Production of tantalum by aluminothermic reduction in plasma reactor

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Abstract

Tantalum is a very interesting metal for industry due to some properties such as high melting point, ductility, high corrosion resistance, besides attractive electric and thermal conductivities. In the present work, the production of metallic tantalum (Ta) has been investigated through the reduction of Ta₂O₅ by aluminothermic reduction technique (ATR), using hydrogen plasma to trigger the exothermal reaction. Ta₂O₅ and Al mixtures were previously processed by mechanical alloying during 2, 6 and 10 h. The results obtained by XRD and SEM show that it is possible to obtain a compound rich in tantalum through the technique of aluminothermic reduction by plasma.

Keywords: Tantalum; Aluminothermic reduction; Plasma; Mechanical alloying; Scanning electron microscopy; X-ray diffraction

1. Introduction

Tantalum exhibits very interesting properties such as high melting temperature, ductility, corrosion resistance and significant thermal and electric conductivities [1]. Currently, its largest application is in the production of capacitors, due to the suitable properties of its oxides [2]. Other applications of tantalum are as carbide (TaC), additive in the cutting tools manufacturing [3,4], in form of tantalum carbide, and in the catalysts manufacturing [5]. Electrolytic capacitors, made with the anode of sintered tantalum powder, have been a major contribution to the miniaturization of electronic circuits and have made progress in the application of such circuits in extreme environments [6].

Ta powder is usually produced by the reduction of its oxides by elements such as C, Si, Ca, Na, Mg and Al [7–9]. The commercial process for the production of tantalum is the reduction of K₂TaF₇ by sodium [8]. In this process the raw material is dissolved in HF solution, separated and purified by liquid–liquid extraction using organic solvents. The purified solution is used to produce K₂TaF₇ (K-salt) precipitated in the form of small crystals, which are used as an initial material for tantalum reduction from a melt by sodium [10]. In the case of Al, the reaction is called aluminothermic reduction (ATR). The technique is also used to produce Nb. The Al excess used in the reaction and Al₂O₃, which is product of the reaction, can be removed by mechanical separation and thermal refining [7,11–14].

In conventional ATR, aluminum reacts with Ta₂O₅. Metallic Ta and Al₂O₃ are formed. The reaction starts with an external source of heat, but self-propagates because it is strongly exothermal [15]. Gomes [15] showed that the final product (metallic tantalum) obtained in the conventional ATR process solidifies and form a dense block. This material can be further purified by an electron beam furnace. The powder can be produced from the refined material by a hydration-milling-dehydration process [16].

In this work, a variation of the technique of aluminothermic reduction is presented that uses the hydrogen
plasma to trigger the reaction. In the present case, the ATR product is directly obtained in the form of powder.

2. Experimental procedure

Tantalum oxide (99.98%) and aluminum (99.86%) powders were used as reactants in the ATR process by plasma. \( \text{H}_2 \) (99.99%) was used to produce the plasma. Fig. 1a and b are SEM micrographs of \( \text{Ta}_2\text{O}_5 \) and Al powders, respectively. \( \text{Ta}_2\text{O}_5 \) particles tend to agglomerate, forming flakes. The mean particle size determined by laser scattering for \( \text{Ta}_2\text{O}_5 \) and Al was 0.8 \( \mu \text{m} \) and 5.2 \( \mu \text{m} \), respectively. In this test was used as dispersant the RENEX 95 surfactant (Nonilfenol Etosiliado), normally used in the composition of detergents. The proportion used was 400 ml of water (volume of recipient in the granulometer) to 10 drops of dispersant.

In previous works accomplished by Brito [17], stoichiometric and overstoichiometric \( \text{Ta}_2\text{O}_5/\text{Al} \) mixtures were reacted under plasma. In the stoichiometric mixture part of the tantalum oxide did not react. In the other case, the superstoichiometric mixture, containing 5 wt.% Al in excess, exhibited much higher level of reduction. In present work, the samples were prepared using only the overstoichiometric composition. The reduction is described by Eq. (1):

\[
3\text{Ta}_2\text{O}_5 + 10\text{Al} \rightarrow 6\text{Ta} + 5\text{Al}_2\text{O}_3
\] (1)

The Al and \( \text{Ta}_2\text{O}_5 \) powder mixtures were prepared by hand mixing and also by milling in a planetary mill. In all cases, 10 g of \( \text{Ta}_2\text{O}_5 \) and 2.14 g of Al were used. This corresponds to an excess of 5 wt.% Al with regard to the stoichiometric quantities given by Eq. (1). A sample was hand mixed for 15 min. The others were milled for 2, 6 and 10 h in a planetary mill, using hardmetal balls (diameter: 15 mm; total mass: 100 g) and a ball-to-powder weight ratio of 1:10. The milling speed was set at 5, in a scale from 0 to 10.

A schematic of the plasma reactor is shown in Fig. 2. It consists of a glass cylinder with two stainless steel flanges and two electrodes. The flange in the top of the reactor functions like the own anode. The electrode in the bottom of the reactor is the cathode, and is also machined with stainless steel. It is a hollow cathode and works as the sample holder. All reductions were performed under the same conditions: temperature – 800 °C, hydrogen flow –
16 cm$^3$/min, pressure – 300 Pa and heating rate of approximately 20°C/min. The power source has maximum output voltage and DC current of 1500 V and 1.5 A, respectively. Voltage, current, pressure and cathode temperature are measured and controlled in the control panel.

