Surfacing With Tungsten-containing Ores

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Abstract. Experimental research has been carried out into AN 26C flux surfacing with flux cored wires made of dust-like carbon and fluorine containing components and tungsten-containing ores. The investigations have revealed the fact that tungsten can be reduced immediately from tungsten-containing oxide materials. The chemical composition of added metal has been determined, as well as slag compositions after surfacing; hardness, wear resistance have been investigated and metallurgical tests have been carried out. Thermodynamic calculations of reactions of WO3, as well as W2C and WC carbides reduction to W by carbon and carbon oxide have been made in standard conditions at temperature T = 1500 – 6000 K. The obtained thermodynamic characteristics of reactions have demonstrated that in the course of WO3 reduction tungsten is most likely to be obtained in terms of thermodynamics, subsequently W2C and WC carbides. After these reactions those of W2C and WC carbides obtaining are thermodynamically possible via reduced tungsten and carbon composition.

Introduction

Efficient use of tungsten is of particular importance due to its high value, shortage and high production cost. Flux cored wires containing tungsten are widely applied for surfacing high wear resistant steels; reduced tungsten is used as a filling material in these wires in the form of ferroalloys, alloys and metal powder of various grades. Moreover, silicides, borides, carbides and other compounds of tungsten are applied to achieve definite service characteristics. W2C and WC are tungsten carbides, which are used in wires of this kind. The technology of flux cored surfacing is relevant for practical application, which presupposes tungsten oxide and carbon-containing reducer as a filler material. Theoretically, tungsten and its carbides are possible to be obtained in direct reduction.

This paper submits thermodynamic calculations and provides consideration of the possibility to reduce tungsten oxides from flux cored wires by a carbon-containing reducer in the course of flux surfacing. Tungsten concentrate of KSH-4 grade according to State Standard 213-83 produced at the open joint stock company “Mining company “AIR” with 54% of WO3 concentration was used in experiments, as well as ores containing 0.372% of WO3 and enriched rejects with 0.07% concentration of WO3. Dust-like carbon and fluorine containing wastes of metallurgical production were used as a carbon-containing reducer; chemical composition in mass concentration (%) is as follows: Al2O3 = 21-43.27; F = 18-27; Na2O = 8-13; K2O = 0.4 – 6%; CaO = 0.7- 2.1; SiO2 = 0.5-2.48; Fe2O3 = 2.1-2.3; Cgen = 12. 5-28.2; MnO = 0.03-0.9; MgO = 0.04-0.9; S = 0.09-0.46; P = 0.1-0.18.

The purpose of research is to determine the potential of tungsten reduction by carbon as the result of which W2C and WC carbides form when surfacing.
Results and discussion

Previously conducted investigations [1-6] have demonstrated that carbon and fluorine containing dust-like wastes of metallurgical production make it possible: 1) to extract hydrogen by fluorine-containing compounds (like Na₃AlF₆, CFₓ (1 ≥ x > 0) etc.), as the result, a gaseous compound HF forms; 2) to deoxidize a weldpool by carbon in form of CO and CO₂, which are generated when carbon fluoride CFₓ (1 ≥ x >0) reacts with dissolved in steel oxygen; 3) to improve the stability of arc combustion by means of potassium and sodium making ionization in arc column easier. Therefore, tungsten reduction can be made by carbon according to the reaction and reacts with tungsten, as the consequence, W₂C and WC carbides are generated.

Table 1 provides compositions of fusion mixtures of flux cored wires under consideration, as well as block coefficients of manufactured wires. The selected correlation is accepted on the ground of stoichiometric calculations provided that complete reduction from tungsten-containing ores both of tungsten, silicon and manganese is possible to be carried out by carbon, which is a part of dust-like metallurgical wastes. The following correlation in the wire is accepted: 111 – according to stoichiometric calculations, 112 – double surplus of carbon, 331 – double shortage of carbon, 441 – triple surplus of carbon, 551, 661 – according to stoichiometric calculations for ore and rejects.

AN 26C flux surfacing was carried out by tractor ASAW 1250. Surfacing conditions are provided in Table 2.

Chemical composition of added metal was determined by roentgen-fluorescent method with spectrometer XRF-1800 and atomic emission method with spectrometer DFS-71. Hardness was measured with ultrasonic hardness testing instrument UZIT - 3.

Chemical composition of added metal and hardness (after surfacing and thermal treatment) are provided in Table 3. As one can see from the aforementioned data of Tables, tungsten has been reduced completely in all samples of wires, except sample 331 (extraction was approximately 96.31%) because of the shortage of a reducer.

Metallographic investigations into micro-sections were carried out with optical microscope OLYMPUS GX-51 in a bright field at various zooming in alcoholic solution of nitric acid, and in solution of hydrofluoric acid.

