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Dissolution of high-purity lead and subsequent crystal growth during the preparation of corrosion coupons

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High-purity lead discs were prepared using several combinations of polishing, rinsing and ultrasonic treatment. Physical degradation of the lead surface and the premature generation and deposition of oxides on the surface were observed for certain combinations of preparation steps. Ultrasonic treatment of the discs was found to be particularly detrimental as it induced significant crystal growth and, in several instances, deterioration of the polished surface. Simple air drying of freshly rinsed discs also led to oxide formation on the surface after as short a time as 1 min. An effective method for preparing discs from high-purity lead is described.

1. Introduction

In recent years there has been great interest in the corrosion behaviour of lead and lead alloys in aqueous and atmospheric environments [1–3]. This interest stems from the ubiquity of lead in past and modern manufacturing processes, as well as the known health implications when lead is released into the environment. Lead, when alloyed with other elements such as calcium, finds its principal use as the plate and post material in lead–acid batteries [4, 5]. The malleability and ductility of lead have also made it a very attractive material for processing, and among its most common applications are as sheeting for roofs [1], and in solders, bearings and lubricants [6, 7]. Chemical corrosion and wear of lead can result in the degradation of the material and the release of potentially toxic and chemically active and aggressive lead compounds [6].

The chemical aggressiveness of lead compounds is of particular concern in the nuclear industry where the presence of lead and lead alloys has been implicated as a primary feature in the premature degradation of nickel-based alloys that are used in the manufacture of critical components [8–11]. Of particular concern to date has been accelerated attack on Inconel 600, the preferred alloy for the manufacture of steam generator tubes in first-generation nuclear plants. Copson and Dean [12] were the first to identify the accelerating effect of lead on the transgranular and intergranular attack of Inconel 600 in aqueous systems, whether or not the lead was initially in contact with the alloy. Subsequent studies on 300 series stainless steels [13], Inconel 600 and other advanced steam generator tube alloys such as Inconel 690 [14] and Incoloy 800 [15] have been conducted, and the degradative effect has been found to be a function of the nickel content of the alloy, the temperature, the pH, the exposure time and the method used in alloy manufacturing. Despite the fact that the actual mechanism through which the material degradation is assisted by the presence of lead is still under debate, there is some evidence for the presence of metallic lead on the alloy surfaces [14].

Although metallic lead may play a key role in the corrosion of the tube alloys, the process leading to its deposition at tube surfaces is complex and has not been elucidated to date. There is sufficient evidence, however, to implicate the corrosion of lead and lead-containing materials as the first step in the process. Studies of lead levels in drinking-water distribution systems [3, 15, 16] and nuclear stations [17], show quite clearly that metallic lead does degrade and solubilize in aqueous systems. The chemical, thermal and operating conditions that are specific to nuclear plants have not been studied extensively with regard to their impact on lead corrosion. The results that are reported in this paper stem from our interest in the corrosion behaviour of lead in simulated secondary heat transport systems (feedwater) of CANDU® (registered trademark of Atomic Energy of Canada Limited (AECL)) nuclear generating stations.

In the course of the disc fabrication step in these experiments, it was observed that the methodology employed in the processing of the lead had a significant impact on the nature of the working surface, one that in certain instances interferes with the formation

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of corrosion films and also the final interpretation of subsequent corrosion experiments. This paper describes observations that were made during the processing and recommends methodology to ensure a reproducible working surface on lead discs.

2. Experimental procedure

The end use of the lead discs described below was for corrosion experiments in several aqueous environments (including submersion in aqueous solutions, and suspension in wet steam environments). These experiments require that the discs be mounted in autoclaves or tubular loops and, hence, the processing had to yield a stable surface that could be removed from the polishing fluid and stored temporarily.

