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著者	TANIUCHI Kentaro, MIMURA Koji
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Arc-plasma Reduction of Vanadium Oxide with Carbon*

Kentaro TANIUCHI and Koji MIMURA

The Research Institute of Mineral Dressing and Metallurgy

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Synopsis

The reduction of vanadium pentoxide by carbon has been investigated in an argon plasma-arc furnace. Briquettes of vanadium pentoxide and carbon mixtures have been examined and the results are as follows:

1) The optimum mixing ratio of carbon and vanadium pentoxide, C/V_2O_5 , is approximately 4.5 and is smaller than the stoichiometric ratio of 5. When the mixing ratio is less than 4.5, the oxygen remaining in the product increases, while the vanadium carbide content increases when the ratio is greater than 5.

2) The sample is fused within 45 seconds by the plasma-arc and the reduction of vanadium oxide proceeds rapidly to nearly 90% vanadium content in the melt. Subsequent reduction in the molten state is slow. Within 10 minutes the vanadium content reaches a maximum of 96%.

3) Preliminary sintering of the briquette results in good recovery of vanadium due to the diminished loss of the sample under the plasma flame.

4) An increase of the vanadium content is not observed as temperature is increased from 2100 to 2800°C.

5) The hardness of the product with the highest vanadium content is about H_V 290 and is much larger than that of vanadium metal due to the small amount of remaining oxygen and/or carbon.

6) By means of EPMA, it is observed that the well developed, dendritic, primary crystals contain a small amount of carbon and oxygen in solid solution is observed.

In this study, a vanadium metal of 96% purity has been produced within 10 minutes in spite of the strong affinity of vanadium for carbon or oxygen.

I. Introduction

Metallic vanadium is used as an alloying element in alloy steels and the construction material of atomic reactors. However, in Japan the production of this metal is very small at present^(1,2). Ordinary smelting processes involve the reduction of oxide or chloride with calcium or magnesium metals^(3,4) and the thermal decomposition of iodide⁽⁵⁾.

As for the reduction of oxide with carbon, the experimental reports are few except in the study of the reduction in the solid state under a reduced carbon

* The 302th report of the Research Institute of Mineral Dressing and Metallurgy, originally published in Japanese in the Bulletin of the Research Institute of Mineral Dressing and Metallurgy, Tohoku University, **33** (1977), 71.

- (1) S. Matoba et al, *Kinzoku Seiven Gijutsu Handbook (Handbook of Metallurgical Smelting Technics)*, Asakura Shoten, (1963), 645.
- (2) Y. Kumamoto, *Shin-Kinzoku Databook (New Metals Databook)*, Agne, (1977), 296.
- (3) R.K. McKechnie and A.V. Seybolt, *J. Electrochem. Soc.*, **97** (1950), 311.
- (4) A.P. Beard and D.D. Crooks, *ibid*, **101** (1954), 597.
- (5) O.N. Carlson and C.V. Owen, *ibid*, **108** (1961), 88.

monoxide pressure at approximately 1600°C^(6,7).

Recent developments in the technology of the plasma-arc furnace have led to many studies on the reduction of metallic compounds, the production of alloys, and the formation of carbides or nitrides at high temperature^(8,9).

We have carried out an investigation of the arc-plasma reduction of metallic compounds. These compounds have high melting points or are refractory in nature and are found to be difficult to reduce. In this paper, our results of the carbon reduction of vanadium pentoxide are presented. While the arc-plasma reduction of vanadium oxide has already been reported by Akashi et al⁽¹⁰⁾, we feel that a sufficient explanation has not been made.

II. The apparatus and experimental methods

A plasma-arc furnace by Tōei Industry Co. Ltd. is used. This furnace is a direct current, arc plasma type and has a maximum power output of 20 KW. Fig. 1 shows the schematic diagram of the furnace including the plasma torch and the reaction vessel. The reaction vessel is a cylinder of stainless steel. Its inner diameter and height are 26 cm and 20 cm respectively. The diameter of the copper nozzle (anode) is 0.7 cm.

Sample materials in a water-cooled, copper crucible are reduced by the transferred type arc. The distance between the top of the plasma torch and the sample is about 2 cm.

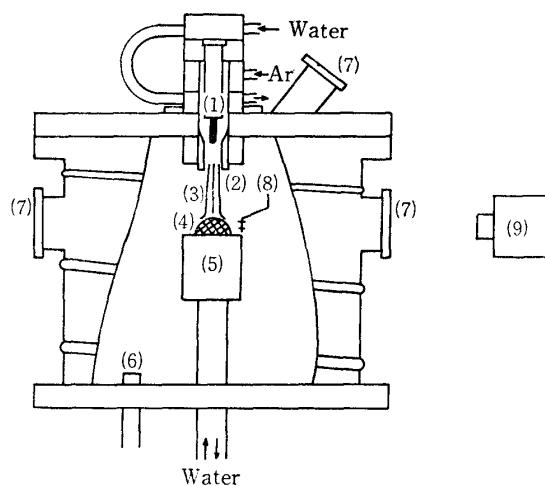


Fig. 1. Schematic diagram of the plasma-arc furnace.

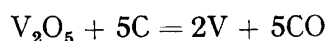
(1) Cathode ($W+ThO_2$), (2) Anode (copper nozzle), (3) Plasma flame, (4) Sample, (5) Copper crucible, (6) Gas outlet, (7) Viewing port, (8) Radiation sealed molybdenum plate with small hole (2 mm × 2 mm), (9) Two-colour-eye pyrometer.

