Microstructure and cyclic oxidation behavior of W–Cr alloys prepared by sintering of mechanically alloyed nanocrystalline powders

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1. Introduction

Tungsten (W) is considered worldwide as a material of interest for high temperature applications, because of its high melting point of 3420 °C. Moreover, its high density (≈19.3 g/ml), impressive values of hardness (≈9.75 GPa) and elastic modulus (≈407 GPa), low coefficient of thermal expansion, excellent thermal conductivity as well as the low vapor pressure [11] justify, why W or W-alloys are considered as interesting candidate materials for various types of strategic and engineering applications. These alloys are of particular interest in systems, where heat is used as a driving force for various functions (e.g., engines, reactors, rockets, etc.). However, the applications of W and its alloys are somewhat limited, because of their susceptibility to oxidation at relatively moderate temperatures [2–5].

Alloying of W with elements, which oxidize preferentially with respect to other alloying elements to form protective oxide scales such as Cr₂O₃, Al₂O₃ and SiO₂, is a prospective approach. These oxide scales offer protection from further oxidation by acting as effective barrier against ionic migration [6–8] due to their continuous and impervious nature, which in turn is attributed to (i) their low growth rate, (ii) stoichiometric compositions, as well as (iii) their strong bonding with the alloy substrate lying underneath. However, alloying with elements having relatively low melting points, such as aluminum (Al) and silicon (Si) needs to be avoided, since the presence of these elements in the W-alloy adversely affects its high temperature capabilities. On the other hand, addition of chromium (Cr) as alloying element is preferred, since the W–Cr alloy is an isomorphous system with a miscibility gap below 1677 °C [9]. Moreover, the Gibbs free energy for formation of Cr₂O₃ is more negative than that of WO₃ [10], which indicates that the former oxide is more stable. Therefore, in the W–Cr alloy, Cr is expected to oxidize preferentially compared to W. Moreover, if the activity of Cr in the alloy is sufficiently high, stoichiometric and continuous oxide scale of Cr₂O₃ is expected to form.

However, consolidation of the W–Cr alloys without adding Group VIII elements (low melting sintering activators) is quite difficult [11], because inter-diffusion in W–Cr alloys is known to be very slow at high temperatures [12]. Further, it has been reported that the most efficient sinter-activator for W–Cr alloys is palladium (Pd) [11]. Itagaki and Yoda [13,14] have studied both sintering and oxidation characteristics of W–Cr alloys containing (0.14–2.27) at.% Cr alloys containing (0.14–2.27) Pd. In these studies, Pd has been used to activate diffusion in the W–Cr binary system by forming a molten Cr–Pd phase during sintering. Further investigations on high temperature oxidation behavior of these alloys have confirmed that their oxide scales are stable and protective in nature. But, the presence of relatively low melting sintering activators in the W-alloy limits its high temperature capabilities by reducing the solids temperature of the alloy. Moreover, Pd is considered as rare and expensive. A recent study in this laboratory has shown a drastic reduction in the sintering temperature of elemental W from the conventional temperature of ≥2500 °C to relatively modest range of 1700–1800 °C, through decrease in W powder particle size to nanometric scale through high energy mechanical milling (MM) prior to sintering [15]. Therefore, it is expected that the sinterability of the W–Cr alloys can also be enhanced by following this procedure. Therefore, the effects of nanostructure formation on densification deserve a comprehensive study. Moreover,
the oxidation behavior of the W–Cr alloys prepared by sintering of the nano-size powders also needs to be examined for optimization of process parameters and composition for practical applications. Hence, the present investigation has been undertaken with its major objectives as: (i) to examine the phase formations induced by mechanical milling of W_{1−x}Cr_{x} (x = 0.3, 0.5 and 0.6, compositions are given in atomic percent throughout this paper) elemental powder blends, and sintering behavior of their compacts; (ii) to study cyclic oxidation behavior of selected alloys, and (iii) to analyze the oxidation mechanisms of these alloys, based on theoretical and experimental evidences.

2. Experimental approach

2.1. Materials and processing

Elemental tungsten (W) powders (99.95% purity, 3–4 μm particle size) and chromium (Cr) powders (99.95% purity, 10–15 μm particle size) were used as raw materials in the present study. Prior to sintering, the average powder particle size of the W–Cr elemental blends containing 30 at.% Cr (W_{0.7}Cr_{0.3}), 50 at.% Cr (W_{0.5}Cr_{0.5}) and 60 at.% Cr (W_{0.4}Cr_{0.6}) were reduced to nanometric dimensions by using high energy planetary ball mill (Pulverisette 5, Fritsch GmbH, Idar-Oberstein, Germany). The problem of contamination during milling was minimized by the use of hard grinding media (WC balls), and a process control reagent (toluene). The milling speed was 300 revolutions per minute (rpm), and the ball to powder weight ratio was 10:1. A recent study in this laboratory [15] has shown that ball milling of W beyond 5 h resulted in a considerable amount of WC contamination. Therefore, in order to minimize erosion of the grinding media as well as strain hardening of the W particles, the duration of milling in the present study was restricted to 5 h. The milled samples were taken out at predetermined intervals for their further characterization. Then, the nanostructured powders obtained by ball milling were compacted to pellets using an automatic hydraulic press (Pellet press, Insmart Systems, Hyderabad, India) operated uniaxially with a load of 10 T. Subsequently, the green compacts were sintered in reducing atmosphere of hydrogen (H₂) at 1500 °C and 1700 °C for 5 h.