Lead coupons were cut from high-purity bar stock (Johnson–Mathey; 12 mm diameter; 99.9999% stated purity). The discs were dry polished using 240, 360 and 600 grit emery paper followed by wet polishing using 3 μm alumina polishing compound on a rotating polishing wheel. Several options for the final surface preparation have been published, including the following: rinsing in distilled water and air drying [18, 19]; exposing the disc to a warm ammonium acetate solution [20]; cathodic polarization to induce hydrogen evolution [21]; ultrasonic cleaning [22]. Cathodic polarization is only practical for cases where the lead disc has been fabricated for ultimate use as an electrode; otherwise excessive sample handling is required. That the discs were ultimately to be used in aqueous corrosion experiments, with additives such as ammonia and acetate, precluded the use of these chemicals for the disc preparation process. Ultrasonic cleaning, which has proven to be effective for cleaning and degreasing metal specimens, was initially selected as the method for final preparation of the lead discs. As described in Section 3, the ultrasonic cleaning method was extended to include a combination of rinses with the ultrasonic treatments.

The generation and deposition of crystalline material and deterioration of the disc surfaces were followed by recording scanning electron micrographs on an ISI DS-130 microscope. Powder X-ray diffraction (XRD) patterns were recorded directly from the disc surfaces using a Rigaku Rotaflex diffractometer using nickel-filtered Cu Kα radiation to identify the corrosion products.

3. Results and discussion

The use of progressively finer polishing grits to prepare metal and metal oxide samples is a commonly used procedure, as is the use of laboratory ultrasonic cleaners and distilled water as a final step in the surface cleaning process. Three 5 min immersions in a low-power ultrasonic cleaner (L&R model T14; 120 W; 1 A) were used to treat the disc, which was subsequently allowed to air dry at room temperature. A post-sonication scanning electron microscopy (SEM) examination revealed a number of crystals on the surface of the disc (Fig. 1). There were three main types of crystals identified on the surface: large flake-like crystals with diameters in the 20–50 μm range, needle-like crystals that approached 50 μm in length, and smaller octahedral crystals approximately 1–4 μm in diameter. Energy-dispersive X-ray analysis confirmed the presence of lead in all the crystal types and, coupled with the absence of signals attributable to the silicon or aluminum, ruled out the possibility that the crystals were residual polishing compound. The XRD patterns were measured and revealed the presence of massicot (PbO) and lead oxide hydrate ($3PbO \cdot H_2O$), in addition to the underlying lead metal. Based on the partial matching of some of the weak powder XRD peaks, the large flake-like crystals are believed to be a member of the lead carbonate family (either hydrocerrusite ($2PbCO_3Pb(OH)_2$) or plumbonacrite ($6PbCO_33Pb(OH)_2PbO$)).

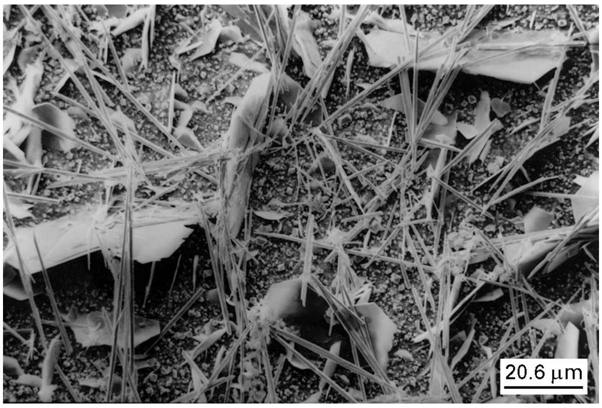

Figure 1 Low-magnification scanning electron micrograph of the variety of crystals formed on the surface of a polished lead disc following three 5 min treatments in a low-power ultrasonic cleaner. (Magnification, 486 ×.)

