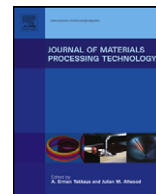




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## Effects of low-content activators on low-temperature sintering of tungsten

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## ABSTRACT

Tungsten compacts are processed by the activated sintering technique at low temperatures near 1200 °C, whereby either nickel, iron or a combination of the two are employed as additives. Despite very small contents of additives of a few monolayers and below, the processing technique is found viable for providing enhancing effects to the sintering kinetics of tungsten, and the sintered materials remain in the partially densified stage. Nickel is proved to be a superior activator, which induces a reduction of the activation energy as its content increases.

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## 1. Introduction

Owing to its very high melting point of 3422 °C, tungsten (W) has been a material of choice for a number of refractory uses including heating, electrical and welding applications. Commonly, W is processed by sintering which allows near-net shape manufacturing of components at temperatures below their melting points, and full sintered density can be achieved when temperatures as high as 2700 °C is employed. Research studies by German and Ham (1976) and German and Munir (1976) have however demonstrated that addition of Group VIII transition metals including Ni, Pd, Pt, Co, and Fe can beneficially enhance the sintering kinetics of W powder, and thus reduce its sintering temperatures. It was found that a sintering additive which is insoluble in W can segregate to the contact zone between W particles, provide a high diffusivity transport path for W atoms, and consequently lower the activation energy for bulk transport of W (Li and German, 1984; Hwang et al., 2000). To obtain high theoretical densities (TD) above 90%, German and Munir (1976) have shown that 4 monolayers of either Ni, Pd, or Pt are required as a W-additive for sintering in the temperature range of 1100–1400 °C.

While the prior studies on activated sintering have concentrated on highly densified W sintered compacts, fundamental studies

of W with low sintered density are limited. From the point of view of property control, functionality, and economics, partial sintering (~<80%TD) is in fact of importance for many applications, including those that benefit from the presence of porosity and weight reduction. For example, melt-infiltration processes for fabrication of metal matrix composites require preforms with interpenetrated open porosity (Peng et al., 2000), a tungsten component with high energy absorption capability can be engineered through an introduction of porosity (Boade, 1969), and finally, to provide decent emission properties, a high current density tungsten cathode impregnated with electron emissive materials must be partially-sintered (Selcuk and Wood, 2005). The development and understanding of effective routes for processing of partially densified tungsten components are thus essential. In this study, we therefore extend the prior studies on activated sintering of W and systematically examine the feasibility of the use of small contents of activators (i.e. <3 monolayers), namely Ni and Fe, to fabricate partially densified W sintered compacts. Various additive contents below 3 monolayers are investigated at different sintering temperatures in the low-temperature range near 1200 °C, and sintering properties, sintering mechanisms and activated energy of the systems are analyzed.

## 2. Experimental procedure

High purity W powder manufactured by GE Lighting Components (Cleveland, OH) is used in the study. The powder has a mean particle size of 1.2 μm, and contains negligibly low content of Ni

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and Fe of 0.0005 and 0.001 wt.%, respectively. Various contents of either Ni, Fe, or both Ni and Fe (1:3 and 3:2 weight ratios) additives, ranging approximately from 0.01% to 0.18% by weight, were incorporated into the base powder, resulting in 0.6, 1.3 or 2.6 average monolayer coverage of the sintering activators on the surface of W powders. The average monolayer coverage parameter,  $\bar{M}$ , is calculated by integrating monolayer coverage over the particle size distribution, assuming spherical particles:

$$\bar{M} = \frac{\int P(r)r/2a[(1 + c\rho_w/\rho_a(1 - c))^{1/3} - 1] dr}{\int P(r) dr} \quad (1)$$

where  $r$  is the particle radius of W,  $P(r)$  the number population of W powders at any particle size,  $c$  and  $a$  the concentration and atomic radius of sintering activators, respectively, and  $\rho_w$  and  $\rho_a$  the theoretical densities of W and additives. Sintering activators generally can be added to W with an aqueous deposition method (Li and German, 1984) or a dry mixing method (Moon et al., 1984). While the first can result in a more uniform coating, the latter is practically useful for an industrial setting and thus was chosen for this study. In particular, Ni (2.2–3  $\mu\text{m}$ ) and Fe (1–3  $\mu\text{m}$ ) powders were added to the W powder and the materials were mixed in a high-energy powder mixer for 30 min.