2.2. Characterization

The densities of the sintered specimens were evaluated by the Archimedes principle using the Sartorius density measurement kit (averaged out of 5 successive calculations). A high resolution X-ray diffractometer (Philips PW 3040/60, Panalytical B.V., Almelo, Netherlands) was used for recording the X-ray diffraction (XRD) patterns obtained from powders and sintered specimens. In addition, a scanning electron microscope (SEM) (Zeiss Evo 60, Carl Zeiss NTS GmbH, Oberkochen, Germany) was used for examining the microstructures of sintered specimens. Further, the chemical compositions of the phases constituting the microstructure was studied using an energy dispersive spectroscopy (EDS) (Oxford instruments, AZtechEnergy, Oxfordshire, UK) attached to the SEM.

Vickers microhardness of the sintered samples was measured by a microhardness tester (Micromet 5103, Buehler Ltd., Lake Bluff, IL, USA) operated under 0.5 N load with dwell time of 10 s. Results of hardness measurements with standard deviations were averaged out of ten successive indentations for each specimen.

2.3. Cyclic oxidation tests

The sintered specimens were polished to 400 grit finish, and subsequently ultrasonically cleaned first in acetone and then in methanol. Cyclic oxidation tests were performed at 800 °C, 1000 °C and 1200 °C in air using a muffle furnace (Okay furnaces with Kanthal super heating element, Bysakh & Co, Kolkata, India). These tests involved placing the specimens in alumina crucibles, which were then exposed for 0.5 h at the test temperature, and subsequently air-cooled to room temperature. The changes in weight were measured using a semi-microbalance (CPA 224S, Sartorius, Goettingen, Germany) with an accuracy of ±0.1 mg. The above-mentioned procedure was repeated for 30 cycles, such that the cumulative time of exposure at the chosen temperature was 15 h. Top surfaces of the oxidized specimens, which were directly in contact with air, were analyzed using XRD for identification of the phases present in the oxide scales. The exposed samples of the alloy, which was found to be the most oxidation resistant through the study of kinetics as described above, were cross-sectioned, hot mounted using bakelite-copper mixture, and then metallographically polished for observation on the SEM, where the presence of Cu in the mount ensured its electrical conductivity.

3. Results and discussion

3.1. Characterization of ball-milled powders

The phases present in the W_{0.5}Cr_{0.5} elemental blend ball-milled for different time periods are displayed in the XRD patterns shown in Fig. 1. These patterns depict continuous broadening of W peaks with reduction in their intensities, which may be attributed to the residual strains in the W-rich phase, and the refinement of W crystallite size in the powders subjected to ball milling. As expected, a progressive decrease in the crystallite size (Fig. 2) and increase in r.m.s. stain with increase in duration of milling is observed. The average crystallite sizes after milling for 5 h have been found as 32.8, 41.7 and 49.1 nm in W_{0.7}Cr_{0.3}, W_{0.5}Cr_{0.5} and W_{0.4}Cr_{0.6} alloys, respectively. The crystallite sizes in the as milled powders of these alloys is found to be higher than that in the powders of pure W ball milled under similar conditions [15], indicating the cushioning effect of Cr in the blends during the impact of the WC balls on the W particles. In fact, higher extent of cushioning effect is found in the higher Cr containing samples as indicated in Fig. 2. For instance, crystallite sizes of the powders milled for different durations up to 5 h are found to be high for the alloy having the highest concentration of Cr, that is, W_{0.4}Cr_{0.6} (Fig. 2). Similar trends have also been observed during ball milling of pure W and W–Cu elemental blends [16].

A close look at W_{110} peaks in Fig. 1 indicates shift in its position towards slightly higher angle side as compared to pure W, evidencing slight decrease in the lattice parameter of W with milling time. Such a trend is expected, because atomic radius of Cr (r_{Cr} = 0.128 nm) is less compared to that of W (r_{W} = 0.139 nm). On the other hand, Cr_{110} peaks in the XRD patterns show negligible peak shift indicating no significant dissolution of W in Cr. Similar features have also been
reported previously for milling of the Cr\textsubscript{19}Mo\textsubscript{40}W\textsubscript{40}Pd\textsubscript{1} elemental powders [11].

Bright and dark field TEM images of the W\textsubscript{0.5}Cr\textsubscript{0.5} alloy milled for 5 h sample are shown in Fig. 3(a) and (b), respectively. Examination of these images suggests that the crystallite size varies from 30 to 50 nm, which is in agreement with the average crystallite size derived from analysis of the XRD results shown in Figs. 1 and 2.

The SEM back-scattered electron (BSE) images of W\textsubscript{0.7}Cr\textsubscript{0.3}, W\textsubscript{0.5}Cr\textsubscript{0.5} and W\textsubscript{0.4}Cr\textsubscript{0.6} alloy powders milled for 5 h are displayed in Fig. 4(a), (b) and (c), respectively. Examination of these images indicates that the investigated powders possess flake-like morphology. Furthermore, typical bulk EDS spectra of W\textsubscript{0.7}Cr\textsubscript{0.3}, W\textsubscript{0.5}Cr\textsubscript{0.5} and W\textsubscript{0.4}Cr\textsubscript{0.6} alloys are shown in Fig. 4(d), (e) and (f), respectively, and the results of quantitative EDS analysis for these samples are presented in Table 1. Examination of the data obtained from the bulk EDS analysis indicates that the initial compositions of W–Cr alloys are more or less maintained even after milling for 5 h. Moreover, there is no evidence for the presence of carbon (C) in the milled powders [Fig. 4(d) to (f) and Table 1], which further indicates that the WC contamination of the alloy powders is insignificant for the powders milled for 5 h.