- (6) W.J. Kroll and A.W. Schlechton, *ibid*, **93** (1948), 247.
 (7) S. Takeuchi et al, *Denkikagaku* (J. Electrochem. Soc. of Japan), **33** (1965), 713.
 (8) Y. Hayakawa and O. Matsumoto, *Plasma Chemistry and its Application*, Shōkabō, (1971), 111.
 (9) K. Akashi and R. Ishizuka, *Kinzoku* (Metals), **43** (1973), 50.
 (10) R. Ishizuka, K. Akashi and I. Egami, *Seisan-Kenkyū* (J. Institute of Industrial Science, Tokyo University), **22** (1970), 370.

The surface temperature of the sample materials during the reduction is measured by a Sigma Electron Industrial Co. Ltd., Type C-120, two-colour, optical pyrometer. The upper limit of this measuring device is 3300°C. Radiation from the high temperature, plasma flame, upon entering the pyrometer, causes a full scale deflection of the indicator. Therefore, the surface temperature of the sample cannot be measured. Consequently, as shown in Fig. 1, a molybdenum plate with a 2 mm by 2 mm size hole is attached to the edge of the copper crucible and prevents the incidence of radiation from the plasma flame. To ensure the accuracy of the pyrometer, the melting temperature of tantalum (M.P. $2996 \pm 50^\circ\text{C}$ ⁽¹⁾, purity 99.9%*) and niobium (M.P. $2520 \pm 10^\circ\text{C}$ ⁽¹¹⁾, purity 99.5%) have been measured and are found to be 3100°C and 2550°C respectively. Therefore, this pyrometer is confirmed to be reasonably accurate.

The vanadium oxide used in the present work is powdered pentoxide of 99.56% purity with a particle size of minus 200 mesh. The reducing reagent is graphite powder of minus 300 mesh particle size and its ash content is under 0.05%. Selected ratios of the two materials are mixed for about 2 hours. These mixtures are vacuum briquetted under a pressure of 6 ton/cm². Each briquette is about 15 mm diameter and about 7 to 8 mm in thickness and weighs 3.5 g.

The fundamental reaction of reduction is shown as follows:



Then, the stoichiometric mixing ratio of carbon to vanadium pentoxide, C/V₂O₅, is 5. However, to find the optimum mixing ratio, the reduction of briquettes with the mixing ratios of 3 to 6 has been studied. Further, two kinds of briquettes have been compared. One is a green briquette and the other is sintered at 700~1000°C for 1 hour in an argon atmosphere prior to the reduction.

Industrial, high purity argon is used in the generation of the plasma arc and the gas flow rate is 5 l/min. The relationships between the arc current, the arc voltage, the power input of the furnace and the surface temperature of the sample are shown in Fig. 2.

The reduction temperatures in this study range from 2100 to 2800°C. The melting temperature of metallic vanadium is reported to be 1917°C⁽¹²⁾. Further, changes in the standard free energy with temperature for the reaction of various vanadium oxides⁽¹³⁾ are shown in Fig. 3. Thus, the reaction temperatures in this work are considered to be sufficient for the carbothermic reduction of vanadium oxide.

The time spent to melt down the briquette is approximately 45 seconds. It should be noted that in this work, the instant when the briquette is fused and forms

* Compositions are shown in weight percentage hereafter, unless specified otherwise.

(11) Japan Institute of Metals, *Metals Databook*, Maruzen, (1974), 10.

(12) O.A. Songina, *Rare Metals*, 3rd ed., Israel Program for Scientific Translations (1970), 72.

(13) O. Kubaschewski et al, *Metallurgical Thermochemistry*, (1967), 421.

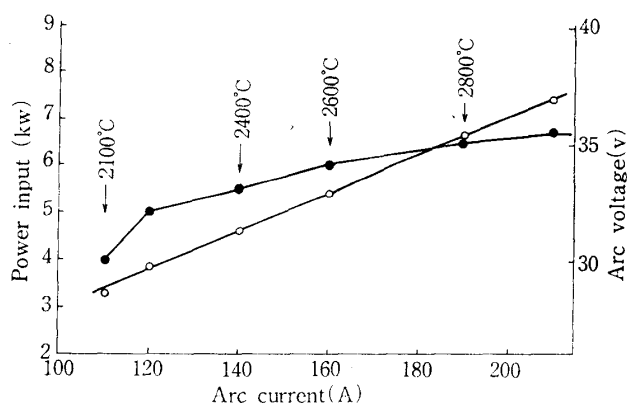


Fig. 2. Correlation between the arc current, the arc voltage and the power of input of the plasma-arc furnace.

