Carbothermic Reduction of the Waste Chromium Oxide Rods from Thermal Spray Processes

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Abstract. The waste chromium-oxide rods from thermal spray processes contained the valuable components of high chromium. The carbothermic reduction with graphite powders can be used to recover the chromium from the chromium-oxide rod. The waste rods were prepared into small pieces with a half-dimensions of 6.3 mm diameter and 5 mm length, and heated under the reducing atmosphere at 1150 – 1350 °C. Besides, the effect of different types and sizes of reducing agent on the reduction was observed. During the heating and cooling period, argon gas was fed into the atmosphere. Chromium carbide formation was promoted when the temperature and time were increased. Cr-O and Cr-O-Al-Si were observed in the microstructures before and after the reduction. The outermost part of the waste rod can be reduced to chromium because of the interphase zone. Consequently, the carbothermic reduction is one possible recycling method for utilizing ceramic rod wastes from the thermal spray process.

Keywords: Waste chromium oxide rod, Thermal spray, Carbothermic reduction

1. Introduction

Ceramic rod containing high chromium oxide is widely used as a raw material in thermal spray coating techniques \cite{1, 2}. There are some remaining parts from the ceramic rod after the process which cannot be reused. However, the waste rods consist of the valuable metals, for example chromium and aluminum. The recycling method is one possible way to recover chromium from the waste rods. Chromium can be extracted by carbothermic reduction is shown in equation (1).

\[
M_xO_y(s)+yC(s) = xM(s)+yCO(g)
\]  

(1)
The carbothermic reduction of chromium oxide is a combination of the reactions below.

\[ \text{Cr}_2\text{O}_3(s) = 2\text{Cr}(s) + \frac{3}{2}\text{O}_2(g) \]  

(2)

\[ 3\text{C}(s) + \frac{3}{2}\text{O}_2(g) = 3\text{CO}(g) \]  

(3)

Combining Equation (2) and Equation (3):

\[ \text{Cr}_2\text{O}_3(s) + 3\text{C}(s) = 2\text{Cr}(s) + 3\text{CO}(g) \]  

(4)

The high Cr-containing wastes from the metallurgical industries, e.g. the slag in steelmaking processes, had been investigated for recycling by the carbothermic processes at temperatures from 900 °C to 1600 °C [3, 4, 6–10]. The high chromium vanadium-titanium pellets were investigated in the reduction atmosphere at 900 °C for two hours and showed the reduction degree increased with increasing reduction time [3]. Research of ZHANG et al. [8] reported that chromium percentage from the reduction of chromite (FeCr$_2$O$_4$) increased from 68.60 to 80.21 wt.% when raising the reduction temperature from 1350 to 1550 °C. Furthermore, the work of MORI et al. [4] showed the slag component from the steelmaking process could be reduced to chromium by the carbothermic reduction at temperature more than 1350 °C [3]. The work of Takano et al. [5] observed metallic phases of Fe-Cr-C in chromium containing slag when it was exposed in carbon at 1500 °C for 10 minutes. In this work, the reduction of the waste rods from thermal spray processes containing high chromium oxide by carbothermic reduction was investigated.

2. Materials and Methods

The chromium-oxide rod wastes from the thermal spray processes were used in this study, the composition is shown in table 1. The green waste-rod samples with a half-dimension of 6.3 mm diameter and 5 mm length were prepared and placed in alumina crucibles with the reduction agents such as anthracite, graphite, and carbon powders. The reducing agents showed different particle sizes, as reported in table 2. The samples were exposed in a horizontal furnace at different temperatures; 1150, 1250, and 1350 °C respectively for both time durations of 30 and 60 minutes. Argon gas was flown into the furnace during heating and cooling. The experiment was conducted in two parts, firstly, the reduction temperature and time were changed to investigate their relationship with the reduction products. Secondly, the effect of the reducing agents was investigated when they were used for the reduction of the ceramic rod. During the steps of the reduction testing, the weight of the samples was measured by a 5-digit digital analytical balance, and after the reduction test, the waste ceramic rod was analyzed by a scanning electron microscope with an energy dispersive spectrometer (SEM-EDS).

| Cr$_2$O$_3$ | Al$_2$O$_3$ | SiO$_2$ | Fe$_2$O$_3$ | MgO |
|------------|-------------|---------|-------------|-----|
| 90.33      | 3.67        | 5.62    | 0.27        | 0.11 |
Table 2. The average particle size of reducing agent.

| Powder   | Particle size (µm) |
|----------|--------------------|
| Anthracite | 265 ± 90          |
| Carbon    | 40 ± 15            |
| Graphite  | 70 ± 20            |

3. Results and Discussion

The effect of temperature for the reduction process was revealed when comparing the mass change of the chromium waste rods at temperatures between 1150 and 1350 °C in the graphite powder, as illustrated in figure 1. At the lowest temperature of 1150 °C, the mass of the waste rods was not much changed after the reduction. However, the mass change increased around 0.8 mg when temperature was increased to 1250 °C and held for 30 min. The reason may be related to the transformation of chromium oxide into carbides such as $\text{Cr}_2\text{C}_6$, $\text{Cr}_7\text{C}_3$, and $\text{Cr}_3\text{C}_2$, which followed the carbothermic reduction reaction in equation (5) to equation (8). These carbides showed stability of formation with a more negative change in Gibbs free energy ($\Delta G^\circ$) at high temperature (figure 2).

