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TUNGSTEN AND ALUMINIUM NANOPARTICLES SYNTHESIZED BY LASER ABLATION IN LIQUIDS

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In this work we explore the viability of laser ablation of W and Al metal targets immersed in acetone and water, respectively, as a technique to produce metal nanoparticles having structural, morphological, and compositional properties that are related to those expected to be created as by-products in next-generation nuclear fusion reactors. The morphology of laser processed particles was investigated by means of scanning electron microscopy (SEM). Information regarding their size-distribution was inferred from the SEM micrographs using computer imaging software. Energy-dispersive X-ray spectroscopy (EDAX) analysis was used to reveal the composition of resulting particles. The formation of spherically shaped metal nanoparticles with sizes ranging from few tens of nanometers to several hundreds of nanometers is revealed for all samples. Ablation in acetone appears to result in strong contamination with C and pronounced agglomeration of particles. Ablation in water medium gives rise to much more dispersed particles, allowing for computer imaging software analysis of their size distributions. Both of these morphologies are relevant in terms of future particle treatments and environmental/toxicology studies, as dust created in future fusion reactors is expected to exhibit both a core-shell structure and a simpler structure that is susceptible to rapid oxidation.

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1. Introduction

To date, metal powders made of particles with sizes ranging from several nanometers (clusters) to hundreds of microns have found uses in numerous fields, most notably in industrial applications related to the fabrication of hard coatings and super-alloys [1]. Conversely, the treatment, handling, and removal of such metal powders that are expected to be created as by-products in next-generation nuclear fusion reactors, such as ITER, are major issues. The likely formation of tritiated dust following the erosion of the reactor walls could compromise its functioning and safety. Moreover, the treatment, removal, and handling of such products raise serious health and environmental concerns. All these aspects have been taken under severe scrutiny by participants to the European Fusion Development Agreement [2].

Most of the studies related to the treatment and synthesis of metal particles using various laser-based techniques are aimed towards applications in the field of materials science, and only a handful of them relate to possible applications in nuclear reactors [3-5]. Laser synthesis and treatment of metal particles aimed at applications related to the functioning and safety of fusion reactors is a niche of scientific research, which has not been approached in detail thus far.

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In this work we explore the viability of laser ablation of W and Al metal targets immersed in acetone and water, respectively, as a technique to produce metal nanoparticles having properties related to those of powders expected to be created as by-products in next-generation nuclear fusion reactors. Our work is a first step towards more in-depth studies on the properties and treatment of such particles. To this end, laser ablation of metal targets in liquids is a particularly appealing synthesis technique, making it possible to produce not only pure nanoparticles, but also oxides, carbides, and various alloys. Moreover, this method has other significant advantages, such as a relatively simple experimental setup, ease of preparation and size control [6-8].

2. Experiment

The setup used for the synthesis of metal particles by laser ablation of a metal target in liquid medium is presented in Figure 1. A lens having a focal distance of 30 cm was used to focus the laser beam on the metal target (Al or W, respectively) immersed under ~30 ml of liquid in a rotating receptacle. This particular choice of targets is closely tied to the materials used for the construction of fusion reactors, namely Be and W. Given the high toxicity of Be, Al was chosen as a substitute due to some common physical and chemical properties that it shares with Be.

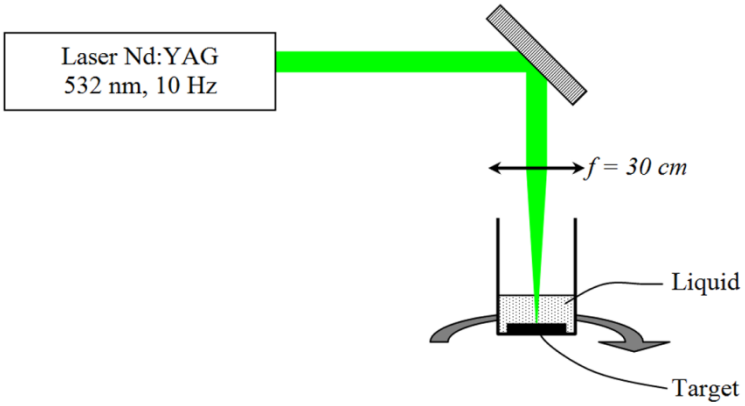

Fig. 1. Schematic representation of the experimental setup.