This unexpected growth of crystalline material on the disc surface prompted a more detailed examination of the effect of sonication on the state of the lead surface using a more powerful ultrasonic cleaner (Cole Parmer model 8891; 47 kHz; 80 W; 1.2 A) with the same set of three 5 min sonications, followed by air drying. Once again, there was significant growth of the various crystals but, in addition, there was generation of pits and craters, and general deterioration of the surface of the disc (Fig. 2a). Reducing the exposure time in the ultrasonic cleaner to three 1 min immersions reduced the incidence of surface pitting and erosion but resulted in the formation of a densely packed layer of octahedral crystal on the surface (Fig. 2b). The size distribution of the crystals, estimated from the scanning electron micrographs, was quite narrow and fell in the range 1–4 μm. XRD studies indicated that the crystals were lead oxide hydrate ($3PbO \cdot H_2O$). It is interesting to note the differences in the density of the small crystals on the discs that were treated in the two different ultrasonic cleaners. Evidently the ultrasonic energy is assisting the dissolution of lead from the surface of the discs, the higher-energy case apparently leading more readily to supersaturation at the surface which promotes the formation of the uniform distribution of particles on the surface.

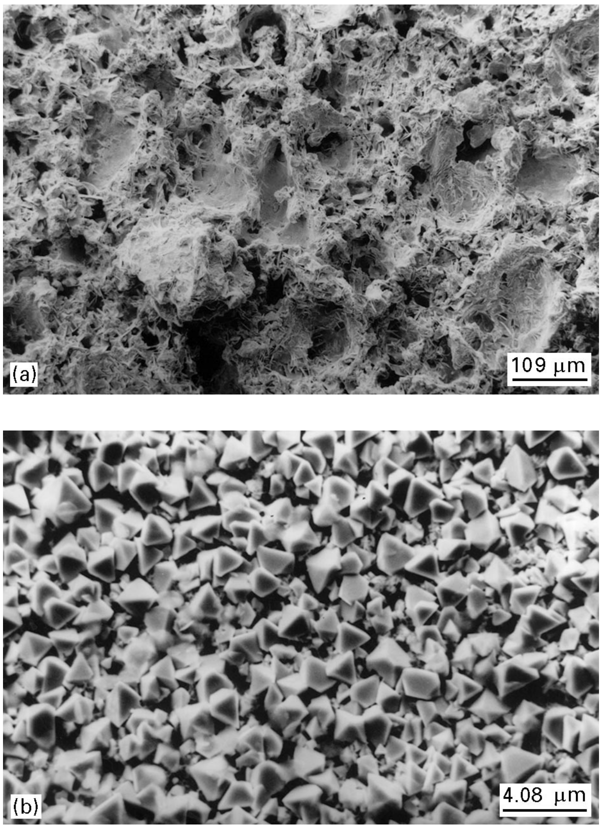

Figure 2 (a) Low-magnification scanning electron micrograph of the surface of a polished lead disc following three 5 min treatments in a high-power ultrasonic cleaner. Note the significant erosion of the surface. (Magnification, 92 × .) (b) Lead oxide hydroxide crystals formed on the surface of a lead disc following three 1 min treatments in a high-power ultrasonic cleaner. (Magnification, 2450 × .)

