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CARBOTHERMIC REDUCTION AND ELECTRON BEAM MELTING OF VANADIUM

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Summary

Carbothermic reduction of V_2O_5 in vacuum at temperatures higher than 1400 °C results in much loss of metal owing to the relatively high vapour pressures of vanadium and its oxides. The reduction at the lower temperatures is not powerful enough to decompose residual subcarbide and suboxide to the metal phase. The subsequent electron beam melting of the reduction products was found to be effective for preparing vanadium with low carbon and oxygen contents, although the working conditions must be strictly controlled. In this operation the oxygen may be easily eliminated as VO and CO and the carbon may be removed as CO. For an adequate elimination of the carbon, an excess of oxygen to carbon of about tenfold should be present in the reduction products to be melted.

1. Introduction

The preparation of high melting point metals by a combination of carbothermic reduction of oxide in vacuum and electron beam melting is becoming possible. The most significant part of this process from a metallurgical standpoint is the purification of metals by vacuum degassing at high temperatures near the melting points. The decarburization via CO and the deoxidation by volatilization of base metal oxides makes it possible to reduce the carbon and oxygen contents to a sufficient degree.

A carbothermic reduction–electron-beam-melting combination process without volatilization of the metals to be reduced was successful for the super refractory metals and alloys such as niobium [1], molybdenum [2] and Nb–Mo alloys [3]. Many examples of the carbothermic reduction of vanadium in vacuum have so far been reported [4 - 6]. However, the results obtained in these investigations show a limited possibility for purifying vanadium because of relatively high vapour pressures of vanadium and the suboxide VO; the reduction products always contained precipitates of the subcarbide and suboxide.

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In the present work, electron beam melting was combined with the reduction process with the aim of lowering effectively the residual carbon and oxygen contents, and the possibilities and conditions for acquisition of metal vanadium by this combination process were examined.

2. Thermodynamic conditions

The conditions for a reduction may be expected on the basis of the equilibrium thermodynamic data on the V–C–O system. Although such thermodynamic data are incomplete for a complex practical process, much may be gained towards an understanding of the problem from the proper organization of the available data.

The V–C–O solid solution can equilibrate with the suboxide V_4O and subcarbide V_2C phases at temperatures higher than 1200 ℃ according to the following monovariant reaction:

$$V_4O(s) + V_2C(s) = 6V(s) + CO(g) \tag{1}$$

Reaction (1) is of particular importance because it concerns the ultimate CO pressure p_{CO} to obtain metal.

By using the standard free energy change of reaction (1) [7, 8] and by neglecting the solid solubilities between the phases, p_{CO} was calculated as 0.70 Torr at 1400 ℃. This may be a technologically feasible reduction condition.

In the course of reduction of V_2O_5 the volatile suboxide VO is formed as most of the refractory metals tend to form high volatile oxides which in most cases have higher vapour pressures than their metals do. Brewer and Rosenblatt [9] discussed the possibility of purifying metals contaminated with oxide by vacuum melting or by distillation.

The possible degree of purification is expressed by an evaporation ratio R, defined as the ratio of molar concentrations of oxygen to metal in the gas phase and in the condensed phase if kinetic considerations which affect the rates are neglected:

$$R = \frac{(\mathrm{O{:}M})_{\mathrm{gas}}}{(\mathrm{O{:}M})_{\mathrm{metal}}} \tag{2}$$

A favourable purification effect can be expected if R is at least 10 or even greater. Equation (2) can be rewritten in terms of vapour pressures and mole fractions as

$$R = \left(\frac{\Sigma y p_{M_xO_y}}{\Sigma x p_{M_xO_y}}\right)_{\mathrm{gas}} \Bigg/ \left(\frac{N_O}{N_M}\right)_{\mathrm{metal}} \tag{3}$$