The source used for the ablation of the metal targets was a Continuum made laser, Surelite II model, working at a wavelength of 532 nm (2nd harmonic), having a pulse duration of ~7 ns and a pulse repetition frequency of 10 Hz. The value of the working wavelength was chosen in such a way as to minimize attenuation in the media considered for the experiments of ablation in liquids, namely acetone and water. Table I gives a summary of the experimental conditions under which selected samples were obtained.

Table I. Growth conditions of selected samples.

Sample	Target	Liquid	Fluence (J/cm^2)
A	Al	acetone	20
B	Al	water	20
C	W	acetone	20
D	W	acetone	28
E	W	water	20
F	W	water	28

For all samples discussed in this paper, the duration of each experiment was of 30 minutes (18,000 pulses). The spot size on the target surface was of 0.6 mm^2. At the end of the ablation procedure, ~15 ml of solution (around 50% of the initial quantity) were taken and placed in a beaker with a Si substrate placed at the bottom. Particles remained on the surface of the Si substrate following evaporation. This approach gave us the possibility to analyze the morphology of the resulting particles by scanning electron microscopy, Si being a particularly adequate substrate for SEM analysis.

The morphology of the laser processed particles was investigated by means of scanning electron microscopy. Energy-dispersive X-ray spectroscopy analysis was used to reveal the composition of resulting particles. Both characterizations were performed using an FEI Inspect S50 apparatus. The size-distribution histograms of the as-synthesized particles were inferred from the SEM micrographs using computer imaging software analysis.

3. Results and discussions

The SEM images of samples A and B, obtained following the ablation of an Al metal target in acetone and water, respectively, are presented in Figure 2. We should mention that prior to the preparation of the particles on Si substrates the colloidal solutions resulting from the ablation in liquids were transparent, with a brown hue in the case of sample A, processed in acetone, and a white hue in the case of sample B, obtained in water. No coloration of the liquid was visible to the naked eyed when we used a laser fluence of 12 J/cm^2.

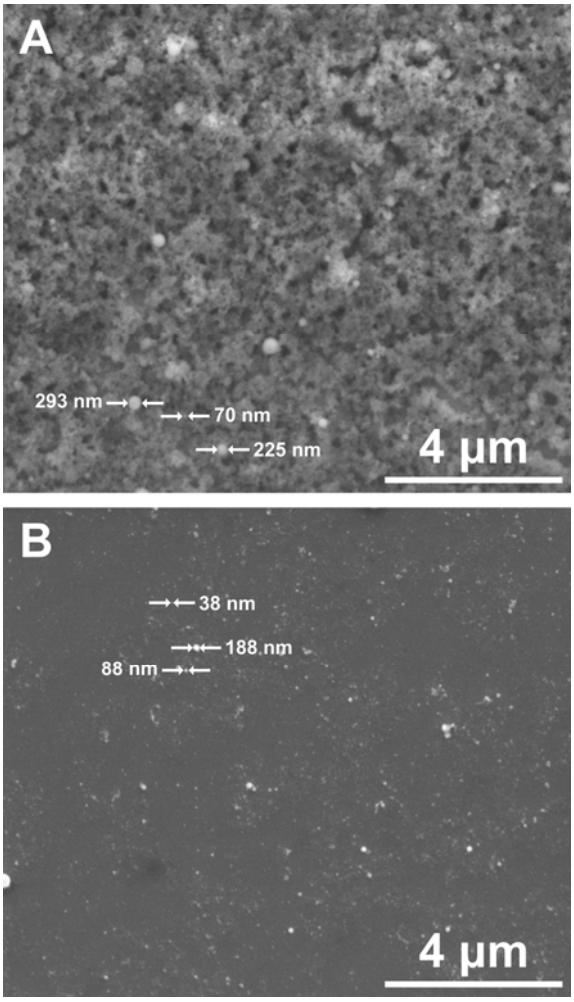

Fig. 2. SEM images of samples A (top) and B (bottom) obtained following the ablation of an Al target in acetone and water, respectively, at a laser fluence of 20 J/cm^2.