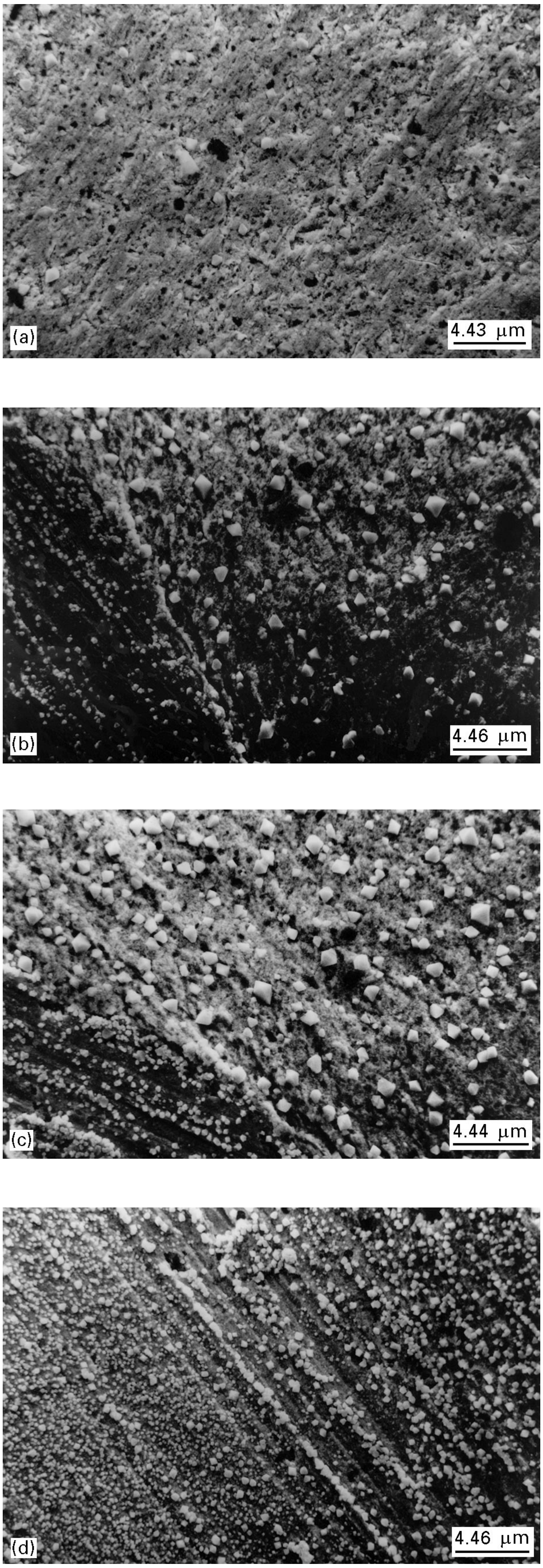

Figure 3 (a) Surface of a polished lead disc that had been blotted dry following rinsing in distilled water. (Magnification, 2260 × .) (b) Surface of a polished lead disc that had been treated in a low-power sonicator for 5 min and blotted dry following rinsing in distilled water. (Magnification, 2240 × .) (c) The same disc as shown in (b) following a 1 min treatment in the high-power sonicator. (Magnification, 2250 × .) (d) The same disc as shown in (c) following two additional 1 min treatments in the high-power sonicator. (Magnification, 2240 × .)

These initial studies suggested that there were probably two different processes that produced the two distinctly different groups of crystals. In an attempt to separate the two principal variables in the disc preparation process, experiments were undertaken to investigate the effect of sonicating discs in the two sonicators for different periods of time with an assisted method of drying the discs, and rinsing the discs in water with no sonication followed by different methods of drying the surface.

Fig. 3a shows the surface of a lead disc that was polished, as described previously, and subsequently rinsed in distilled water and blotted dry using low-lint cleaning tissue (Kim-Wipe) placed in contact with the disc. In this case, the growth of crystals was limited to a few isolated examples, dispersed across the surface. There was no evidence for the formation of the large flakes that had formed when the rinse water was allowed to evaporate. This essentially clean disc was placed in the low-power sonicator for 5 min, rinsed in a stream of distilled water and blotted dry. The crystal density on the surface increased significantly (Fig. 3b), but no flake formation occurred. The disc was subsequently sonicated for 1 min in the high-power sonicator, rinsed and blotted dry, examined using SEM and sonicated twice more for 1 min before the final examination. The micrograph in Fig. 3c of the same region of the disc as is shown in Fig. 3b shows that the 1 min exposure to the more powerful ultrasonic treatment induced further crystal growth. As the exposure was extended for a further 2 min, the lead oxide hydrate crystal density became even greater (Fig. 3d), and there was evidence for the surface damage in some locations.

This set of sequential exposures to ultrasonic treatment, followed by accelerated or assisted surface drying by blotting, demonstrates that the small octahedral crystals that form on the lead discs are generated, at least in part, as a result of the sonication treatment. To confirm that the flakes that are shown in Fig. 1 could be attributed to the drying process, a further set of experiments was performed to evaluate the effect of drying condition on the state of the disc surface.

