# The Study of Synchronous Reduction-carbonization of $V_2O_3$, $Cr_2O_3$ and W-Co Composite Oxides in Fluidization

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**Abstract**

*One append way of liquid state inhibitor was investigated, which putting V, Cr into W-Co composite solutions in the form of ionization. After spray drying and being calcined, W-Co composite oxides could come into being. Then taking fluidization techniques, well-proportioned W-Co composite powder compounded with inhibitor could be produced in the end.*

**Keywords : VC,$Cr_3C_2$, Fluidization, Reduction-carbonization**

## 1. Introduction

At present, WC-Co composite powders with 70nm sub-grain size can be produced by high temperature fluidization technology[1]. However, the grain size of all inhibitors used at home and abroad is more than 1μm and the doped way of inhibitor is wet-ball milling. It is still in question that whether this grain size and doped way of inhibitor can or can not effectively restrain grain growth of cemented carbide during sintering.

In order to solve this problem a new measure has been taken, namely the inhibitor element are doped and well-distributed into W-Co composite solution in the form of ion. After spray drying, the composite oxide powders are carried out synchronous reduction-carbonization by high temperature fluidization technology, enabling the inhibitor to distribute between WC-Co composite powder homogeneously and dispersively. In this paper, two commonest elements V, Cr were chosen to study the synchronous reduction-carbonization problem in the process of fluidization.

## 2. Experimental and Results

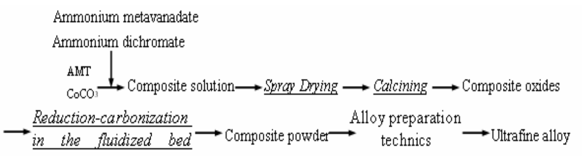



**Fig. 1. Flowchart of tests.**

After dissolving, AMT was transformed into meta-wolframate through ion exchange column. W-Co composite solution was produced by equally pouring $CoCO_3$ into container according to proper proportion. Vanadium element was then inputted into solution in the form of ammonium metavanadate, which is the same as chromium in the form of ammonium dichromate. The next procedures for producing composite oxides were spray drying and calcination. Composite oxides were then deposited in fluidized bed, reduced by $H_2$, and carbonized by methane. Finally, WC-Co composite powder containing inhibitors were obtained with WC grain size about 70 nm by adjusting the dissociative carbon in powder.

**The homogeneously doping of V and Cr**

The first step is that V and Cr should be able to form homogeneous solution with W. For this, ammonium metavanadate and ammonium dichromate were dissolved first in this study. After pouring them into W-Co composite solution, a well-distributed composite solution was obtained with clear and transparent character.

According to the requirement of cemented carbide, the content of VC and $Cr_3C_2$ should be 0.2% and 0.3% in composite powder, respectively. These specifications were also applied in this study. Table 1 shows the composition after doping V and Cr.

**Table 1. Chemical compositions of composite solution**

| Composition | $WO_3$ | Co | V | Cr |
|---|---|---|---|---|
| Content (g/L) | 567.2 | 35.38 | 0.741 | 1.354 |

By converting these dates, the values were 0.177% VC and 0.302% $Cr_3C_2$ in composite powder, respectively.

The chemical compositions of composite oxide after spray drying and calcining of composite solution are shown in Table 2.

**Table 2. Chemical compositions of composite oxide**

| Composition | $WO_3$ | Co | V | Cr |
|---|---|---|---|---|
| Content (%) | 71.36 | 5.85 | 0.10 | 0.22 |

After converting, the contents of VC and $Cr_3C_2$ were 0.150% and 0.309% in composite powder, respectively.

The chemical compositions of composite powder are shown in Table.3 after reduction-carbonization of composite oxide in fluidized bed.

**Table 3. Chemical compositions of composite powder**

| Element | W | Co | V | Cr |
|---|---|---|---|---|
| Content (%) | 85.72 | 7.06 | 0.15 | 0.26 |

After converting, the content of VC and $Cr_3C_2$ were 0.185% and 0.312% in composite powder, respectively.

Comparing the theorical calculation with experiment results of V and Cr contents, the difference between the two was not so big in every procedure. It means V and Cr can be doped into composite powder and well-distributed mixture powder with W-Co can be formed, basically without loss throughout the whole process.

