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TEM observations of particles obtained by electro-erosion in kerosene

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Abstract Nano spherical iron compounds particles produced by spark-erosion using kerosene as dielectric were observed by transmission electron microscopy (TEM) and analyzed by X-ray energy dispersive spectrometry (EDS). The observed material was formed by spherical particles of carbon compounds whose size belong to a specific distribution, with a mean value of about 37 nm and their crystallites belonging to a size distribution whose mean value is about 6 nm.

Introduction

The spark-erosion or electro-discharge machining process (EDM) is a technique developed many years ago [1, 2], applied to carve, cut or slice and give form to conductive materials by means of electric discharges in a dielectric media [3]. The dielectric can be: organic, (like kerosene), water or liquid gases. It is a thermal process involving heating, melting, vaporizing, fast cooling and diffusion, all far from equilibrium. The process consists of a swift electric energy discharge—led by a pulsed power source—striking on a reduced area. In this way the surface energy density is very high raising the temperature to the melting and even the boiling point of the electrodes. A bubble is formed on the electrodes surface and when it explodes, very small spherical droplets are ejected from the condensed vapor of the bubble [4]. Due to the created depression, part of the liquid metal that remains on the surface is sucked into the dielectric and suddenly solidified acquiring the spherical shape of the larger particles [5]. Ejected as well as vapor solidified particles fit a bimodal size distribution [6], corresponding to micro and nanoscopic sizes respectively.

On the other hand craters appear on the surface of the electrodes forming a resolidified layer known as ‘‘white zone’’, similar to that formed by welding. The material in the layer is different from the rest of the electrodes due to the solidification process and the incorporation of elements belonging to the dielectric. Crater size, composition and thickness of the white zone depend on the current, duration of the discharge and dielectric [7–9].

Micro spherical metallic particles are widely used for applications of powder metallurgy and several well-known methods are employed to produce them [10]. In a previous work [11] we focussed our attention on the study of the ejected material by the EDM process to obtain spherical iron particles using kerosene as dielectric and this method [12] was also applied to produce and study U-Mo spherical particles using pure water as dielectric [13]. In this work we have analyzed by TEM and EDS the smaller particles produced by a common industrial EDM equipment and kerosene as dielectric with both electrodes manufactured in iron.

Experimental details

Electro-discharge machine (EDM)

Our experiments were performed in a commercial EDM (CT Electromecánica Ltd®, Argentina) using a rectangular

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electric current pulse of 25 Amp. The pulse consisted of an active time t_0 of 3,072 μs and an inactive t_1 of 25,589 μs, a power of 2,000 W and an energy of 6.14 J per discharge. The dielectric was an aeronautical JP1 kerosene. To collect the powders resulting from the electro-discharge, a device consisted in a box and filters was specially designed, see Fig. 1.

Studied material

The material studied in this work came from the electrodes, called the masterpiece and the tool respectively, being both manufactured in iron, whose composition in ppm was: Mn < 800, C < 200, S < 150. The tool and masterpiece were machined in a cylindrical form and the masterpiece had an axial hole.

EDM process

The iron tool was fixed in a rotating holder, its circular and axial movements along the vertical axis improved the removal of the particles from the working zone. The particles were sucked by a centrifugal pump through the sample hole and pushed to external paper filters. The particles retained by the filters were washed, cleaned, and dried with ethanol, see Fig. 1

Preparation of samples for TEM

The particles observed by TEM were 325 mesh sieved and those smaller than 44 μm TEM observed. The samples preparation for TEM observation was made as follows: a Cu grid was covered with an amorphous carbon layer, the particles were put in a small recipient, mixed with methanol and separated by sonication. A small drop of the mix containing the suspended particles was deposited on the grids and laid on the carbon film.

Techniques of analysis

TEM observations and the simultaneous EDS were performed in a Philips CM 200 with EDAX equipment operated at 200 kV. X ray diffractograms were taken with Co-K_α radiation.

Results

Microscopic spheres are clearly seen after the EDM process by SEM micrographs and metallographies, Figs. 2, 3, 4. Figure 3 is a SEM micrograph showing the cross section of an hollowed microscopic sphere with a Widmanstätten pattern, in the same picture appear other spheres without holes and Fig. 4 is an optical metallography of the cross section of a continuous sphere with a Widmanstätten pattern as well.