3.2. Microstructure and properties of as-sintered W–Cr alloys

The average densities of the sintered products obtained by measurements using the Archimedes principle are reported in Table 2. From these results, it is confirmed that relative densities of the investigated alloys sintered at 1500 °C and 1700 °C are 7–9% and 12–15%, respectively, higher than that in the product obtained by sintering of nanostructured W powder under similar conditions [15]. Furthermore, densification of these alloys are found to be enhanced remarkably from 87–90% to 96–97.5%, by increasing the sintering temperature from 1500 °C to 1700 °C. For subsequent studies on oxidation, only defect-free samples possessing higher relative densities have been considered in order to ensure the reproducibility of results. An earlier study by Kofstad and Lillerud [17] has shown that mass transport through the micro-cracks in the samples leads to enhancement of oxidation kinetics in the initial stages.

An XRD pattern indicating the presence of both W-rich (W\textsubscript{ss}) and Cr-rich (Cr\textsubscript{ss}) phases in the microstructures of the as-sintered alloys is shown in Fig. 5. Furthermore, the variation of lattice parameter of the W-rich phase with its Cr content is shown in Fig. 6. From this figure, it is obvious that the lattice parameter decreases with increasing Cr content. This trend is well-expected, as the atomic radius of Cr is less than that of W. Calculated lattice parameter values of the investigated alloys are in good agreement with those reported earlier by Naidu et al. [9].

Typical SEM images depicting the microstructures of the sintered W–Cr alloys are shown in Fig. 7(a) through (c). Examination of these images indicates the presence of two phases having relatively brighter and darker contrast, which by EDS analysis (Table 3) have been found to be enriched in W and Cr, respectively. This observation is consistent with those of the XRD analysis, which confirms the co-existence of both W\textsubscript{ss} and Cr\textsubscript{ss} phases in the microstructures of each alloy. This observation is also consistent with the nature of phases expected from the W–Cr binary equilibrium phase diagram [9]. The W\textsubscript{ss} phase present in the microstructure of W\textsubscript{0.7}Cr\textsubscript{0.3} alloy exhibits primarily a blocky morphology with Cr\textsubscript{ss} phase appearing as darker channels in between, as shown in Fig. 7(a). However, part of the microstructure shows lamellar morphology for both W\textsubscript{ss} and Cr\textsubscript{ss} phases. In contrast, the microstructure of W\textsubscript{0.5}Cr\textsubscript{0.5} and W\textsubscript{0.4}Cr\textsubscript{0.6} shows primarily lamellar microstructure, as shown in Fig. 7(b) and (c), respectively.

The image analysis of the microstructures of the as-sintered W–Cr alloys reveals that: (i) the area fraction of the Cr\textsubscript{ss} phase in the alloys is increased with increase in Cr content (Table 2), and (ii) the average grain size of the W-rich phase in the W\textsubscript{0.7}Cr\textsubscript{0.3} alloys is 7.89, whereas average lamellar widths of W\textsubscript{ss} in W\textsubscript{0.5}Cr\textsubscript{0.5} and W\textsubscript{0.4}Cr\textsubscript{0.6} are 1.35 and 5.62 μm, respectively (Table 2). Based on the data in Table 2 and SEM (BSE) images depicted in Fig. 7, it is obvious that among the investigated alloys, the W\textsubscript{0.5}Cr\textsubscript{0.5} alloy exhibits the lowest interspacing and the most uniform distribution of W\textsubscript{ss} and Cr\textsubscript{ss} with lamellar...

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**Fig. 2.** Plots showing variations of crystal size of W in W–Cr elemental blends with milling time up to 5 h.

**Fig. 3.** (a) Bright-field and (b) dark-field TEM images of the 5 h milled W\textsubscript{0.5}Cr\textsubscript{0.5} alloy.
morphology. It may be further noted that the grain sizes of these alloys appear to be ~2 to 8 times finer than that in the product obtained by sintering of the nanostructured W powder under similar conditions [15,18]. No cracks could be observed in the microstructures even at higher magnification, confirming reasonably uniform densification of the sintered samples.

Bar charts depicting Vickers hardness of the W–Cr alloys with different Cr contents are shown in Fig. 8. This figure indicates that the values of hardness measured for the investigated alloys are higher than that of pure W, and the alloy with 50 at.% Cr shows the highest hardness value. Higher hardness of this alloy is attributed to finer interlamellar spacing and more uniform distribution of the phases present in its microstructure compared to that in the other two alloys investigated.

3.3. Oxidation behavior

3.3.1. Kinetics

Cyclic oxidation behavior of both pure W and W–Cr alloys at different temperatures has been studied by recording the variation of weight gain per unit surface area (Δm/S) with time (t), and the results are depicted in Fig. 9. The net weight gained by each of the investigated samples exposed to air at 800 °C, 1000 °C and 1200 °C for 15 h (30 cycles) is listed in Table 4.

At 800 °C, the values of Δm/S recorded for the W0.7Cr0.3 alloy is 3 and 5 times higher than those of W0.5Cr0.5 and W0.4Cr0.6 alloys, respectively. This observation confirms that the oxidation resistance at this temperature scales with the Cr content of the investigated alloys. Upon exposing to 1000 °C, pure W shows gradual weight gain up to 5 h, and later a significant amount of the powdery mass is stripped from the oxide scale, followed by its accumulation in the alumina crucible. This observation confirms that pure W does not form a protective oxide scale on its surface. Similar results have been reported in the past about the oxidation behavior of pure W at these temperatures [2–5]. Even at 800 °C, the values of Δm/S of the investigated W–Cr alloys are found to be more than 4 times lower than that of pure W. This observation suggests that the oxidation resistance of the W–Cr alloys is superior to that of pure W in the temperature range of 800–1200 °C. Therefore, it is inferred that alloying with Cr contributes to protection against oxidation at elevated temperatures, which deserve further investigation.

