# Vacuum-Plasma-Sprayed Titanium-Manganese Electrode Layers for MnO₂ Deposition

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Vacuum-plasma-sprayed titanium-manganese alloy electrode layers are intended to improve the economy and efficiency of the synthesis of electrolytic manganese dioxide, which is commercially used as cathodic material in primary batteries. Titanium anodes with a high content of manganese offer high electrochemical activity and corrosion resistance, but poor mechanical stability. Therefore, dense and well-bonded coatings of this brittle alloy were vacuum plasma sprayed onto ductile substrates using commercially pure titanium and manganese powder mixtures as well as mechanically alloyed powders. The mechanically alloyed powders, fabricated in a planetary ball mill, are suitable for the plasma spray process. The microstructure and electrochemical properties of the anode coatings produced by these two methods are discussed. Results are compared to commercially pure titanium anodes.

1. Introduction

ACTIVE manganese dioxide is used primarily as a depolarizer in dry cell batteries. Several types of synthetic MnO_2 are produced commercially, the most important of which is electrochemically deposited manganese dioxide (EMD) (Ref 1, 2). The production of EMD usually starts from manganese ore, which is first reduced to MnO and then leached with sulfuric acid to form a manganese sulfate solution. The chemical basis for the electrochemical process is the oxidation of Mn^{2+} ions to form a solid phase deposit of MnO_2 on the anode:

$$MnSO_4 + 2H_2O \rightarrow MnO_2 + H_2SO_4 + H_2$$
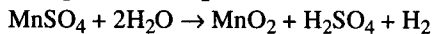
Then the product is mechanically removed from the anode, crushed, and ground to the desired particle size.

It is difficult to design an electrochemically active, mechanically stable, and corrosion-resistant anode for the production of EMD. Individual materials such as carbon, lead, or lead alloys have been investigated (Ref 3). Unfortunately, these electrodes provide poor mechanical stability, leading to contamination of the product during its separation from the anodes.

Nevertheless, lead and carbon are still being used, although current EMD production technology favors the use of titanium anodes, which are characterized by high mechanical stability and corrosion resistance. The main disadvantage of titanium anode material is its high sensitivity to passivation. Because of this factor, the current density must be reduced to relatively low values, negatively affecting the economy of the EMD process (Ref 4).

Several attempts have been made to overcome this restriction. However, for various reasons, none has found application at the present time (Ref 5-8). It has been established that the electrochemical activity of a titanium anode for use in concentrated acid solutions at high current densities could be significantly increased by alloying the titanium with manganese (Ref 9). At the same time, titanium-manganese alloys containing larger

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amounts of manganese are not suitable for the EMD process because of their brittleness.

In order to increase the mechanical stability of such coatings, these alloys were sprayed onto different ductile substrates by means of vacuum plasma spraying (VPS). Commercially pure powder mixtures as well as mechanically alloyed powders were used. The production of VPS alloy coatings using pure powders applied through separate powder feeders appears to be very economical, but presents various problems (Ref 10). Prealloyed powders result in more homogenous coatings, which is beneficial with respect to their electrochemical behavior.

2. Experimental

2.1 Mechanical Alloying

The mechanical alloying (MA) process is a high-energy, dry milling technique used to produce composite metal powders characterized by submicron homogeneity (Ref 11, 12). The process takes place under inert atmosphere in a high-energy ball mill, a vibratory ball mill, or an attritor-type ball mill. The metal powder particles are trapped between the colliding balls, strongly deformed, and cold welded, resulting in a characteristic sandwich structure. Additional milling further refines the microstructure (Fig. 1), and in many cases true alloying ultimately takes place. Reference 13 provides a detailed description of the MA process.

The authors' experiments employed a conventional planetary ball mill (Fritsch, pulverisette 5). Commercially pure titanium and manganese powders with a particle size of less than 45 μm were mixed and placed with the balls in a cylindrical milling container. To avoid oxidation, the container was sealed and evacuated to 10^{-2} hPa. The leakage of helium was checked and determined to be less than 10^{-8} hPa/s. In order to keep the milling temperature low and thus eliminate the need for cooling, the milling process was performed in 15 min intervals separated by 15 min of rest (Ref 14, 15). Containers and balls made of various materials (e.g., sialon, zirconia, tool steel, and austenitic steel) served as milling tools. The milling behavior of 10 and 20 mm diam balls also was investigated. Additional experiments were performed with 10 mm diam tungsten carbide balls in a tool steel
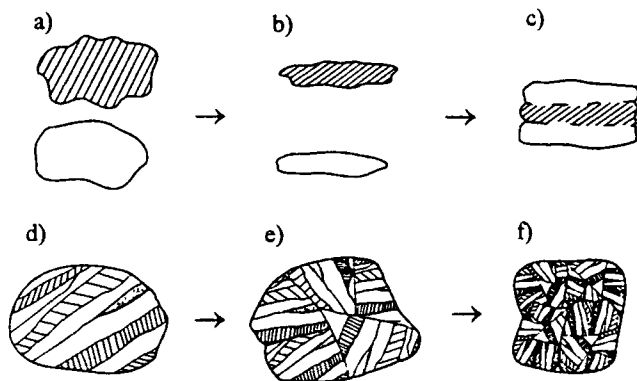
Fig. 1 Schematic of several stages during mechanical alloying of ductile metals according to Ref 13. (a) Starting powders. (b) Particle flattening. (c) Welding of particles. (d) Equiaxed particles. (e) Random welding orientation. (f) Steady-state particle size