Following dry mixing, green compact specimens were prepared using a single-action cold press and a stainless-steel die of rectangular cross section. A compaction pressure of 21 MPa was employed, resulting in compact densities of 50%TD, with specimen dimension of 25 mm  $\times$  8 mm  $\times$  3 mm. These green specimens were then sintered in a furnace programmed with a heating rate of 5  $^{\circ}\text{C}/\text{min}$  and an isothermal hold at 1177  $^{\circ}\text{C}$  for either 0.5, 1 or 2 h. Additionally, some sets of specimens were sintered isothermally at 1200 and 1250  $^{\circ}\text{C}$  for 0.5 h. In all cases, slow furnace cooling was employed after firing. To prevent the oxidation of W, the processing was carried out in a dry 3%  $\text{H}_2$ –97%  $\text{N}_2$  atmosphere. At least two specimens were prepared for each processing condition, and for comparison, sintered W specimens containing no additives were also prepared using similar processing procedure. After sintering, sintering properties including linear shrinkage ( $\Delta L/L_0$ ) and sintered density ( $\rho_s$ ) were determined from the measured mass and dimensions of the as-fired specimens. Microstructure of the specimens was examined using a scanning electron microscope.

### 3. Analysis of sintering kinetics

The controlling sintering mechanism and the activation energy for diffusion of W atoms can be determined by examining their sintering kinetics. In the initial stage of sintering, linear shrinkage of a material,  $\Delta L/L_0$ , may be assumed to follow (Kang, 2005):

$$\frac{\Delta L}{L_0} = \left(\frac{Kt}{T}\right)^m \quad (2)$$

$$\text{where } K = B \exp\left(\frac{-Q}{R_g T}\right) \quad (3)$$

In Eqs. (2) and (3),  $K$  is a diffusion coefficient,  $B$  a constant which relates to diffusivity, surface energy, atomic volume, and particle size,  $t$  time,  $T$  temperature,  $Q$  activation energy for atomic diffusion,  $R_g$  the gas constant (8.3 J/mol K), and  $m$  a sintering exponent whose value depends on the dominant diffusion mechanism. For grain boundary diffusion, volume diffusion and viscous flow, the values of  $m$  are 0.33, 0.5, and 1 respectively (Kang, 2005). According to Eq. (2),  $m$  may be estimated from a slope of a log–log plot of linear shrinkage versus time at a constant temperature. Using a fixed value of linear shrinkage and corresponding sintering time presented in isothermal log–log shrinkage–time plots, the value of  $K$  can also be

determined. Finally, from Eq. (3), the value of  $Q/R_g$  can be obtained from the slope of a  $\ln(K) - 1/T$  plot, following the general procedure discussed in Pathak (2004) and Kang (2005).

### 4. Results and discussion

Fig. 1 presents the linear shrinkage and sintered density of W specimens prepared at 1177  $^{\circ}\text{C}$  for 1 h as a function of types and contents of additives. For all specimens containing additives, sinterability was enhanced over that of the pure W specimen, whose linear shrinkage and sintered density were respectively 0.5% and 51.4%TD. With low-firing temperature of  $\sim 1200$   $^{\circ}\text{C}$  and very small additive content below 3 monolayers, all W sintered compacts were partially sintered with sintered density below 70%. In particular, the microstructure of the specimens comprised of irregular pores and W particles that were bonded to one another, indicating that sintering remained in the initial stage. Details of the microstructure of activated W compacts sintered at low temperatures are discussed by Boonyongmaneerat (2007).

The data in Fig. 1 also illustrates that Ni is a very effective sintering activator as compared to Fe, and that the sintering of W is enhanced with increasing amount of Ni added. On the other hand, sintering improved with an increase of Fe content until it reached 2.6 monolayers, after which a drop in linear shrinkage and density was detected. The observation that Ni helps activate the sinterability of W more pronouncedly than Fe agrees well with previous studies (German and Munir, 1976; Li and German, 1984). With the use of 2.6 monolayers of Ni, which is the maximum impurity content employed in this study, maximum shrinkage and sintered density of 7.8% and 65.4%TD, respectively, were obtained.

Activated sintering process was enabled when both Ni and Fe were used together (Fig. 1). With the same monolayer coverage, W specimens containing both Ni and Fe additives with the weight ratio of 3:2 appeared to sinter better than those with 1Ni:3Fe. This may be due to the higher content of Ni, the superior activator, present in the first case. Alternatively, this may be explained by considering the co-existing phases of the materials upon sintering, using a W–Ni–Fe pseudo-binary phase diagram (Raynor and Rivlin, 1981). Unlike W with 1Ni:3Fe additive, that with 3Ni:2Fe additive avoids the formation of intermetallic phases, which can inhibit W transport during sintering. Consequently, it may be expected that the activation energy for diffusion of W atoms is relatively low for W

