

SOLID-STATE SINTERING OF TUNGSTEN HEAVY ALLOYS

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ABSTRACT

Solid-state sintering is a technologically important step in the fabrication of tungsten heavy alloys. This work addresses practical variables affecting the sinterability: powder particle size, powder mixing, and sintering temperature and time. Compositions containing 1 to 10 micrometer (μm) tungsten (W) powders can be fully densified at temperatures near the matrix solidus. Blending with an intensifier bar provided good dispersion of elemental powders and good as-sintered mechanical properties under adequate sintering conditions. Additional ball milling increases powder bulk density which primarily benefits mold and die filling. Although fine, 1 μm W powder blends have high sinterability, higher as-sintered ductilities are reached in shorter sintering times with coarser, 5 μm W powder blends; 10 μm W powder blends promise the highest as-sintered ductilities due to their coarse microstructural W.

INTRODUCTION

Tungsten heavy alloys are pressed and sintered from elemental powders of W, nickel (Ni), iron (Fe), and/or cobalt (Co), and sometimes copper (Cu). Alloys of $>85\%$ W can be liquid-phase (LP) sintered to high densities but with some slumping and loss of shape that diminishes as the W content increases. The slumping can be controlled by first solid-state (SS) sintering to full density and potting the part in refractory "sand" before the LP sintering. Alloys $<85\%$ W must be SS sintered to avoid "settling" of the W phase⁽¹⁾ as well as severe slumping; such low W alloys can be worked and SS annealed into materials having the consistently high ductilities and strengths typical for a wrought material.⁽²⁾ For these reasons the SS sintering of the full range of W heavy alloys to full, 100%, densities is of interest.

(a) Operated by Battelle Memorial Institute for the U.S. Department of Energy.

This work addresses some of the primary variables affecting SS sintering: W powder particle size and powder mixing; sintering data were developed for alloys of 40%, 70%, 80%, and 90% W, alloyed with either Ni-Fe or Ni-Co. Tungsten powders used were limited to some of those commercially available and do not include specially prepared, sub-micron powders such as freeze-dried powders⁽³⁾ which are highly sinterable, sintering to full density several hundred degrees Celsius below the matrix melting temperature, 1460°C. Nickel, Fe, and Co elemental alloying additions activate the SS sintering of W powders to high densities,⁽⁴⁾ sintering being further enhanced by smaller W particle sizes.⁽⁵⁾ However, the highest ductilities and lowest hardnesses are obtained from larger as-sintered W particle sizes in both LP sintering⁽⁶⁾ and in SS sintering;⁽²⁾ for this reason, the sinterability of powder mixes using 10 μm W powders is investigated in addition to the typical 1 and 5 μm W powders.

EXPERIMENTAL PROCEDURES

The characteristics of the powders used are listed in Table 1. The W particle sizes measured after laboratory milling (listed in parentheses) are thought to most closely represent the true, deagglomerated W particle size (the W powder agglomerates are -200 mesh, and the Fe, Ni, and Co agglomerates are -300 mesh). The weighed elemental powders mixtures were blended in a twin-shell blender for 30 min with the intensifier bar running 1 min of every 5 min.

Table 1. Powder Characteristics

Powder	Source/Grade	Particle Size, $\mu\text{m}^{(a)}$	Apparent Density, $\text{g}/\text{cm}^3^{(b)}$	C, ppm	O, ppm
1- μm W	Teledyne Wah Chang/C5	1.12 (1.00)	2.01	32	880
5- μm W	Teledyne Wah Chang/C10	4.60 (3.68)	3.57	8	160
10- μm W	Teledyne Wah Chang/C40	13.00 (10.00)	3.75	1	100
Ni	INCO 123	4.07	1.93	650	610
Fe	GAF HP	6-8 typ.	1.9 max	1000	3000 max
Fe	BASF CM	6.2	--	200	2000
Co	Carolment EF	1.39	1.02	300 max	5300

(a) Fisher subsieve size, American Society for Testing and Materials (ASTM) B330. Particle size in parentheses taken after lab milling.

(b) Scott Volumeter, ASTM B329.

Except where noted the blended powders were dry ball milled for 16 hours to break up agglomerates, provide intimate mixing, and uniformly disperse the elemental powders. The milling was done in 1 gallon, rubber-lined jars using typical dry grinding parameters: jar half filled with 1/2-in. diameter, 440 stainless steel balls, powder volume equal to 1/4 the mill volume, and mill speed equal to 65% of the critical speed (62 rpm).