The powder sample of around 0.1 g was placed in the sample holder. The reactor was closed and pumped until the pressure reaches 300 Pa. The electrodes were polarized and hydrogen was introduced in the reactor chamber. The gas was ionized and the temperature was raised up to 800°C. The heating rate was controlled by appropriately adjusting the voltage. After reaching the final temperature, the power was turned off. The reaction takes place instant during heating. After cooling, the samples were characterized by SEM (using a Philips XL 30 ESEM) and XRD (in a Shimadzu Diffractometer, using Cu K-α radiation, with 2θ varying between 10° and 80° and scattering velocity of 2° min$^{-1}$).

3. Results and discussion

XRD patterns of the hand mixed and milled powder mixtures are shown in Fig. 3. The intensity of the peaks of Ta$_2$O$_5$ and Al decrease and their width increases with the milling time. These effects are related to the strain (distortion) of the crystalline lattice and decrease of the crystallite size and are caused by the high energy of the ball-powder-ball collisions. In the case of extreme milling intensity, the phases can become amorphous. This was not verified in this study.

During milling, morphology, size and composition of the particles change continually [18–20]. High energy milling causes strain of the crystal lattice, deformation of the ductile phases, cold welding of the particles and fracture of the brittle phases. The ductile Al particles are deformed, getting the shape of plates. The Ta$_2$O$_5$ flakes are fragmented and the smaller hard fragments are embedded in the ductile Al by the collisions. As milling continues, different Al plates weld and break successively [18–22]. The final result is the formation of particles in which tantalum oxide fine particles are dispersed in a lamellar Al matrix [22,23].

In powders milled during 6 h, the largest particles are around 36 μm (Fig. 4). This value is the arithmetic average of diameters of the largest particles showed in Fig. 4, obtained using the image analysis software Image-Pro Plus version 6.0.

In conventional ATR process, the reaction propagates throughout the material. Previous investigations showed that the propagation of the aluminothermic reaction does not necessarily occur in the complete volume of material, but in individual volumes of particles [24]. This propagation is dependent mainly on the existence of contacts among the reacting phases, Ta$_2$O$_5$ and Al. Therefore, the better dispersion of the phases imply in larger the contact area between them. For this reason, the reactivity of the milled Ta$_2$O$_5$/Al mixtures is expected to be high, in comparison to the hand mixed mixture, since the reacting phases are intimately mixed, having a large contact area. The reaction propagation is similarly favored. As a consequence, the reaction yield, that is, the amount of Ta$_2$O$_5$ that is reduced, is higher for the milled powders than for the hand mixed one.

In Fig. 5, XRD patterns of the reduced samples are shown. The powders effectively reacted with the hydrogen plasma as reaction trigger. The milling time influenced the reaction yield. The longer the milling, the better the dispersion of the phases. Therefore, the higher the reactivity of the mixture. This can be seen in the stronger peaks of Ta and the absence of Ta$_2$O$_5$ in the powders milled for 10 hours, after reduction.

In the conventional ATR procedure, the whole material (reactants and reduction products) is molten. After cooling, the material is in the form of dense blocks (ingots). In the ATR by plasma, each particle is separately reduced and the material is produced in form of powder. The particles are constituted of metallic Ta, Al$_2$O$_3$, Ta$_2$O$_5$ not reacted and the excess Al. The particles are bulky and larger than before the reaction (Fig. 6a). Partial molten occurs and...
promotes the enlargement of initial composite particles by agglomeration. Complete molting did not occur due to the high thermal loss of the particles to the surrounding atmosphere. The existence of unreacted Al and Ta$_2$O$_5$ after cooling is a consequence of both short reaction time and bad dispersion.

In conventional ATR process, the reaction occurs in both solid and liquid phases. When the whole material is liquid, the dispersion improves. But in the present case the melting is partial. This means that each particle agglomerates is an individual reducing system. If in certain agglomerate, there is more Ta$_2$O$_5$ than the stoichiometry, then there will be residual Ta$_2$O$_5$ in the particles, otherwise, the whole Ta$_2$O$_5$ present in the particle will be reduced.

The structure of the particles of the reduced material consists of a Al$_2$O$_3$ and dispersed Ta grains, as shown in Fig. 6b, a micrograph in the back scattered mode. The bright area, marked by Al is reach in Ta, while the dark area is reach in aluminum, according to EDS analysis.

The use of this powder in catalysis is a possibility, since Ta is already supported in alumina.

4. Conclusions

A plasma reactor can be used to promote the alumino-thermic reduction of tantalum oxide. The dispersion of the reactants influences strongly the yield of the reaction. Milled mixtures present higher reaction yield than hand mixed ones. The milling time also influences the reaction yield. Milling produces particles that contain both reagents, forming a large contact area. This increases the reactivity of the mixture and eases the propagation of the reaction. Each particle reacts separately. The reaction product is a powder whose particles have metallic Ta and Al$_2$O$_3$ in their structure.

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References