In the case of sample A, the dark hue of the colloidal solution suggests the fact that we are dealing with the presence of carbon in the ablated products, either as carbon particles or as C-coated Al particles [9]. According to Ref. [10], the high temperature plasma generated after each laser pulse at such fluences decomposes acetone molecules, resulting in the release of C atoms. Some of these C atoms will then bind to synthesized metal particles, forming a carbon shell. On the other hand, in the case of sample B, the white hue of the colloidal solution suggests the likely oxidation of the Al particles. This hypothesis is also supported by the white coloration of the Al target in the ablated region.

The most obvious difference between the morphologies of samples A and B is the fact that in the case of sample A particles seem to form a compact conglomerate, while in sample B they remain dispersed. This effect is due to the different nature of particles in the two samples, but also stems from the fact that, during sample preparation, evaporation of acetone is more rapid and energetic than that of water, which favours the formation of conglomerates in the case of the former.

The arrows in Figure 2 point to a few selected particles. Corresponding diameters are also shown (with an error of ±6 nm) in order to give the reader a rough image of particles sizes in the two samples. Particles have a spherical shape, their diameter being in most of the cases of the order of few tens of nanometers, in some cases going up to few hundreds of nanometers. As mentioned, particles can be distinguished more easily in the SEM image of sample B. Almost no agglomeration effect is visible in this case, making it possible to distinguish particles with much smaller diameters than in the case of sample A.

The ablation of W in liquids (acetone and water, respectively) yields similar results. Experiments on W targets were conducted at two laser fluences (20 and 28 J/cm^2, respectively). This was due to the fact that at 20 J/cm^2 the coloration of the W colloidal solutions was much fainter than that of Al colloidal solutions, likely due to the higher ablation threshold of W with respect to that of Al. A 40% increase of laser fluence resulted in similar colorations of the colloidal solutions as compared to those of Al.

In Figure 3 we show the SEM images for samples obtained following the ablation of W in acetone at fluences of 20 and 28 J/cm^2, respectively, whereas Figure 4 illustrates the same result for the case of W ablation in water. Increasing fluency by a factor of 40% (from 20 to 28 J/cm^2) yields different results in the considered media. In the case of acetone (samples C and D), a net increase of the number metal particles with increasing fluence is observed. There is only a quantitative difference between particles in samples C and D, both of them exhibiting formation of conglomerates. The agglomeration effect is more prominent in the case of sample D due to a higher density of particles of the surface of the Si substrate. Particles sizes in samples C and D show no significant variations and are comparable to those of sample A.

