Vanadium Recovery from Combustion Ash of Orinoco Tar in Venezuela

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Abstract: Vanadium is added to the special steel like tool, ship and pipe. Vanadium is produced as a by-product of other metals or recovered from petroleum refining catalyst. Recently, attention has been given to Orinoco tar combustion ash as vanadium resource, because the ash contains more than 20 mass% V_2O_5.

In the first step, vanadium recovery was tried from the combustion ash of Orinoco tar in the present work. The ash mixed CaO was reduced with carbon at 1773K. The mixed sample melted completely and separated into slag and metal containing vanadium carbide at the temperature. Vanadium was not observed in slag phase, and it meant that all of vanadium in ash was recovered as VC in the metal phase. The metal was Fe-Ni alloy.

In the second step, Fe-Ni-V-C quo-ternary isothermal section phase diagram was experimentally assembled at 1773K.

As the result, the mechanism of vanadium recovery from Orinoco tar combustion ash by reduction with carbon was discussed based on the Fe-Ni-V-C phase diagram system and generating gas species analysis in the heating process.

Keywords: Reduction, Vanadium, Orinoco tar, Fe-Ni-V-C quo-ternary phase diagram

1. Introduction

Vanadium is an indispensable additive element to the materials of boat, ship, tool steel, and pipeline, and so on. It is, therefore, very important to produce a stable supply of vanadium. Pure vanadium ore does not exist in nature, and vanadium is yielded as a by-product of other metals or recovered from petroleum refining catalyst.

The recovery methods of vanadium from combustion ash of heavy oil have recently been discussed[1-4)]. In those reports, hydrometallurgy is proposed for the recovery method.

1.2 trillion barrels of Orinoco tar are found in northern area of 50,000km^2 in Venezuela. The Orinoco tar reserves that can be mined are 270 billion barrels. It will be possible to supply the tar for 700 years even if its 60 million ton is mined a year. As the viscosity of Orinoco tar is higher than usual heavy oil, dilution is required and its usage has been limited. Therefore, the other new utilization methods have been expected to be developed because of a lot of its reserves. Attention has recently been given to the crude Orinoco tar combustion ash as vanadium resource because it contains V_2O_5, NiO, Fe_2O_3, SiO_2 and Al_2O_3.

The vanadium recovery process from the combustion ash of Orinoco tar mixed CaO and carbon was developed with pyrometallurgical method in the present study, resulting in Fe-Ni-V-C metal and SiO_2-CaO-Al_2O_3 slag phases. The reason is that pyrometallurgical method has the following advantages.

1. The capital investment is lower than that in hydrometallurgical process.

2. The productivity is comparable high than other metallurgical processes.
3. It is possible for the recovery to be low when cheap reducing agent is used.

The basic information of the Fe-Ni-V-C system phase diagram was necessary in the present work where carbon was used as cheap reducing agent. Therefore, the metal system phase diagram was investigated. Temperature of 1773K was chosen based on melting point of the slag produced in the present proposing reduction method.

2. Experimentals

The combustion ash of the Orinoco tar, of which composition is shown in **Table 1**, was used for recovery of vanadium in the present study. The ash was mixed with CaO and C powder, as shown in **Table 2**, and compacted to tablet shape.

Table 1 Orinoco tar combustion ash composition

V_2O_5	NiO	Fe_2O_3	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	S	C	Total (mass %)
20.53	13.18	18.62	15.61	9.80	0.83	1.06	1.06	0.30	0.22	5.08	86.30

Table 2 Mixing ratio of sample

Ash	C	CaO	Total(mass %)
78.89	7.00	14.11	100

The compacted sample was put in a carbon crucible and heated to 1773K at the rate of 200K/hr in Ar atmosphere. After holding for 3hr at 1773K, the sample was withdrawn with a Mo wire from the inside of a reaction tube and quenched by impinging He gas. The obtained sample was cut and observed with SEM-EDS/WDS.