Metallographic analysis of added layers has revealed the following facts: sample 111 (Figure 1) has a definitely pronounced Widmanstatten pattern with thin needles deviating from ferritic net, which is located on the edges of initial austenite grains. The dimensions of grains correspond to 3 - 4 points.

Table 1. Component composition and block coefficient of manufactured wires

| Wire | Component, mass fraction, % | Block coefficient of a wire, % |
|------|-----------------------------|--------------------------------|
| 111  | 48.54 51.46 - - | 12.37 |
| 112  | 31.85 68.15 - - | 9.36 |
| 331  | 66.67 33.33 - - | 12.86 |
| 441  | 25 75 - - | 10.76 |
| 551  | - 50 50 - | 8.72 |
| 661  | - 50 - 50 | 10.95 |

1 - WO₃ concentrate, 2 – carbon and fluorine containing dust-like wastes of metallurgical production, 3 – tungsten ore, 4 – rejects after reduction of tungsten ores.

Table 2. Surfacing conditions

| Stamp | Iₜ(A) | Uₜ(W) | Vₜ(m/h) | The number of added layers |
|-------|-------|-------|---------|---------------------------|
| 111   | 490   | 30    | 28      | 5                         |
| 112   | 490   | 32    | 27      | 5                         |
| 331   | 410   | 27    | 24      | 5                         |
| Stamp | $I_a$ (A) | $U_a$ (W) | $V_a$ (m/h) | The number of added layers |
|-------|-----------|-----------|------------|---------------------------|
| 441   | 430       | 28        | 24         | 5                         |
| 551   | 420       | 28        | 24         | 5                         |
| 661   | 420       | 28        | 25         | 5                         |

*Table 3. Chemical composition and hardness of added metal*

| Sample | Mass fraction of elements, % | Hardness HRC* |
|--------|-------------------------------|---------------|
|        | C    | Si   | Mn   | Cr   | Ni   | Cu   | Ti   | W   | V   | Mo  | Co  |       |
| 111    | 0.35 | 0.31 | 0.49 | 0.07 | 0.12 | 0.13 | 0.001| 0.67| 0.008| 0.005| 0.007| 27.2  |
| 112    | 0.29 | 0.25 | 0.50 | 0.07 | 0.12 | 0.12 | 0.001| 1.29| 0    | 0.002| 0.006| 19.2  |
| 331    | 0.13 | 0.15 | 0.43 | 0.06 | 0.12 | 0.11 | 0.001| 1.90| 0.01 | 0.03 | 0.007| 30.4/52|
| 441    | 0.26 | 0.31 | 0.43 | 0.06 | 0.12 | 0.10 | 0.002| 0.58| 0.01 | 0.03 | 0.006| 26.2/47|
| 551    | 0.11 | 0.34 | 0.38 | 0.05 | 0.12 | 0.09 | 0.001| 0.02| 0.01 | 0.03 | 0.005| 21.6  |
| 661    | 0.23 | 0.46 | 0.33 | 0.05 | 0.12 | 0.08 | 0.001| 0.01| 0.01 | 0.02 | 0.005| 22.1  |

* - numerator: hardness after surfacing, denominator – after thermal treatment

**Figure 1. Sample 111**

**Figure 2. Sample 112**

**Figure 3. Sample 331**

**Figure 4. Sample 441**
Sample 112 (Figure 2) has Widmanstatten pattern with thin needles deviating from ferritic net, which is located on the edges of initial austenite grains. The dimensions of grains correspond to 4 points.

Sample 331 (Figure 3) has a granular ferrite – carbide structure. The dimensions of carbides are within the range of 1 - 5 micrometer.

Sample 441 (Figure 4) has Widmanstatten pattern with a significant number of thin needles inside the grains. The dimensions of grains correspond to 3 points.

Sample 551 (Figure 5) has a structure, which consists mainly of ferrite with small localizations of perlite.

Sample 661 (Figure 6) has Widmanstatten structure with bulky needles and thick ferrite net. The dimensions of grains correspond to 3 points.

Therefore, the investigations have revealed a principal potential of tungsten oxides reduction from ores by a carbon-containing reducer and generation of tungsten carbides in an added layer within the range of 1-5 micrometers.