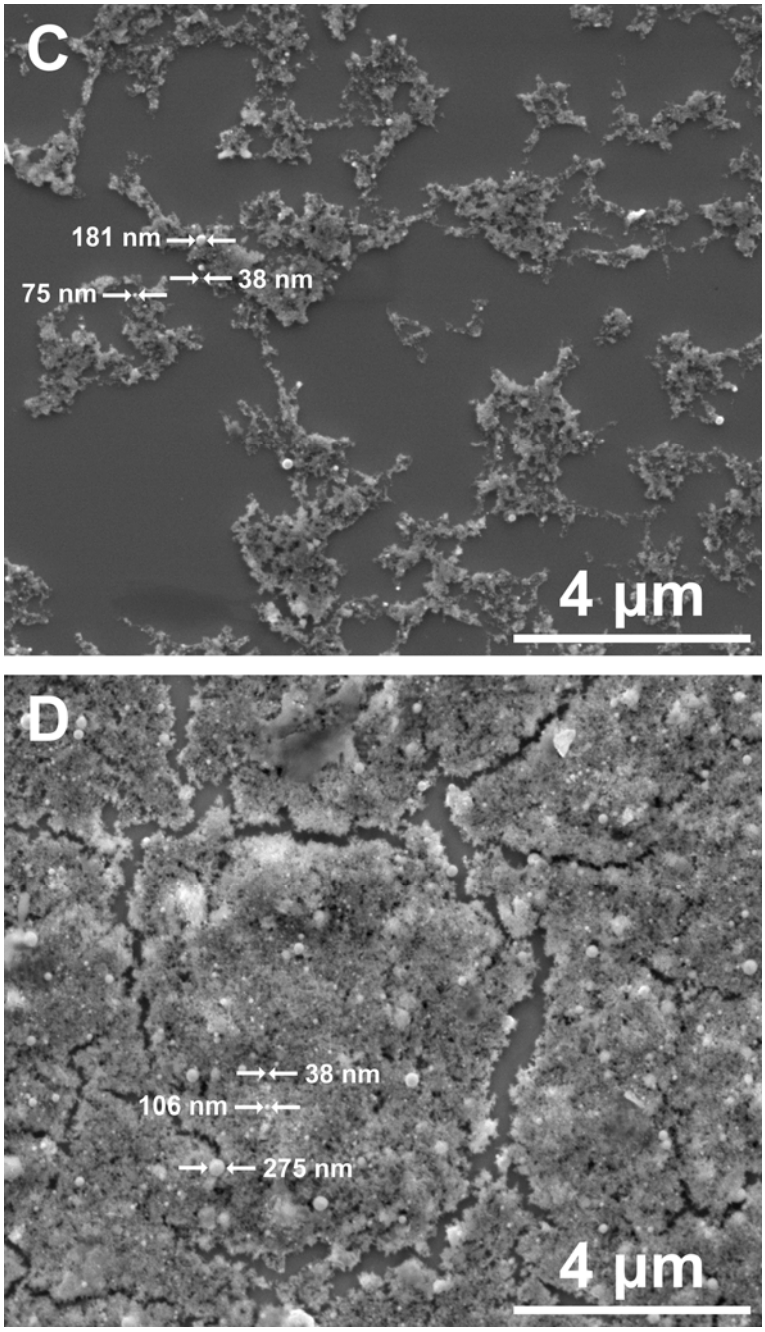

Fig. 3. SEM images of samples C (top) and D (bottom) obtained following the ablation of a W target in acetone at laser fluences of 20 and 28 J/cm^2, respectively.

A different outcome is observed for samples E and F, which exhibit qualitative differences in morphology (Figure 4). The higher statistical weight of particles having sizes in excess of hundreds of nanometers in samples F suggests a change in the formation mechanism of these particles. A likely cause for this occurrence is the transition from an ablation regime in which a plasma of atomic vapours is generated to one in which large clusters are ablated from the W target, resulting in the formation of bigger particles following condensation.