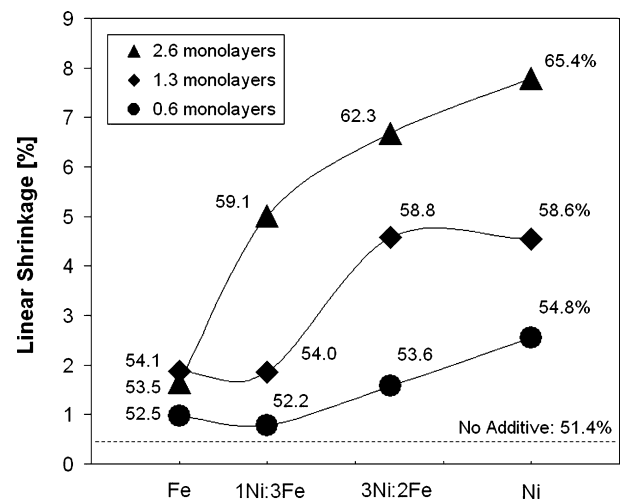
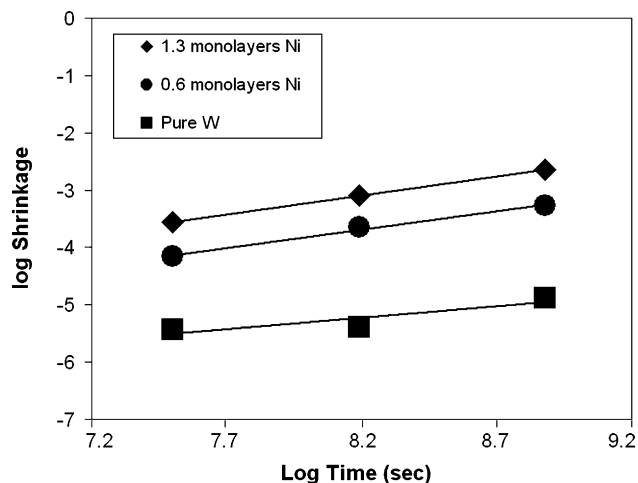


Fig. 1. Linear shrinkage of W compact specimens, which were activated by Fe and Ni at various concentrations, and were sintered at 1177  $^{\circ}\text{C}$  for 1 h. The sintered densities (in % theoretical density) are indicated next to the data points.

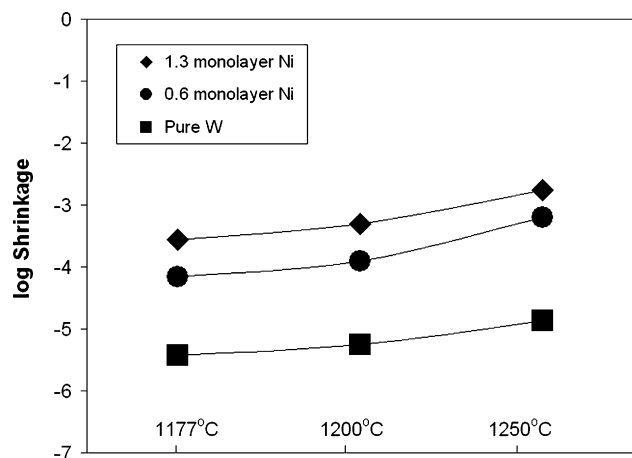


**Fig. 2.** Natural log–log plot of linear shrinkage of W compacts and time. The specimens contained various contents of Ni activator and were sintered at 1177 °C for 0.5, 1, and 2 h. Sintering exponents ( $m$ ) can be determined from slopes of the trendlines.

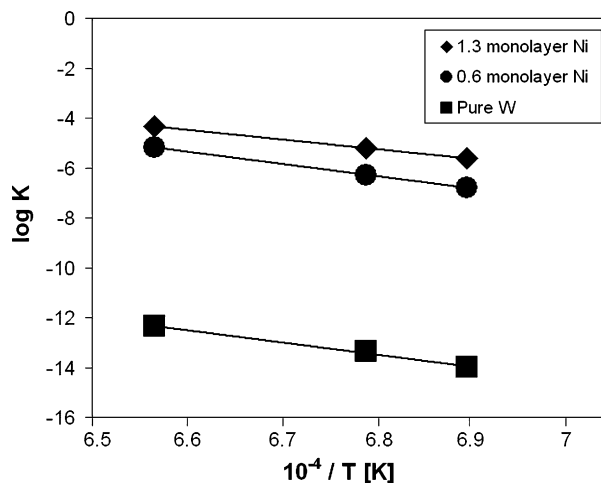
with 3Ni:2Fe additive. From the experiment, it was also observed that the degree of sintering of W was generally higher in the case of specimens containing only Ni additives, as compared to those with both Ni and Fe of the same total monolayer coverage.

