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# Oxide reduction during triggered-lightning fulgurite formation

B.E. Jones[a], K.S. Jones[a,*], K.J. Rambo[b], V.A. Rakov[b], J. Jerald[a], M.A. Uman[b]

[a]*Department of Materials Science and Engineering, University of Florida, 100 Rhines Hall, Gainesville, FL 32611, USA*
[b]*Department of Electrical and Computer Engineering, University of Florida, 100 Rhines Hall, Gainesville, FL 32611, USA*

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**Abstract**

In this study triggered-lightning induced fulgurites were formed in 99.9% pure binary oxides of manganese (MnO) and nickel (NiO) in order to study oxide reduction mechanisms. The fulgurite formation process involved packing the oxide in PVC holders and using the standard rocket-and-wire technique to trigger a lightning strike through the oxide at the International Center for Lightning Research and Testing in Camp Blanding, Florida. These two oxides were chosen from the thermodynamic extrapolation of the oxide stability using the Ellingham Diagram. This diagram indicates that NiO is significantly less stable than MnO. Fulgurites from the pure oxides were analyzed in a scanning electron microscope (SEM); secondary electron images, backscattered images and energy dispersive spectroscopy (EDS) were used to determine the microstructure and composition of the fulgurites. SEM/EDS analysis of the NiO and MnO prior to fulgurite formation confirmed they were pure binary oxides with no metallic contamination. After fulgurite formation, it was found that the nickel oxide fulgurite contained metallic nickel particles; the manganese oxide fulgurite showed no metallic phase formation. Transmission electron microscopy (TEM) examination confirmed that the MnO was a pure oxide with no sign of metallic phase formation. However, TEM results of the NiO showed that approximately 50% of the NiO was reduced to metallic face-centered cubic Ni. The Ni and NiO were observed to be coherent with the [1 0 0]Ni//[1 0 0]NiO and [1 1 0]Ni//[1 1 0]NiO. These results are consistent with the aforementioned thermodynamic stability calculations and show that the presence of carbonaceous material or mixtures of oxides is not necessary for oxide reduction during fulgurite formation. These studies do not rule out the possibility that electrolysis plays a role in oxide reduction. However, these fulgurites were made simultaneously during the same lightning strike and therefore were subjected to the same electrical current, and thus it is proposed the thermodynamic stability of the oxide must play a role in oxide reduction.


*Keywords:* Lightning; Fulgurite; Oxides; Reduction

## 1. Introduction

Lightning is known to produce air temperatures as high as 30,000 K (Uman, 2001). Fulgurite formation is a well-known phenomenon associated with lightning striking the surface of the earth (e.g. Frondel, 1962; Pye, 1982; Rakov, 1999). The general macroscopic characteristics of fulgurites have been studied by many groups (Anderson, 1925; Gifford, 1999; Daly and Buseck, 1993; Pye, 1982; Carron and Lowman, 1961). These studies have reported that the macroscopic, morphological, and textural features of fulgurites are

*Corresponding author. Tel.: +1 352 392 9872; fax: +1 352 392 8381.
*E-mail address:* kjones@eng.gufl.edu (K.S. Jones).

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consistent with melting and solidification of the surface sediment.

Microscopic studies of the composition and microstructure have also been conducted (Anderson, 1925; Essene and Fisher, 1986; Wasserman et al., 2002; Carron and Lowman, 1961). These studies have reported that metallic phase formation from the reduction of oxides can occur during fulgurite formation. There has been much speculation as to the origin of this metallic phase formation. One of the principle issues has been whether carbon is necessary for oxide reduction. The purpose of this study was to produce fulgurites in pure binary oxides in an effort to better understand the mechanism behind the reported oxide reduction process.

## 2. Experiment

Two 8 cm lengths of 2.54 cm diameter PVC pipe were filled with 250 g of either MnO or NiO. A very fine copper wire was installed along the axis of the PVC in order to help control the fulgurite formation process. Lightning was then artificially initiated from natural thunder clouds using the rocket-and-wire technique (Davis et al., 1993; Rakov et al., 1998) at the International Center for Lightning Research and Testing at Camp Blanding, Florida. The triggered lightning current that created the fulgurite transferred 27 C of charge in about 350 ms and consisted of an irregular current flow with a peak value of about 550 A. After fulgurite formation the contents of each tube were filtered through a fine screen and the subsequent fulgurite material analyzed. After weighing the fulgurite material, pieces of the two fulgurite samples, along with oxide that was not subjected to lightning (control samples) were prepared for SEM analysis. This involved lapping the fulgurites using 1200 grit SiC paper in order to produce a flat surface for SEM analysis. A FEI Dual beam (DB-235) focused ion beam (FIB) was used to produce the TEM sections from the fulgurites. Each section was approximately 10 μm long 5 μm deep and 0.2 μm thick (electron transparent).

