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Effect of Cu-Melt Infiltration Technique and Furnace Atmosphere on Density and Microstructure Evolution of W-20Cu Sintered Compacts

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ABSTRACT

In this study, experiments were conducted to evaluate the effectiveness of environmental furnace on microstructure and hardness of W-20Cu sintered compacts. The copper melt was furnished by placing thin high purity copper sheets of 13-14mm diameter and 0.2 mm thickness under the W-20Cu green compacts. These arrangements were introduced into alumina tube furnace and sintering at 1150°C for 2h under different furnace atmospheres as protective environment. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX), were utilized to examine and characterize the microstructure, the inter boundary layer and the contamination levels of the sintering compacts. The results showed that the sintered specimens under hydrogen gas and Cu-Melt infiltration presented the best results (99.92% of theoretical density).

***Keywords**:*
W-Cu composites.
Liquid phase sintering.
Liquid infiltration.

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1 INTRODUCTION

Tungsten-copper (W-Cu) composites are promising materials for thermal managing applications such as microelectronic devices because of the low thermal expansion coefficient of tungsten and the high thermal conductivity of copper. The low solubility between W and Cu elements, makes it difficult to attain nearly-full density of W-Cu composites using solid-state sintering (SSS) or liquid phase sintering (LPS) or/and liquid infiltration (LI) techniques [1,2,3]. W-Cu composites are very important for many applications and these applications depend on the fraction of W into the composites. Some applications for W-Cu composite materials are electrical contacts, heat sinks for thermal management and packaging materials [4]. A high tungsten volume fraction (e.g., 80 wt.%) is necessary to achieve a low coefficient of thermal expansion (CTE), as needed for microelectronic heat sinks [5,6]. The most popular methods for the fabrication of W-Cu composite materials are by the infiltration process [7,8] and liquid phase sintering [9,10]. However, densification of W-Cu composites by liquid phase sintering is attained mainly by the tungsten particle rearrangement due to the capillary force and surface tension of Cu matrix [11,12].

The primary objective in synthesizing composites is to combine more than one chemically and physically different material. The interfacing between the surfaces of different elements is very important [13,14]. It has been known that, when the contact angle decreased, the wettability enhanced resulting in a significant improvement in densification in liquid phase sintering. Low contact angle helps in the liquid spreading over the solid grain particles homogeneously, thus pervasion a capillary attraction that assists densification system. The high contact angle of Cu elements with several oxides hinder the process of infiltration. [1,15]. Unsurprisingly all metals of technical importance respond to the gas of their surrounding atmosphere, and are more influenced when treated at high temperatures. The primary cause for using particular sintering atmospheres is to provide protection against oxidation of the sintering powders. There are many sintering atmospheres, which have the ability to control the basic process of sintering. They resulted in reduction of the oxides and facilitate gas atmosphere to enter the sintering compact through the interconnected pores. It is possible that the gas atoms of the sintering atmosphere may diffuse into the metal and alter its chemical composition [16].

In general, there are many kinds of furnace atmospheres such as vacuum, hydrogen, argon, and mixture of argon/hydrogen and nitrogen/hydrogen and. These furnace environments have a strong effect on the densification of W-Cu composites. The main concern of using these gases during the consolidation process of metals is the partial pressure of the reactants and the products in the equilibrium with one another at the sintering temperature. In this study four furnace environments (vacuum, hydrogen gas, pure argon and argon/hydrogen of 95/5 wt.% ratio) were employed to consolidate W-20Cu composite. The effect of these environments on the densification of W-20Cu composite was also reported.

2 MATERIALS AND METHODS

In this work, tungsten powder produced by Strem-chemicals with particle size average of 12μm and purity of >99.9%, Cu (99.7% purity, 63μm, Merck's supplier). The sintering additive powder was Ni (99.9 % purity, 7 μm, Fluka chemise's supplier). SEM micrograph of the as-received powders is illustrated in Fig. 1. The basic and additive element powders were mixed manually in a small glass container for 30 min to avoid any particle segregation due to gravity and grain size effects. All powder mixtures were die-pressed at 400 MPa to produce cylindrical shape compact of approximately 13.14mm in diameter and 2-3mm in height depended on their Cu volume fraction content. The pure Cu sheet weight was 0.5 ±0.03 grams and 13.5 ±0.5mm in diameter and placed under the green compact. Isothermal sintering was conducted in alumina tube furnace at temperatures of 1150˚C for 2hr under different protective gases (H_2/Ar with weight ratio of 5/95; hydrogen, pure argon and vacuum). The heating rate was 4^oC/min., cooling rates was 10^oC/min and the protective gas flow rate was 4.5 L/min. The sintered density of the samples was measured using Archimedes technique and SEM was used for microstructure observations.