The TEM micrographs in Figs. 5 and 6 show an overall view of particles, extending from low to higher magnification.

Smaller particles are shown in Fig. 7 and the corresponding crystallites in the dark field of Fig. 8, which was obtained from one ring of the diffraction pattern of Fig. 9. Figure 10 shows the smallest particles of the studied material.

From different dark field micrographs, similar to that shown in Fig. 8, we measured the crystallite sizes distributed as shown in the diagram of Fig. 11. The particle size distribution was obtained from bright field micrographs, see Fig. 12 and Table 1.

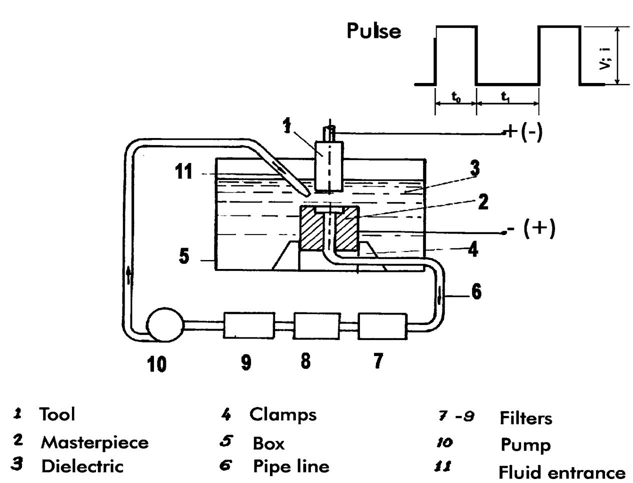

Fig. 1 Device for obtention and collection of the expulsed electro-erosioned particles; V = 80 V, i = 25 Amp, t_0 = 3,072 μs

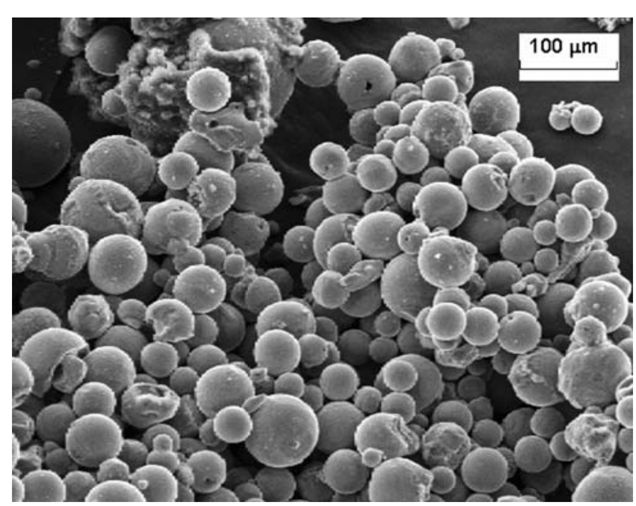

Fig. 2 SEM micrograph showing a group of spherical particles at low magnification

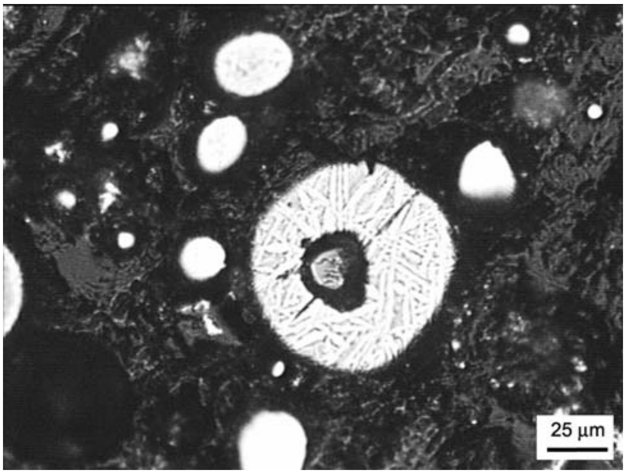

Fig. 3 SEM micrograph taken on a cross section of a hollowed sphere and others on a homogeneous one