Fig. 2 Normalized particle size distribution after different milling times

Table 1 Spray parameters for coatings applying mixed and mechanically alloyed powders

Parameter	Mixed powder	MA powder
Plasma gas		
Argon, L/min	112	125
Hydrogen, L/min	7.5	2.5
Powder feed rate, g/min	36	45
Arc power, kW	77	77
Spraying distance, mm	350	290
Chamber pressure, mbar	40	40

container. The powder weight, the ball-to-powder weight ratio, and the milling intensity corresponding to different energy values of the colliding balls were varied.

The milling process was interrupted at defined intervals, and a small quantity of the milled powder was removed. The container was resealed and evacuated before the next ball milling interval. The powder was investigated using optical and scanning electron microscopy (SEM) and x-ray diffraction. The particle size distribution was measured with an interactive image analysis system. Results are presented in Fig. 2.

2.2 VPS Titanium-Manganese Coatings

Powder mixtures of commercially pure titanium and manganese were used. Alloying during spraying was carried out using two powder feeders that allowed various mixing ratios as well as a homogeneous composition of the spray material. The two powder lines were connected to form a "Y" junction to mix the powders before injection into the plasma. The grit-blasted mild steel substrates were preheated to 800 °C and reverse sputtered by a transferred arc. The spraying parameters for the commercially pure and the mechanically alloyed powders are given in Table 1. Cross sections of the coatings were analyzed by optical microscopy and SEM.

The electrochemical behavior of titanium coatings was determined in $1N$ H_2SO_4 aqueous solution against a calomel electrode at room temperature. The solutions were aerated during measurement of the polished sample surface.
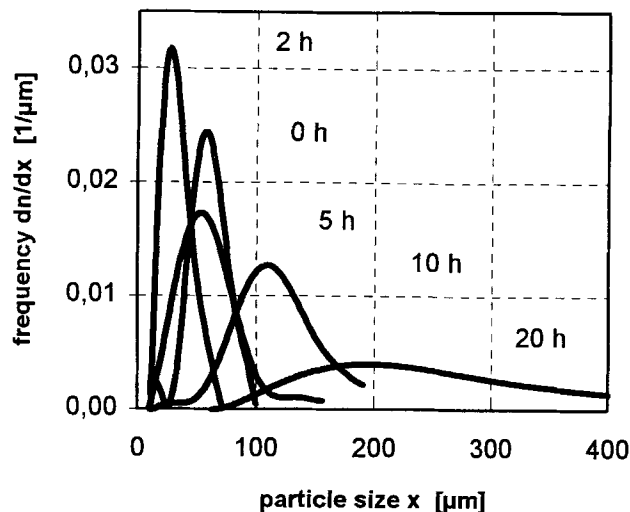
Test runs were performed in a laboratory electrolyzer with a 2 l capacity to evaluate the behavior of the coatings for the electrolytic deposition of manganese dioxide. The temperature of the $MnSO_4/H_2SO_4$ electrolyte was kept constant. The polished surface of a coated sample served as the anode; graphite was used as the cathode material.

3. Results and Discussion

3.1 Synthesis of Mechanically Alloyed Titanium-Manganese Powders

Generally, the mean particle size of the powder mixture initially decreases. Strong deformation and cold welding processes then form composite particles with a typical lamellar microstructure. Extended processing results in additional welding and plastic deformation of the composite particles, further refining their microstructure as the particle size increases.

Milling of titanium powder mixtures present other problems. Because of the strong welding tendency of titanium, coarser particles that are unsuitable for spraying applications are formed after longer milling times. Furthermore, the powder welds to the balls and the container walls.

The addition of small quantities of surface-active organic agents, such as stearic acid or paraffin, decreases the pure metal-to-metal contact and moderates the strong welding tendency (Ref 16). These "process control agents" provide controlled welding and fracturing of the powder particles—the basis of the mechanical alloying process (Ref 11). The required amount of agent depends on the composition of the desired alloy, generally decreasing with increasing manganese content.