The relative density of compacts was calculated according to the rule of mixture method:

$$m_t = m_W + (m_{Cu1} + m_{Cu2})$$

$$A = m_W/m_t$$

$$B = (m_{Cu1} + m_{Cu2})/m_t$$

$$1/\rho_t = A/\rho_{t,W} + B/\rho_{t,Cu} \quad (1)$$

Where:

ρ_t is the theoretical density of the composites,

A and B are the percentage of weight fraction of tungsten and copper respectively,

m_{Cu2} is the weight fraction of infiltrated pure Cu-sheet into W-Cu composites (process via liquid infiltration),

m_{cu1} is the weight fraction of copper powder into W-Cu compacts before sintering,

$\rho_{t,w}$ and $\rho_{t,cu}$ are the theoretical density of tungsten and copper respectively,

m_t is the total composites weight and m_w is the tungsten powder weight.

The densification of sintering compacts was calculated according to this equation (2) [17]:

$$\Psi = \frac{\rho_s - \rho_g}{\rho_T - \rho_g} \quad (2)$$

Where Ψ is the densification, ρ_s is the sintering density, ρ_g is the green density and ρ_T is the theoretical density.

3 RESULTS AND DISCUSSION

3.1 Microstructures

The morphology of the as received tungsten and copper powders are shown in Fig. 1. The SEM images reveal different particles size, shapes and agglomerate. Table 1 shows that, properties of W-Cu sintered compact are completely affected by the different types of furnace environments used as well as by the method of fabrication. It was very clear that the highest sintering density was attained using inset method (Cu-MI, combine liquid phase sintering and liquid infiltration) under hydrogen gas as sintering furnace atmosphere. The presence of oxygen throughout the sintering process led to discontinue the infiltration, whereas the sintering under hydrogen gas provided the best results. Using hydrogen as protective-environmental gas demonstrated superior results when compared with other environmental such as vacuum and argon/hydrogen mixture in range (95/5 wt.%). When argon/ hydrogen mixture gas was used as a protective gas, the final density was slightly higher than the compacts sintered under vacuum as shown in Table 1. Moreover, the results showed that a pure argon as a furnace environment resulted in a very low sintering density when compared with other environmental furnace. Besides, it also showed that the microstructure has a high level of porosity as shown in Figure 2.

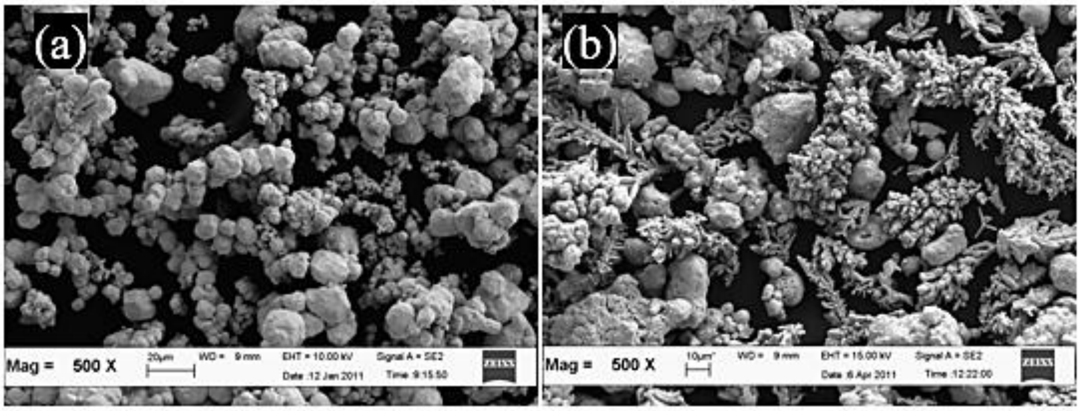

Figure 1. *SEM micrographs of the raw materials powders: (a) W, and (b) Cu*

Table 1. *The sintering and relative density and densification of 80W-Cu sintered compact prepared by Cu-MI as well as LPS at 1150°C and with different furnace environments*

