The flow rates of those gases were 9 l/min and 30-35 l/min respectively.

$SiCl_4$ was introduced into the plasma through three small copper pipes attached along the outer wall of the dc plasma torch, at the flow rate of $3.5x10^{-3}$mol/min with Ar (2l/min) as a carrie gas. NH_3 was injected horizontally at the flow rate of 3.5 l/min with the cooling gas from the upper part of the quartz tube. The time for introduction of $SiCl_4$ and NH_3 was 15-20 min. The dc input power was 3-5 KW, and the maximum output power of the rf generator, a part of which was coupled with the dc power, was about 15 KW. The brown and yellow powder was deposited on the inner wall of the water cooled quartz tube just under the rf coil region. The white fine deposit was obtained on the lower end of the dc plasma torch. The X-ray diffraction analysis of the deposit was carried out. It revealed that both Si and NH_4Cl were contained in the deposit. But, only Si was detected in the deposit dried after washing with water or heated in a vacuum at 400°C and 1000°C for 1 h. The intensity of diffraction lines showing the presence of Si was made remarkably strong by the heating in a vacuum. The mean diameter of particles constituting the deposit was estimated to be 400 Å by electron microscopy.

The equilibrium concentration of various constituents to be present in the Ar-Ti-Cl-H-N system at high temperatures were examined by the thermodynamical calculation based on the known thermochemical data(Ref.2), following the example of the Ar-Ti-Cl-H system. An example of the calculated results was shown in Fig.5. The formation of Si_3N_4 may be difficult because it can be decomposed at higher temperatures.

4. CONCLUSION

The optimum operating conditions of new types of combined plasma torches were examined. The stable and enlarged plasma was generated succesfully. A few experiments were carried out to clarify the characteristics of vapor phase reactions in the enlarged plasma. But there is much left to study in those points.

REFERENCES

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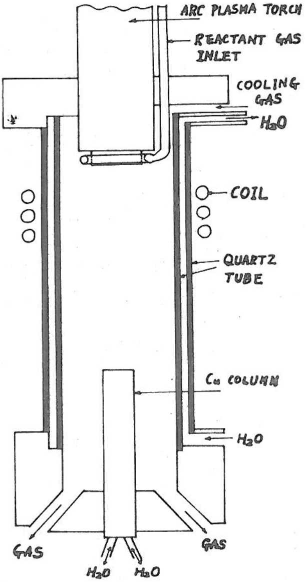

FIG.1 COMBINED TYPE I OF DC AND RF TORCHES

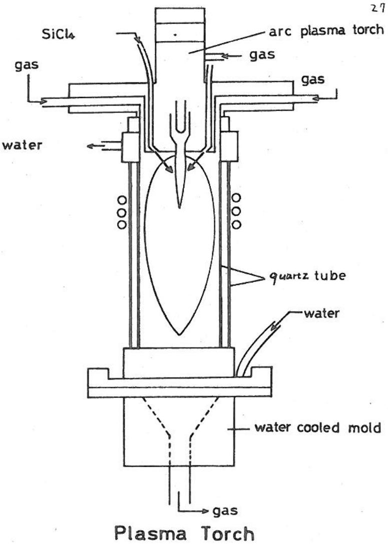

FIG.2 COMBINED TYPE II OF DC AND RF PLASMA TORCHES

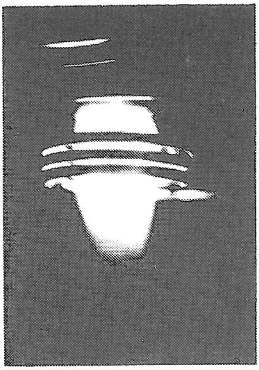

FIG.3 STABLE AND ENLARGED PLASMA GENERATED BY INDUCTIVE COUPLING OF RF POWER WITH DC PLASMA JET

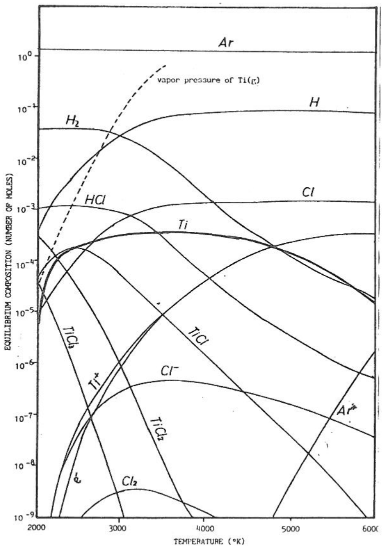

FIG.4 DIAGRAM OF EQUILIBRIUM CONCENTRATIONS OF VARIOUS CONSTITUENTS IN Ar-Ti-Cl-H SYSTEM AT HIGH TEMPERATURES

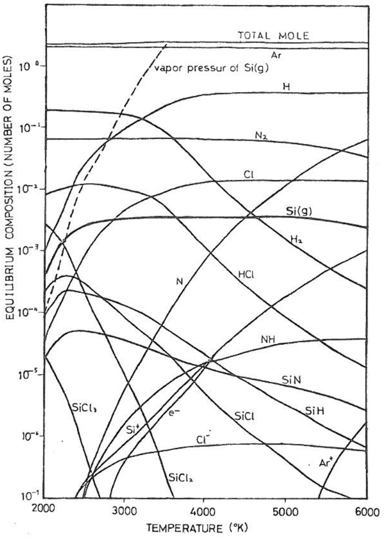

FIG.5 DIAGRAM OF EQUILIBRIUM CONCENTRATIONS OF VARIOUS CONSTITUENTS IN Ar-Si-Cl-H-N SYSTEM AT HIGH TEMPERATURES