In the next stage, phase diagram experiment on Fe-V-C, Ni-V-C and Fe-Ni-V-C systems was made in the present work. In this experiment, electrolysis Fe, Ni and carbon powder were mixed and compacted to tablet shape. The sample was put on V crumbs in an Al_2O_3 crucible as shown in **Fig. 1.**

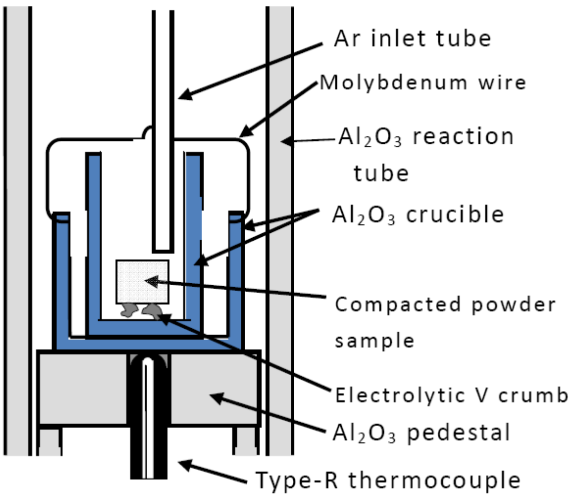


Fig.1 Experimental apparatus

3. Experimental Results

3.1 Reduction experiment of Orinoco tar combustion ash

The mixed sample melted completely and separated into metal and slag phases at 1773K as shown in Fig. 2. The sample was observed with SEM. The metal phase separated into vanadium carbide and Fe-Ni alloy. As V was not contained in slag phase, it was observed that V in ash was almost completely recovered as vanadium carbide in metal phase. The chemical composition of metal phase was analyzed by SEM-EDS/WDS. It is shown in **Table 3**. A was a vanadium carbide phase composed of C, O, and V. B was the matrix of metal phase composed of O, Si, Fe, and Ni. The metal phase coexisted with both of vanadium carbide and C phases.

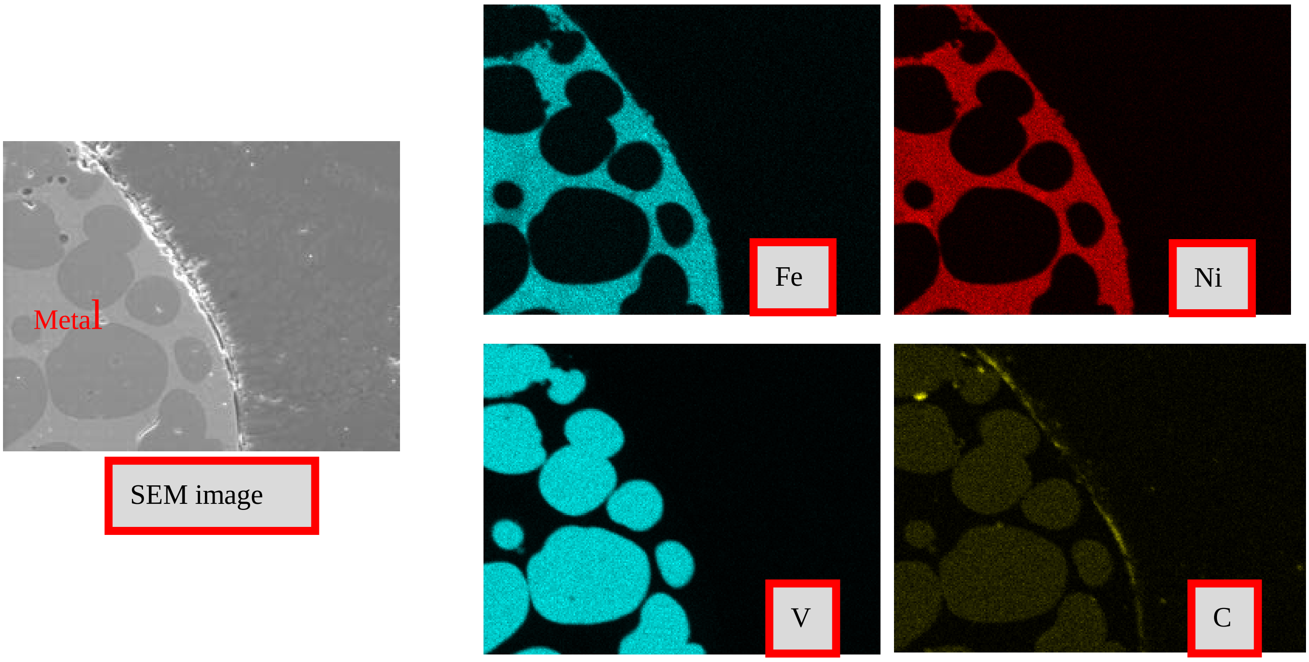
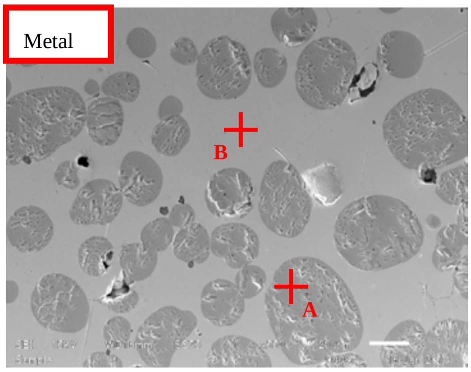