where $p_{M_xO_y}$ is the equilibrium partial pressure of the gaseous oxide M_xO_y being considered and N_O and N_M are the mole fractions of oxygen and metal in the condensed phase. As a limiting case, calculations of the ratio R were carried out for the oxygen concentration at which the vanadium metal is saturated with oxygen. The vapour pressure of the monoxide VO over the V–O solid solution was measured by Hörz [10] and gives 1.05×10^{-8} atm at 1400 °C for the solubility limit of oxygen (11.8 at.% [8]). The vapour pressure of vanadium over the oxygen-saturated vanadium was estimated to be 6.0×10^{-9} atm at 1400 °C using the pressure value for pure vanadium [7] and taking 0.88 for the activity of vanadium in the oxygen-saturated vanadium. The magnitude of R calculated in this manner is 4.8; this low R value indicates a limited possibility for purifying vanadium at high temperatures and in vacuum. However, deoxidation of vanadium will be achieved to a higher degree by the use of carbon because carbon, particularly under reduced pressures, has a very high affinity for oxygen.

3. Carbothermic reduction of V_2O_5 in vacuum

Powdered V_2O_5 of 99.9% purity was mixed with the graphite powder of 99.6% purity in a V_2O_5:C mole ratio of 1:5, according to the stoichiometric reaction

$$V_2O_5 + 5C = 2V + 5CO \tag{4}$$

and this mixture was cold pressed in the form of a square bar of dimensions 10 mm × 10 mm × 50 mm under a pressure of 500 kgf cm^{-2}.

A vacuum furnace with a graphite heating element was employed for the reduction. The temperature was controlled by means of an SCR gate-controlling system using the electromotive force of a W–WRe_{26} thermocouple.

The reduction was carried out in a graphite crucible under continuous evacuation. The reduction of oxide proceeds with gas evolution with rising temperature; it began noticeably at about 650 °C. Because the melting point of V_2O_5 is very low (650 °C) the temperature of the sample was kept constant at 650 °C until the degassing had almost ceased, *i.e.* until the V_2O_5 had decomposed to V_2O_3 of high melting point (2073 °C). When the temperature had reached 1400 °C, the sample was maintained at this temperature and a pressure of 1×10^{-4} Torr for 2 h. The sample was then quenched by transfer into the cold zone of the furnace. The final products did not adhere to the graphite crucible and exhibited a porous and sponge-like state.

The results of carbothermic reduction of V_2O_5 for various V_2O_5:C ratios, the X-ray analyses and determinations of carbon and oxygen are summarized in Table 1. Figure 1 shows the relationship between the carbon and oxygen contents of the samples after the reduction and it can be seen that the contents are inversely proportional to each other.

The compositions of the reduction products were also plotted in the tentative V–C–O phase diagram represented in Fig. 2 which was constructed according to various investigations [11 - 14]. The residual C:O ratios in the reduction product greatly depend on the C:O mole ratios in the starting materials. Figure 3 shows the relationship between the C:O mole ratio in the starting

TABLE 1

Carbothermic reduction of V_2O_5 in vacuum

Sample	*C:O mole ratio*	*Temperature* (°C)	*Ultimate pressure* (Torr)	*Refining time* (h)	*Analysis*		
					C (wt.%)	*O* (wt.%)	*X-ray (phases)*
1	1.00	1400	1×10^{-4}	2	10.3	0.4	V_2C, V_4O, VO
2	0.65	1400	1×10^{-4}	2	1.1	9.8	V_4O, VO
3	0.70	1400	1×10^{-4}	2	2.3	9.5	V_2C, VO, V_4O
4	0.75	1400	1×10^{-4}	2	2.9	5.9	V_2C, V_4O
5	0.80	1400	1×10^{-4}	2	6.2	4.0	V_2C, V_4O, VO
6	0.90	1400	1×10^{-4}	2	6.7	2.2	V_2C, V_4O
7	0.85	1400	1×10^{-4}	2	5.7	4.7	V_2C, V_4O
8	0.95	1400	1×10^{-4}	2	7.8	1.3	V_2C, V_4O
9	0.60	1400	1×10^{-4}	2	1.6	14.9	VO, V_4O, V_2C
10	0.65	1400	1×10^{-4}	2	2.1	10.6	V_4O, VO, V_2C