Contrary to the behavior observed at 800 °C, the weight gain of the W0.5Cr0.5 alloy has been found to be lower than that of other investigated alloys for the tests carried out at 1000 °C and 1200 °C. This observation suggests that at these temperatures, the oxidation resistance of the W0.5Cr0.5 alloy is superior to that of the other investigated W–Cr alloys with either lower or higher Cr content. This observation also suggests that there is an upper limit of the Cr content in the W–Cr alloys, which is necessary to maintain a stable and protective oxide scale at temperatures above 1000 °C. Possible reason for such behavior is explained later in Section 3.3.4.

On comparison of the mass gains of the investigated alloys, the oxidation kinetics of the W0.7Cr0.3 alloy is found to be 2 and 1.8 times more sensitive to temperature changes than those of W0.5Cr0.5 and W0.4Cr0.6 alloys, respectively in the range of 800–1200 °C. This

### Table 1

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Wt.%</th>
<th>At.%</th>
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<tbody>
<tr>
<td></td>
<td>W</td>
<td>Cr</td>
</tr>
<tr>
<td>W0.7Cr0.3</td>
<td>89.6</td>
<td>10.4</td>
</tr>
<tr>
<td>W0.5Cr0.5</td>
<td>78.3</td>
<td>21.7</td>
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<tr>
<td>W0.4Cr0.6</td>
<td>68.6</td>
<td>31.4</td>
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### Table 2

<table>
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<th>Composition</th>
<th>Sintered density (%)</th>
<th>At 1700 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1500 °C</td>
<td>1700 °C</td>
</tr>
<tr>
<td>W0.7Cr0.3</td>
<td>97.3</td>
<td>96.5</td>
</tr>
<tr>
<td>W0.5Cr0.5</td>
<td>90.6</td>
<td>97.9</td>
</tr>
<tr>
<td>W0.4Cr0.6</td>
<td>91.4</td>
<td>97.4</td>
</tr>
</tbody>
</table>

Fig. 4. SEM (BSE) images of 5 h milled W–Cr alloy powders and the corresponding EDS spectrums: (a) and (d) W0.7Cr0.3; (b) and (e) W0.5Cr0.5; (c) and (f) W0.4Cr0.6.
observation may be attributed to the increase in susceptibility of the investigated alloys to oxidation with decrease in their Cr content.

The variation of $\Delta m/S$ with time ($t$) in the range of 800–1200 °C has been used to determine the kinetic parameters, namely, the general rate constant ($k$), oxidation exponent ($n$), parabolic rate constant ($k_p$), and the activation energy ($Q$). The relation between $\Delta m/S$, $k$ and $n$ is expressed as:

$$\Delta m/S = S^{\frac{1}{n}} = kt$$

To obtain the general rate constant ($k$) and oxidation exponent ($n$), curve fitting has been carried out for the plots of $\Delta m/S$ against $t$ using the classical Freundlich model ($y = ax^b$) through the Microcal Origin software. Comparison of the Freundlich model with Eq. (1) yields $n = 1/b$ and $k = a^n$. The results of this analysis for the W–Cr alloys at different temperatures are shown in Table 4. The proposed function has been used to fit the experimental data obtained at all three temperatures with the correlation factor ($R^2$) ≥ 0.9. The values of $n \approx 2$ obtained for oxidation rests on the W$_{0.5}$Cr$_{0.5}$ alloy indicate that approximately parabolic rate law is being followed in the range of 800–1200 °C. Moreover, almost similar behavior has been observed for the W$_{0.5}$Cr$_{0.5}$ alloy. In contrast to the nature of results for the higher Cr-containing alloys, the values of $n$ as determined for the W$_{0.7}$Cr$_{0.3}$ alloy ($1 < n < 2$) indicate that the rate of oxidation is faster than that predicted by the parabolic rate law, and slower than that for linear relationship between $\Delta m/S$ and $t$. Based on the values of $n$, it can be interpreted that the alloy with 30 at.% Cr is significantly more prone to oxidation than those having greater Cr content.

According to Mrowec and Stoklosa [19], minor deviation from the parabolic behavior is not necessarily an intrinsic characteristic of an alloy. One of the reasons for such deviations is probably the erroneous interpretation of the experimental data. For example, in the present investigation, weight gain per unit surface area ($\Delta m/S$) has been measured based on the initial surface area of the sample. However,
it should be noted that the effective surface area of a given sample is reduced continuously with the progress of oxidation. For precise calculations, one must consider the instantaneous surface area by incorporating suitable corrections. In reality, experimental evolution of the actual such surface area after each cycle of high temperature exposure is a difficult task, and sometimes the top surface of the oxide scale is damaged during handling. Moreover, non-uniform (non-planer) growth of the oxide scale may also alter the effective metal-oxide interfacial area, which in turn may contribute to inaccurate results.

Parabolic rate constant \((k_p)\) has been determined for \(W_0.5Cr_0.5\) and \(W_0.4Cr_0.6\) alloys using the following relationship:

\[
(\Delta m/S)^2 = k_p t + C
\]  

(2)

The parabolic rate constants have been obtained from the slope of the best-fit lines for the plot of \((\Delta m/S)^2\) against \(t\), representing the oxidation tests carried out for \(W_0.5Cr_0.5\) and \(W_0.4Cr_0.6\) alloys at different temperatures, as shown in Fig. 10(a) through (c). The values of \(k_p\) obtained for the tests at different temperatures are presented in Table 5. It can be observed that the values of \(k_p\) increase steadily with increase in the test temperature, as expected.

Furthermore the parabolic rate constant, \(k_p\), is a function of absolute temperature \((T)\) and apparent activation energy \((Q)\) according to the Arrhenius relationship:

\[
k_p = k_0 \exp\left(-\frac{Q}{RT}\right)
\]  

(3)

where \(k_0\) is the Arrhenius constant and \(R\) is the universal gas constant \((8.314\ J/K.\ mol)\).