(—○—; power input, —●—; arc voltage, the flow rate of Ar gas=5 (l/min))

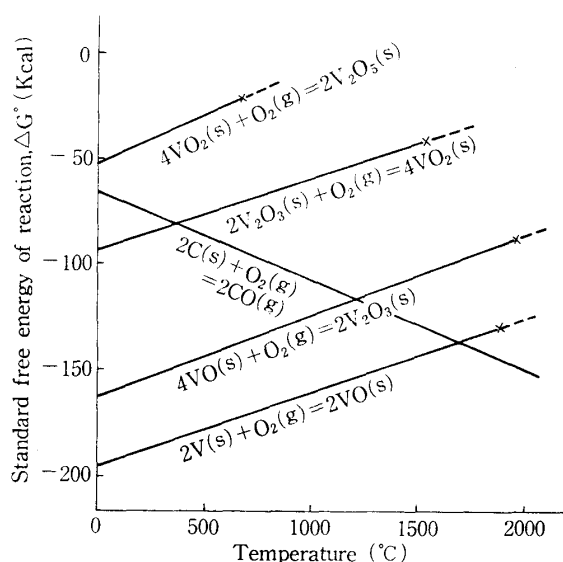


Fig. 3. Changes in standard free energy with temperature for the reaction of vanadium oxides (Kubaschewski et al.).

a liquid button is considered to be the starting time of the reaction. After this time, the reaction is continued for a given number of minutes, the sample material is turned over, and the reduction is continued for an equal time interval. The total time of both heat treatments is taken to be the reaction time.

X-ray diffraction analyses, Vickers hardness measurements, microscopic observations, and EPMA analyses for the reduction products have been carried out. The content of vanadium is analysed by chelatometry and the remaining carbon is analysed by the method of coulometric determination. The remaining oxygen is calculated by the following equation:

$$O \text{ (wt.\%)} = 100 - V - C$$

To confirm the accuracy of the calculated quantity, oxygen of two sample products have been analysed by the method of argon gas fusion-coulometric

determination. These results are shown in Table 1. Because the results from the chemical analysis agree well with the calculated values, the calculated values from the above-mentioned equation are considered to be reasonable.

Table 1. Analysis of V, C and O of the products

Sample number	V(wt. %)	C (wt. %)	O (wt. %)
1	93.5	3.5	2.7
2	95.8	2.5	1.2

III. Results and discussion

The appearance of the briquette at various stages in the plasma-arc treatment can be examined in Photo. 1. As shown in this photograph, the briquette sintered for 1 hour at 1000°C, Photo. 1(B), is darker than the green briquette, Photo. 1(A). The top and cross-sectional views of a green briquette treated with the plasma-arc for 30 seconds is shown in Photo. 1(C). The upper section of the sample adjacent to the plasma flame has undergone reduction to a large extent. This portion has a metallic luster and appears as a much lighter phase in the photograph. Small pores are observed near the interface between the light and dark regions and are considered to be due to bubbles of CO gas generated by the reduction reaction. A sample reduced for 6 minutes forms a metallic button as shown in Photo. 1 (D).

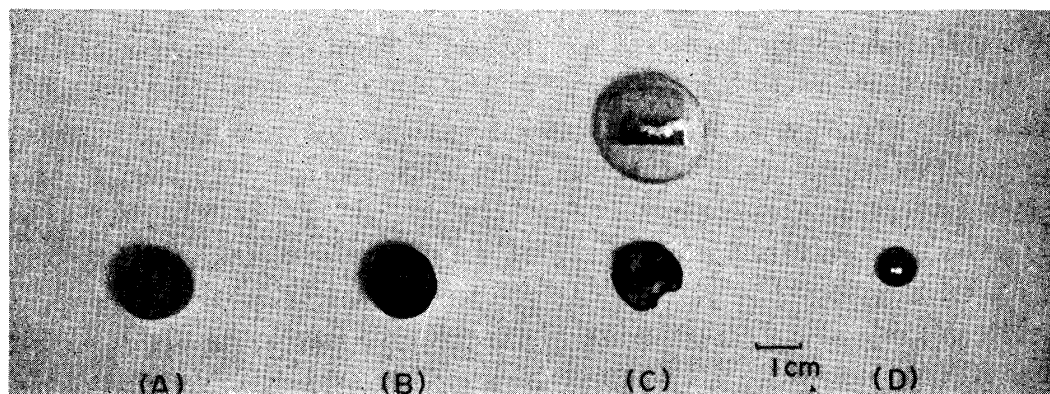


Photo. 1. Photographs of the sample materials before and after the plasma-arc treatment; (A) Not-sintered, (B) Sintered 1 hr at 1000°C, (C) Treated for 30 sec, upper photograph shows the vertical cross section, (D) Sample heated for 6 min after the melting down (that is, reaction time 6 min).

1. The effect of the mixing ratio, C/V_2O_5

Vanadium has various valencies from 2 to 5 and has a strong affinity for carbon and oxygen. To find the most suitable reducing condition, the mixing ratio, C/V_2O_5 , in the briquettes has been varied from 3 to 6. Fig. 4 shows the dependence of vanadium, carbon and oxygen contents of the reduction products on the ratio, C/V_2O_5 , at a reaction temperature of 2100°C. The results for three reaction times, 0, 6 and 20 minutes, are shown in this figure. The curves indicating the

residual carbon and oxygen correspond to a reaction time of 20 minutes. As shown in this Fig. 4, the optimum mixing ratio is approximately 4.5 which is somewhat less than the stoichiometric ratio of 5. Additionally, the highest vanadium content of the product has reached 95.9% after 20 minutes of reaction. The contents of the residual carbon and oxygen in this product are 2.3% and 1.8% respectively. When the mixing ratio is less than 4, the residual oxygen in the