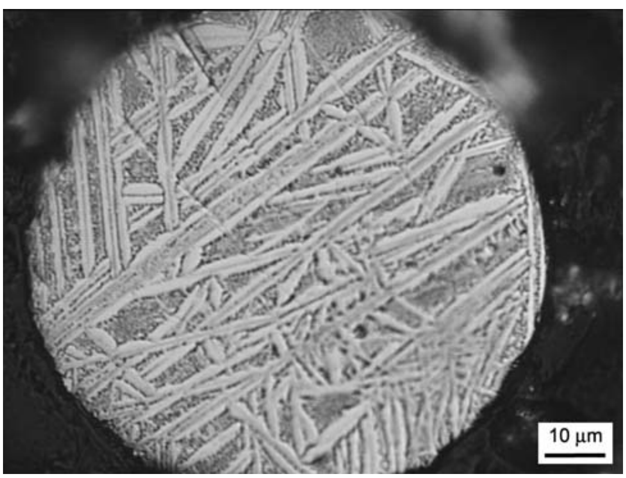

Fig. 4 Optical metallography taken on a cross section of a homogeneous sphere with Widmanstätten pattern

The composition of the nanoparticles was obtained with the EDS detector in the TEM equipment with an uncertainty of ±5 at.%.

Figure 13 displays three diffractograms corresponding to pure iron, indicated as α-Fe, to particles between 44 and 53 µm labeled as –44, and particles smaller than 44 µm, the lines on the top of Fig. 13 corresponds to Fe_3C.

Discussion

Even if there is a similar method employing electro-discharges to produce particles, it consists of a different specific device [6]. The difference with our method is that we have used a conventional EDM with a simpler apparatus, which may be effortless built.

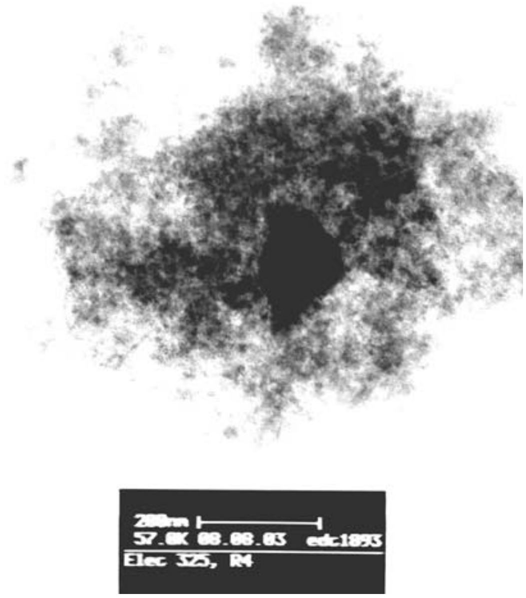

Fig. 5 TEM micrograph showing a general view of spherical nanoparticles

Fig. 6 TEM micrograph of an isolated nano-particle, showing the layer formed by very small particles

Microscopic continuous solid spheres are the most common shape obtained by electro-erosioning iron with kerosene as dielectric and when water is the dielectric the hollowed spheres are predominant [11]. In the case of the U-Mo electro-erosioned with water [13], both

