Journal of Alloys and Compounds 632 (2015) 161–164

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Thermodynamic analysis and effect of temperature on surface hardening of tungsten heavy alloys using ethanol

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ARTICLE INFO

Article history:
Received 8 December 2014
Received in revised form 22 January 2015
Accepted 24 January 2015
Available online 31 January 2015

Keywords:
Metals and alloys
Gas–solid reactions
Microstructure
Mechanical properties
X-ray diffraction
Thermodynamic modelling

ABSTRACT

Surface hardening of 92.5W–5.25Ni–2.25Fe (wt.%) heavy alloy was investigated at 1200–1500 K using ethanol as carbon source. The hardened surfaces were characterized by XRD, optical microscope and microhardness tester. Microhardness of the alloy increased from $HV_{0.3}$ 318 to 1640 with temperature. This was attributed to both increased thickness of WC shells formed on W grains and increased reaction depth as a result of higher C diffusion. Reaction pathways leading to WC formation were explained using thermodynamic and experimental results.

1. Introduction

Tungsten heavy alloys are composite materials consisting of round tungsten grains in a ductile Ni-rich FCC matrix phase. The alloys are commonly produced by liquid-phase sintering of tungsten, nickel and iron powder mixtures with tungsten contents up to 98 wt.% in the presence of hydrogen at temperatures around 1773 K [1]. They are used for various applications including kinetic energy penetrators, inertial components (balance weights), radiation shields and sport materials owing to combination of good mechanical properties and high density. They have, however, relatively poor surface characteristics such as wear and corrosion resistance. A classical approach to improve these properties is to increase surface hardness and modify surface composition of the alloys. But, scanty information on this issue has been reported.

Surface hardening of 92.5W–5.25Ni–2.25Fe (wt.%) heavy alloy was investigated previously by Eroglu et al. [2] using CH_4 as carbon source at a constant temperature of 1473 K. It was reported that heavy alloy with high surface hardness was obtained by carburization of tungsten grains. The present study differs from the previous one in the following aspects. (i) Different carbon source, ethanol, was used because it is produced in large quantities from various sources such as biomass, plants. (ii) Effects of temperature on thickness, composition and hardness of modified surface layers were also explored. (iii) In addition, thermodynamic analysis in the W–C_2H_5OH–Ar system was carried out to predict the conditions for single WC phase formation and to better understand the process.

2. Thermodynamic analysis

The thermodynamic analysis has been carried out by the method of minimization of the Gibbs' free energy of a system [3]. For a system of given input composition, it computes both the equilibrium gas phase and condensed phase contents at constant pressure and temperature. The calculation requires specifying all possible species and condensed phases known to exist in the temperature range of interest. In the present study, W and C_2H_5OH were used as initial reactants. In addition, Ar was included in the analysis because it was used to carry C_2H_5OH vapor into the reaction zone. Ni and Fe were excluded from the calculations for the sake of clarity. Therefore, equilibrium calculations were carried out in the W–O–C–H–Ar system. In this system, 47 species were considered to be as the constituents of the gas phase including H_2, H_2O, CO, CO_2, CH_4, CH_3, C_2H_4 and CH_2O. Solid equilibrium phases were assumed to be WO_3, WO_2, W, W_2C, WC and C. Input thermodynamic data in the form of Gibbs' free energy of the formation of the constituents were obtained from the thermochemical tables [4,5]. Thermodynamic calculations of the complex equilibria were performed using a modified version of Eriksson's computer program SOLGASMIX [6].

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http://dx.doi.org/10.1016/j.jallcom.2015.01.211
0925-8388/

Fig. 1 shows equilibrium solid stability diagram computed as a function of temperature (1200–1500 K) and input C_2H_5OH mole fraction (~0–1) for Ar/C_2H_5OH molar ratio of 12.7 (which is experimentally attainable). Input C_2H_5OH mole fraction is defined as $n^\circ_{C2H5OH}/(n^\circ_{C2H5OH} + n^o_W)$ where n^o represents the initial number of moles. The boundaries in the diagram divide different phase fields in which the indicated phases are expected to form. As seen from Fig. 1, there are W + WC, WC and WC + C phase fields for the conditions studied. WC phase (the desired phase) forms as single phase in a narrow range of input parameters. The equilibrium calculations generally indicate that input C_2H_5OH mole fraction should be around 0.5 for the formation of single phase WC. WC phase field gets slightly wider with decreasing temperature. In addition, free C is expected to form along with WC phase at the input mole fractions above 0.5 at the temperatures studied.

3. Experimental procedures

The experimental set-up used for the present study essentially consists of a hot-wall furnace with SiC heating elements, a bubbler, a quartz tube (20 mm in diameter and 500 mm in length) and Ar gas flow meter. Liquid ethanol was kept in a bubbler at ~297 K. Ethanol vapor was carried into the reaction zone by Ar flowing through the liquid. The flow rate of gaseous ethanol ($F^o_{ethanol}$) was calculated by the following equation:

$$F^o_{ethanol} = \frac{F^o_{argon} P_{ethanol}}{P_{total} - P_{ethanol}} \qquad (1)$$

where (F^o_{argon}, $P_{ethanol}$, and P_{total} are flow rate of the carrier gas Ar (40 standard cm^3/min, sccm), vapor pressure of ethanol (0.073 atm at 297 K) and total pressure (1 atm), respectively. The flow rate of ethanol was calculated to be 3.15 sccm corresponding to Ar/C_2H_5OH molar ratio of 12.7. Prior to the surface modification experiments, coupons (~2 mm × 10 mm × 10 mm) were cut by a diamond disc from 92.5W–5.25Ni–2.25Fe (wt.%) heavy alloy rod. The rod was produced by liquid-phase sintering of turbula mixed W, Ni and Fe powders in H_2 atmosphere at 1753 K for 30 min. The sintered density of the alloy was measured to be higher than 99.6% of the theoretical density (17.6 g/cm^3). The amount of liquid phase in the alloy was determined to be ~15 vol.%. The details of the sample preparation techniques and properties of the as-sintered alloy were given elsewhere [7]. Surface modification of the coupons was carried in the atmosphere having Ar/C_2H_5OH molar ratio of 12.7 at 1200, 1300, 1400 and 1500 K for 60 min.