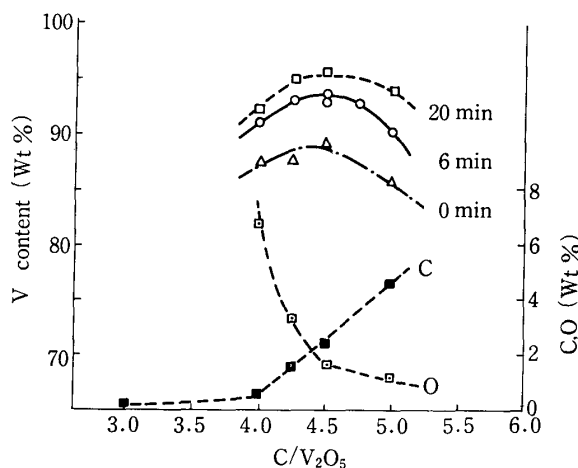


Fig. 4. Dependence of V, C and O contents of the products on C/V_2O_5 at 2100°C (not-sintered).

product increases because of the shortage of carbon for reduction. Conversely, when the mixing ratio exceeds 5, the presence of excess carbon leads to the formation of vanadium carbide in the reaction product. When the mixing ratio is 6, the peak for the carbide, V_8C_7 , is observed in the X-ray diffraction pattern of the product and the postulation of carbide formation by the excess carbon is confirmed. From the above-mentioned discussions, the optimum mixing ratio is considered to be approximately 4.5.

Further, as shown in Fig. 4, the vanadium content of the product approaches 90% at the reaction time of zero. As the initial content of vanadium in the briquette is about 43%, the reduction of the briquette proceeds rapidly before the sample is completely molten. During this period, the reduction reaction of liquid vanadium oxide with solid carbon is considered to proceed rapidly.

2. The effect of preliminary sintering

Preliminary sintering of the briquette prevents the sample material from scattering during plasma-arc heating. Moreover, the electrical conductivity of the briquette increases which helps to stabilize the plasma flame. While the recovery of vanadium from the green briquette is 86~88%, the briquette sintered for 1 hour at 1000°C in an argon atmosphere shows an increase in its recovery to 94~95% for a mixing ratio between 4 and 5. However, when the mixing ratio is less than 4 or greater than 5.5, both kinds of briquettes show a decrease in vanadium recovery due to the increased loss of the sample. In both these cases, the shape

of the liquid sample is not spherical and a disc-shaped product is formed possessing a rough surface.

Peaks of V_2O_4 and C and peaks of V_2O_3 and C are observed in the X-ray diffraction patterns of briquettes sintered for 1 hour at 700°C and at 1000°C , respectively. Therefore, the reduction is considered to begin during preliminary sintering. Further, the losses in weight during sintering are 10 to 11% at 700°C and 20 to 21% at 1000°C and correspond to the above-mentioned peaks in the X-ray diffraction patterns.

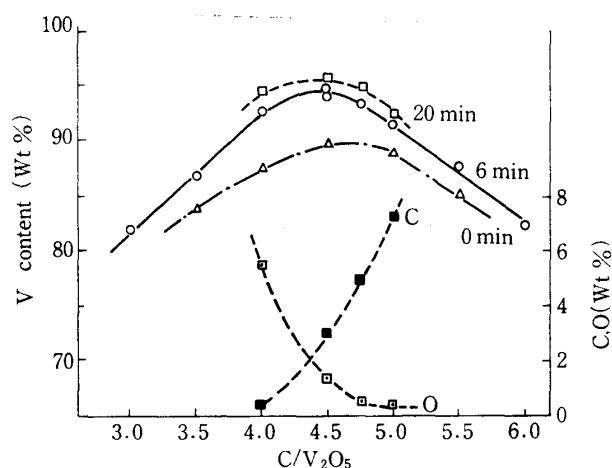


Fig. 5. Dependence of V, C and O contents of the products on C/V_2O_5 at 2100°C (sintered 1 hr at 1000°C).

For the briquette sintered for 1 hour at 1000°C and reduced at 2100°C , Fig. 5 shows the dependence of V, C and O contents of the products on the ratio, C/V_2O_5 , in the same manner as in Fig. 4. In this case, the results are similar to those obtained for green briquettes. The optimum mixing ratio is again approximately 4.5 and the maximum vanadium content attained is 95.3%. However, the residual carbon content in the product increases slightly while the residual oxygen decreases. The reason for this phenomenon is considered to be that the oxygen content diminishes in the sintering steps and correspondingly, some carbide is formed. However, the presence of carbide is not confirmed by the X-ray diffraction analysis of the sintered briquette.

3. The effect of reduction temperature and reaction time

By increasing the power input to the plasma-arc, the reaction temperature is raised from 2100°C to 2800°C and the effect of temperature on improving the content of vanadium in the product is observed. The results are shown in Fig. 6. In this figure, the abscissa and the ordinate indicate the reaction temperature and the vanadium or carbon content respectively. In this study, the samples with a mixing ratio of 4.5 are sintered for 1 hour at 1000°C and are reduced for 10 minutes. When the reaction temperature is raised, the sample in the crucible vibrates violently

and the reduction rate is expected to be enhanced by this agitation. However, as shown in the figure, the enhancement of the reaction by increasing the temperature above 2100°C is not observed in the vanadium content. Also the X-ray diffraction pattern does not change. From these results, it can be stated that the majority of the reduction occurs at 2100°C.