SEM microstructural analysis was conducted on a JEOL 6400 SEM with a Link EDS system. Secondary images as well as back-scattered images of the surfaces were taken. EDS analysis was done on both virgin oxides as well as the lapped fulgurite surfaces. In addition EDS analysis was conducted on the light and dark regions of the back-scattered image. A FEI dual beam focused ion beam system (DB-235) was used to prepare the TEM samples. TEM analysis was conducted on a JEOL 200CX. Both bright field and dark field images as well as selected area diffraction patterns were taken.

## 3. Data

Using the SEM, micrographs of the fulgurites were taken at low magnification prior to lapping (Fig. 1). The MnO fulgurite was more tube-like in its morphology than the NiO fulgurite. Pieces of each fulgurite were polishing flat prior to SEM analysis in order to eliminate possible shadowing effects during EDS analysis. Multiple backscattered electron images of each fulgurite were taken to determine if any metallic phase was formed.

Fig. 2 shows the backscattered image of the polished surface of the NiO fulgurite. The NiO fulgurite showed regions rich in heavier elements (bright regions in Fig. 2) whereas the MnO sample did not show any signs of phase separation (no bright regions). Energy-dispersive spectroscopy was used to determine the chemical composition of each sample. Fig. 3 shows a pair of EDS spectra from NiO sample. Fig. 3a is from the dark

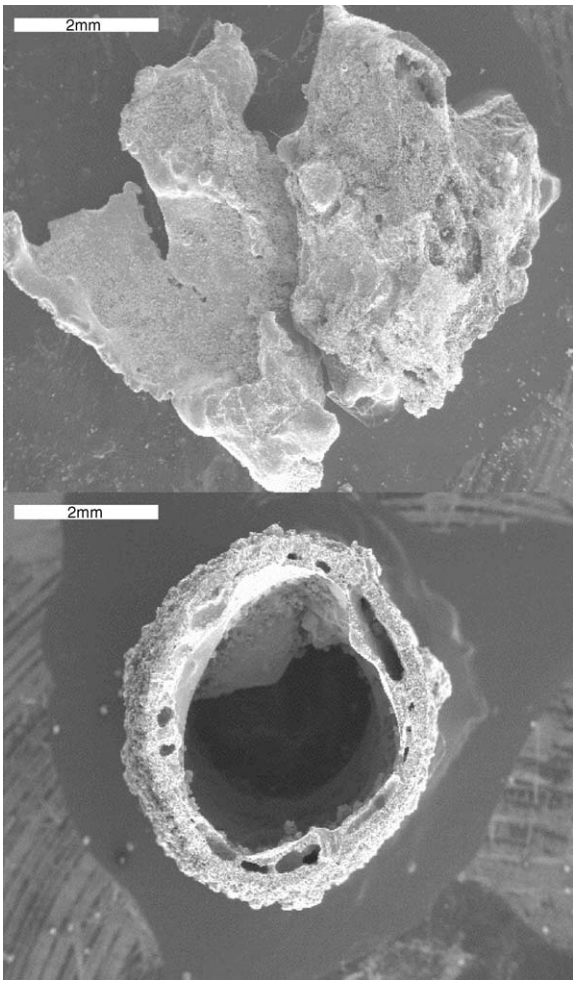


Fig. 1. Low-magnification SEM image of NiO fulgurite (top) and MnO fulgurite (bottom).

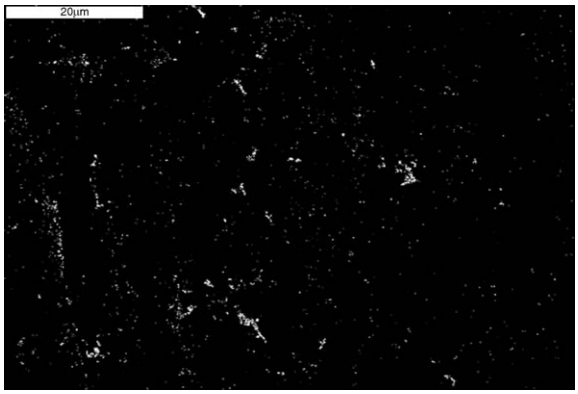


Fig. 2. NiO backscattered electron image; bright spots are metallic Ni particles.