This relation can be further simplified as:

\[
\ln(k_p) = -\frac{Q}{RT} + C
\]  

(4)

From the Relation (4), it is obvious that the value of \(Q\) can be obtained from the slope of the best fit line for the plot of \(\ln(k_p)\) against \(1/RT\), as shown in Fig. 10(d). Through the aforementioned analysis, the activation energies for oxidation in the range of 800–1200 °C have been found to be 135.65 kJ/mol and 207.13 kJ/mol for \(W_0.5Cr_0.5\) and \(W_0.4Cr_0.6\) alloys, respectively. Explanation for the results obtained in terms of the kinetic parameters requires a thorough evaluation of the oxidation mechanisms through study of oxide scale, which have been discussed in Sections 3.3.2 and 3.3.4.

3.3.2. Oxide scales

3.3.2.1. Phase identification. The XRD patterns obtained from the oxide scales of the W–Cr alloys subjected to 15 h exposure at different temperatures are shown in Fig. 11(a) through (c). The results of XRD analysis as shown in these figures, confirm that the products of oxidation at 800 °C and 1000 °C for each of the alloys are primarily mixtures of \(Cr_2O_3\), \(Cr_2WO_6\) and \(WO_3\). Almost similar composition was identified in the oxide scales of \(W_0.7Cr_0.3\) and \(W_0.4Cr_0.6\) samples exposed at 1000 °C. Conversely, the major peaks in the XRD patterns from the oxide scales formed on the \(W_0.5Cr_0.5\) alloy exposed at 1000 °C represent only the \(Cr_2WO_6\) phase. Furthermore, the XRD patterns from the oxide scales formed on the samples of \(W_0.5Cr_0.5\) and \(W_0.4Cr_0.6\) alloys exposed at 1200 °C show major peaks representing the \(Cr_2WO_6\) phase (Fig. 11(c)). In contrast, the XRD pattern from
the spalled oxide powders obtained from oxide scale of the W0.7Cr0.3 alloy exposed to 1200 °C (Fig. 11(c)) shows the presence of WO3 as the predominant constituent. Thus, based on the examination of the XRD patterns at different temperatures, it is appropriate to infer that superior protection of the W0.5Cr0.5 alloy at higher temperatures (>800 °C) might be due to the presence of relatively larger amount of Cr2WO6 in its oxide scale. The oxide scale constituents as identified in the present study are in agreement with those found in course of the oxidation studies performed on 10W90Cr, 20W80Cr and 30W70Cr alloys, which were prepared by using Pd as an activator for sintering [20].

3.3.2.2. Morphology. The morphologies of top surfaces of the oxide scales formed on the specimens exposed for 15 h at different temperatures are shown in Fig. 12. Examination of these images suggests that the oxide scale morphologies depend on the Cr content of the alloys as well as on the temperature of exposure. In the alloy with the least Cr content (W0.7Cr0.3), considerable amount of powdery mass formed by spallation and stripping from the surface of the specimen has been found. Furthermore, complete degradation of this alloy has been observed on exposure at 1200 °C. From these observations, it is inferred that the presence of 30 at.% Cr in the W–Cr alloy is not sufficient to develop a protective oxide scale at the alloy surface. In contrast, the oxide scales formed on other two alloys having higher Cr content appear to be more adherent to the alloy surface. Previous studies on the W–Cr alloys have also confirmed that the Cr concentration of ≥50 at.% would be required to maintain a stable and protective oxide scale [21,22].

Typical SEM (SE) images of the top surfaces of the oxide scale formed on the W0.5Cr0.5 alloy, which has been found to be the most oxidation resistant in the course of exposure at 800–1200 °C for 15 h, are shown in Fig. 13(a) through (c). In these images, two different morphologies of the constituent phases can be clearly identified, namely equiaxed (more or less spherical) and whisker-shaped. Based on the results of EDS analyses, the oxide phases with high aspect ratios appear to be rich in W, while those with equiaxed shapes are found to be depleted in W and enriched in Cr.

Table 4
Results of the cyclic oxidation tests on the investigated W–Cr alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Temperature, °C</th>
<th>Weight gain, Δm/S (mg cm⁻²)</th>
<th>y = axᵇ</th>
<th>(Δm/S)² = k</th>
<th>n = 1/b</th>
<th>k = cᵃⁿ</th>
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<tr>
<td>W0.7Cr0.3</td>
<td>800</td>
<td>54.12</td>
<td>10.37</td>
<td>0.623</td>
<td>0.987</td>
<td>1.605</td>
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<tr>
<td>W0.5Cr0.5</td>
<td>800</td>
<td>18.24</td>
<td>6.516</td>
<td>0.382</td>
<td>0.946</td>
<td>2.617</td>
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<tr>
<td>W0.5Cr0.5</td>
<td>1000</td>
<td>103.88</td>
<td>47.79</td>
<td>0.684</td>
<td>0.993</td>
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<tr>
<td>W0.5Cr0.5</td>
<td>1200</td>
<td>91.36</td>
<td>22.46</td>
<td>0.512</td>
<td>0.990</td>
<td>1.953</td>
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<tr>
<td>W0.4Cr0.6</td>
<td>800</td>
<td>336.45</td>
<td>42.26</td>
<td>0.772</td>
<td>0.987</td>
<td>1.295</td>
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<tr>
<td>W0.4Cr0.6</td>
<td>1000</td>
<td>142.36</td>
<td>37.33</td>
<td>0.459</td>
<td>0.981</td>
<td>2.178</td>
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<tr>
<td>W0.4Cr0.6</td>
<td>1200</td>
<td>174.08</td>
<td>53.91</td>
<td>0.439</td>
<td>0.970</td>
<td>2.277</td>
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</table>