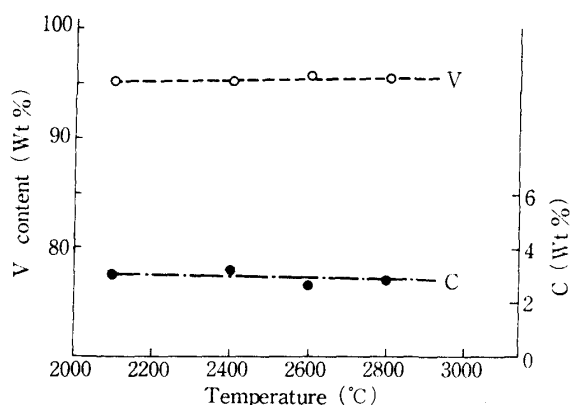


Fig. 6. Reduction temperature dependence of V and C contents of the products (C/V_2O_5 4.5, sintered 1 hr at 1000°C, time 10 min).

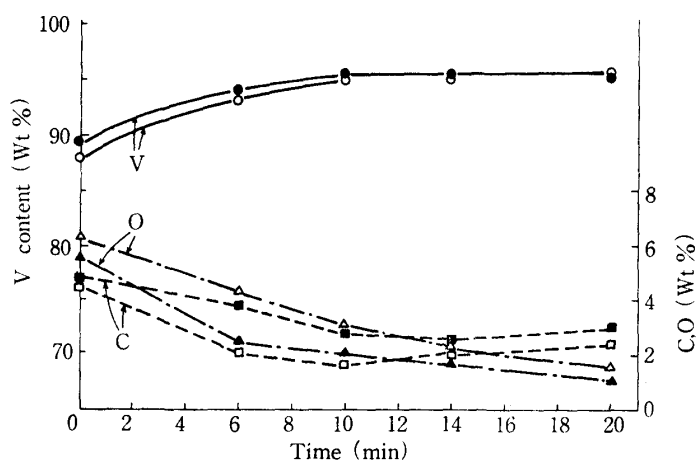


Fig. 7. Dependence of V, C and O contents of the products on the reaction time at 2100°C (C/V_2O_5 4.5, \circ , Δ , \square : not-sintered, \bullet , \blacktriangle , \blacksquare : sintered 1 hr at 1000°C).

The dependence of the vanadium, carbon and oxygen contents of the products on the reaction time is shown in Fig. 7. These results are for briquettes with a mixing ratio of 4.5 reduced at 2100°C. As described earlier, upon application of the plasma-arc, the sample melts and forms a button within 45 seconds. During this period the reduction of vanadium oxide proceeds rapidly and the vanadium content approaches 90%. Subsequently, the reduction proceeds slowly for about 10 minutes and the vanadium content increases to approximately 96%. Correspondingly, the carbon and oxygen contents decrease. When the reaction time exceeds 10 minutes, further reduction of the oxide does not occur. Also, the

remaining carbon and oxygen contents do not decrease below certain limits. The stagnation of the reduction process after the melt down period is considered to be caused by the following effect. When the contents of carbon and oxygen dissolved in molten iron are small and the pressure of carbon monoxide is kept constant, Hamilton's equation holds between the carbon and oxygen contents as follows⁽¹⁴⁾:

$$[C][O] = K.$$

For the melts studied in this work, the above equation is confirmed to be valid, as shown in Fig. 8. Namely, the curve indicating the relationship between the carbon and oxygen contents of the products which have a mixing ratio of 4 to 5 and a reduction time of 20 minutes at 2100°C is almost hyperbolic. Using these values of carbon and oxygen contents in weight percent, the calculations of the constant, K, by the least squares method gives the following relationship:

$$[O] = 3.82 [C]^{-1.09}.$$

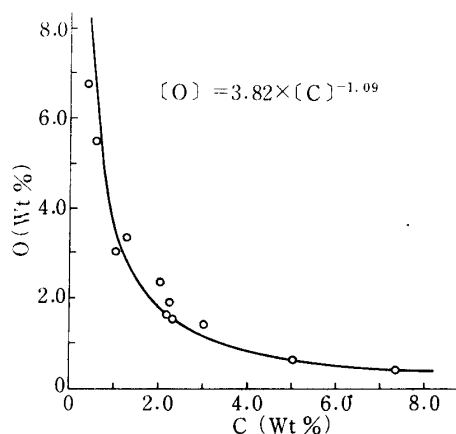


Fig. 8. Relation between C and O contents of the products at 2100°C (reaction time 20 min).

In this case, the correlation coefficient is calculated to be 0.98. In this experiment, the pressure of CO around the sample is considered to be small because argon gas is injected into the furnace and flows at a high flow rate. Nevertheless, the pressure of CO is estimated to be sufficient to disturb the advance of the reduction to some extent.

The values of the carbon and oxygen contents in Fig. 8 are large compared with the case of molten iron. One reason for this is considered to be the strong affinity of vanadium for carbon and oxygen⁽¹⁵⁾. Therefore, some doubt still remains as to the validity of using Hamilton's equation in this case.

(14) T. Araki et al, *Tekkō-Seiren no Kiso (The Fundamentals for the Smelting of Iron and Steel)*, Asakura Shoten, (1971), 90.

(15) W.L. Worrell and J. Chipman, *Trans. AIME.*, **230** (1964), 1682.