The milled powders were either isostatically pressed at 27 kips per square in. (ksi) (without lubricant) or uniaxially pressed at 40 ksi with lithium stearate die-wall lubricant, and sintered in a cold-wall furnace with 100% hydrogen atmosphere (typical dew points of -20°C). Typical heating rates were $500^{\circ}\text{C}/\text{h}$, and included a 1-hour hold at 900°C and a 1-hour ramp to 1100°C during heating for oxide reduction.

Green densities were measured from dimensions and mass. As-sintered immersion densities were measured according to ASTM B311. Tensile tests, according to ASTM E8, were run at 0.01 in./min to the yield point and then 0.05 in./min to failure. Tensile bars were either MPIF standard powder bars or they were machined from as-sintered slabs to ASTM E-8 dimensions.

EFFECTS OF BALL MILLING

Three alloys were studied: 1) 40% W ($1\ \mu\text{m}$) with Ni/Fe ratio of 8/2 (using the BASF CM Fe), 2) 70% W ($5\ \mu\text{m}$) with Ni/Co ratio of 2/1, and 3) 80% W ($5\ \mu\text{m}$) with Ni/Co ratio of 2/1. The starting ball mill powder loadings for equal volumes were dependent on the calculated bulk density of the elemental powder alloy mixes and were 4400 g, 5000 g, and 5500 g, respectively. As-blended powders were ball milled as described previously and 100 g samples of powder were withdrawn periodically to follow the progress of milling induced changes in powder density and sinterability.

For each 100 g sample the "pour density" was measured by gently spooning the 100 g sample into a 100 graduated cylinder, and the "tap density" was measured after vibrating the loaded graduated cylinder for 3 min on an oscillating drum packer. Cylindrical pellets, 0.45-in. diameter by 0.45 in. long, were uniaxially pressed at 40-ksi and sintered at 1425°C for either 1 or 3 hours.

The effects of ball milling time are shown in Figure 1, where densities are plotted as percent of theoretical (11.1, 14.1, and 15.5 g/cc for the 40% W, 70% W, and 80% W alloys, respectively). There is a remarkable similarity in behavior for all three alloys despite the wide variation in W content and the Fe and Co alloying elements. As shown in Figure 1, the "pour" and "tap" densities were significantly increased during the first 3 hours of milling, which certainly benefits mold or die filling. Conversely, green strength (qualitatively measured by hand on 1/8-in.-thick uniaxially pressed pellets) decreased continuously with milling time (i.e., the edges chipped easier and the bend strength fell with time). Although green densities are not strongly affected by milling, short-time, 1 hour, as-sintered densities are improved significantly, climbing from near 93% to 96% with 15 hours of milling.

However, with longer (3 hours) sintering time, density increases for all milling times, and the range is much narrower, between approximately 97.5% and 99%.

Except for a drop in porosity as density increased, there was little microstructural change in the sintered samples with milling time; very little change in the degree of W dispersion or in W particle size was observable after sintering. Milling did not influence the tensile properties of MPIF bars sintered for 3 hours, as shown in Table 2; in fact, the tensile properties of both the 70% W and 80% W alloys from unmilled powders are adequate for subsequent hot working. At the longer milling times the MPIF tensile bar pressings cracked and laminated during pressing, again indicating lowered, and for these uniaxial pressings, inadequate green strength; isostatic pressings, however, could be made from even the longest-milled powders.

EFFECTS OF W PARTICLE SIZE

Since W powder is a large fraction of most W heavy alloys, the W particle size has a controlling influence on sinterability, as well as as-sintered mechanical properties. These effects were investigated