All of the MA powders provide a spherical morphology and nearly constant particle size, which is excellent for thermal spraying. Figure 3 shows an MA powder with a manganese content of 10 wt% and a particle size of 14 ± 6 μm. The milling parameters for powder production are given in Table 2. Best results are obtained using tool steel balls and containers. The use of ceramic milling tools leads to a high contamination of the powder
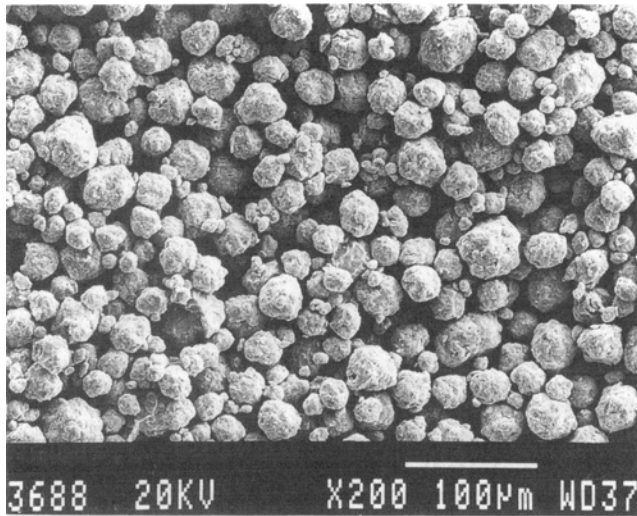
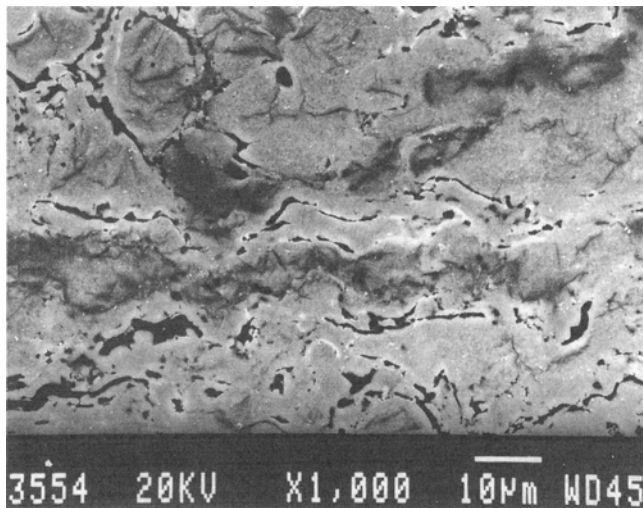**Fig. 3** Mechanically alloyed titanium-manganese powder with 10% Mn, 100 h milling time

Fig. 5 SEM image of VPS titanium-manganese coating applied using MA powder (30% Mn)

Fig. 4 SEM image of VPS titanium-manganese coating applied using mixed powder (10% Mn)
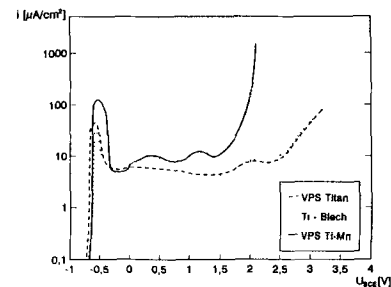
Fig. 6 Current density versus potential curve of VPS titanium-manganese coating applied using MA powder, compared with VPS titanium layer and titanium plate. $1N$ H_2SO_4, air rinsed, $dU/dt = 12$ mV

Table 2 Milling parameters for producing mechanically alloyed titanium-manganese powder

Parameter	
Milling tool	
Container	Steel
Balls	Steel (10 mm)
Powder	
Titanium, g	21
Manganese, g	9
Process control agent	
(stearic acid), %	0.5
Ball-to-powder ratio	13.5:1
Milling	
Atmosphere	Vacuum (10^{-2} hPa)
Intensity, rev/min	180
Time, h	80

particles even after short milling times. Wet chemical analysis demonstrates that alloy product milled in steel containers with steel balls contains less than 0.2 wt% iron impurities caused by the ball milling process. Increasing contamination is also observed at higher milling intensities and at higher ball-to-powder weight ratios.