4. X-ray diffraction analysis of the reduction product

The reduction product is ground into powder and X-ray diffraction patterns are obtained. The patterns for green briquettes reduced for 20 minutes at 2100°C are presented in Fig. 9. As shown in this figure, the strongest vanadium peaks and the weakest carbide, V_2C , peaks are obtained when the mixing ratio is 4.5. When the mixing ratio increases to almost 5.5, the peaks of V_2C are intensified substantially. Further, when the ratio exceeds 6, the peaks of the carbide, V_8C_7 , which contains more carbon than V_2C are observed. When the mixing ratio decreases and approaches 4, the locations of the peaks are shifted slightly from those of vanadium. This shift is attributed to the strains produced in the lattice by the presence of relatively large quantities of carbon and oxygen.

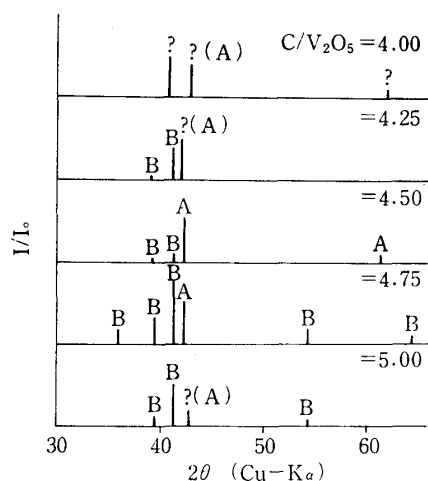


Fig. 9.

Fig. 9. Dependence of the X-ray diffraction pattern on C/V_2O_5 (not-sintered, temperature 2100°C, time 20 min) (A:V, B: V_2C).

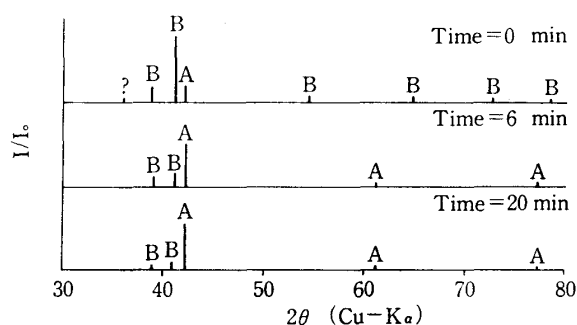


Fig. 10.

Fig. 10. Dependence of the X-ray diffraction pattern on the reaction time (C/V_2O_5 4.5, not-sintered, temperature 2100°C) (A:V, B: V_2C).

When sintered briquettes are reduced, the X-ray diffraction patterns show similar tendencies to those observed for green briquette reductions. However, the former case results in a relative increase in intensity of the peaks of V_2C .

Fig. 10 shows the relationship of the X-ray diffraction pattern and the reaction time. Green briquettes with a mixing ratio of 4.5 have been reduced at 2100°C for 0, 6 and 20 minutes. Increasing the reaction time results in stronger vanadium peaks and a gradual decrease in the peaks of V_2C . These results trace the advancement of the reduction with reaction time. However, it is difficult to clearly define the difference between the patterns for the reaction times of 20 minutes and 6 minutes. Thus, an increase in the reaction time does not result in substantial improvements in the product vanadium content. These findings coincide with the chemical analyses results described above. A similar tendency is observed for sintered briquettes.

5. Reduction product hardness measurements

The hardness of metals such as V, Nb and Ta increases rapidly when small quantities of carbon or oxygen are present.

The Vickers hardness of the products reduced at 2100°C has been measured. Fig. 11 shows the dependence of the hardness of the products on the mixing ratio. The minimum hardness number of the product occurs at a mixing ratio of

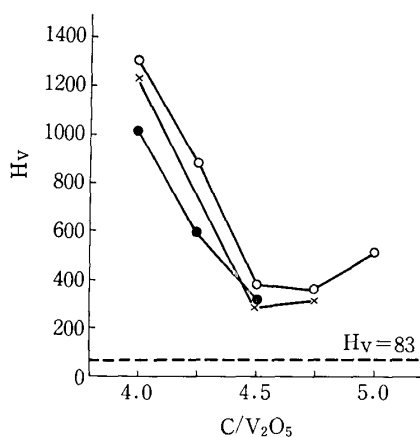


Fig. 11.

Fig. 11. Dependence of Vickers hardness of the products on C/V_2O_5 (temperature 2100°C, —○—: not-sintered, —×—: sintered 1 hr at 700°C, —●—: sintered 1 hr at 1000°C)

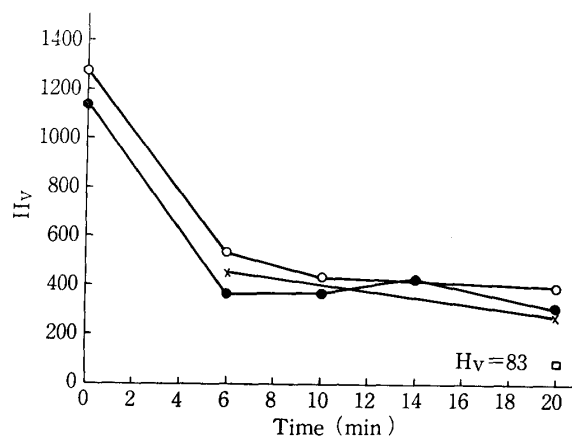


Fig. 12.