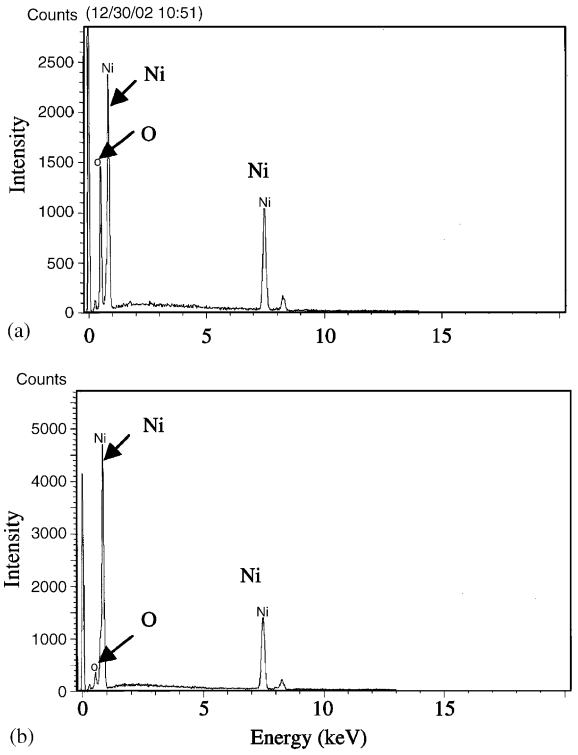


Fig. 3. EDS results of bright and dark regions in Fig. 2 (a) strong presence of oxygen in darker regions of Fig. 2, however (b) shows EDS spectrum of bright particle from Fig. 2 showing a lack of oxygen.

regions of the NiO micrograph in Fig. 2. This spectrum is identical to the virgin binary nickel oxide powder before fulgurite formation. Fig. 3b shows the EDS results from the bright regions of the NiO sample in Fig. 2. It is obvious that the oxygen concentration is greatly reduced in these bright regions. Quantitative analysis of the EDS spectra is given in the table in Fig. 4. The EDS indicates the bright particles are at least 87% Ni. However the regions are too small ($<1\,\mu m$) to get an accurate nickel/oxygen ratio. Its possible there is pure Ni in the sample but it is not possible to discern it from the SEM results.

In order to better understand the microstructure of the phases formed after fulgurite formation TEM analysis was done. Thin (2000 Å) thick slices 10 µm long by 5 µm deep were made from each fulgurite using the FIB. Figs. 5a and b show bright field images of the NiO and MnO fulgurites, respectively. The NiO image was taken at the [0 0 1] pole where as the MnO was taken down the [0 −1 1] pole as shown in the diffraction patterns in Figs. 6a and b, respectively. The NiO clearly shows a two phase mixture has formed. The diffraction pattern in Fig. 6a shows two distinct phases present along with a set of double diffraction spots. The spots with the smaller reciprocal lattice spacing (labeled 1–3) were determined based on their symmetry and inter-planar spacings to arise from pure cubic NiO (Fig. 7). The spots with the larger reciprocal lattice spacing (4–6) were determined to arise from pure cubic Ni. The double diffraction arises because the two phases were coherent with the (2 0 0) planes of NiO parallel to the (2 0 0) of Ni and the (2 2 0) planes of NiO parallel to (2 2 0) planes of Ni. Simulation of the diffraction pattern was done using a program called Desktop Microscopist® and the results matched the diffraction pattern of Fig. 6a exactly. Dark field images were done using the Ni (2 0 0) spot to produce the image and it was shown that the dark phase in Fig. 5a I the Ni phase. Quantitiative analysis of the Ni portion of the image estimated the fraction to be 50% Ni ± 5%. Thus a significant portion of the Ni is reduced during fulgurite. Fig. 5b shows that the MnO appears to be simply a highly defective single phase. This is confirmed in the diffraction pattern in Fig. 6b. The diffraction pattern was indexed and shows only pure MnO as indicated in the table in Fig. 7. Thus no oxide reduction was observed in the case of the MnO fulgurite.

| Fulgurite | Atomic % Ni | Atomic % Mn | Atomic % O |
|---|---|---|---|
| NiO (dark region fig. 2) | 52% ± 5% | | 48% ± 5% |
| NiO (bright region fig. 2) | 83% ± 5% | | 17% ± 5% |
| MnO (all regions) | | 45% ± 5% | 55% ± 5% |

Fig. 4. Table quantifying the EDS results by SEM.