3.2 VPS Titanium-Manganese Coatings

Figures 4 and 5 exhibit cross sections of coatings sprayed using commercially pure and mechanically alloyed titanium-manganese powders under optimized parameters. Adding manganese increases the porosity of the coatings produced from mixed powders, as shown in Fig. 4. Zones of higher manganese content (light areas) and nearly pure titanium (dark areas) are visible. In comparison, the coatings produced using MA pow-
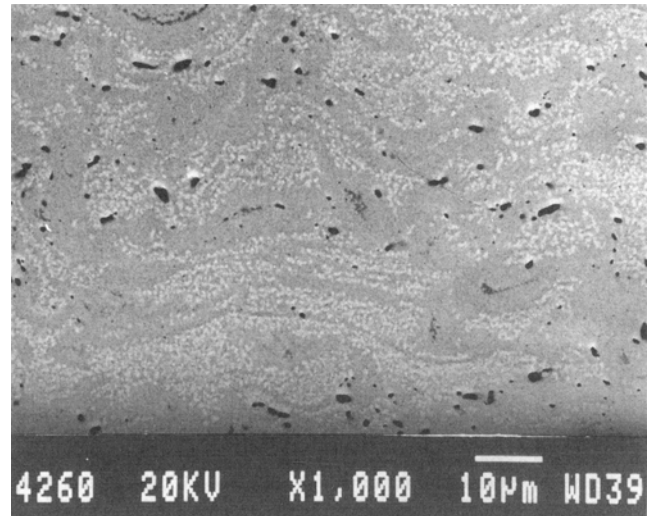
ders (Fig. 5) provide a dense structure, with porosity values of less than 2 vol%. A very fine microstructure and homogeneous composition is evident. The manganese content of the coating shown in Fig. 5 was determined as 30 wt%. The thickness of the coatings measures about 250 μm.

Figure 6 presents the results of the polarization measurements. The current density versus potential curve of a VPS coating of MA titanium-manganese powder (VPS Ti-Mn) is
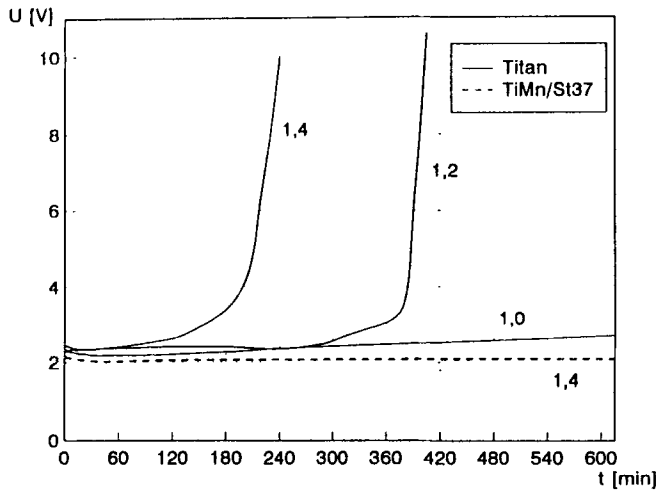
Fig. 7 Cell voltage versus time of titanium anode and VPS titanium-manganese coated anode at different current density values (A/dm^2)

compared to the electrochemical behavior of a VPS titanium coating (VPS Titan) and of a pure titanium plate (Ti-Blech). The results show that it is possible to produce VPS titanium coatings with electrochemical behavior comparable to that of pure titanium. The titanium-manganese alloy also is passive over a wide range of potentials. However, if the potential is higher than 1.8 V, current density increases, and at the same time, oxygen begins to evolve. In comparison to titanium, the overvoltage for this electrochemical reaction is lower on the titanium-manganese surface. This confirms that alloying titanium with manganese leads to a considerable acceleration of anodic processes (Ref 9). Furthermore, due to the low passive current density, the VPS titanium-manganese coatings can be expected to exhibit very good corrosion resistance.

Laboratory electrolysis tests confirm the results concerning the high electrochemical activity of titanium-manganese anodes. The anode potential of commercially pure titanium begins to rise extensively after a critical transition time at high current densities. In Fig. 7, the behavior of a titanium anode at different current densities is compared with an electrode coated by VPS titanium-manganese with 30 wt% Mn. No increase in cell voltage is observed during the deposition time of 9 h at a current density of $1.4 A/dm^2$ employing the titanium-manganese electrode. The electrodeposited MnO_2 forms a dense layer with good bonding to the electrode. After the process is halted, the deposit can be removed without damaging the electrode surface. In contrast, the MnO_2 partially peels off the polished titanium anode.

4. Conclusions

Mechanical alloying has been successfully adapted to the production of titanium-manganese powders for vacuum plasma spraying. The MA powders have a spherical morphology and a nearly constant particle size. Vacuum-plasma-sprayed coatings

of MA titanium-manganese powder revealed lower porosity and a more homogenous structure in comparison to coatings produced using commercially pure powders. Laboratory tests confirmed that anodes coated by VPS titanium-manganese did not passivate at higher current densities during the electrolytic deposition of MnO_2. This fact increases the economy of the EMD process.

Acknowledgment

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