Table 5
Parabolic rate constants (kp, in cm⁶ g⁻¹ h⁻¹) for W0.5Cr0.5 and W0.4Cr0.6 alloys at different temperatures.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Temperature, °C</th>
<th>kp, cm⁶ g⁻¹ h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>W0.5Cr0.5</td>
<td>800</td>
<td>20.52</td>
</tr>
<tr>
<td>W0.4Cr0.6</td>
<td>1000</td>
<td>540.01</td>
</tr>
<tr>
<td>W0.4Cr0.6</td>
<td>1200</td>
<td>1156.8</td>
</tr>
<tr>
<td>W0.5Cr0.5</td>
<td>800</td>
<td>6.782</td>
</tr>
<tr>
<td>W0.5Cr0.5</td>
<td>1000</td>
<td>1708.6</td>
</tr>
<tr>
<td>W0.5Cr0.5</td>
<td>1200</td>
<td>2014.5</td>
</tr>
</tbody>
</table>

Fig. 10. Plots showing variation of (Δm/S)² against t for the W0.5Cr0.5, and W0.4Cr0.6 alloys exposed to (a) 800 °C, (b) 1000 °C and (c) 1200 °C for 15 h (30 cycles); (d) variation of ln(kp) against 1/RT for the W0.5Cr0.5, and W0.4Cr0.6 alloys exposed to 800–1200 °C for 15 h (30 cycles).
The SEM (BSE) images depicting the oxide scale cross-sections in the samples of W0.5Cr0.5 alloy exposed at 800 °C are shown in Fig. 14. Examination of these figures shows the presence of three distinct layers within the oxide scale with a significant amount of porosity and cracks in the outermost layer. From the studies of compositions through EDS analysis and elemental X-ray maps, the innermost relatively dense layer formed on the samples exposed at 800 °C is found to be enriched in Cr, while the outer layer shows the presence of W. Based on the results of EDS and XRD analysis, it is inferred that the oxide scale contains layers of Cr2O3, Cr2WO6 and WO3 in sequence from alloy–oxide to oxide–air interface.

An SEM image depicting the oxide–alloy interface in the W0.5Cr0.5 alloy exposed at 1200 °C is shown in Fig. 15. It shows an almost uniform composition throughout the outer oxide scale. Based on the results of XRD and EDS analysis, it is therefore inferred that Cr2WO6 is the main constituent of this region.

3.3.3. Probable oxidation reactions and thermodynamic analysis

The probable chemical reactions involved in the formation of the oxidation products such as WO3, Cr2O3 and Cr2WO6 oxides are as follows:

\[ W(s) + \frac{3}{2}O_2(g) \rightarrow WO_3(s) \]  \hspace{1cm} (5)

\[ 2Cr(s) + \frac{3}{2}O_2(g) \rightarrow Cr_2O_3(s) \]  \hspace{1cm} (6)

\[ 2Cr(s) + WO_3(s) \rightarrow Cr_2O_3(s) + W(s) \]  \hspace{1cm} (7)

\[ W(s) + Cr_2O_3(s) + \frac{3}{2}O_2(g) \rightarrow Cr_2WO_6(s) \]  \hspace{1cm} (8)

\[ Cr_2O_3(s) + WO_3(s) \rightarrow Cr_2WO_6(s) \]  \hspace{1cm} (9)

Further, the thermodynamic data including the standard Gibb's free energy (\( \Delta G \)) [10], the equilibrium constant (K), and the partial pressure of oxygen \( P_{O_2} \) for selected reactions are presented in Table 6. The standard free energy of formation of Cr2O3 is more negative than that of WO3 at all temperatures, which confirms that the former oxide is more stable. Moreover, the calculated partial pressures of oxygen for Reactions (5) and (6) show that \( P_{O_2} (WO_3) > P_{O_2} (Cr_2O_3) \) for all temperatures.

In the XRD patterns representing W0.5Cr0.5 and W0.4Cr0.6 alloys exposed to relatively higher temperature (1200 °C), major peaks corresponding to Cr2WO6 phase could be observed. The absence of
\(\text{Cr}_2\text{O}_3\) and \(\text{WO}_3\) peaks in the XRD patterns of the oxide scales formed at 1200 °C is attributed to the fact that these oxides are unstable at this temperature. While \(\text{WO}_3\) is known to vaporize at temperatures \(\geq 1000 \degree \text{C}\) [4,5], \(\text{Cr}_2\text{O}_3\) is expected to be converted into volatile \(\text{CrO}_3\) in contact with air or oxygen through Reaction (10) [23]. As these volatile oxides tend to escape from the oxide scale at 1200 °C, their presence is not expected in the oxide scales formed at this temperature.

\[
\text{Cr}_2\text{O}_3(s) + (3/2)\text{O}_2(g) \rightarrow 2\text{CrO}_3(g). \tag{10}
\]

However, from the results related to weight gains (Fig. 9 and Table 4) during high temperature exposure of the investigated alloys, it is obvious that the volatility related weight loss is much less significant compared to the oxidative weight gains. The loss in weight due to volatilization of \(\text{CrO}_3\) at temperatures more than 1000 °C is probably avoided, because of the consumption of \(\text{Cr}_2\text{O}_3\) in the formation of \(\text{Cr}_2\text{WO}_6\) through Reaction (9).