Fig.2 Sample mapping

Table 3 Chemical composition analysis result of metal phase



Phase	C	O	Si	Ti	V	Fe	Ni	Total (mass%)
A	19.43	6.68	0.03	1.57	71.52	0.61	0.16	100
B	2.13	10.60	12.25	0.02	0.72	37.41	46.40	100

3.2 Isothermal section of Fe-Ni-V-C system at 1773K

The samples were observed with SEM. An example is shown in **Fig.3**. A black part was a carbon phase, a gray round portion was a vanadium carbide phase, and the surroundings were a metal phase. The composition of each phase was analyzed by SEM-EDS/WDS quantitatively. The result of the chemical composition analysis by WDS was plotted on the isothermal section of Fe-V-C, Ni-V-C, and Fe-Ni-V-C system in **Figs. 4**, **5** and **6**, respectively. Solidus and liquidus lines in these phase diagrams were decided based on the present experimental results.

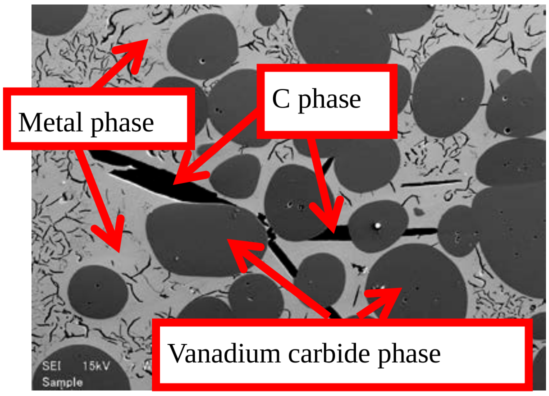