After polishing down to the 3 μm grit level, three discs were rinsed with distilled water and allowed to air dry for 1, 5 and 10 min before being blotted dry, and a fourth disc was allowed to dry fully in air, a process that required 45 min. Fig. 4 shows the effect of drying time on the surface morphology at the region of the water–air interface. The effect is quite spectacular and demonstrates the aggressiveness of distilled water on polished lead surfaces. The accumulation of crystalline matter at the interface region is consistent with evaporation of the water from the lead surface and the relative concentrating effect that this will have on dissolved solutes in the droplet. The disc that was left exposed to water for 1 min had a minor region that demonstrated the difference on the two sides of the interface (Fig. 4a). Extending the contact time to 5 min resulted in a significant increase in the number of small octahedral crystals on the surface and also the onset of the growth of the larger flakes (Fig. 4b). The crystal density grew further for the 10 min exposure (Fig. 4c) with a significant increase in the number of flakes in the interfacial region. The disc that was allowed to dry fully over a 45 min period had a high density of the flake-like material of varying size (Fig. 4d). The obvious conclusion is that the polished lead discs are extremely susceptible to corrosive attack when left to dry naturally following a rinse in distilled water.

The evidence that was gathered from the tests described above reinforced the sensitivity of the lead surface to undergo facile oxidation or corrosion in high-purity oxygenated water. The final investigation of this series of tests was conducted to assess the impact of a rinse solvent on the state of a freshly polished disc, and a disc that had been allowed to grow a layer of oxide crystals by allowing it to air dry. A disc that was polished using the procedure described previously, rinsed with distilled water and then rinsed immediately with acetone was completely free of crystals on the surface. Acetone rinsing was also found to be an effective method of displacing water from the surface of a disc that had oxide growth on the surface without disrupting the morphology of the surface. This is an important consideration for lead corrosion experiments where the disc is to be removed from an aqueous solution for subsequent *ex-situ* examination since the results of this study indicate that remaining traces of water will tend to contribute to continued oxide growth during the drying period.