Studies using XRD analysis (Fig. 11) have shown that \(\text{Cr}_2\text{WO}_6\) is formed on the surfaces in the oxide scales, and its formation is enhanced at the expense of that of \(\text{WO}_3\) and \(\text{Cr}_2\text{O}_3\) with increase in the temperature of exposure. The equilibrium phases in the ternary

![Fig. 12. Surface appearances of the investigated W-Cr alloys after exposing to 800 °C, 1000 °C and 1200 °C for 15 h (30 cycles).](image)

![Fig. 13. SEM images of the oxide surface of W_{0.5}Cr_{0.5} alloy after exposing to (a) 800 °C, (b) 1000 °C and (c) 1200 °C for 15 h (30 cycles).](image)
W–Cr–O system have been investigated in the past, and are well-documented [24–28]. The Cr₂WO₆ phase has been found to be stable in the range of 900–1350 °C in the pseudo-binary Cr₂O₃–WO₃ systems [26]. Based on the results of an earlier investigation, the possible chemical reactions leading to the formation of Cr₂WO₆ are Reactions (8) and (9). It may be proposed that in the initial stages of oxidation, Cr₂O₃ may react with W through Reaction (8) leading to the formation of Cr₂WO₆. At a later stage, the Cr₂WO₆ is more likely to form by the reaction between WO₃ and Cr₂O₃ (through Reaction (9)).

### 3.3.3. Oxidation mechanism

Based on the experimental evidences and thermodynamic analysis as discussed in Sections 3.3.1–3.3.3, it is possible to propose oxidation mechanisms for the investigated W–Cr alloys. In W₀.₅Cr₀.₅ and W₀.₄Cr₀.₆ alloys, simultaneous oxidation of W and Cr through Reactions (5) and (6) appears to occur in the initial stages, which leads to the growth of both Cr₂O₃ and WO₃ at the top of the alloy surface. In the later stages, the grains of WO₃ grow preferentially due to the faster outward diffusion of W³⁺ ions compared to that of Cr³⁺. Moreover, as the P₀₂ required for the formation of WO₃ is greater than that for Cr₂O₃, the presence of former oxide in the outermost layer can be further justified. As a result, the Cr₂O₃ grains are covered on the outer side with a polycrystalline WO₃ layer. As Cr₂O₃ is also expected to form by reduction of WO₃ by Cr (Reaction (7)) at the alloy–oxide interface, growth of the former oxide as inner layer at the alloy–oxide interface is further promoted.

It is interesting to note that at 1000 °C and 1200 °C, the W₀.₅Cr₀.₅ alloy is more oxidation resistant than W₀.₄Cr₀.₆, while the trend is opposite at 800 °C. The relatively finer interlamellar spacing in the microstructure of the W₀.₅Cr₀.₅ alloy than that in the W₀.₄Cr₀.₆ leads to larger interfacial area in the former alloy, which provides short-circuit path for diffusion of Cr³⁺ ions, and enhances the kinetics of Cr₂O₃ scale formation. It is intuitive that diffusion of Cr³⁺ plays a dominant role in Cr₂O₃ formation at temperatures ≥1000 °C, whereas that of O²⁻ is more significant at lower temperatures.

Diffusion of W from the base alloy to the alloy–oxide interface and its reaction with Cr₂O₃ leads to the formation of Cr₂WO₆ [Reaction (8)]. As predicted by thermodynamic analysis in Section 3.3.3, Cr₂WO₆ can also form by reaction between Cr₂O₃ and WO₃ [Reaction (9)]. Therefore, a continuous and dense layer of Cr₂WO₆ is able to form between the layers comprising WO₃ and Cr₂O₃. The layers of Cr₂WO₆ and Cr₂O₃ are believed to be responsible for protection against oxidation at 800 °C. At temperatures greater than 1000 °C, when the WO₃ vaporizes from the outer layers, the Cr₂WO₆ layer acts as a barrier for inward diffusion of oxygen, and inhibits further oxidation of Cr₂O₃ to volatile CrO₃ through Reaction (10). According to Bayer [24], the crystal structure of Cr₂WO₆ is inverse tri-rutile (space group p4/mmm (Z = 2) [29] type. It forms stable valances of Cr³⁺ and W⁶⁺, which may be expected to be very stable at higher temperatures as well. Hence, it is intuitive that in the case of W₀.₅Cr₀.₅ and W₀.₄Cr₀.₆ alloys, protection against oxidation at temperatures ≥1000 °C is supported by preferred growth of Cr₂WO₆ layer in the oxide scale. The oxidation resistance of the W₀.₄Cr₀.₆ alloy has been found to be worse in comparison to that of W₀.₅Cr₀.₅ at 1000 °C and 1200 °C probably because higher Cr content of the former alloy causes the formation of greater amount of Cr₂O₃ than WO₃ in the oxide scale. In that case, the surplus amount of Cr₂O₃ to WO₃ is greater in the Cr₂O₃ scale, which leads to Cr₂O₃ being the protective oxide phase.

### Table 6

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Temperature</th>
<th>ΔG (kJ/mol)</th>
<th>K</th>
<th>P₀₂ (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2/3)W + O₂ → (2/3)WO₃</td>
<td>800 °C</td>
<td>−381.32</td>
<td>3.66×10¹⁸</td>
<td>2.73×10⁻⁹</td>
</tr>
<tr>
<td>1000 °C</td>
<td>349.32</td>
<td>2.15×10¹⁴</td>
<td>4.63×10⁻⁸</td>
<td></td>
</tr>
<tr>
<td>1200 °C</td>
<td>317.32</td>
<td>1.79×10¹¹</td>
<td>5.58×10⁻¹²</td>
<td></td>
</tr>
<tr>
<td>(4/3)Cr + O₂ → (4/3)Cr₂O₃</td>
<td>800 °C</td>
<td>−504.32</td>
<td>4.65×10²⁷</td>
<td>2.15×10⁻⁸</td>
</tr>
<tr>
<td>1000 °C</td>
<td>−536.32</td>
<td>1.01×10²²</td>
<td>9.82×10⁻⁸</td>
<td></td>
</tr>
<tr>
<td>1200 °C</td>
<td>−504.32</td>
<td>7.66×10¹⁷</td>
<td>1.30×10⁻⁸</td>
<td></td>
</tr>
<tr>
<td>(2/3)W + (2/3)</td>
<td>800 °C</td>
<td>−388.06</td>
<td>3.80×10¹⁴</td>
<td>2.62×10⁻¹⁵</td>
</tr>
<tr>
<td>1000 °C</td>
<td>−355.33</td>
<td>2.75×10¹¹</td>
<td>3.63×10⁻¹²</td>
<td></td>
</tr>
</tbody>
</table>
is expected to remain in the scale after WO₃ is completely consumed by Reaction (9). This residual Cr₂O₃ is likely to oxidize further to volatile CrO₃, which in turn is lost by vaporization.