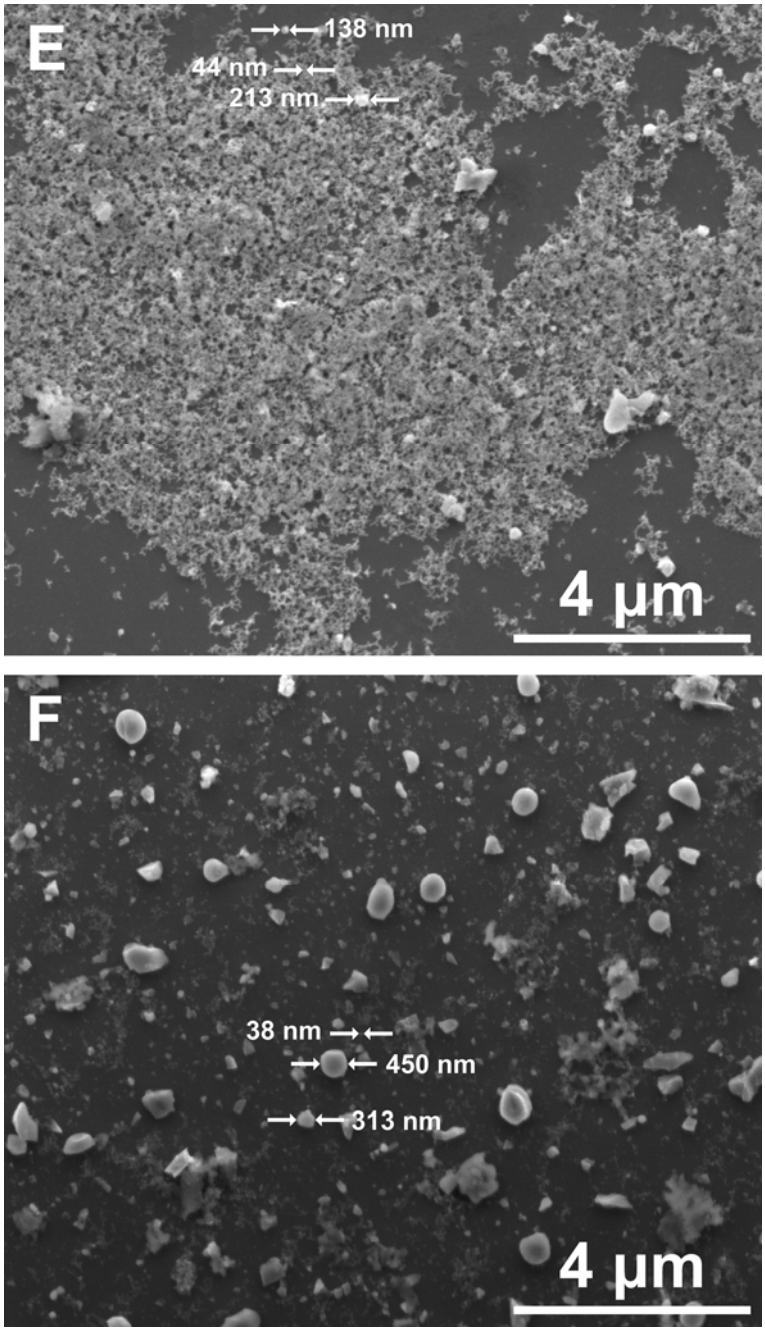

Fig. 4. SEM images of samples E (top) and F (bottom) obtained following the ablation of a W target in water at laser fluences of 20 and 28 J/cm^2, respectively.