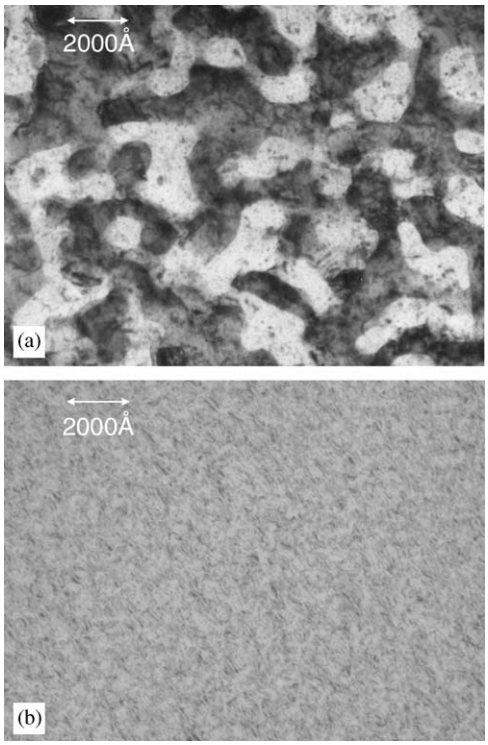


Fig. 5. Bright field TEM images of (a) NiO and (b) MnO fulgurites. NiO is clearly a two-phase mixture but the MnO fulgurite is a defective single phase.

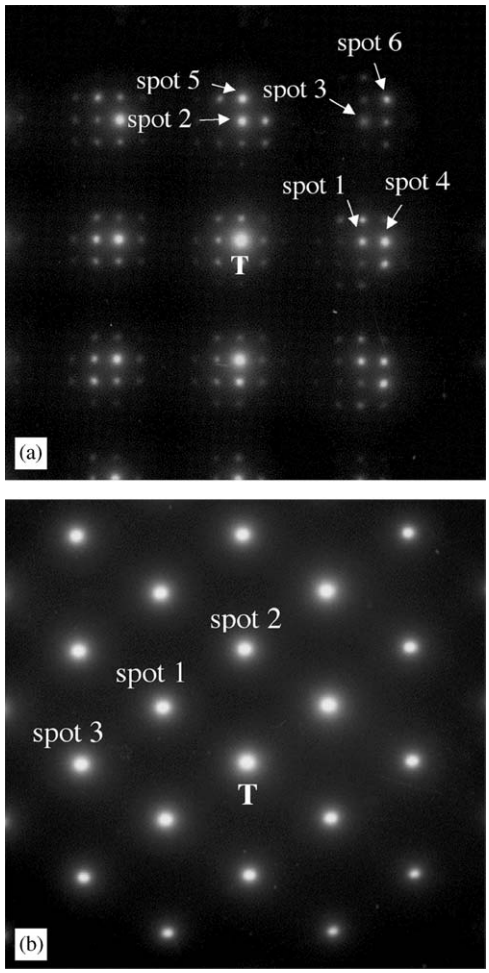


Fig. 6. Selected area diffraction pattern of fulgurites (a) NiO [0 0 1] zone axis (b) MnO [0 −1 1] zone axis.

## 4. Discussion

It has been previously reported that metallic oxide reduction can occur during fulgurite formation and many possible explanations were proposed. One possible explanation was the thermodynamic instability of the oxide at high temperature with respect to the metal (Essene and Fisher, 1986; Wasserman and Melosh, 2001). A second possible explanation involved the presence of carbon acted as a reducing agent through the formation of CO or other compounds (Essene and Fisher, 1986; Wasserman et al., 2002) The possibility that carbon was responsible for the oxide reduction process, could not be eliminated by Essene because of the existence of carbonaceous material in the soil. A third possibility is electrolysis from the high current associated with the lightning (Essene and Fisher, 1986). A fourth possibility is that the shockwave may induce reduction (Rowan and Ahrens, 1994). A fifth possibility is that one oxide converts to a more oxidized state thereby reducing a less stable oxide.