The oxidation mechanism of the W₀.₇Cr₀.₃ alloy is completely different from those of the alloys with higher Cr content. In the initial stage, the oxidation mechanism is probably similar to that of the other two alloys with higher Cr content. However, due to lower Cr concentration in the alloy, the flux of Cr atoms to the alloy/oxide interface appears to be insufficient for the formation of continuous and protective Cr₂O₃ scale. Hence, the formation and growth of porous WO₃ scale is promoted, as confirmed by XRD results shown in Fig. 11(c). In the later stages, therefore, the ingress of oxygen through the porous oxide scale occurs in an unabated manner. As a result, WO₃ grows continuously at the oxide–alloy interface of the W₀.₇Cr₀.₃ alloy. It is also noted from the results in Fig. 9 that the amount of degradation is significantly increased with increase in temperature due to simultaneous increase in diffusivities of both W⁴⁺ and O²⁻ ions. The evidence of damage in the W₀.₇Cr₀.₃ alloy after exposure for 15 h at 800 °C is presented in Fig. 16, which illustrates spheroidal precipitates located along the grain boundaries. The results of EDS elemental analysis confirm that these dispersed precipitates are Cr oxides. This observation suggests that internal oxidation is promoted in this alloy through short circuit diffusion of oxygen anions through the grain boundaries or interphase interfaces. Conversely, in the other two alloys, there is no evidence of internal oxidation. Internal oxidation is expected to accelerate the process of degradation, as both diffusion of the O²⁻ and localized dilution by formation of oxides at the alloy grain boundaries leads to generation of high internal stress, which in turn causes cracking followed by spallation. While the aforementioned mechanism of oxidation appears to be operative during exposure of the W₀.₇Cr₀.₃ alloy in the range of 800–1000 °C, the vaporization of WO₃ is expected to cause further degradation of the alloy at temperatures ≥ 1000 °C.

3.4. Impact of this study

The results of the present study have shown that sintering of W₁₋ₓCrₓ (x = 0.3, 0.5 and 0.6) alloys is possible at relatively low temperatures, without using any sintering activators like Pd or Ni. Subsequent cyclic oxidation studies on these alloys have shown that either Cr₂O₃ (at ≤ 800 °C) or W₂O₅ (at > 800 °C) provides an impervious protective scale, which can act as a barrier to the inward diffusion of oxygen. The oxidation resistance of all the alloys is a function of both the concentration of Cr and the temperature of exposure. All three investigated alloys have shown sound oxidation resistance at 800 °C. On increasing the temperature of exposure to ≥ 1000 °C, the alloys with 50 and 60 at.% Cr (W₀.₅Cr₀.₅ and W₀.₄Cr₀.₆) have shown superior oxidation resistance following more or less parabolic-rate kinetics. The oxidation resistance of the alloy with lower Cr content (W with 30 at.% Cr) is poor in the range of 1000–1200 °C, indicating that > 30 at.% of Cr would be required in the W–Cr alloy to form and maintain a stable protective oxide scales at temperatures up to 1200 °C.

4. Conclusions

(a) The average density achieved by sintering of nanocrystalline W–Cr elemental blends at 1700 °C for 5 h has been found to be ≥ 96%, which is nearly 8–10% higher than that of pure W sintered under similar conditions.

(b) Studies of the microstructures of sintered samples have shown crack-free surfaces, and dual phase microstructures with the presence of both W-rich (W₆₅) and Cr-rich (Cr₆₅) phases. In W₀.₅Cr₀.₅, the W₆₅ has mainly blocky appearance with channels of Cr₆₅ in between, whereas these phases exhibit lamellar morphology in W₀.₅Cr₀.₅ and W₀.₄Cr₀.₆. Among the investigated alloys, the W₀.₅Cr₀.₅ has shown the finest interlamelar spacing and more uniform distribution of both the phases, which in turn is responsible for its hardness (~112% of that of pure W) being more than those of the other investigated alloys.

(c) The cyclic oxidation tests at 1000 and 1200 °C have shown the oxidation resistance of W₀.₅Cr₀.₅ alloy to be superior to that of the alloy with higher or lower Cr content. Higher oxidation resistance of the W₀.₅Cr₀.₅ alloy compared to that of W₀.₇Cr₀.₃ is attributed to lower Cr content in the latter alloy, because it is insufficient for formation of a stable and protective oxide scale. On the other hand, the oxidation resistance of the W₀.₄Cr₀.₆ alloy has been found to be inferior to that of W₀.₅Cr₀.₅, because greater interlamellar area in the latter alloy leads to higher diffusion rate of Cr atoms, which in turn enhances the kinetics of the Cr-rich protective oxide scale.

(d) Examination of the oxide scale using XRD, SEM and EDS analyses suggests that the protective oxide scales formed on the surfaces of W–Cr alloys are mainly constituted by Cr₂WO₆, WO₃ and Cr₂O₃. The formation of Cr₂WO₆ in the oxide scale becomes more significant for protection against oxidation at temperatures ≥ 1000 °C, to prevent loss of volatile oxides, WO₃ and CrO₃.

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References