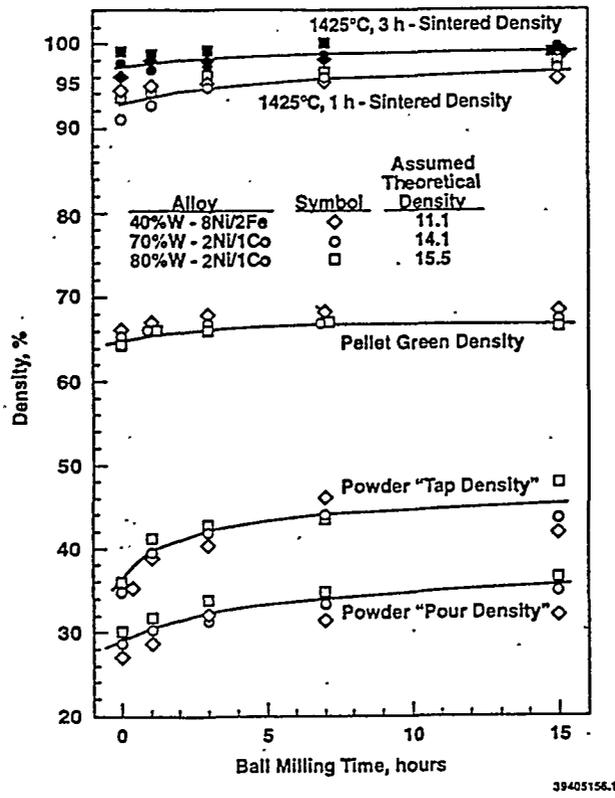


Figure 1. Effect of ball milling time on powder and pellet densities for 40% W, 70% W, and 80% W alloys.

Table 2. Influence of Ball Milling Time on As-Sintered Tensile Properties of 70% W and 80% W Alloys (alloyed with 2Ni/1Co and sintered 3 hours at 1425°C)

Milling Time - h	Density - g/cc	Yield Strength - ksi	Ultimate Strength - ksi	Elongation - %
<u>70% W</u>				
0 (as-blended)	13.83	78	151	33
1	14.00 (14.1)	80	160	32
3	14.10	85	163	35
7	} cracked or laminated during pressing at 40 ksi			
15				
<u>80% W</u>				
0	15.36	89	155	20
1	15.49 (15.5)	92	158	20
3	} cracked or laminated during pressing at 40 ksi			
7				
15				

using powder mixtures made from 1, 5, and 10 μm W powders (Table 1) that were milled, isopressed, and sintered in hydrogen according to the procedures described earlier. The most complete data were developed for the 70% W alloy; complementary data for 80% W and 90% W alloys are also presented.

The sinterabilities of 70% W alloys using 1 and 5 μm powders is illustrated in Figure 2. The high sinterability of powder mixtures containing 1 μm W is readily apparent; high densities are reached at relatively low temperatures and short times. As sintering time and temperature increase, hardness falls (Figure 2) as the W particles coarsen (Figure 3). For the less sinterable 5 μm W powder mix, hardness increases continuously with density, full densification being attained above 1 hour and 1400°C.

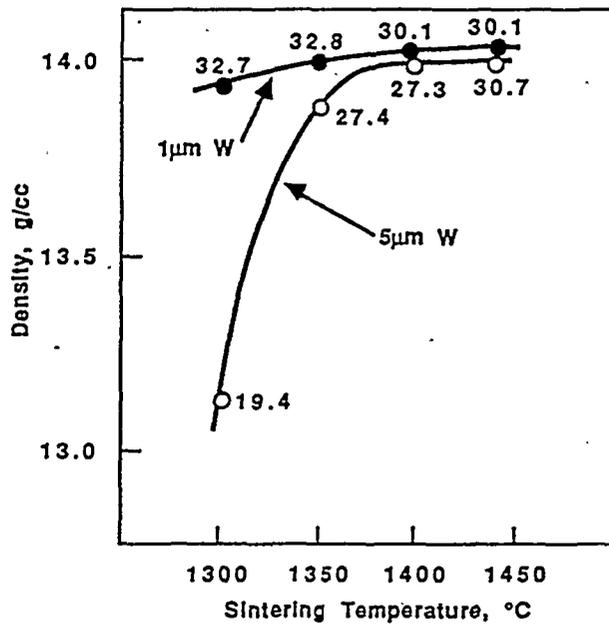
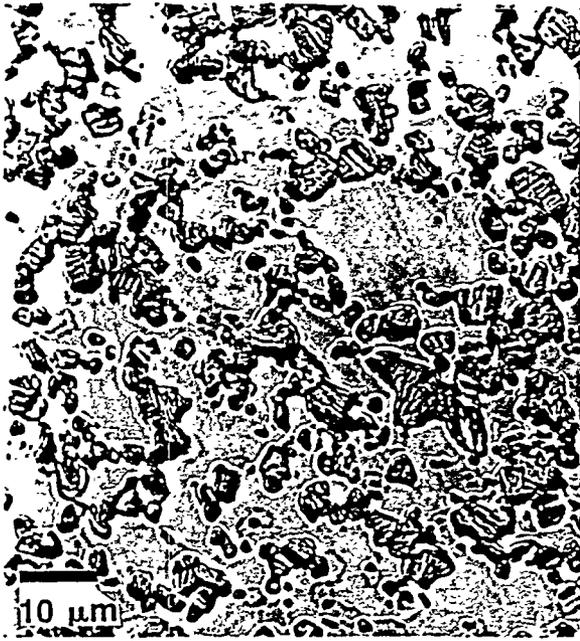
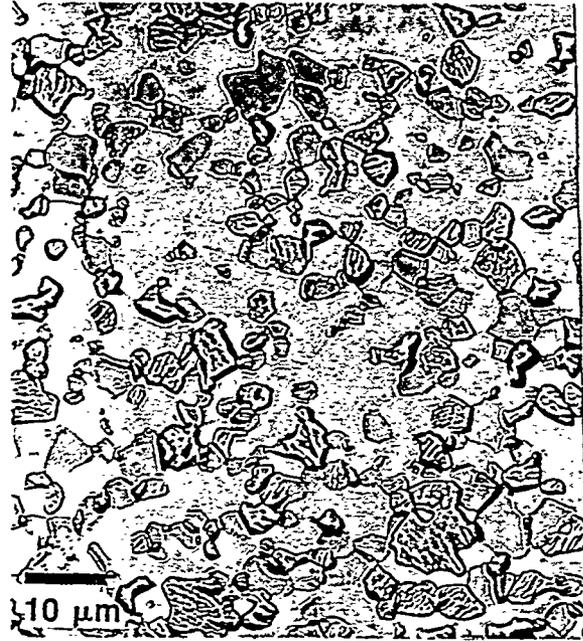