Fig. 12. Dependence of Vickers hardness of the products on the reaction time at 2100°C. (—○—: not-sintered, —×—: sintered 1 hr at 700°C, —●—: sintered 1 hr at 1000°C)

approximately 4.5 and coincides with a maximum content of vanadium. The same result is observed when sintered briquettes are reduced. Following a fusion treatment in the plasma-arc furnace, commercially available, electrolytic, vanadium metal of 99.8% purity gives a Vickers hardness of 83*. This value is indicated with a dotted line in Fig. 11. However, in this study, the minimum hardness value is 286 and this larger value, relative to pure vanadium, is attributed to the small quantities of carbon and oxygen in the product. When the mixing ratio is greater or less than 4.5, the hardness of the product increases. Although the vanadium content is similar, when the mixing ratio is 4.25 and 4.75, the hardness number of the former ratio is much larger. This is due to the fact that oxygen has a far greater effect than carbon on the product hardness⁽¹⁶⁾.

Fig. 12 shows the dependence of the Vickers hardness of the products on the reaction time. The product at zero reaction time is very hard because of the relatively large amounts of remaining oxygen and carbon. As the reduction advances, the hardness of the product decreases. When the reaction time

* H_V value of the vanadium metal of 99.8% purity (Its impurities are as follows: C 0.05%, O 0.08%, N 0.04%, H 0.008%) is reported to be 93. (Nippon Kinzoku Gakkai, *Metals Databook* (1974), 147).

(16) N. Kainuma et al, The Summary of the 1977 Spring Meeting of Nippon Kinzoku Gakkai (1977), 70.

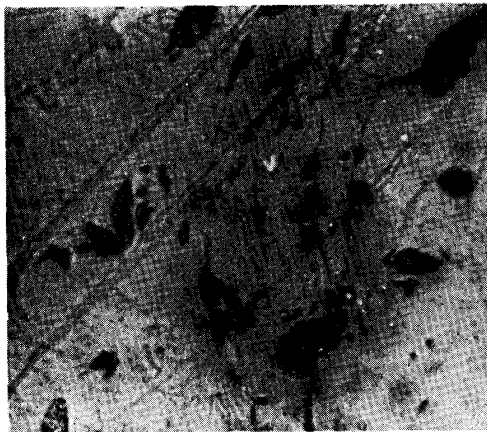
exceeds 6 minutes, the hardness becomes constant and H_V is approximately 300. This result is in agreement with the above-mentioned chemical analysis of the product.

6. Microscopic examination of the structure and a qualitative EPMA analysis

The structure of the reduced briquettes with a mixing ratio of 4.5 is examined microscopically and the vanadium, carbon and oxygen contents are qualitatively determined by means of EPMA. The samples are polished but not etched.

Photo. 2 shows the microstructure of the sample with a reaction time of zero. In this micrograph, many black regions are observed and it is difficult to determine whether these dark zones are newly formed carbide or remaining oxide phases. However, the hardness is greater than that of the surrounding structure. At this stage, the sample is still not uniformly reduced.

Photo. 3 shows the structure of the sample reduced for 20 minutes, containing about 96% vanadium. The dendritic crystals are distributed uniformly over the whole area. At a magnification of $1110\times$, Photo. 4 and Photo. 5 show the microstructures of the products reduced for 6 and 20 minutes respectively. While both



10 μ m

Photo 2. Microstructure of the product (C/
 V_2O_5 4.5, not-sintered, time 0 that is just
after the melting down)
Contents analysed: V 86.1%, C 4.8%,
O 7.1%.



10 μ m

Photo. 3. Microstructure of the product
(C/ V_2O_5 4.5, not-sintered, time 20 min)
Contents analysed: V 95.9%, C 2.3%,
O 1.8%.

show similar dendritic structures, the crystals of the latter are larger than the former. Therefore, a greater degree of reduction leads to the growth of larger dendrites.

To determine the distribution of vanadium, carbon and oxygen between the dendritic phase and the matrix, a qualitative analysis has been performed by means of EPMA. The electron beam is scanned across the sample as indicated by the white, center line in each photograph at a velocity of $5 \mu\text{m}/\text{min}$. As shown by the analysis in Photo. 4, the carbon content decreases in the dendritic phase while the vanadium content increases. Conversely, the carbon content in the surrounding phase is relatively large. Similar behaviour is observed in the analysis of a

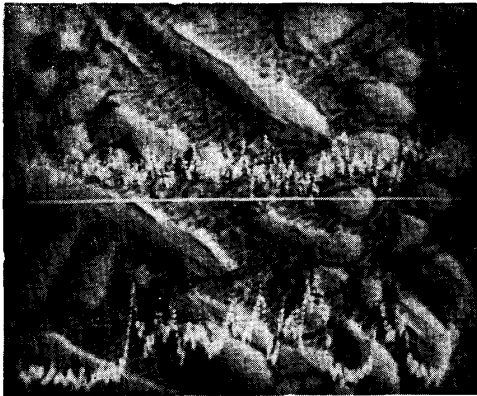


Photo. 4. Line scanning profiles by EPMA for V and C
($\text{C}/\text{V}_2\text{O}_5$ 4.5, not-sintered, time 6 min)
Contents analysed: V 93.3%, C 2.2%, O 4.5%.

V- $\text{K}\alpha$ (2 Kcps)

C- $\text{K}\alpha$ (500 cps)

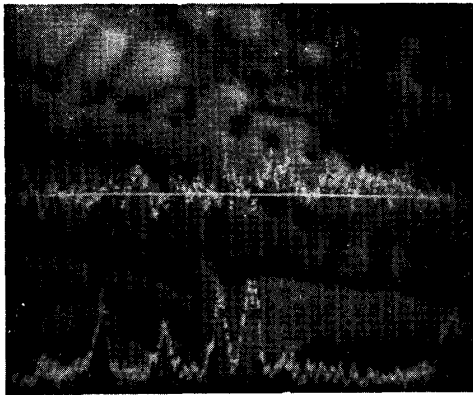


Photo. 5. Line scanning profiles by EPMA for V and C of the sample shown on Photo. 3.