In this experiment, for the first time fulgurites were formed in pure binary oxide samples of NiO and MnO. Both fulgurites were formed simultaneously with the same lightning strike. The SEM results showed metallic particle formation in the NiO but not in the MnO. The TEM results confirm this and show that a significant portion (50%) of the NiO was reduced to pure Ni whereas the MnO remains pure MnO. The NiO fulgurite was also found to be highly conducting after fulgurite formation, however, the MnO was found to be insulating. The TEM results explain the origin of the conductivity in the NiO fulgurite. The observation of metallic phase in the pure NiO fulgurite samples indicates that the presence of carbon is not necessary for oxide reduction. In addition since the oxide was pure the presence of two different oxides is not necessary for metallic phase formation. There were concerns that the thin Cu wire might oxidize and contribute to oxide reduction however this is discounted because (a) the amount of Cu was very small (less than 1% of the fulgurite by weight) and (b) no CuO was observed, only a couple of very small particles of metallic Cu in the

| TEM SADP data | | | JCPDS Files | | |
|---|---|---|---|---|---|
| Fulgurite | Spot | d spacing (Å) | Mineral | d spacing (Å) | Planes |
| MnO | 1 | 2.6 | MnO | 2.568 | (111) |
| | 2 | 2.3 | | 2.22 | (200) |
| | 3 | 1.6 | | 1.57 | (022) |
| NiO | 1 | 2.09 | NiO | 2.08 | (200) |
| | 2 | 2.08 | | 2.08 | (200) |
| | 3 | 1.48 | | 1.48 | (220) |
| | 4 | 1.9 | Ni | 1.8 | (200) |
| | 5 | 1.87 | | 1.8 | (200) |
| | 6 | 1.3 | | 1.25 | (220) |

Fig. 7. Table indexing selected area diffraction patterns. Spot number corresponds to Fig. 6. d spacings determined from the diffraction pattern using the standard camera constant relationship. Results show that NiO fulgurite is a coherent mixture of cubic Ni and cubic NiO whereas MnO fulgurite is still pure MnO.

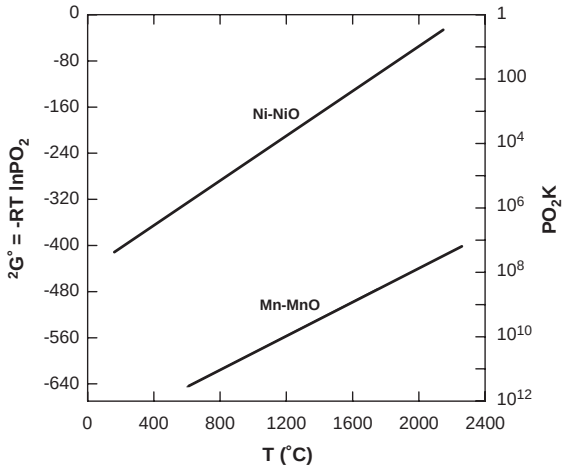


Fig. 8. Ellingham diagram of oxide stability at 1 at of oxygen. Note MnO is significantly more stable than NiO (DeHoff, 1993).

SEM results and nothing in the TEM results. It is possible that electrolysis or shock is responsible for oxide reduction. However previous studies of naturally produced silica fulgurites did not show any formation of any stishovite which is the high-pressure phase associated with meteor impact formation (Jones, 2003) suggesting that the shock wave associated with fulgurite formation is not as significant as an impact event. The final explanation is simply that the oxides are thermodynamically unstable at high temperatures. The Ellingham diagram in Fig. 8 predicts that the temperature at which the NiO becomes unstable with respect to the metallic phase (~2300 °C) is considerably lower than that of MnO (~5000 °C) (DeHoff, 1993). This is consistent with experimental observations. Thus it is possible that the thermodynamic instability of the oxide at the very high temperatures achieved during fulgurite formation is responsible for the metallic reduction observed in these fulgurites.

In conclusion, it has been shown that it is possible to reduce pure NiO to Ni during lightning-induced fulgurite formation whereas pure MnO appears to stay in its oxidized state. These results allow us to better understand the origin of the oxide reduction process observed during fulgurite formation.

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