Figure 2. Sintered Density of 70% W Alloy as a Function of Sintering Temperature (1 hour at temperature) and W Powder Size (as-sintered hardness, HRC, indicated at each data point)

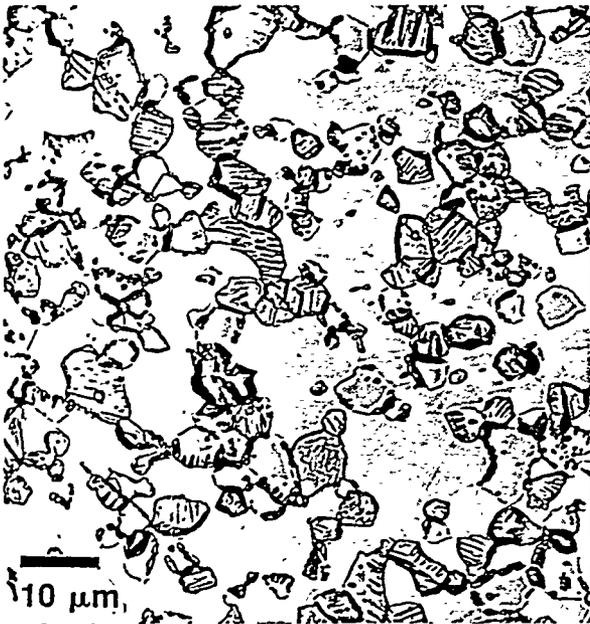
Tensile properties for fully densified, 14.0 g/cc, 70% W alloys are given in Table 3; although the hardness of all specimens was HRC (Rockwell "C" hardness) 30 ± 1 , there are significant differences in yield strength and elongation which are related to microstructural W particle size. After 1 hour at 1400°C the 1 μm W mix is fully densified, but has relatively high yield strength and low elongation, which is due to the microstructural fineness, shown in Figure 3a. In contrast, 5 μm W mix reaches a ductile state of high elongation combined with low yield strength after only 1 hour at 1440°C; 4 hours at 1440°C are required for the 1 μm W mix to approach the same properties, and similar W microstructure as shown in Figures 3c and 3d. The slightly lower ductility for the 1 μm W mix (after 4 h—1440°C) relative to the 5 μm mix (after 1 h—1440°C) with similar W particle size may be due to higher carbon content in the 1 μm W powder (Table 1). (As-sintered oxygen contents were similar for both 1 μm W and 5 μm W mixes, ranging from 8 to 12 ppm.) The one necessary conclusion from this information is that while finer W mixes are more sinterable, longer sintering times are required to reach maximal ductilities, which are slightly lower than that obtainable from a coarser W powder mix. Therefore, the optimal choice is the coarsest W powder mix that will sinter to full density in a reasonably short time, say 1 to 3 hours.



