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Review

# Lower sintering temperature tungsten alloys for space research

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ABSTRACT

In the early 1900s the sintering temperature for tungsten was 2800 °C or higher. At that time direct electrical discharge (self-heating) was used to induce sintering densification. A reduced sintering temperature for tungsten arose in forming radiation containment structures. By 1938 the sintering temperature was 1500 °C for tungsten alloyed with Ni–Fe or Ni–Cu using liquid phase sintering. Activated sintering arose between 1946 and 1961, relying on low concentrations of Pd, Pt, Ni, or other late transition metal additions, enabling densification at temperatures in the 1200 to 1400 °C range. In 1991, W–Ni–Mn alloys were identified and became the precursor to W–Ni–Cu–Mn alloys that densify at 1200 °C, a temperature associated with steel sintering. The lower sintering temperature W–Ni–Cu–Mn system is now critical to research on microgravity processing (densification, distortion, and coarsening) since it matches with furnace capabilities on the International Space Station. Details on the experiments are given in this article.

**Contents**

## 1. Introduction

One of the early important applications for sintering was tungsten for use in lamp filaments [1–3]. This review examines the progressive change in tungsten sintering temperature and the recent evolution of low sintering temperature formulations designed for microgravity processing on the International Space Station.

Initially it was a struggle to attain the high temperatures required to sinter tungsten. Sintered ingots were required as precursors to wire drawing. Self-heating by direct current discharge was one of the few means to reach the required high temperature. In essence, the idea of spark sintering arose from Acheson's developments in the late 1800s and Moissan's *Electric Furnace* publication in the early 1900s. Sintering using current discharge was applied to incandescent lamp filaments by Voelker [4], and subsequently tungsten filaments by Lux [5] and Coolidge [6]. Subsequent trials employed pulsed currents and external pressure, in what is termed resistance sintering under pressure [7]. Variants today include spark sintering, spark plasma sintering, and various electric field assisted sintering concepts.

Low sintering temperature tungsten alloys are applied when elevated temperature properties are not a concern; for example in ammunition, projectiles, radiation shields, watches, sporting equipment, wing weights, vibrators, machining supports, and other inertial components. For microgravity research, tungsten alloys provide the high density desired to amplify the role of gravity in small samples [8]. Indeed, tungsten alloys are a mainstay for isolating the gravitational role in sintering [9–21]. Now microgravity sintering research is moving to the International Space Station using the European Space Agency's Low Gradient Furnace. Unfortunately the new facility only operates to a maximum

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temperature of 1200 °C. To accommodate this limitation, while employing large solid–liquid–vapor density differences, requires new low sintering temperature tungsten composites. Accordingly, research was required to develop W–Ni–Cu–Mn compositions for microgravity sintering.

## 2. Background

Table 1 gives an outline of the historically significant steps in reducing the sintering temperature for tungsten compositions [22–31]. For pure tungsten, direct sintering (also termed spark sintering) provided ingots needed for wire drawing. Subsequently, liquid phase sintering provided desirable radiation containment materials using tungsten sintered with Ni–Cu or Ni–Fe additions [23,24,32]. Lower sintering temperature compositions (W with Ni–Cu–Mn, Cu–Sn–Fe, Co–Mn, Ni–Mn, or Ni–Fe–Mn) densify at 1100 to 1300 °C [28–37]. Recent focus has been on 1200 °C sintering as possible with W–Ni–Cu–Mn alloys [31]. It is noteworthy how these compositions are sintering in the temperature range associated with ferrous powder metallurgy.

Early tungsten sintering was driven by the desire to form durable filaments for incandescent lamps. The precursor to today's incandescent light was patented in 1874 by Woodward and Evans. They sold the patent to Edison, who used an evacuated version with carbon filament to achieve 13 h life in 1879, becoming the basis for his famous light bulb patent. Edison hired Acheson to invent longer life filaments. Acheson relied on intense electric discharges to form SiC as a filament. Ten years later, Moissan applied Acheson's concept to form WC and other compounds, reaching temperatures of 3,500 °C, for which he was awarded the 1906 Nobel Prize.

Acheson's ideal of direct electric discharge provided the means to sinter refractory metals without a high temperature furnace infrastructure. Subsequently, Voelker [4] patented spark sintering to form filaments. In 1906 Lux [5] patented pulsed electric current sintering (1 s pulses of 10 A/mm$^2$) in vacuum to make brittle tungsten filaments. Experiments by Braun [27] concluded about 2500 °C was the typical temperature. In sintering literature, Lux's patent is incorrectly attributed to Bloxam, who was the patent agent, not the inventor.

It took thirty years from Edison's patent until Coolidge [22] developed a long-lasting ductile tungsten filament for alternating current systems using concepts traced back to Acheson. To work the tungsten lamp filament problem, Edison hired Whitney, a former student of Nobel Prize winner Ostwald. In turn, Whitney recruited Coolidge and Langmuir. Coolidge developed sintered ductile tungsten and Langmuir designed the coiled filament operating with gas filled bulbs to control evaporation. Langmuir subsequently won a Nobel Prize.