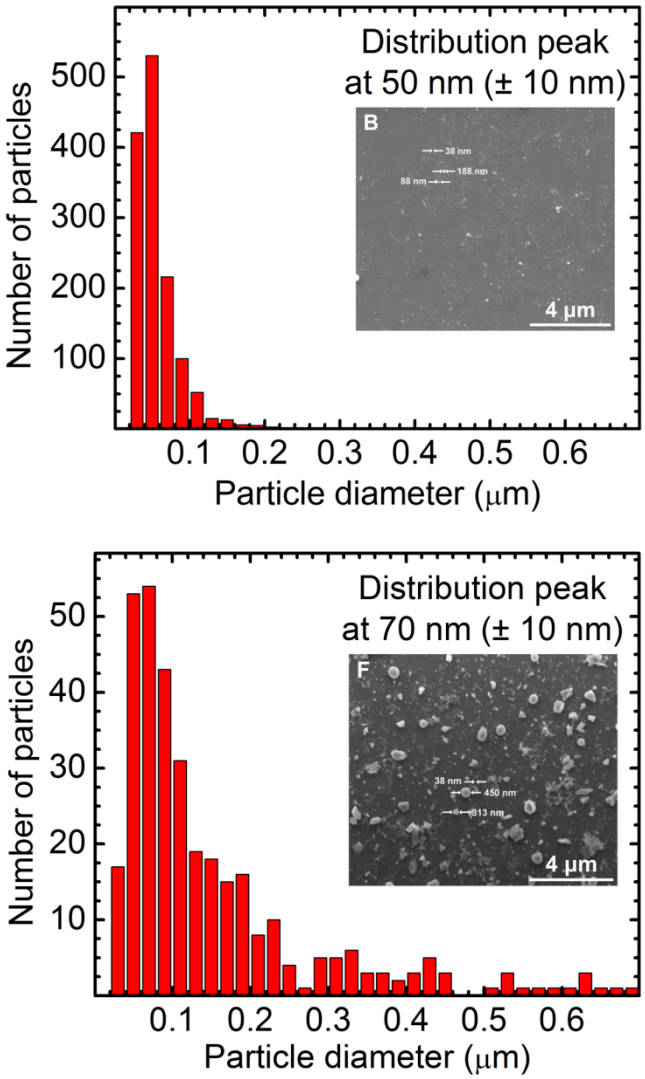

Fig. 5. Computer imaging software generated histograms of particles sizes for samples B (top) and F (bottom). The width of each bin is 20 nm.

Computer imaging software analysis of particles size distributions yielded meaningful results only in the case of samples in which particles were dispersed. The histograms of particles sizes for samples B (Al in water, 20 J/cm^2) and F (W in water, 28 J/cm^2) are illustrated in Figure 5. The width of each bin is 20 nm. Although the two distributions peak at comparable values, 50 nm for sample B and 70 nm for sample F, respectively, there are two significant differences between them: i) sample B exhibits a fairly narrow and symmetric distribution of particles sizes, whereas the formation of a significant number of particles having diameters of the order of hundreds of nanometers leads to an asymmetric broadening of the histogram of sample F; ii) the number of particles with diameters peaking at 50 nm in sample B is one order of magnitude higher than that of those peaking at 70 nm in sample F. These observations suggest that, quantitatively, most of the ablated material is retrieved as large particles, several hundreds of nanometers in diameter, in the case of sample F, and as many small particles, ~50 nm in diameter, in the case of sample B.

Compositional analysis of the resulting particles by means of energy-dispersive X-ray spectroscopy proved to be particularly challenging due to the very thin layer of material / particles covering the Si substrate. This translated into extremely poor detection capabilities, especially for the case of W whose principal transition in the EDAX spectra was completely masked by the overlapping signal coming from the Si substrate.

EDAX mappings of samples synthesized from Al targets identified spherical particles observed in SEM images as containing Al. Contributions from C and O however could not be resolved due to the very low detection efficiency of the system for these elements.

4. Conclusions

We performed laser ablation experiments of Al and W targets in acetone and water, respectively. SEM analysis of synthesized particles reveals that they are generally spherically shaped, with diameters usually of the order of several tens of nanometers, in same cases going up to hundreds of nanometers. Therefore, we can assert that for both targets (Al and W, respectively) and for both media considered (acetone and water, respectively) the synthesis of nanoparticles was achieved.

Significant differences between the nanoparticles states of aggregation on the substrate following evaporation have been observed. Nanoparticles processed in water maintain a better dispersion on the substrate surface, as compared to those obtained in acetone, allowing for the determination of their size distributions using computer imaging software. Particles size distributions peak are relatively narrow, peaking at 50 - 70 nm. There are, however, notable differences between the shapes of the distributions of Al particles sizes processed in water at a laser fluence of 20 J/cm^2 and that of W particles obtained in water at a laser fluence of 28 J/cm^2, a significant portion of these latter ones having sizes in excess of several hundreds of nanometers.

A pronounced agglomeration of Al and W particles, as well as strong C contamination, was observed for all samples processed in acetone. The agglomeration of Al nanoparticles has also been reported in Ref. [9]. Al particles size distributions measured using a laser particle size analyzer (LPSA) and reported in Ref. [9] are strikingly similar to those reported in this paper for sample B, suggesting that our computer assisted imaging analysis approach was accurate.

EDAX measurement confirmed the presence of Al in nanoparticles observable in the SEM images of samples A and B presented in this work. A transmission electron microscopy (TEM) photograph in Ref. [9] reveals the core-shell structure of some of the Al nanoparticles processed in acetone, which is likely to occur in our experiments as well. Given these results, future experiments of treatments and environmental/toxicology studies of by-products expected to be created in next-generation nuclear fusion reactors could be initiated using such particles.

Acknowledgments

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