Fig.3 An example of sample SEM image

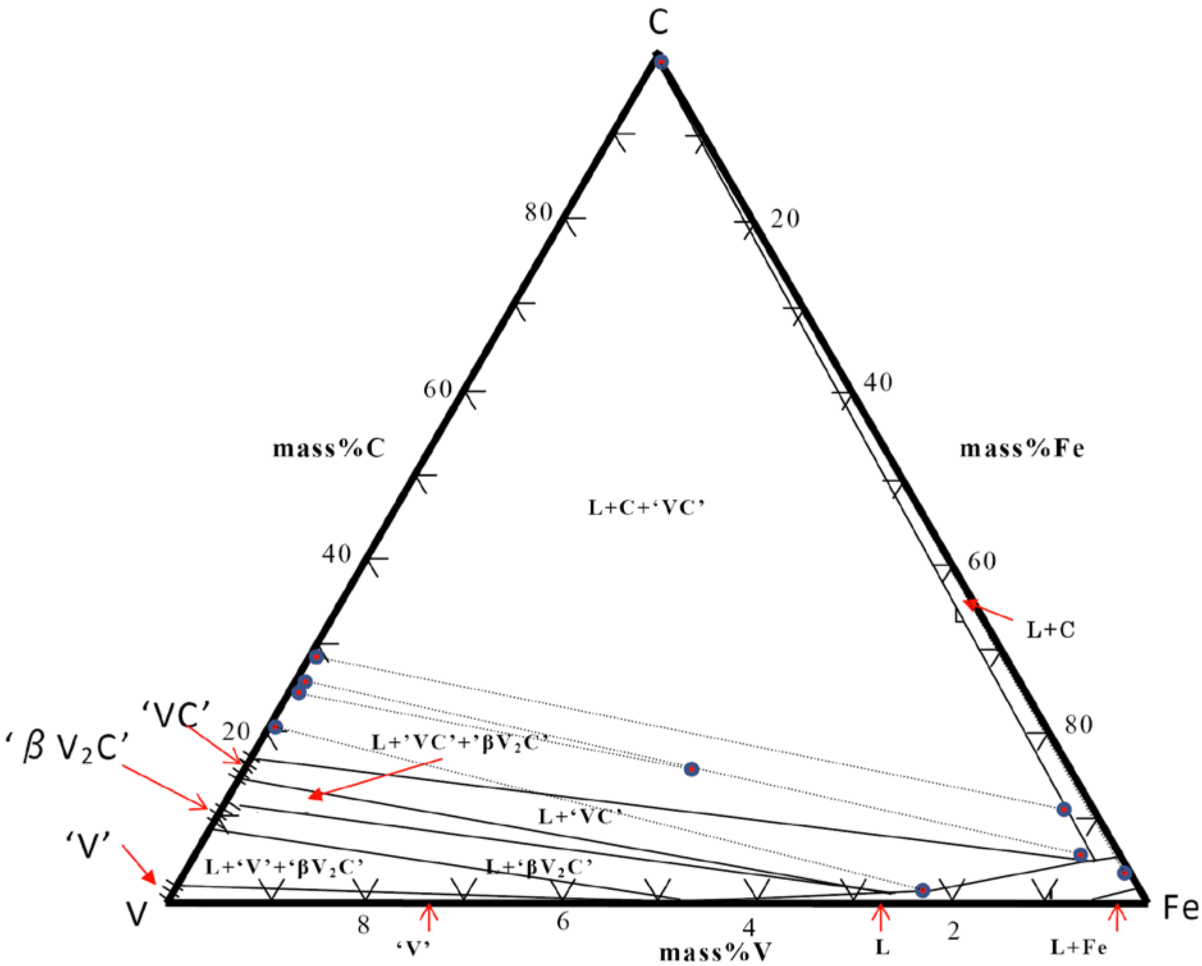


Fig.4 Iso-thermal section of Fe-V-C phase diagram at 1773K

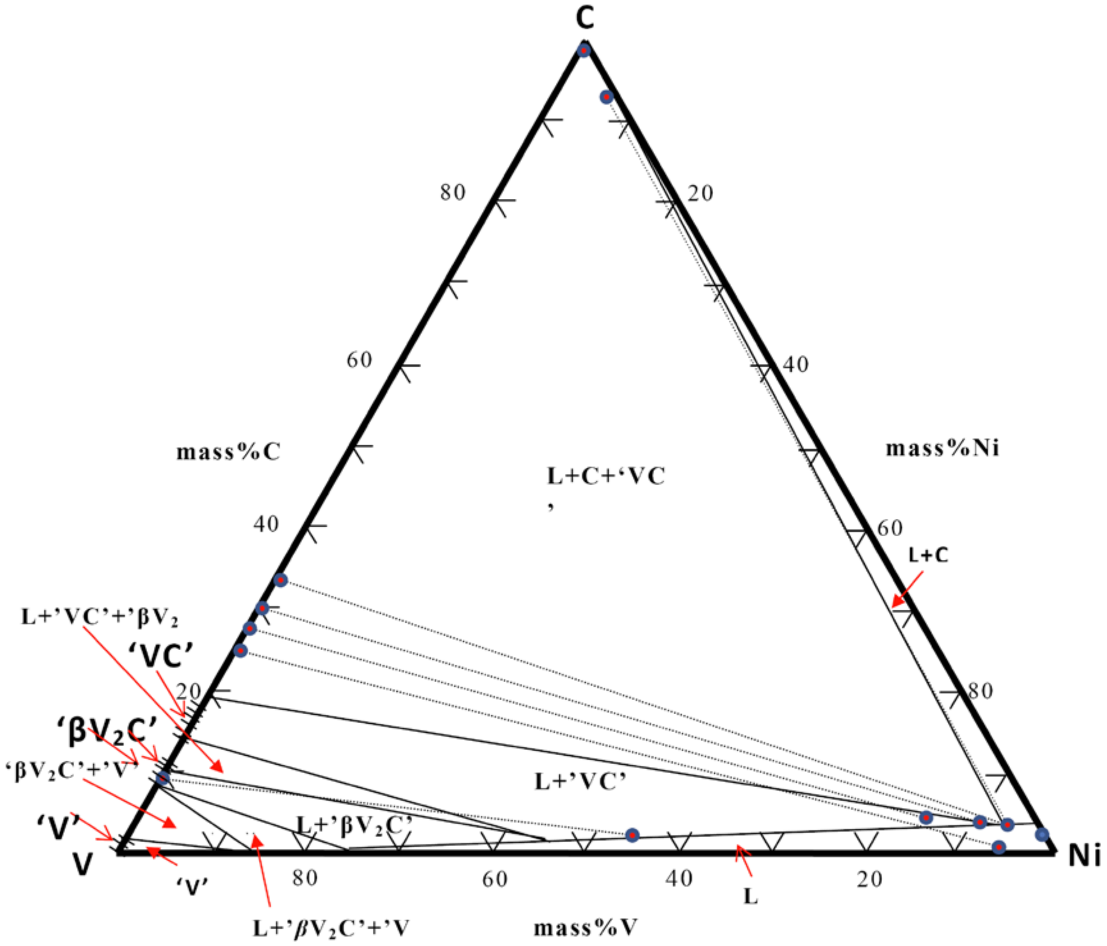


Fig.5 Iso-thermal section of Ni-V-C phase diagram at 1773K

4. Discussion

Amara *et al.*[5] reported the phase diagram of Fe--V-C system. They reported that the solid phases formed from liquid phases as follows;

At e_1 of 1420K which is the ternary eutectic of 92.84mass%Fe, 2.91mass%V and 4.26mass% C,

$$\text{Liq} \rightarrow \gamma + VC_{x=0.89} + Fe_3C$$

At p of 1643K which is the ternary quasi-peritectic of 87.19mass%Fe, 10.71mass%V and 2.10mass%C,

$$\text{Liq} + \alpha(\text{FeV}) \rightarrow \gamma + VC_x$$

At e_2 of 1663K which is the ternary eutectic of 65.76mass%Fe, 32.72mass%V and 1.52mass%C,

$$\text{Liq} \rightarrow \alpha(\text{FeV}) + VC_{x=0.62} + V_2C\ (VC_{0.40})$$

e_1, p locates in the area of liquid phase at 1773K in the Fe-V-C phase diagram iso-thermal section shown in Fig.4. According to the result of Amara *et al.*[5], liquid phase disappears at 1420K and 1643K of e_1 and p. Therefore, the present result agrees with that of Amara *et al*. However, e_2 dose not locate in liquid phase region at 1773K.

The present experimental samples of which composition located in L+'VC' area transferred into α(FeV) and VC_x phases during cooling process. Similarly, the samples in L+'VC'+'βV_2C' area did into α(FeV), VC_x and 'V_2C' phases during cooling process. The samples in L+'βV_2C' area did into α(FeV) and 'V_2C' phases during cooling process. These agree well with the result of Amara *et al.*[5]. But the samples in L+'V' area did into α(FeV) and 'V_2C' phases during cooling process. This disagrees with the result of Amara *et al*.