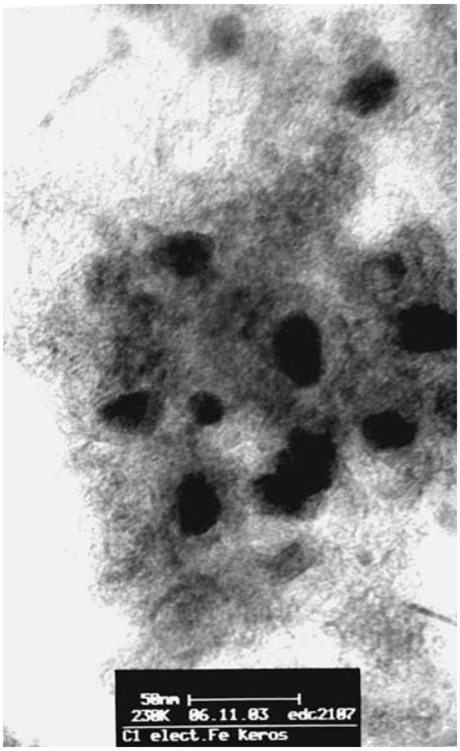

Fig. 7 TEM bright field micrograph showing nanoparticles

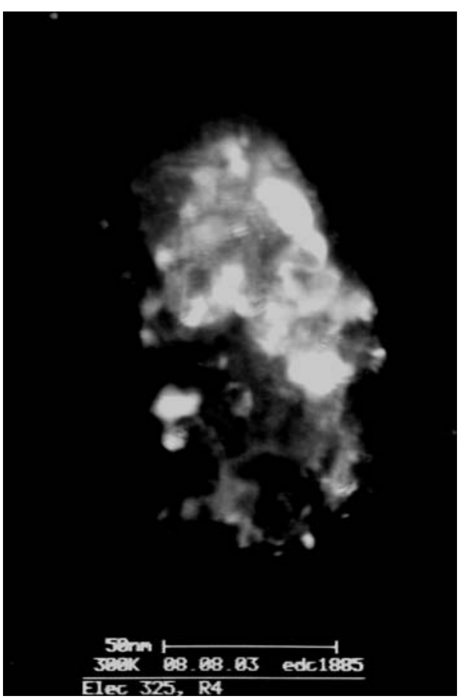

Fig. 8 TEM dark field showing crystallites. The crystallites are smaller than particles of Fig. 7

hollowed and non-hollowed spheres are present. In this work the TEM observations showed only continuous spheres.

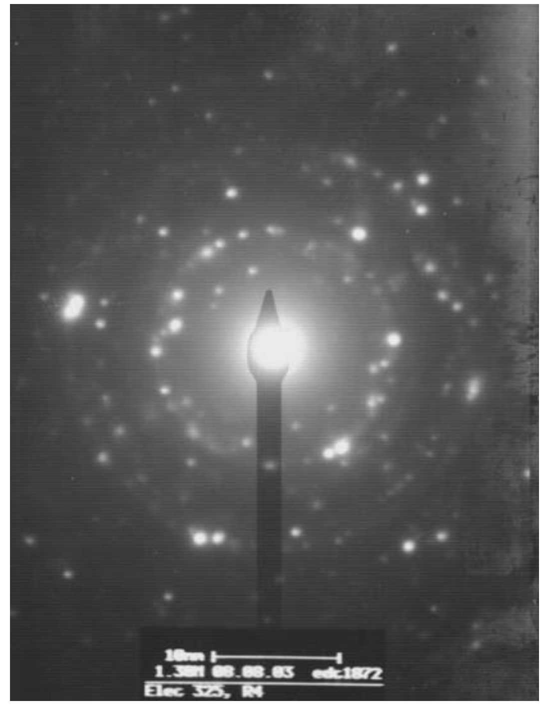

Fig. 9 Electron diffraction pattern of –44 μm particles, the rings correspond to iron carbides

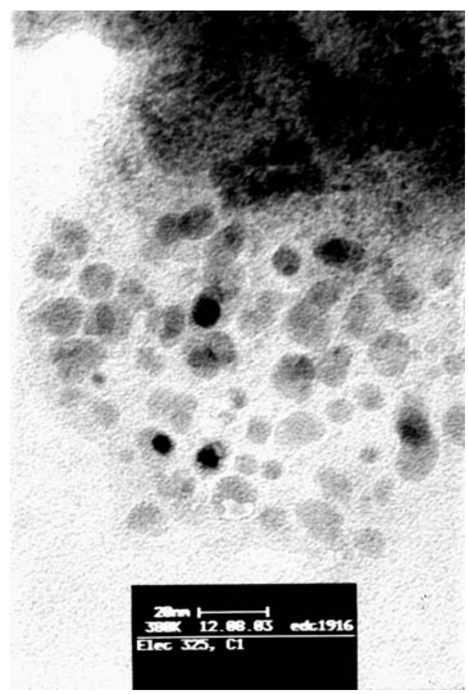

Fig. 10 TEM micrograph showing the smallest observed particles

The nanoparticles studied in this work contain carbon as result of the interaction between iron and the kerosene and they are carbides like those found in [11]. The XRD also gives this evidence, see Fig. 13. The type of carbides is similar to those obtained by planning electro erosion [7–9], but some