Sintered compact	Furnace environment	SD (g/cm^3)	RD (% of TD)	Hardness (Hv)
		By using LPS technique		
80W-Cu	Vacuum	12.51	80	115
80W-Cu	Arg./H_2 gas	13.5	86.3	127
80W-Cu	H_2 gas	13.76	88.13	150
		By using Cu-MI method		
80W-Cu	Vacuum	12.46	79.7	127
80W-Cu	Arg./H_2 gas	14	89.9	166
80W-Cu	H_2 gas	15.62	99.92	253

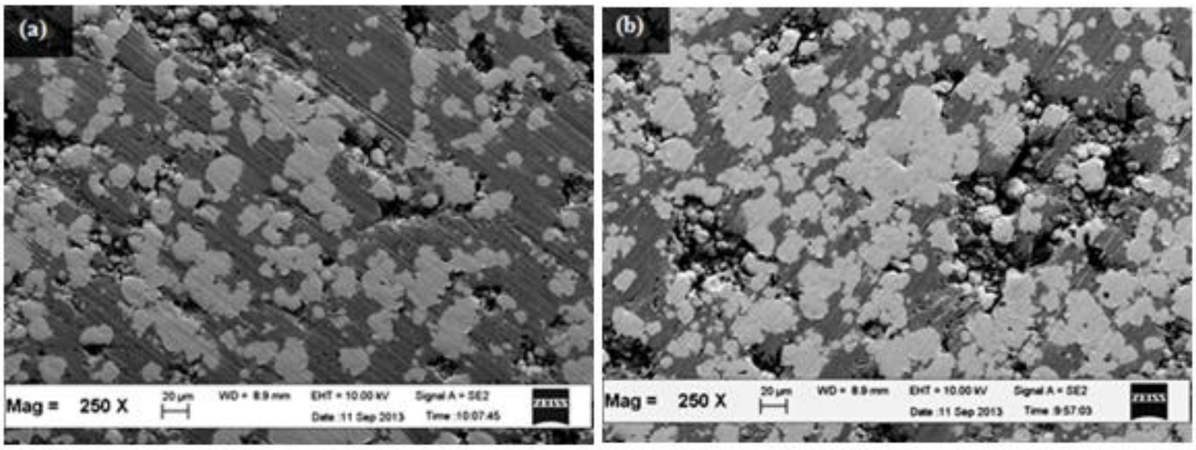

Figure 2. *The SEM micrographs of sintering compacted at 1150˚C under Argon gas with different fabrication techniques: (a) using LPS techniques and (b) using Cu-MI technique*

In this context, the effect of oxygen and carbon contents for the same sintered compact and using different furnace environment are examined and detected by EDX spot and line scan analysis. The quantity of carbon and oxygen are focused at the surrounding area of the W grains. As tungsten and copper are immiscible in each other, segregation elements of carbon and oxygen can influence the wettability of tungsten by copper. Oxygen forms oxides with W and Cu. Consequently, these oxides can increase the contact angle (high wetting angle) between W and Cu and in turn can hinder the densification of W-Cu. The oxidation compound of WO_3, CuO and Cu_2O are volatile and can lead to loss in sample weight during sintering process. Besides, their different thermal expansion coefficient values can cause swelling [18, 19].

The contamination of carbon element in low level content may enhance the mechanical properties by forming tungsten carbide, and at the same time the carbon element fills the pores and impedes pore liquid closure. This argument is supported via the high content of oxygen in the EDX result of the cracked particle surface as shown in Figure 3 (a) and (b).