$$\begin{align*}
\text{Cr}_x\text{O}_y(s) + 2yC(s) &= \text{Cr}_x\text{C}_y(s) + yCO(g) \\
23\text{Cr}_2\text{O}_3(s) + 81C(s) &= 2\text{Cr}_2\text{C}_6(s) + 69CO(g) \\
7\text{Cr}_2\text{O}_3(s) + 27C(s) &= 2\text{Cr}_7\text{C}_3(s) + 21CO(g) \\
3\text{Cr}_2\text{O}_3(s) + 13C(s) &= 2\text{Cr}_3\text{C}_2(s) + 9CO(g)
\end{align*}$$

After increasing temperature to 1350 °C, the mass change surprisingly increased by 4.75 times compared to the previous temperature (1250 °C). It should be noted that the carbide formation can be promoted at higher temperatures and the results were in good agreement with the previous work which reported that the carbide $\text{Cr}_2\text{C}_6$ could be appeared in pellets containing chromium oxide after reduction at temperature around 1400 °C for 1800 s [4]. Besides, $\text{Cr}_2\text{O}_3$ still existed because of the high oxide stability ($\Delta G^\circ_{1400 \, ^\circ\text{C}} \sim -45,000$ J mol$^{-1}$ O$_2$) and a short reduction time.
Figure 1. Mass change of ceramic rod after reduction in graphite for 30 minutes.

Figure 2. Ellingham diagram for chromium oxide and chromium carbides was plotted following by thermodynamic data from Kubaschewski et al. [11]
Figure 3 showed the mass change of reduced chromium rods in different three reducing atmospheres, which compared the effect of reducing agents (carbon, graphite, and anthracite powders). The mass change under anthracite powders showed lowest value at every reduction temperature and time. Concerning the mass loss of chromium rods which heated for 30 min in graphite at 1150 °C and in anthracite at 1250 °C for 30 min, it can be concluded that the carburization reaction did not occur and volatile matters in the green chromium rods, such as water, were evaporated following volatilization reaction during heating. Besides, CrO$_2$(OH)$_2$ and CrO$_3$ gases which are a kind of hexavalent chromium vapors were formed by chromium oxide in dry air and wet air respectively at the temperature above 400 °C, [12–14]. These reasons can lead to the mass loss of chromium rods for those conditions. The larger particle of anthracite of around 265 µm may have caused the carbon diffusion in waste rods to be slow in comparison to the other reducing agents. The high value of the mass change was obtained from the reduction in carbon and graphite powders with nearly similar size range. Furthermore, the mass change by carbon powder was small even if temperature changes. However, the mass change by graphite powder at low temperature was lower than that at high temperatures. For this reason, carbon power was more effective for carbothermic reduction over a wide operating temperature range.

![Figure 3](image-url)

**Figure 3.** Mass change of ceramic rod after reduction test with different reduction agents, time durations, and temperatures.
The microstructures of waste chromium oxide rods before and after the reduction test were compared, as shown in figure 4. Before the reduction, microstructure consisted of two phases; white and black. The grain sizes significantly increased after the reduction test. The SEM-EDS analysis showed the oxide rich in Cr and O in the white phase, and Cr, Si, Al, and O in the black phase. The outermost part of chromium oxide rods, which was next to the reducing agent, was thoroughly observed and revealed high Cr percentage as depicted by a plot of EDS line scans, as shown in figure 5. Consequently, the white area which is rich in Cr and O was almost reduced to pure chromium at approximately 86.30 and 83.37 wt.% corresponding to the EDS spectrum 1 and 2, respectively, in figure 6. The results were similar to a research work of MORI et al. [4], which presented the reduction degree of 91% for the carbothermic reduction of Cr$_2$O$_3$ at 1350 °C for 60 minutes. However, they found two compounds i.e. Cr$_7$C$_3$ and Cr$_{23}$C$_6$ following the direct reduction. In addition, the reduction of chromite (FeCr$_2$O$_4$) in the self-reducing agglomerate comprised of petroleum coke, Portland cement and fluxing agents (hydrated lime and silica) [5] showed 58 wt.% Cr at the similar area of this work between the self-reducing agglomerate and solid graphite powder.

Figure 4. Cross section morphology of ceramic rod (a) before reduction, and (b) after reduction in graphite at 1350 °C for 60 minutes.
Figure 5. SEM cross-section morphology with EDS line scans of the waste ceramic rod after reduction in graphite at 1350 °C for 60 minutes.

Figure 6. SEM cross-section morphology and composition in wt.% of the waste ceramic rod after reduction in graphite at 1350 °C for 60 minutes.
4. Conclusions

- The mass change of waste chromium rods increased when increasing temperature from 1150 to 1350 °C and held for 30 min because of the carbide formation.
- The waste rods had the lowest mass change after reducing with anthracite powder as a result of larger particle size and slow carbon diffusion.
- Carbon powder is suitable agent for carbothermic reduction at temperatures higher than 1150 °C.
- \( \text{Cr}_2\text{C}_6, \text{Cr}_7\text{C}_3, \) and \( \text{Cr}_3\text{C}_2 \) presumably formed after carbothermic reduction at 1150 – 1250 °C, and some Cr formed at 1350 °C when heated for 60 min.
- After the reduction at 1350 °C for 60 minutes, the grain size of the Cr-O and Cr-O-Si-Al rich phases increased because of the effect of high temperature.
- The reduction of the waste rods started to reduce at the outermost part due to the interphase between the entire waste rod and the reducing agent.

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