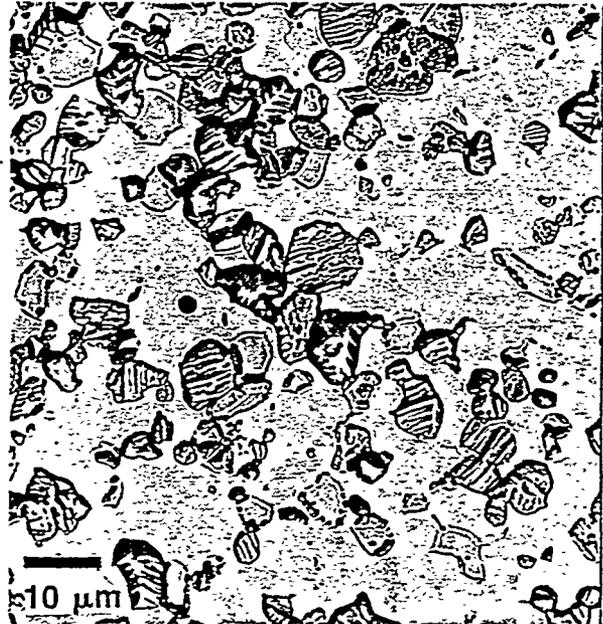
(a) 1 μm W, 1 h—1400°C



(b) 1 μm W, 1 h—1440°C



(c) 1 μm W, 4 h—1400°C



(d) 5 μm W, 1 h—1440°C

Figure 3. As-sintered 70% W microstructures. (Note definite coarsening of the 1 μm W powder billets with increasing temperature and time: a, b, and c. Compare (b) and (c) with 5 μm W powder billet (d) after sintering at 1440°C for 1 hour.)

Table 3. Sintered Properties of 70% W Alloys from 1 and 5 μ m W

Sinter Cycle ^(a)	W Size μ	Yield ksi	Ultimate ksi	Elongation %
1400°C - 1 h	1	93	146	20
1440°C - 1 h	1	87	146	25
	5	81	141	38
1440°C - 4 h	1	81	144	30
	5	80	142	34
1440°C - 6 h	1	82	143	30
	5	79	140	34

(a) Vacuum degassed 30 min at 1000°C after sintering and machining into 0.17-in.-thick tensile bars. Sintered density of all specimens was 14.0 g/cc.

Alloys of 80% W and 90% W have sinterabilities, similar to the 70% W alloys, as shown in Figure 4. With 5 μ m W powder mixes, high densities are reached in a few hours; Figure 5 contains typical microstructures.

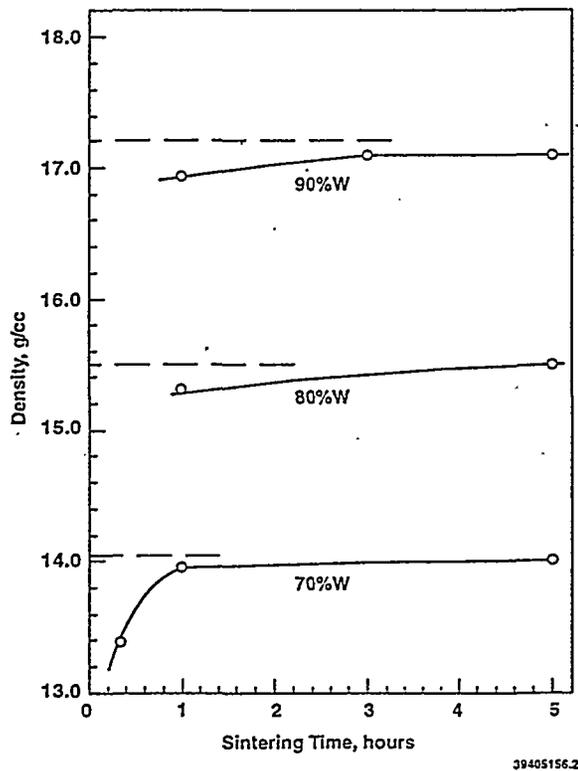


Figure 4. Sintering curves for alloy powders made with 5 μ m W. (Dashed lines indicate 100% densities. 90% W: 8Ni/2Fe at 1425°C; 80% W: 8Ni/2Fe at 1425°C; 70% W: 7Ni/3Fe at 1400°C.)