V- $\text{K}\alpha$ (2 Kcps)

C- $\text{K}\alpha$ (200 cps)

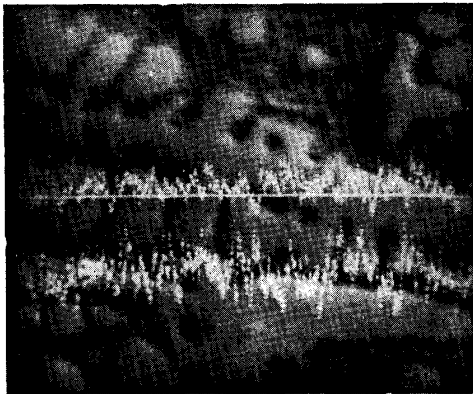


Photo. 6. Line scanning profiles by EPMA for V and O of the sample shown on Photo. 5.

V- $\text{K}\alpha$ (2 Kcps)

O- $\text{K}\alpha$ (200 cps)

5 μm

second sample, as shown in Photo. 5. This latter sample is also analysed for oxygen and the results are presented in Photo. 6. The oxygen is distributed almost uniformly between the two phases.

An explanation of the observed differences in the distribution of vanadium, carbon and oxygen between the two phases is presented with the aid of the vanadium — carbon phase diagram by Storms et al.⁽¹⁷⁾, Fig. 13, and the vanadium — oxygen diagram by Alexander et al.⁽¹⁸⁾, Fig. 14.

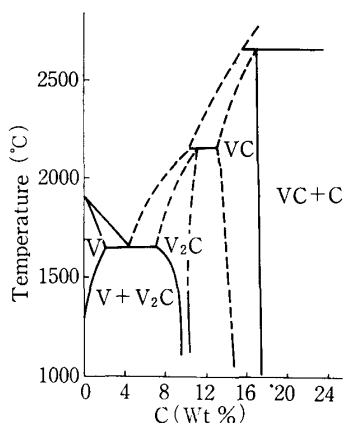


Fig. 13.

Fig. 13. Phase diagram of the V-C binary system (Storms et al.).

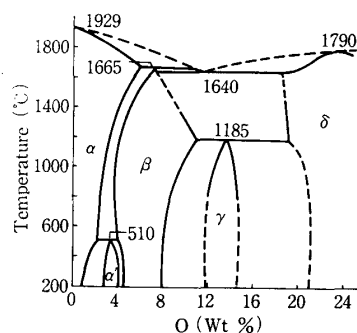


Fig. 14.

Fig. 14. Phase diagram of the V-O binary system (Alexander and Carlson).

The reduction products containing less than a few percent of residual carbon lie on the vanadium-rich side of the V-V₂C eutectic. Therefore, during solidification, the sample will form a primary, dendritic phase of vanadium containing a small amount of carbon. The remaining liquid solidifies at the V-V₂C eutectic.

The oxygen solubility in the vanadium metal is 1.03% at room temperature, 2.14% at 510°C and approximately 6% at the peritectic reaction temperature of 1665°C, according to Fig. 14. Therefore, it is assumed that almost all the residual oxygen in the reduction product remains in solid solution, either in the primary dendritic or the eutectic phase.

IV. Conclusions

The carbon reduction of vanadium pentoxide has been investigated in a plasma-arc furnace. The sample is a mixture of vanadium pentoxide and graphite, vacuum pressed under a pressure of 6 ton/cm² into a briquette. Argon has been used as the arc gas.

The results are as follows:

- 1) The optimum mixing ratio of carbon and vanadium pentoxide, C/V₂O₅, is

(17) E.K. Storms and R.J. McNeal, *J. Phys. Chem.*, **66** (1962), 1401.

(18) D.G. Alexander and O.N. Carlson, *Met. Trans.*, **2** (1971), 2805.

about 4.5 and is smaller than the stoichiometric ratio of 5. When the mixing ratio is less than 4.5, the oxygen remaining in the product increases, while the vanadium carbide increases when the ratio is greater than 5.

2) The sample, weighing 3.5 g is fused within 45 seconds by plasma-arc heating and the reduction of vanadium pentoxide proceeds rapidly to approximately 90% V during this period. The reduction that follows in the molten state is slow. Within 10 minutes, the maximum vanadium content reaches 96%. Longer times of plasma-arc heating are almost useless for the reduction.

3) Preliminary sintering of the briquette results in good recovery of vanadium due to the diminished loss of the sample under the plasma flame.

4) An increase in the vanadium content is not observed as the temperature is increased from 2100 to 2800°C.

5) The hardness of the product with a maximum vanadium content is about H_V 290 and is much larger than that of vanadium metal due to the remaining oxygen in particular.

6) The presence of the well developed, dendritic, primary crystals is observed in the reduction product high in vanadium content.

In this study, pure vanadium metal is not obtained because of the strong affinity of vanadium for carbon or oxygen. However, vanadium of 96% purity is produced within a short time.

In combination with a suitable refining process, plasma-arc reduction is considered to be an useful process for the production of vanadium metal.

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