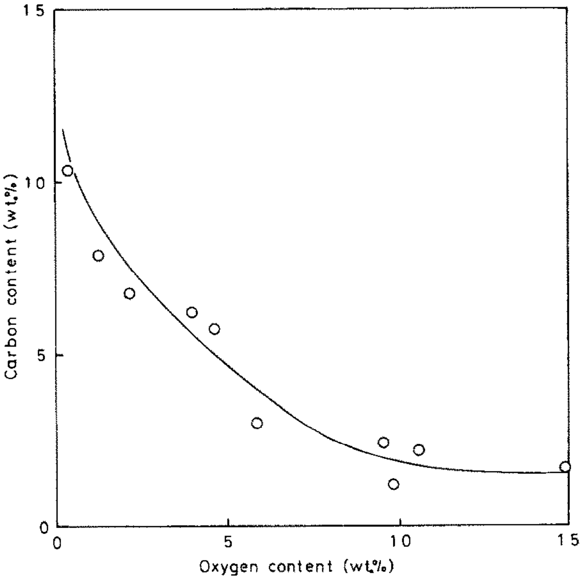

Fig. 1. Carbon and oxygen contents in the reduction products obtained by the carbothermic reduction in vacuum at 1400 °C.

material and the carbon and oxygen contents in the reduction products. From the thermodynamic conditions of the reduction, the degassing of CO is considered to be predominant throughout the reduction. However, as the reduction is (in practice) performed by raising the temperature, the degassing of CO_2 will also take place during the initial reduction stage when the temperature is relatively low. Moreover, the degassing via the volatile oxide VO has to be taken into account particularly during the final reduction period. The dissociation paths for the carbothermic reduction of V_2O_5 are also

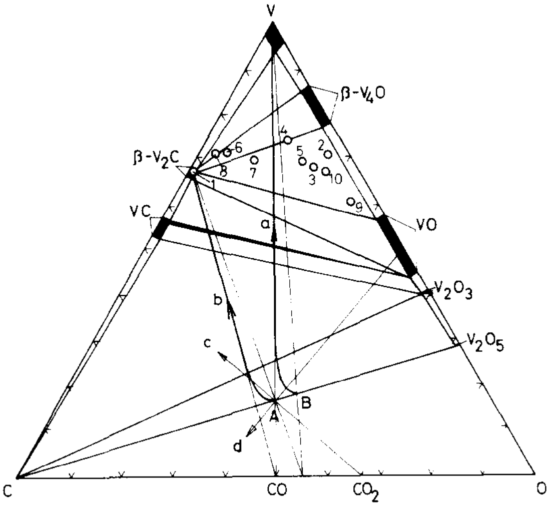

Fig. 2. A tentative V–C–O phase diagram at 1400 °C and the dissociation paths for the carbothermic reduction of V_2O_5.

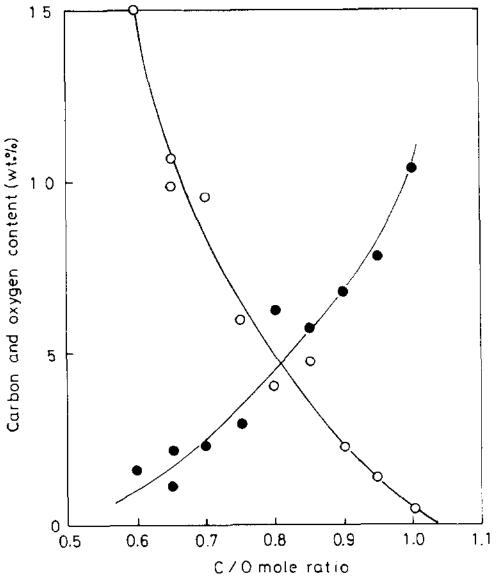

Fig. 3. The relationship between the C:O mole ratio in the starting material and the carbon and oxygen contents in the reduction products: ○, oxygen; ●, carbon.

drawn in Fig. 2. The point A is the mixture of V_2O_5 and carbon in which the C:O mole ratio is unity and the direction *a* is an ideal dissociation path along which carbothermic reduction proceeds according to reaction (4). In reality, since the degassing of CO_2 and VO, the paths of which are in the directions *c* and *d* respectively, occurs in parallel with the degassing of CO, the overall dissociation path would take the direction *b* towards the composition of the reduction product 1. Therefore, if we aim for the vanadium corner, we must take the starting material of the composition B, which has a shortage of carbon.