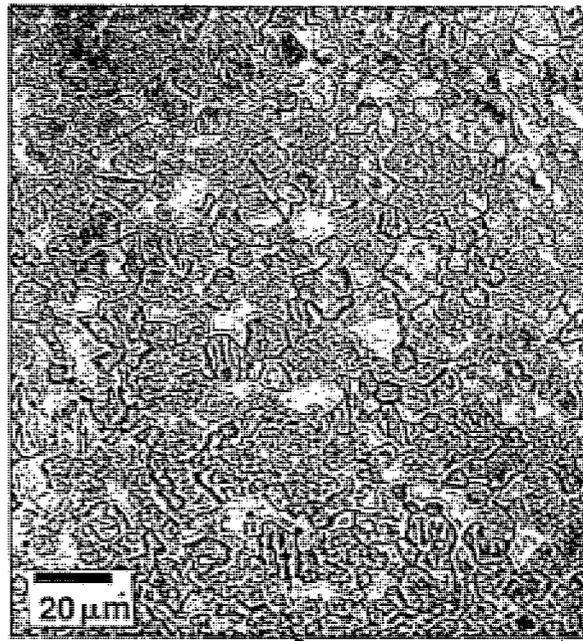
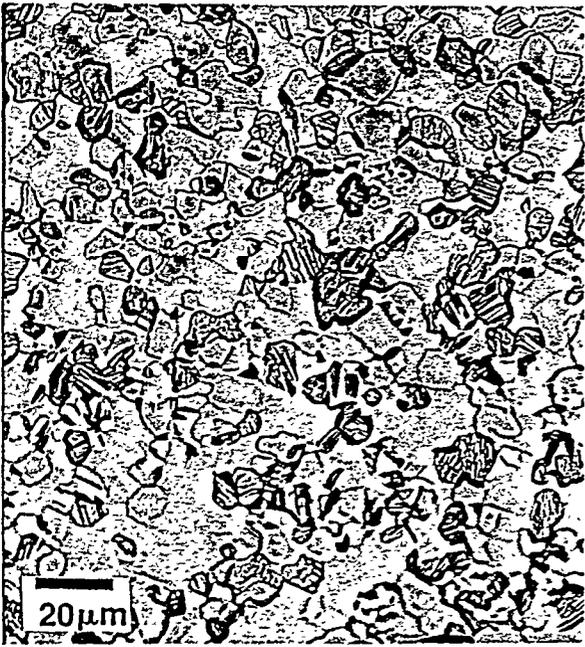


Figure 5. As-sintered microstructures of 80% W (left) and 90% W (right) alloys from 5 μm W Powder (sintered 5 hours at 1425°C).

Based on the conclusion that the coarsest W powder mix will yield optimum as-sintered ductiles, the sinterability of coarse, 10 μm W powder mixes was investigated for 70%, 80%, and 90% W alloys. It was quickly learned that full densification could not be reached; some finer W powder had to be substituted to enhance sinterability. Addition of fine powder may compromise the expected ductility gains from 10 μm W powder; however if a very fine, say 1 μm , W is added, the compromise may be negligible for two reasons:

1. During SS sintering, W coarsening occurs; that is, W dissolved preferentially from the small grains is transported to the large grains by diffusion. The finer the W substitution, the higher its solubility relative to the 10 μm W grains⁽⁷⁾ and therefore the higher the driving force for coarsening. Coarsening also occurs more rapidly at higher W contents because the diffusion path through the matrix is shorter and there is more grain boundary contact area.⁽³⁾
2. The matrix will hold a significant amount of the 1 μm W in solid solution: If 30% W solubility in the matrix is assumed (typical for Ni/Fe ratio of 8/2), 13% of the 70% W in the 70% W alloy goes into solid solution; the amount of W going into solid solution decreases with total W content, to 9% in the 80% W alloy and 4.3% in the 90% W alloy.

Following this reasoning, alloys of 70%, 80%, and 90% W were formulated with 0 to 30% of 1 μm W substituted for the 10 μm W. They were milled, isopressed and sintered at 1425°C and 1440°C for 1 to 5 hours. The resulting sinterability curves are shown in Figure 6. It is readily apparent that the higher W alloys require more substitution of the 1 μm W, due to the increasing dominance of 10 μm W particles on sinterability relative to the finer Ni and Fe. It is also apparent that the 1440°C sintering temperature enhances sintering markedly relative to 1425°C; this result implies that optimal SS sintering should be done as close as possible to the matrix solidus ($\sim 1460^\circ\text{C}$) as practical. Skirting closely to the solidus will require accurate and uniform temperature control (burying the parts in "refractory sand" promotes temperature uniformity within the part). Selected high