Mixing tungsten with other metals prior to sintering was explored during the race to develop lamp filaments. Early variants employed cadmium and mercury, which evaporated as the tungsten was sintered. By 1938 tungsten alloys arose for radioisotope containment [23,24,32]. An example microstructure is shown in Fig. 1 corresponding to 95 wt.% tungsten with 3.5 wt.% Ni and 1.5 wt.% Fe (95W–3.5Ni–1.5Fe). The tungsten grains form a three-dimensional skeleton while the matrix phase fills between the grains. When heat treated, this composite reaches tensile strength of 950 MPa with 25% elongation to fracture. The discovery of liquid phase sintered tungsten paralleled the success in sintered cemented carbide (WC–Co), creating composites with desirable hardness, strength, and toughness.

**Table 1**
Progression in tungsten sintering temperature reports.

| Year | Author | Temperature, °C | wt.% W | Key aspects | Ref. |
|---|---|---|---|---|---|
| 1906 | Lux | Not reported | 100 | Direct discharge sintering | [5] |
| 1908 | Hirst | Not reported | 100 | Reviews several efforts | [3] |
| 1910 | Coolidge | “White heat” | 100 | Direct discharge, no details | [22] |
| 1935 | McLennan et al. | 1350 | 90 | W–Ni–Cu, 96% dense, hours | [23] |
| 1938 | Price et al. | 1400 | 93 | W–Ni–Cu, dense, 6 h $H_2$ | [24] |
| 1946 | Kurtz | 1650 | 99 | Activated sintered | [25] |
| 1959 | Vacek | 1300 | 99 | Activated sintered with Ni | [26] |
| 1960 | Braun | 2500 | 100 | 15 min discharge sintering | [27] |
| 1991 | Bose et al. | 1300 | 90 | Ni–Mn added, 95% dense | [28] |
| 2002 | Elliott | 1100 | 52 | W–Cu–Sn–Fe, 96% dense | [29] |
| 2006 | Johnson et al. | 1360 | 90 | W–Co–Mn, 99% dense | [30] |
| 2012 | Young et al. | 1200 | 80 | Ni–Cu–Mn, 97% dense, 1 h $H_2$ | [31] |

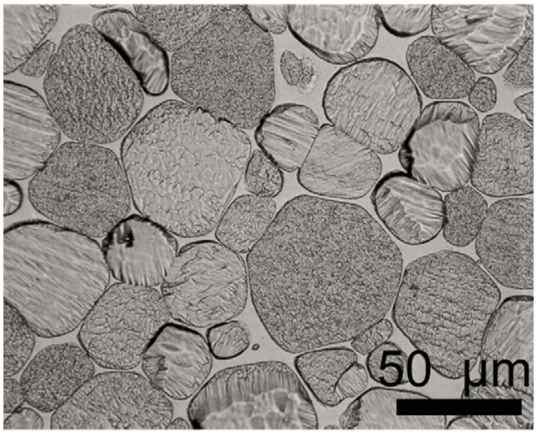

**Fig. 1.** An example microstructure of the connected solid grains in a ground-based liquid phase sintered tungsten alloy consisting of 95W–3.5Ni–1.5Fe.

The next step in tungsten sintering temperature reduction came with activated sintering. The high diffusivity of tungsten dissolved in an activator phase, segregated to the tungsten grain boundaries, results in rapid low-temperature sintering [25,26]. Activated sintering employs about 0.3 wt.% additive (Ni and Pd are optimal) to reach full density near 1300 °C. A recent variant [29] combines tungsten–bronze with Fe activated sintering to form ammunition by sintering at 1100 °C. Although the bronze is liquid at the sintering temperature, effectively it acts to simply fill the pores as the tungsten skeleton sinters via activated sintering.

Recent efforts with lower sintering temperatures revolve around tungsten alloyed with Ni–Mn, Mn–Co, or Ni–Cu–Mn compositions sintered at 1300, 1360, or 1200 °C, respectfully [28,30,31]. Again, the microstructure consists of single crystal tungsten grains bonded to one another with an interpenetrating alloy matrix. Attention on the W–Ni–Cu–Mn system has resulted in qualification of this system for upcoming space flight experiments to understand gravitational effects on densification, distortion, and coarsening.

## 3. Microgravity sintering

Tungsten alloys are a favorite for microgravity research, in part because the sintering behavior is well understood and the high density amplifies gravitational effects in small samples [38]. For experiments in inhabited quarters, safety during the sintering run is a dominant factor. Accordingly, containment of the experiment as well as vehicle power limitations require small sample sizes. After passing several barriers, such as tests for vapor containment, vibration resistance, toxicity, crucible compatibility, weight loss, compression strength, and leakage, W–Ni–Cu–Mn compositions are now qualified for microgravity sintering on the International Space Station.

The samples start with a mixture of solid, liquid, and pore phases. The density differences are large (19 versus 10 versus 0 g/cm$^3$) at the onset of sintering. Gravity plays a major role during sintering on Earth, with a surprising effect on densification due to pore buoyancy, giving pore migration to the top of the compact. A noticeable effect is slumping with an obvious negative impact on net shaping [13,39,40].

Microgravity sintering experiments allow isolation of the gravity role on densification and distortion. Analysis is limited to post-flight inspection, meaning only the initial and sintered dimensions are measured to