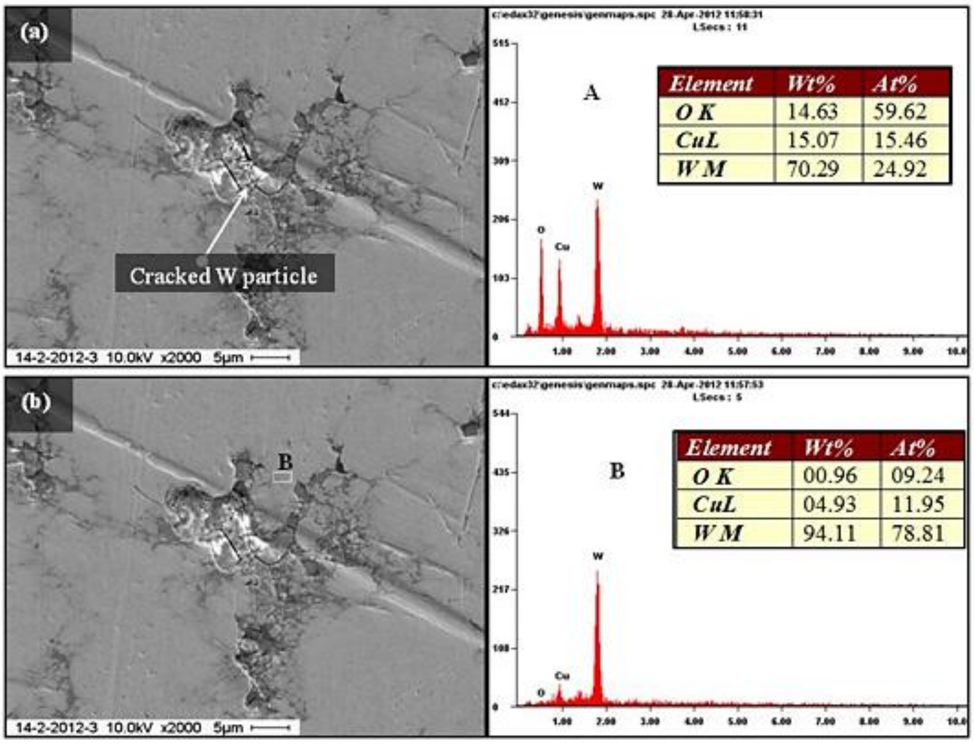

Figure 3. *SEM images coupled with EDX scan for the consolidation of W-Cu composite produced by LPS at 1150°C under H_2 gas as furnace atmosphere:(a) SEM micrograph coupled with EDX result on selected area A and (b) SEM micrograph coupled with EDX result on selected area B.*

On the other hand, the mean oxygen contamination content in W-Cu sintered compact produced by Cu-MI method and using different environmental furnace was quantified and the results are shown in Figure 4. The analysis was carried out using standardless ZAF alteration method in the Genesis software from EDX. The scans were conducted on W-20Cu sintered compact without adding transition elements as sintering activator. The highest oxygen content was detected in the sample consolidated under argon gas resulting in low sintering density when compared with hydrogen, mixture of hydrogen and argon and vacuum as furnace environments (as shown previously in Table 1). The results obtained from Table 1 and Figure 4 indicated that, using hydrogen gas as a furnace atmosphere sintering gives a low content of oxide and high relative density compared with other environmental sintering furnaces. From this test, it is evident that there is a positive impact of low oxygen content on densification of W-Cu system.