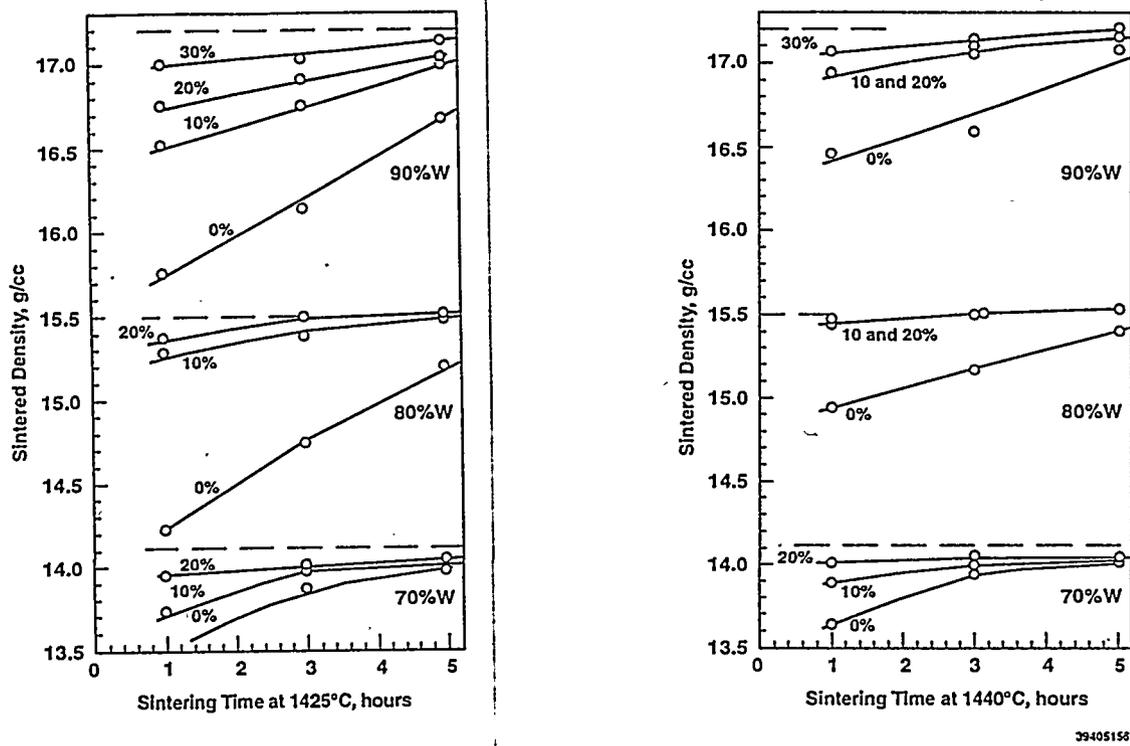


Figure 6. Sintered densities of 70%, 80%, and 90% W alloys made with 10 μm W as a function of sintering time $^{\circ}\text{C}$ and amount of 1 μm W substituted for the 10 μm W (e.g., 90% W powder with 30% 1 μm W has 60%-10 μm W). (Theoretical densities indicated by dotted line. Left: 1425 $^{\circ}\text{C}$ Sintering Temperature. Right: 1440 $^{\circ}\text{C}$ Sintering Temperature.)

density microstructures of the three alloys with 10% 1 μm W substituted, Figure 7, illustrate the coarse, and potentially high ductility, microstructures available from 10 μm W powders. Compare these with the microstructures shown in Figures 3 and 5.