The following reactions have been considered to obtain a thermodynamical assessment of WO₃ oxide reduction by carbon and carbon oxide CO:

\[
\begin{align*}
WO_3 + 3C &= W + 3CO & (1) \\
WO_3 + 3/2C &= W + 3/2CO_2 & (2) \\
WO_3 + 3CO &= W + 3CO_2 & (3) \\
W + C &= WC & (4) \\
W + 1/2C &= 1/2W_2C & (5) \\
WO_3 + 5/2C &= WC + 3/2CO_2 & (6) \\
WO_3 + 2C &= 1/2W_2C + 3/2CO_2 & (7) \\
WO_3 + 5CO &= WC + 4CO_2 & (8) \\
WO_3 + 4CO &= 1/2W_2C + 7/2CO_2 & (9)
\end{align*}
\]

Thermodynamic characteristics of reactions necessary to evaluate the properties of reduction (1) – (9) in standard conditions \([\Delta H^\circ(T), \Delta S^\circ(T), \Delta G^\circ(T)]\) were calculated by the known methods [7] in the range of arc temperatures (1500 – 6000) K according to thermodynamic characteristics \([[H^\circ(T) - H^\circ(298.15 K)], S^\circ(T), \Delta H^\circ(298.15 K)]\) of reagents WO₃, W, C, CO, CO₂ as they are in reference book [8]. Thermodynamic properties of WC and W₂C carbides depending on the temperature as they are in Tables, accepted in [8], were calculated separately with regard to the data from reference books [9, 10]. Here, the following states were selected as standard ones for reacting substances in the range (1500 – 6000) K: \(W(s,l), WO_3(s,l), WC(s), W_2C(s), C(s), CO_{lg}, CO_{2lg}\).

Calculated standard Gibbs energies of reactions (1)–(9) are shown in Table 4 and in Figure 7.
Table 4. Standard Gibbs energy of reactions (1) – (9) in dependence on temperature

| Reaction | \( \Delta G^\circ(T) \), kJ |
|----------|-----------------|
|          | 1500K | 2000K | 2500K | 3000K | 3500K | 4000K | 4500K | 5000K | 5500K | 6000K |
| (1)      | -258.35 | -490.24 | -703.90 | -911.09 | -1113.40 | -1315.15 | -1514.59 | -1710.28 | -1902.54 | -2091.62 |
| (2)      | -121.56 | -226.64 | -315.92 | -400.80 | -482.60 | -565.47 | -647.50 | -727.11 | -804.56 | -880.01 |
| (3)      | 15.23 | 36.97 | 72.06 | 109.48 | 148.20 | 184.21 | 219.60 | 256.05 | 293.41 | 331.59 |
| (4)      | -47.76 | -54.97 | -63.57 | -73.34 | -83.87 | -91.57 | -98.83 | -107.52 | -117.72 | -129.45 |
| (5)      | -35.11 | -47.77 | -61.80 | -76.87 | -92.47 | -104.97 | -116.69 | -129.50 | -143.40 | -158.42 |
| (6)      | -169.32 | -281.61 | -379.48 | -474.15 | -566.48 | -657.04 | -746.32 | -834.64 | -922.29 | -1009.46 |
| (7)      | -156.67 | -274.41 | -377.71 | -477.67 | -575.08 | -670.44 | -764.19 | -856.61 | -947.96 | -1038.43 |
| (8)      | 58.66 | 157.73 | 267.15 | 376.33 | 484.86 | 592.43 | 698.84 | 803.97 | 907.67 | 1009.88 |
| (9)      | 25.72 | 77.06 | 139.60 | 202.71 | 265.99 | 329.13 | 391.94 | 454.28 | 516.00 | 577.05 |

The data show that reaction (1) is the most thermodynamically possible reaction of WO₃ reduction – reduction by carbon to tungsten and CO, followed by reactions (7) and (6) – these ones of obtaining W₂C and WC carbides, respectively, and CO₂. Reaction (2) of WO₃ reduction by carbon to tungsten and CO₂ is the forth likely one. Then, carbide formation follows from tungsten and carbon to W₂C and WC – reactions (5) and (4). The next likely possible reactions are reaction (3) of WO₃ reduction by carbon oxide (II) to tungsten, as well as reaction (9) to W₂C. The least possible reaction is reaction (8) – WO₃ reduction by CO to WC carbide. Thermodynamic probability of reactions (1), (2), (4) – (7) increases as temperature grows, and that of reactions (3), (8), (9), falls, on the contrary.

**Figure 7.** Standard Gibbs energy (kJ) of reactions (1) – (9) in dependence on temperature

**Conclusions**

1. In terms of carried out calculations obtaining of tungsten is thermodynamically the most likely one as the result of WO₃ reduction by carbon, followed by W₂C and WC carbides. Then, W₂C and WC carbides are thermodynamically possible to be obtained via reaction of tungsten with carbon.

2. Provided that a reducer is in a plenty tungsten carbide can be obtained when surfacing with flux cored wire containing tungsten oxides. Here, practical experience has revealed the potential of
tungsten oxides reduction from ores by a carbon containing reducer, as the result, tungsten carbides of grade \((\text{Fe},\text{W})_6\) are obtained, the dimensions are in the range 1-5 micrometers.

The paper is written at Siberian State Industrial University as a project part of State Order of the Ministry of education and Science of the Russian Federation № 11.1531.2014/k.

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