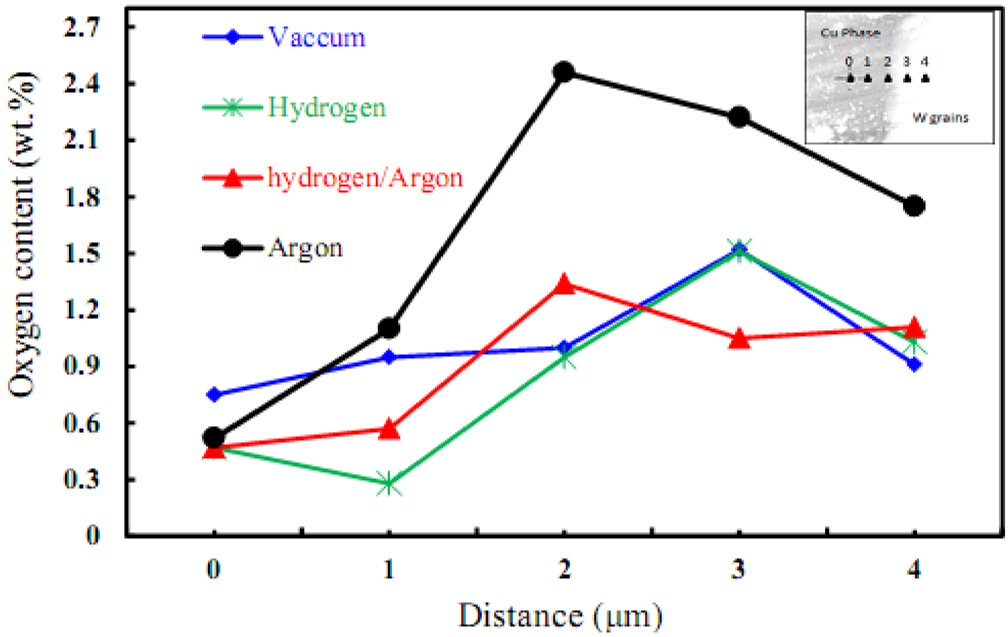

Figure 4. *The EDX results of oxygen elements scanned on the vicinity region of tungsten grain of W-20Cu sintered compact prepared by Cu-MI method under different sintering atmospheres.*

Mechanical properties of tungsten-copper composites strongly depend on the strength of the interface between W and Cu. As W and Cu elements have no solubility with each other and therefore strong interfaces in W-Cu system are assured by enhancing the wettability between W and Cu. On the other hand, segregation of oxygen around the W grain boundary significantly weakness the interface boundary.

3.2 The effect of furnace atmosphere on the contact angle of W-Cu composites

For a system in which both the solid and liquid neglect mutual solubility such as the W-Cu system, sintering of the solid-skeleton defines the densification rate. Copper fills the pores to form the matrix and tungsten form the skeleton. In liquid phase sintering, the contact angle plays a crucial role in the densification of composite. Figure 5 shows sintered compact of 80wt.%W-Cu composites produced by Cu-MI method under same sintering condition but different furnace environments (Figure 5 (a) using vacuum, (b) using argon/hydrogen, and (c) using pure hydrogen). The results obtained from this figure state that, the contact angle completely depends on the type of environmental furnace. Decreasing value of contact angle in the W-Cu system without adding transition elements as sintering activator follow the sequence: i) pure hydrogen gas ($\theta \approx 0°$), (ii) argon/hydrogen gas ($\theta < 45°$) and (iii) vacuum ($90° < \theta > 45°$). The importance of contact angle is that it helps in liquid spreading over the solid particles uniformly, and consequently facilitates the capillary attraction which enhances the densification in the system.

Many researchers have identified the fact that it is difficult to attain full density of W-Cu composites by LPS as a result of insolubility between W and Cu [1, 2, 20]. This problem has been overcome and the nearly-full density of W-Cu composite without adding low concentration of transition elements was accomplished in this work.