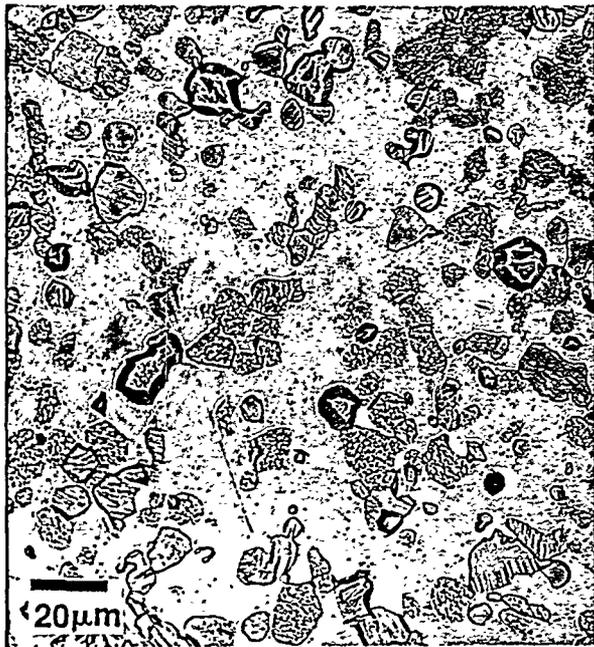
CONCLUSIONS

Tungsten heavy alloys can be SS sintered to full, 100% densities through the use of blended and milled powders that are conventionally pressed and sintered at sub-solidus temperature. Alloying additions of 8Ni/2Fe, 7Ni/3Fe, and 2Ni/1Co are equally sinterable.

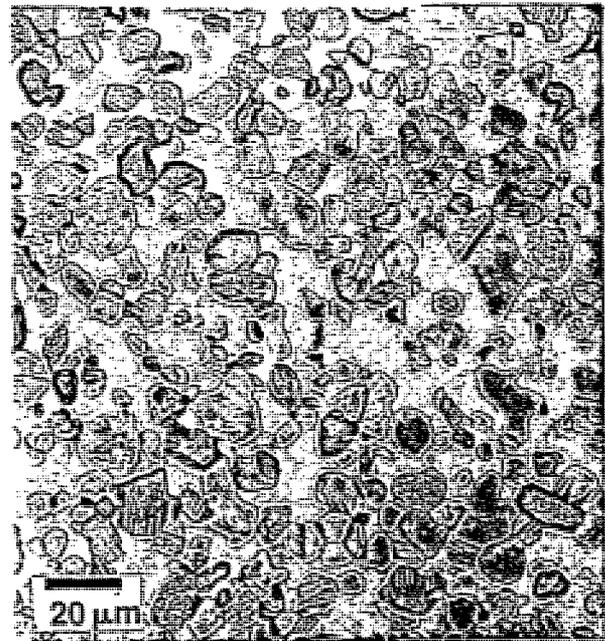
Densification is sensitive to sintering temperature. There is economic incentive to crowd close to the solidus temperature to significantly reduce sintering time and thereby increase furnace throughput.

Blending with an intensifier bar provided adequate dispersion of elemental powders and good as-sintered tensile properties. Ball milling increased powder bulk density (which benefits mold or die filling), pressed densities and, under marginal sintering conditions, sintered densities. With adequate sintering temperature and time, the influence of ball milling on sintered densities diminishes.

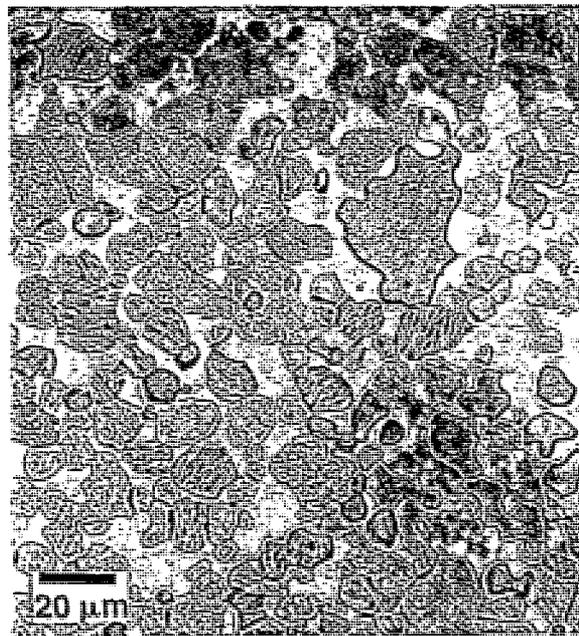
Fine, 1 μm W powders enhance sinterability, but at short sintering times as-sintered ductilities are low and yield strengths are high. Long sintering times are required to coarsen the W particles in the microstructure in order to reach optimal ductility. 5 μm W powders lead to somewhat higher ductilities with short sintering times at 1440 $^{\circ}\text{C}$. These conclusions, for 70% W alloys should apply to other



70% W



90% W



80% W

Figure 7. As-Sintered Microstructures of 70% W, 80% W, and 90% W Alloys Made Using 10% 1 μm W Powder, Remainder 10 μm W Powder (8 Ni/2Fe ratio)

W contents as well. Coarser, 10 μm W powders require the substitution of some 1 μm W powder for adequate sinterability; these materials promise the highest as-sintered ductilities due to their coarse microstructural W.

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