We could follow the proceedings of the reduction by measuring the change in pressure in the furnace. The reduction of V_2O_5 by carbon in vacuum seems to take place in several stages. Below 750 ℃ V_2O_5 was converted into V_2O_3. At about 1000 ℃ the reduction of the V_2O_3 to VO occurred and at about 1300 ℃ the VO decomposed into the β-V_4O phase. In order to decompose V_4O to the metal phase, temperatures higher than 1400 ℃ were necessary. However, the reduction at higher temperatures than 1400 ℃ resulted in significant losses of metal because of the relatively high vapour pressures of vanadium and VO and because the sponge-like materials have large surface-area-to-mass ratios.

4. Vacuum degassing in the solid state

The mechanism of refining of vanadium containing carbon and oxygen with the present method can be characterized by the next steps, *i.e.* carbon is removed by degassing as CO and the elimination of oxygen takes place as CO as well as volatile suboxide such as VO. With respect to these purification reactions the following equations should be assumed:

$$V_2C(s) + V_4O(s) = 6V(s) + CO(g) \tag{5}$$

$$V_2C(s) + [O]_V = 2V(s) + CO(g) \tag{6}$$

$$[C]_V + [O]_V = CO(g) \tag{7}$$

$$[C]_V + V_4O(s) = 4V(s) + CO(g) \tag{8}$$

$$V_4O(s) = 3V(s) + VO(g) \tag{9}$$

$$V(s) + [O]_V = VO(g) \tag{10}$$

where $[C]_V$ and $[O]_V$ represent respectively the amount of carbon and the amount of oxygen dissolved in the metal.

Deoxidation via suboxide, corresponding to reaction (10), has been studied in detail by Hörz [10] from a kinetic point of view, using V–O binary alloys. In this case, the rate of oxygen liberation from solid vanadium was determined by the recombination of oxygen with metal atoms at the surface and the subsequent transfer of the molecules formed into a gaseous space. This rate-limiting step has also been confirmed by other experiments performed on the Nb–O and Ta–O systems using thin wires. In the present investigation we studied the oxide–carbide reaction such as reaction (5).

The degassing experiments were carried out at high pumping rate by using a high temperature vacuum furnace with a tantalum heating element. The temperature of the sample was measured by means of a W–WRe_{26} thermocouple. The temperature was stabilized to ±5 ℃ at 1600 ℃. For the degassing experiments we used the reduction products which contained an excess of carbon with respect to oxygen and the phases present in these samples were V_2C and V_4O. All the samples were crushed to an average grain size of 1 mm.

The courses of the degassing process are shown in Figs. 4 and 5. We noted that the weight of the sample continues to decrease even after carbon and oxygen elimination had almost ceased. This is probably due to the vaporization of the metal. After a short degassing time the oxygen and carbon were removed rapidly, but afterwards the outgassing rate became very slow and further purification could not be expected. The excess of carbon with respect to oxygen in the initial materials was condensed in the metal in the form of subcarbide and carbon dissolved in the metal. In contrast, it may be predicted that, if oxygen is present in excess with respect to carbon in the initial materials, the oxygen can be removed by evaporation of VO even after the carbon is almost eliminated.

5. Electron beam melting

With respect to removal of carbon and oxygen from melts, the rates of purification do not correlate with the data obtained in solid state degassing