**Full carbonization of V, Cr**

Although the above tests indicate that V and Cr can be well doped into composite powder, and at the same time, the thermodynamics analyses also show that V and Cr can be synchronously carbonized with W in fluidized bed, but whether they can be fully carbonized is still unknown.

After many tests, it has been proved that V and Cr can be fully carbonized by the way of effectively adjusting time, temperature and excessive coefficient.

**Table 4. Chemical analysis results of three test batchs**

| No. | Co | Ct | Cf | O | Cr | V | N | Fe | Cc | Cc' |
|---|---|---|---|---|---|---|---|---|---|---|
| 1# | 6.72 | 5.79 | 0.060 | 0.20 | 0.41 | / | / | 0.28 | 5.730 | 5.727 |
| 2# | 7.90 | 5.84 | 0.110 | 0.20 | 0.33 | 0.32 | 0.15 | 0.01 | 5.730 | 5.686 |
| 3# | 6.49 | 5.77 | 0.035 | 0.16 | 0.37 | / | 0.17 | 0.01 | 5.735 | 5.733 |

Note: Cc--test value of combination carbon,
Cc'--calculated value of combination carbon

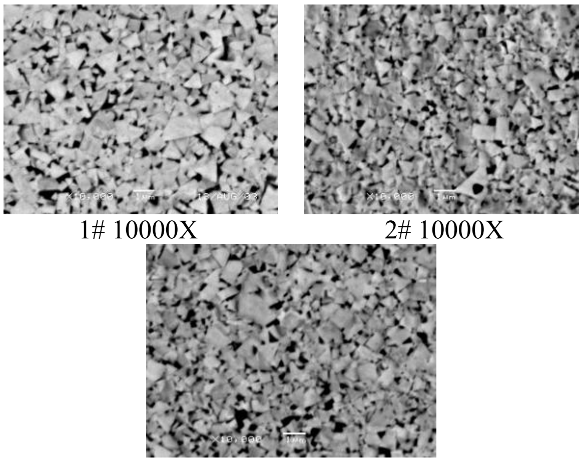
Table 4 clearly shows that factual Cc is much higher than theoretic Cc' (including combination carbon in inhibitors). It means that the carbonizing efficiency of fluidizing reaction is very high, and the inhibitors have been fully carbonized in fluidized bed.

**Effect of VC, $Cr_3C_2$ on cemented carbide**

Due to the fact that doping quantity of V and Cr is very low and it is impossible to exactly determine the phase composition of V and Cr by present instruments, the certification of full carbonization of V, Cr is not very rigorous by above carbonizing efficiency. Therefore, three groups of PS21 sample were compressed and sintered using W-Co composite powder containing inhibitor doped by different way, group No.1 without any inhibitor, No.2 with inhibitor doped during wet ball milling, and No.3 containing inhibitor doped in hydrometallurgy. The aim of these tests is to prove that V and Cr can be fully carbonized during fluidization reaction by properties of cemented carbide. (All samples had not eta-phase and free carbon.)

**Table 5. Comparison results**

| | Coercivity (KA/m) | Hardness (HV30) | Magnetic saturation (%) | Density ($g/cm^3$) | T.R.S (MPa) |
|---|---|---|---|---|---|
| 1# | 23.4 | 1765 | 5.4 | 14.75 | 2183 |
| 2# | 26.2 | 1820 | 5.9 | 14.88 | 3195 |
| 3# | 25.9 | 1810 | 5.9 | 14.79 | 2902 |



1# 10000X 2# 10000X

3# 10000X

**Fig. 2. SEM photos in comparing tests.**

It can be seen from the above results that the inhibitor added in hydrometallurgy affects the restraining grain growth. The properties of cemented carbide made by this way is basically the same as that made by wet ball milling addition. This means that it can be completely realized to synchronous carbonization of $V_2O_3$ and $Cr_2O_3$ with W-Co composite oxide by fluidization technology.

## 4. Summary

In this study, V and Cr could be well mixed with W-Co composite solution in the form of liquor. Furthermore, V and Cr could be synchronously reduced and carbonized with W in fluidized bed.

The inhibitors could be fully carbonized in fluidized bed under the conditions of enough carbonization time and higher potential of carbon. This inhibitor, added in hydrometallurgy, affects the restraining grain growth, but at present it does not show more advantageous properties compared with the effect of solid-solid mixture.

## 5. References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