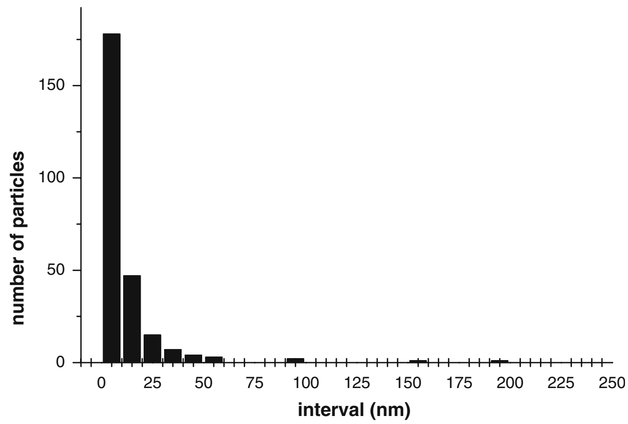

Fig. 11 Crystallites size distribution

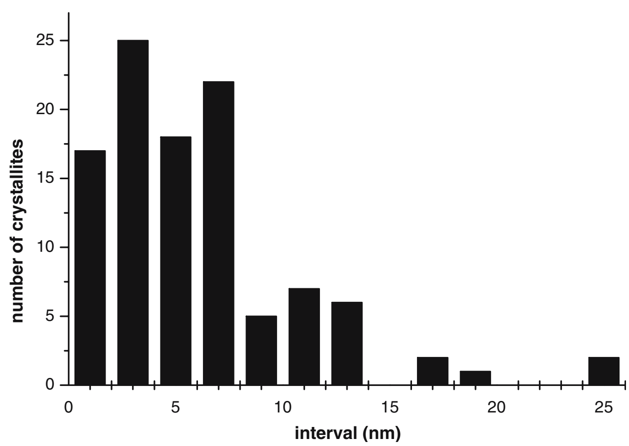

Fig. 12 Particles size distribution

Table 1 Mean dimensions of crystallites and particles

	Mean large (nm)	Measurements
Crystallites	5.9 ± 0.4	105
Particles	37.0 ± 9.0	267

semiquantitative EDS analysis revealed that particles smaller than 50 nm had less iron than those larger than 50 nm.

In iron electro-erosioned in kerosene nanoparticles come from the condensation of vaporized electrodes material [4], and microparticles from the molten pool formed on the surfaces of tools [6]. The distribution size of particles show a mean value of about 37 nm, Fig. 11. It could be seen from Fig. 12, that the mechanism of formation of small particles produces particles with crystallites of about 5 nm that means spheres of about 500 nm^3.

Conclusions

We have confirmed the production of nanoscopic spherical material produced by a commercial EDM electro-erosioning iron in kerosene. In this case carbides were found. The set of measured particles present a monomodal distribution, meaning that this particles may be produced by one singular mechanism during ablation. We found that the observed particles are not magnetic because that the electron diffraction patterns reached the center of the TEM screen. Also the electron diffraction patterns do not show any amorphous state.

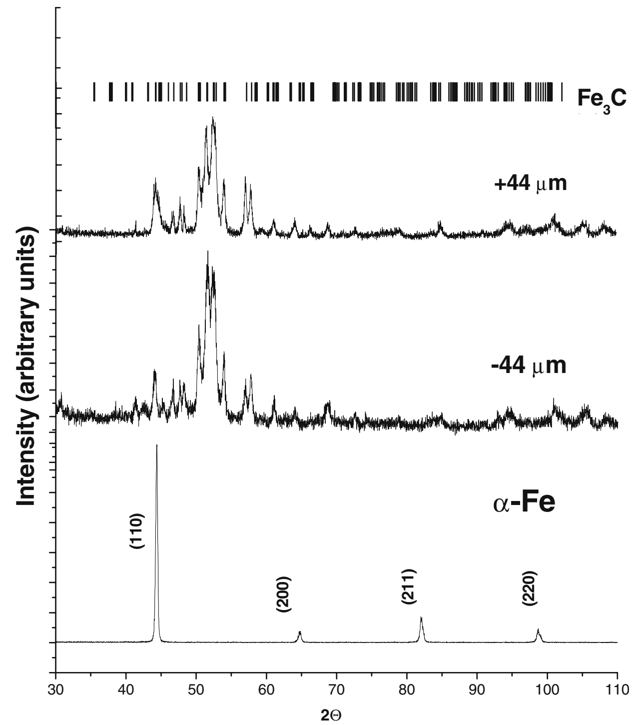

Fig. 13 X-ray diffraction of α-Fe, of particles between 44 and 53 μm and particles smaller than 44 μm

This process would be of interest to produce very small particles with different compositions, sizes and physico-chemical properties depending on the dielectric, material to ablation and EDM parameters. This simple method could be used to produce small particles for many applications like pulvimetallurgy, introducing thermally resistant particles to alloys, medicine, etc.

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