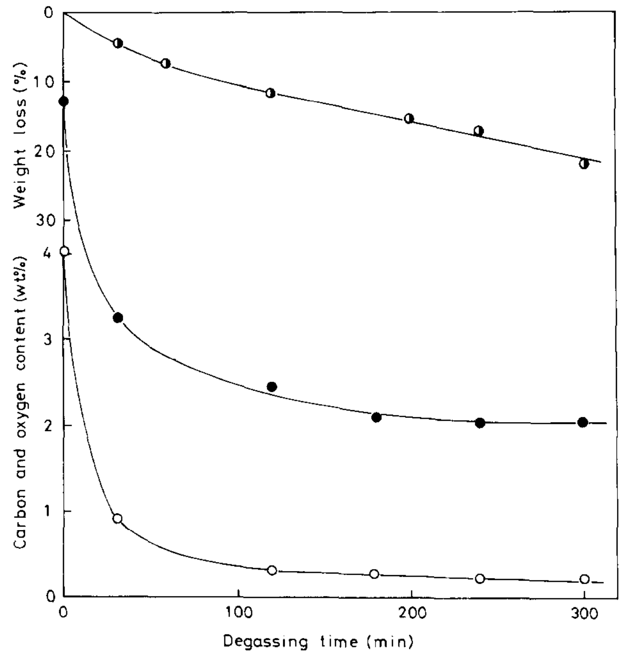

Fig. 4. The lowering of the carbon and oxygen contents and the change in weight of the sample during the isothermal degassing of vanadium in vacuum at 1600 °C: ○, oxygen; ●, carbon; ◑, weight loss.

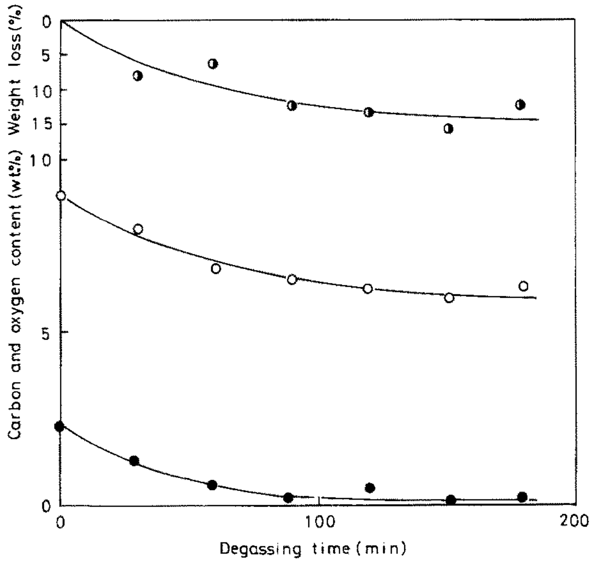

Fig. 5. The lowering of the carbon and oxygen contents and the change in weight of the sample during the isothermal degassing of vanadium at 1600 °C; ○, oxygen; ●, carbon; ◑, weight loss.

in high vacuum. A combination of low pressure, a temperature above the melting point and a lack of contaminating materials in contact with the molten materials provides the necessary conditions for rapid purification reactions.

The products of the carbothermic reduction of V_2O_5 were melted in the form of a button of mass 5 g by using a 10 kV A electron beam furnace. The melting time was 4 min under a vacuum of 2×10^{-5} Torr. The carbon and oxygen levels in the vanadium before and after melting are represented in Fig. 6. It is seen from Fig. 6 that the oxygen removal is much easier than the carbon elimination. The carbon elimination is possible only when an

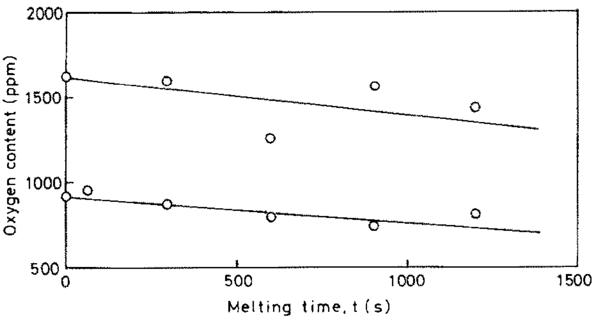

Fig. 6. Correlation of the carbon and oxygen levels in vanadium before and after melting in the electron beam furnace for 4 min.

excess of oxygen is present in the sample before melting. These purification tendencies closely resemble those in the vacuum degassing of the V–C–O system in the solid state. The mechanism of refining in this case is that the carbon is removed only by the degassing of CO and the oxygen can be eliminated by vaporization of both the CO and the VO.