The phases present in the sample surfaces were determined by a parafocusing X-ray diffractometer equipped with a Cu radiation tube ($\lambda_{K\alpha} = 0.15418$ nm) and a monochrometer. Vickers microhardness measurements were carried out perpendicular to the modified surfaces at 0.3 kg load. Cross-sections of the samples were polished using standard metallographic techniques and examined by an optical microscope for morphological analysis.

4. Results and discussion

Fig. 2 displays XRD patterns of original (as-sintered) and surface modified alloys. The pattern of the original sample consists of strong peaks from BCC tungsten and faint peaks at $2\theta_{(111)} = 43.65°$ and $2\theta_{(200)} = 50.60°$ from FCC matrix. After surface modification treatment at 1200 K, intense WC and weak W_2C peaks appear along with those observed from the untreated sample. Furthermore, a broad peak seen at $2\theta \cong 26.5°$ is attributed to the (0002) basal plane of graphite. When surface modification temperature increased to 1300 K, WC peak intensities are seen to be higher than those observed at 1200 K, while W peaks become weak. There are still faint diffraction peaks from the FCC matrix phase. It should be noted that W_2C and C peaks disappear at 1300 K. At higher temperatures (1400 K and 1500 K), the XRD patterns appear to be essentially the same as that observed at 1300 K. A slight decrease in faint W peak intensities is, however, noticeable at 1500 K.

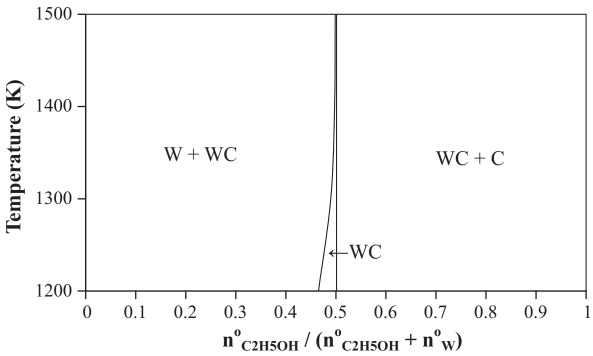

Fig. 1. Equilibrium solid stability diagram predicted by thermodynamic calculations carried out in the W–C_2H_5OH–Ar system as a function of input C_2H_5OH mole fraction and temperature for Ar/C_2H_5OH molar ratio of 12.7.

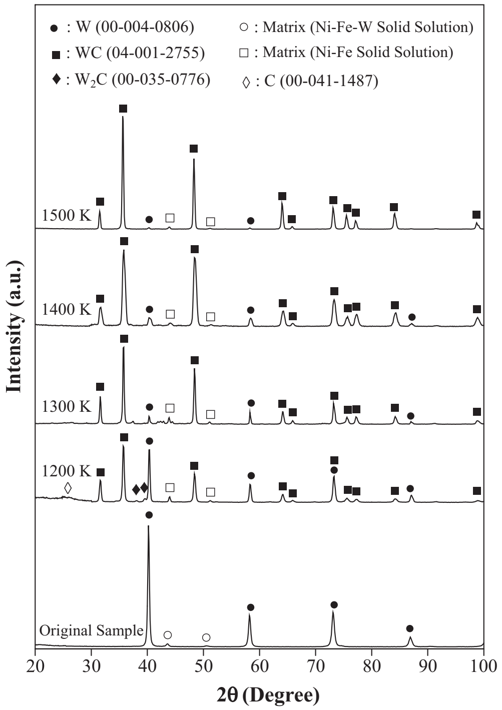

Fig. 2. XRD patterns of the as-sintered heavy alloy and the alloys held in Ar–C_2H_5OH atmosphere at 1200–1500 K for 60 min.

Detailed analysis of XRD patterns revealed that the peak positions of the FCC matrix phase shifted to higher angles after surface treatments, suggesting that chemical composition of the matrix phase changed. The lattice constant of the matrix in the untreated sample was measured to be 0.3601 ± 0.0007 nm in agreement with that of the 50Ni–20Fe–30W (wt.%) solid solution formed during sintering [8]. After surface modification treatments at 1200–1500 K, lattice constant of the matrix phase was calculated to be 0.3566 ± 0.0002 nm, which is close to the lattice constant of 70Ni–30Fe (wt.%) solid solution [9]. The decrease in the lattice constant is attributable to the carburization of W in the Ni–Fe–W solid solution leading to Ni–Fe matrix phase.

Faint W peak intensities do not change significantly at temperatures between 1300 K and 1500 K as revealed by the relevant patterns suggesting that no further carburization takes place with increasing temperature. However, this is not the case as revealed by cross sectional micrographs displayed in Fig. 3. The micrographs show WC shells (dark gray areas) formed on the nearly spherical unreacted W grains (light gray areas) and matrix (designated as M) phase between the grains. Mean WC shell thicknesses were calculated to be 1.24 ± 0.19, 1.77 ± 0.55, 2.93 ± 0.85 and 5.77 ± 1.0 μm for 1200, 1300, 1400 and 1500 K, respectively. The micrographs also reveal that WC reaction depth or effective C diffusion depth