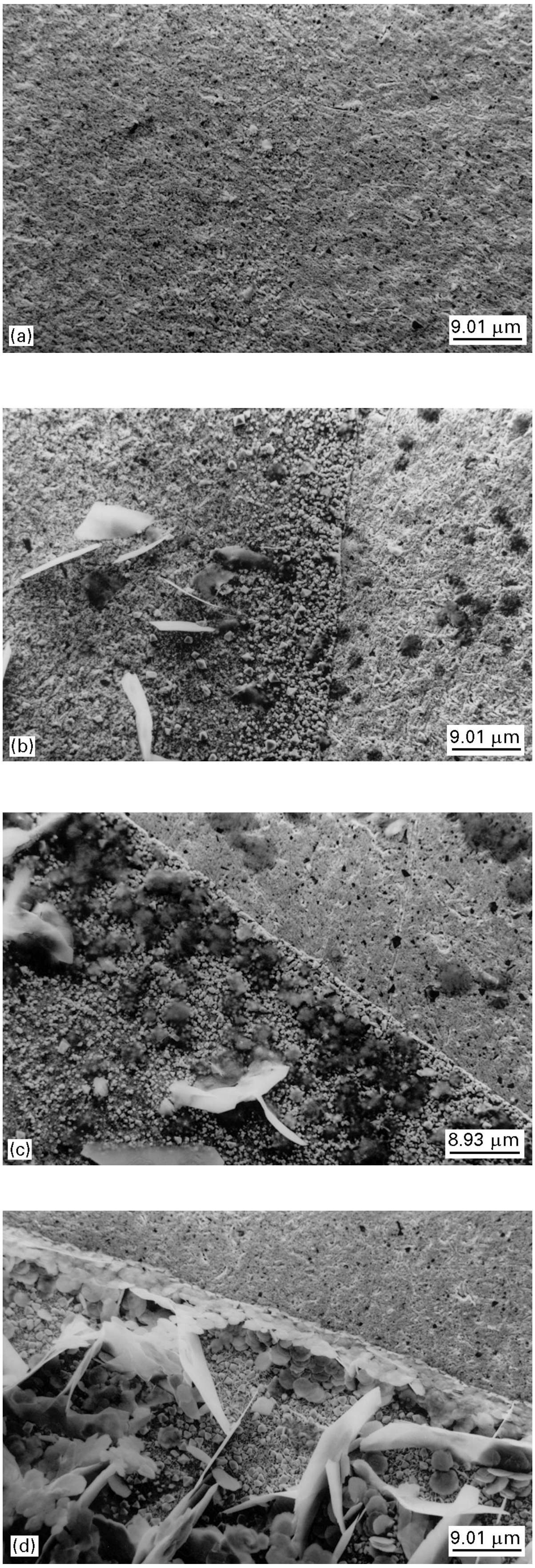

Figure 4 Scanning electron micrographs showing the effect of drying time on the formation of crystals on the surface of a polished lead disc. (a) A disc exposed to a distilled water drop for 1 min. (Magnification, 1110 × .) (b) A disc exposed to a distilled water drop for 5 min. (Magnification, 1110 × .) (c) A disc exposed to a distilled water drop for 10 min. (Magnification, 1120 × .) (d) A disc exposed to a distilled water drop for 45 min. (Magnification 1110 × .)

An examination of the literature revealed that several different methods have been employed when attempting to prepare a lead surface for subsequent oxidation processes, but confirmation of the state of the surface morphology was not a feature of the processing that was reported in the studies that were found. This suggests that the interpretation of some experimental results may in fact be complicated or precluded by the presence of an unsuspected oxide layer on the surface. This is less likely to be the case for many of the electrochemical studies of oxidation processes in aqueous solution where the lead discs were used as electrodes and could be conditioned by passing a cathodic current to evolve hydrogen and to reduce any surface oxides. The situation encountered in the disc preparation in other cases is less certain, particularly if the surface was rinsed with water and allowed to dry prior to use. Shoesmith and Bailey [18], in their work on the anodic oxidation of lead in aqueous carbonate, stated that the results of their experiments were very dependent on the electrode preparation. It seems likely that the preparation method used in their study, which terminated with a rinse in water, may have induced the pre-oxidation of the working surface.

Exposing coupons or discs to laboratory ultrasonic cleaners is used routinely in the preparation of laboratory specimens. Extensive use of ultrasonics to enhance degreasing of surfaces and the removal of particles from pores and fissures is commonly used in research and industrial environments. The results obtained in this study indicate that for some materials, and for lead in particular, the effect of ultrasonic treatment can be pronounced and variable. The cavitation effect was particularly destructive as it produced extensive pitting of the lead surface. Enhancement of the dissolution of the lead surface, which ultimately resulted in the deposition of the oxide crystals on the surface, has been attributed to local heating effects.

Equally important is the method that is employed when removing a lead specimen from an aqueous solution prior to post-experimental examination. Valuable morphological information regarding the nature of dissolution–reprecipitation processes at the surface can be obscured or even lost if proper precautions are not employed to remove the water that may be saturated in lead or other constituents of the process fluid.

4. Conclusions

Using systematic variation of ultrasonic treatment and air-drying steps, the sensitivity and susceptibility of polished lead surfaces to degrade has been documented. In all cases that were considered, ultrasonic treatment in water was found either to induce dissolution and crystallization of lead oxide hydrate on the disc surface or to cause extensive pitting and erosion of the surface. In addition, allowing the discs to dry in air also resulted in significant oxidation of the surface with subsequent deposition of crystals.

The recommended procedure for preparing lead disc specimens, particularly when the surface cannot be treated using cathodic reduction prior to use, is as follows.

1. Dry and/or wet polishing of the surface to a grit size that is appropriate for the experimental requirements should be carried out.
2. The disc should be rinsed immediately in a stream of distilled water, followed by a second rinse in acetone or another low-boiling solvent that is capable of displacing the water and enhancing drying.
3. When the disc is removed from the aqueous solution following a corrosion or oxidation experiment, the surface should be rinsed immediately in a gentle stream of acetone or another low-boiling solvent, to inhibit further growth and deposition of crystals. These procedures have been successfully used to yield lead discs with reproducible and essentially oxide-free surfaces for subsequent oxidation experiments.

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