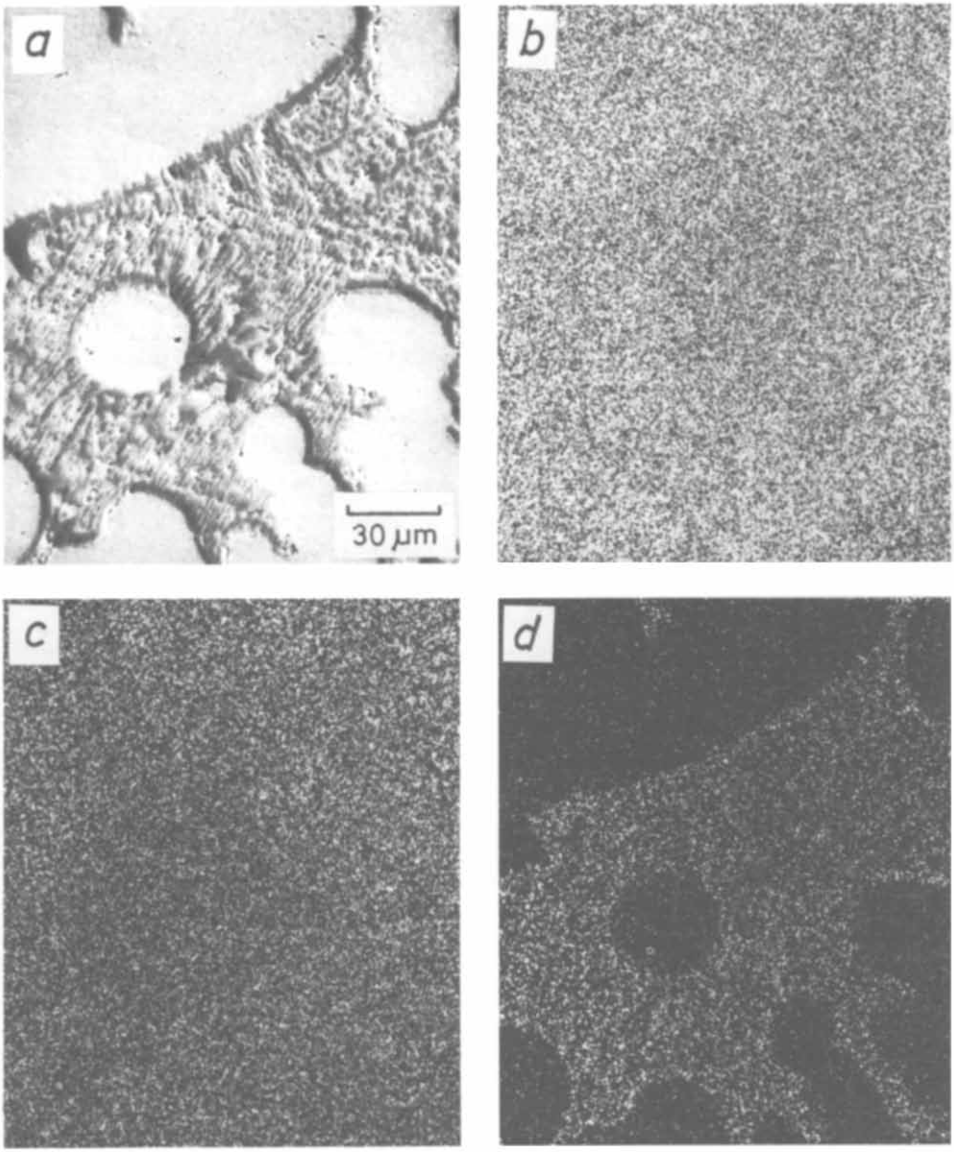

Fig. 7. Electron probe microanalysis of the V–0.6%C–0.5%O alloy melted by electron beam bombardment; (a) backscattered electron image; (b) vanadium map; (c) oxygen map; (d) carbon map.

Electron probe microanalysis was used to provide information concerning the distribution of carbon and oxygen in vanadium solidified after melting. Because the sample was fused in a water-cooled copper hearth in the electron beam furnace, the cooling rate was very rapid; the sample was cooled from the temperature of the molten state to below red heat in about 10 s. Figure 7 shows the backscattered electron image and X-ray maps of the elements obtained from the electron microprobe. The distribution of vanadium and oxygen was uniform but the carbon was condensed in the precipitate.