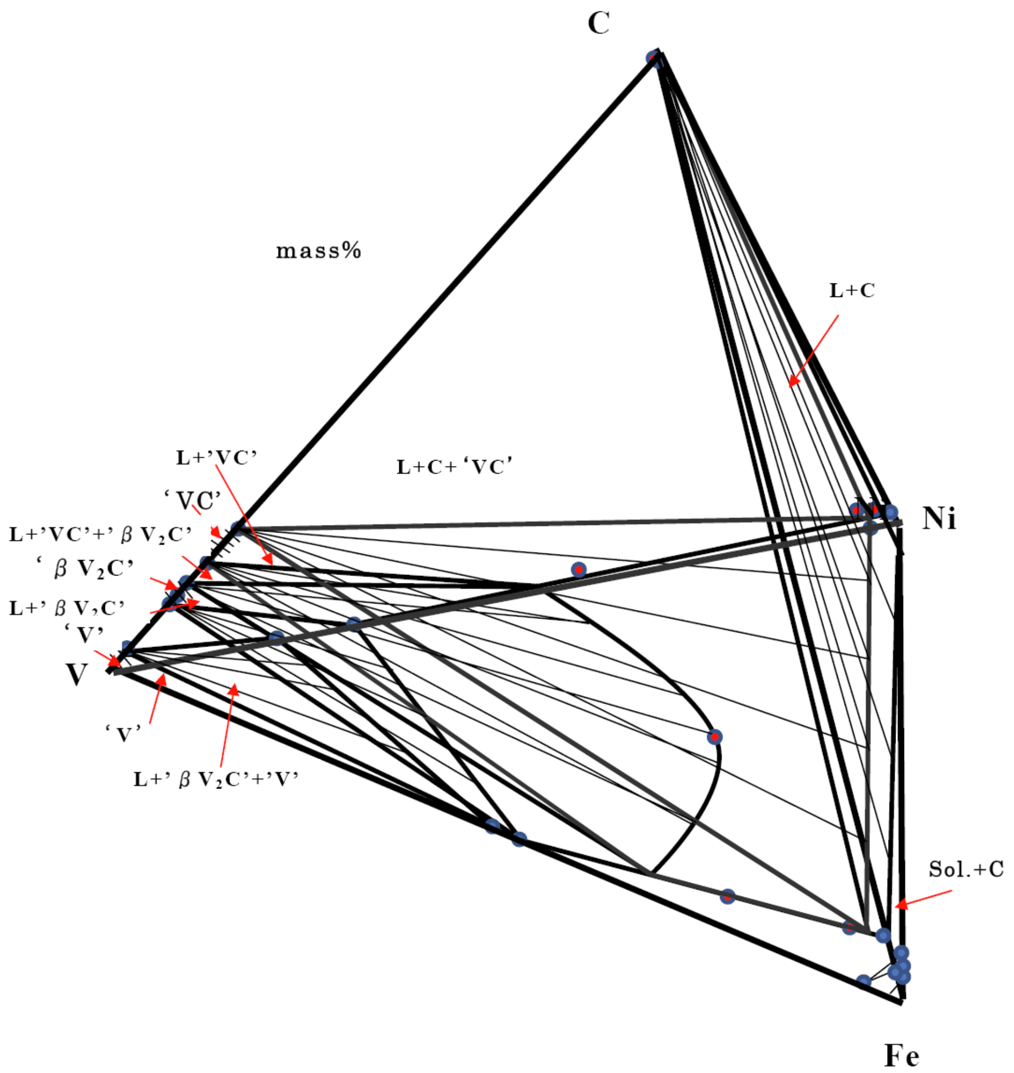


Fig.6 Iso-thermal section of Fe-Ni-V-C phase diagram at 1773K

5. Summery

The followings are concluded in the present study.

1. Orinoco tar ash could be reduced by C. As the results, most of V in the ash could be recovered into Fe-Ni alloy metal as 'VC'.
2. Fe-V-C, Ni-V-C ternary isothermal section and Fe-Ni-V-C quaternary isothermal section were experimentally clarified at 1773K.

Reference

1) Nobuyoshi Mukawa: Trans. Shigen･Sozai, **107**(1991), 295.

2) Kanji Sato: Kogyo Rare Metal, 106(1993), 30.

3) Kunimitsu Tsukakoshi: Energy･Shigen, **18**(1997), 26.

4) Keiichi Miura, Hirosuke Mochiduki, Hirotaka Senba, Toshihisa Maruyama, Kazuaki Hashimoto and Yoshitomo Toda: Inorganic Materials, **6**(1999), 213.

5) Sif Eddine Amara, Rafika Kesri, Nicole Valignat Sylvaine Hamar-Thibault: Mikrochim. Acta, 114/115 (1994), 157.