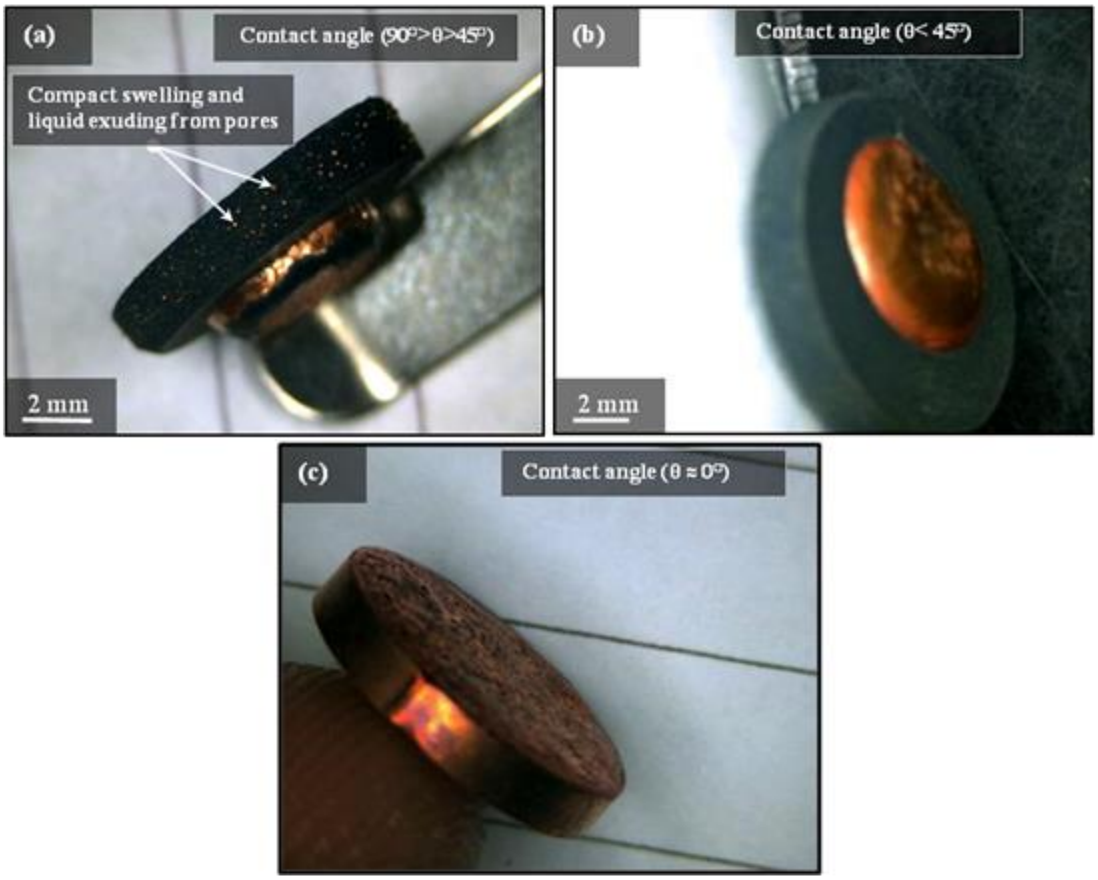

Figure 5. *The photographs of 80W-Cu sintered compact at 1150°C under different furnace environment via Cu-MI method: (a) under vacuum, (b) under Ar./H_2 gas (95/5 wt.%) and (c) under H_2 gas*

4 CONCLUSIONS

Furnace environment is very important during consolidation of W-Cu composites. Sintering of W-20Cu composites with and without infiltration technique at relative low temperature 1150°C and different environmental furnaces was performed. Relative densities in the range of 79.7 to 99.7%TD were achieved. The highest density was obtained under hydrogen gas with high purity Cu sheet (99.7%TD) and the lowest density was obtained under vacuum furnace (79.7%TD). Using hydrogen gas as a protective furnace environment exhibited the best outcome, when compared with other environments such as vacuum and /or hydrogen/argon gas mixture. The presence of hydrogen gas during W-Cu composites was found very important to increase the hardness of the composite.

5 ACKNOWLEDGMENT

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تأثير تقنية تشريب النحاس المصهور وبيئة الفرن على الكثافة والبنية المجهرية لمركب التنجستن والنحاس الملبد

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الملخص

خلال هذه الدراسة، أجريت تجارب لتقييم فعالية بيئة الفرن على تركيب البنية الدقيقة والصلادة لمركب التنجستن والنحاس الملبد. تم تجهيز النحاس المصهور وذلك بوضع صفيحة نحاسية رفيعه بقطر 13-14 مم وسمك 0.2 مم وبدرجة نقاوة عالية تحت مركب التنجستن والنحاس المضغوط. وضعت العينات داخل فرن انبوبي من الألومينا وتم التلبيد عند 1150 درجة مئوية لمدة ساعتين بالفرن تحت بيئات وقائية مختلفة. استخدام كلا من الفحص المجهري الإلكتروني (SEM) وتحليل الأشعة السينية المشتتة للطاقة (EDX) لتقييم وفحص وتوصيف البنية المجهرية والطبقة بين الحدود ومستويات الشوائب للمركب الملبد. أفضل النتائج تم الحصول عليها عند استخدام تشريب النحاس المصهور وغاز الهيدروجين كبيئة واقية حيث ان كثافه المركب الملبد مساويه الى 99.92%من الكثافة النظرية.

الكلمات الدالة:
مركبات التنجستن والنحاس.
التلبيد بالطور السائل.
التشريب.

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