The rate of oxygen pick-up from the melt decreased rapidly when the oxygen level was lowered sufficiently. Because in this case the gas is evolved from the liquid surface, diffusion in the liquid phase may constitute the rate-determining step. The results obtained for vanadium with a low oxygen content were plotted in Fig. 8 and we feel that these levels of oxygen would be limits for its removal in electron beam refining of vanadium.

6. Conclusions

In this work the possibilities and conditions for producing the metal vanadium by the carbothermic reduction–electron-beam-melting combination method have been investigated. The reduction of V_2O_5 at temperatures higher than 1400 °C is unfavourable because of relatively high vapour pressures of the reduction products vanadium and VO, which cause a large amount of loss of metal. The reductions at 1400 °C resulted in the precipitation of vanadium subcarbide and vanadium suboxide and further decomposition is not expected.

Electron beam melting is effective for purifying crude vanadium if the initial carbon content is strictly limited. It has been shown that the excess carbon contained in the reduction product (compared with oxygen) is

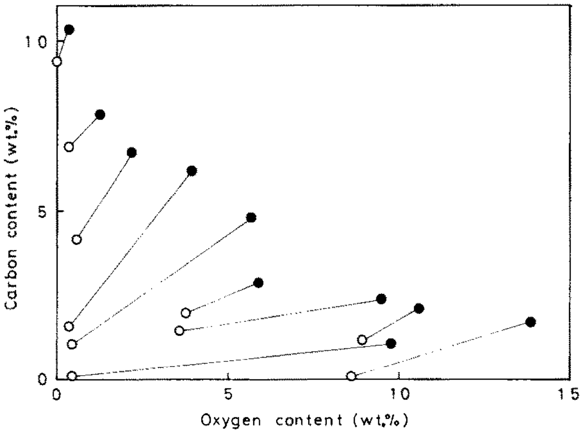

Fig. 8. Electron beam melting of the V–O binary alloys: ●, before melting; ○, after melting.

condensed in the metal after the electron beam melting. Therefore, it is preferable in practice to produce the vanadium containing an excess of oxygen with respect to carbon by carbothermic reduction and subsequently to eliminate the residual oxygen by volatilization of the suboxides in the electron beam furnace. Two unit operations, carbothermic reduction in vacuum and the electron beam melting, are interdependent in producing pure vanadium metal.

References

1 K. Ono, Y. Ueda and J. Moriyama, *Trans. Jpn. Inst. Met., 21* (1980) 321.
2 K. Ono, Y. Ueda and J. Moriyama, *J. Jpn. Inst. Met., 45* (1981) 311.
3 Y. Ueda, K. Ono and J. Moriyama, *J. Jpn. Inst. Met., 43* (1979) 978.
4 M. A. Gurevich and B. F. Ormont, *Zh. Neorg. Khim., 3* (1958) 1237.
5 R. Kieffer, H. Bach and H. Lutz, *Metall. (Berlin), 21* (1967) 19.
6 R. Kieffer, F. Lihl and E. Effenherger, *Z. Metallkd., 60* (1969) 94.
7 O. Kubaschewski and C. B. Alcock, *Metallurgical Thermochemistry*, Pergamon, Oxford, 5th edn., 1979.
8 E. Fromm and E. Gebhardt, *Gases und Kohlenstoff in Metallen*, Springer, Berlin, 1976.
9 L. Brewer and G. M. Rosenblatt, *Trans. AIME, 224* (1962) 1268.
10 G. Hörz, *Z. Metallkd., 60* (1969) 50.
11 W. L. Worrell and J. Chipman, *Trans. AIME, 230* (1964) 1682.
12 D. G. Alexander and O. N. Carlson, *Metall. Trans., 2* (1971) 2805.
13 K. Kohyama and Y. Hashimoto, *Trans. Jpn. Inst. Met., 19* (1978) 291.
14 E. K. Storms, *The Refractory Carbides*, Academic Press, New York, 1967.