Fig. 2 shows a log–log shrinkage versus time plot of W specimens that contained 0, 0.6, and 1.3 monolayers of Ni additive and were sintered at 1177 °C for 0.5, 1, and 2 h. In Fig. 3, shrinkage of the specimens prepared at 1177, 1200, and 1250 °C for 0.5 h is presented as a function of processing temperature. The results shown in these figures indicate that sintering of W was improved with an increase of sintering time or temperature, as can be anticipated. Using the data provided in Figs. 1 and 2 and Eq. (2) and assuming that, within this narrow range of sintering temperatures of concern (1177–1250 °C), the controlling diffusion mechanism of any particular set of materials is the same at different temperatures, the values of diffusion coefficients ( $K$ ) at different processing temperature could be derived, and they are plotted as a function of  $1/T$  in Fig. 4. Parameters  $m$  and  $Q$  of the sintered compacts determined from the slopes of trendlines shown respectively in Figs. 2 and 4 are tabulated in Table 1.

For the case of W without additives, the sintering exponent ( $m$ ) was determined as 0.40. This is comparable to the expected value of sintering exponent for grain boundary diffusion mechanism (0.33),



**Fig. 3.** Linear shrinkage of Ni-activated W compact specimens isothermally sintered at various temperatures for 0.5 h.



**Fig. 4.** Natural log of diffusion coefficient ( $K$ ) of the W sintered compacts with and without Ni activators, plotted as a function of inverse temperature. Slopes of the trendlines give  $Q/R_g$ .

and therefore it is suggestive that, for the case of pure W, the dominant diffusion mechanism involves the transportation of W atoms from grain boundaries (i.e., interparticle boundaries) to interparticle neck regions. The activation energy ( $Q$ ) for this process was determined to be 404 kJ/mol, in agreement with prior studies which reported the activation energy for sintering of pure W between 380 and 460 kJ/mol (Kothari, 1963; Hayden and Brophy, 1964).

As a minority content of Ni (0.6 monolayers) was introduced, the sintering exponent ( $m$ ) was found to increase from that observed in the pure W case to 0.64. This value is slightly higher than the sintering exponent proposed for the volume diffusion mechanism (0.50), and the deviation may be attributed to competitive diffusion mechanisms that occurred simultaneously. The apparent activation energy in this case was found to be 406 kJ/mol, which is comparable to that observed in the case of pure W. The results, therefore, suggest that when a minimal content of Ni was introduced to W, the dominant diffusion mechanism starts to shift from grain boundary diffusion to volume diffusion which involves migration of diffusing species from grain boundary to sintered neck surface through the particle interior. In this case, the “particle interior” could be the activator-rich layer along the surface of W particles. With this very small content of Ni, the increase in diffusion rate arises from the change of dominant transport mechanism without an observable change in activation energy.

When the content of Ni additive was increased to 1.3 monolayers, the sintering exponent ( $m$ ) was determined to be 0.66, which was similar to the case with lower Ni content, suggesting a similar material transport mechanism in the two systems. The activation energy for diffusion ( $Q$ ), however, decreased significantly to 315 kJ/mol. With this reduction in energy barrier for diffusion, the sintering kinetics of W containing 1.3 monolayers of Ni was evidently much faster than that with 0.6 monolayers. Comparing the results obtained here with the activation energy for sintering of W with 4 monolayers of Ni, 280 kJ/mol as reported by German and

**Table 1**  
The sintering exponent ( $m$ ) and the apparent activation energy for sintering ( $Q$ ) of W specimens with and without Ni additives.

Material	$m$	$Q$ (kJ/mol)
Pure W	0.4	404
W + 0.6 monolayer Ni	0.65	406
W + 1.3 monolayer Ni	0.66	315

Munir (1976), it can be seen that activation energy is reduced with increasing activator content.

## 5. Conclusions

The addition of sintering activators, namely Ni and Fe, resulted in the improvement of the sinterability of W powder. In the regime of small activator content, particularly less than 3 monolayers, and low processing temperatures near 1200 °C investigated in the study, the activated W compacts were partially sintered and remained in the initial stage of sintering. Using a dry-mixing processing technique, Ni was found superior to Fe and a combination of Ni and Fe in enhancing the sintering kinetics of W compacts. The sintering exponent was increased when Ni activator with content as small as below 1 monolayer was added, indicating a change of the dominant sintering mechanism from grain boundary diffusion found in pure W. With increasing content of Ni, a reduction of the activation energy occurred, and led to the increase of the diffusion coefficient, explaining fast sintering kinetics of the activated materials. The fundamental studies presented here therefore have provided an insight into the process of activated sintering with minimal additive content, and shown the viability of the process which may be applied for fabrications of partially densified materials for various engineering applications.

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