

Sonoluminescence of Alkali-Metal Atoms in Sulfuric Acid: Comparison between Ultrasonic Horn and Cleaner

硫酸中のアルカリ金属原子のソノルミネッセンス：
超音波ホーンと洗浄器の比較

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1. Introduction

Intense emissions of alkali-metal atoms in sulfuric acid have been reported during both single bubble sonoluminescence (SBSL)¹⁾ and multi-bubble SL (MBSL).²⁻⁴⁾ The literatures have given further insight into the mechanism of how nonvolatile metal cations become heated in a collapsing bubble. In the previous paper, the authors have reported that alkali-atom emissions may occur from ejected daughter bubbles in the region between pressure nodes and antinodes in a standing wave field.⁵⁾

In sonochemistry, there are two types of reactors: ultrasonic horn and cleaner types, as shown in **Fig. 1**. The characters of the reaction fields were reported to be very different.⁶⁾ Sonochemical synthesis of carbon nanotubes, for example, achieved in several minutes by an ultrasonic horn⁷⁾ while in several hours in an ultrasonic cleaner.⁸⁾ It is not understood, however, what the difference results from. It is necessary to compare the reaction fields between the two types of sonochemical reactors.

In this study, we investigate alkali-metal atom emissions during MBSL in sulfuric acid, which are good indices of sonochemical reaction fields. The difference in reaction fields between ultrasonic horn and cleaner is discussed from the results of MBSL.

2. Experimental

The sulfuric acid (H₂SO₄) used was of ultrapure grade (purity: 97.0-98.0%) and sodium sulfate (Na₂SO₄) was of special pure grade (min. 99.0%). H₂SO₄ into which Na₂SO₄ powder was added was degassed under vacuum with stirring and then left under Ar gas atmosphere for a sufficient time to dissolve the gas. The Na₂SO₄ concentration in sulfuric acid was 1 mol/L.

A commercial ultrasonic horn at 20 kHz (Branson, 450) and some commercial ultrasonic cleaning baths at some frequencies around 40 kHz (Branson, 1510 etc.) were used. The spectrum of MBSL was obtained with a quartz glass fiber with 50 ms exposure and 20 times averaging using a

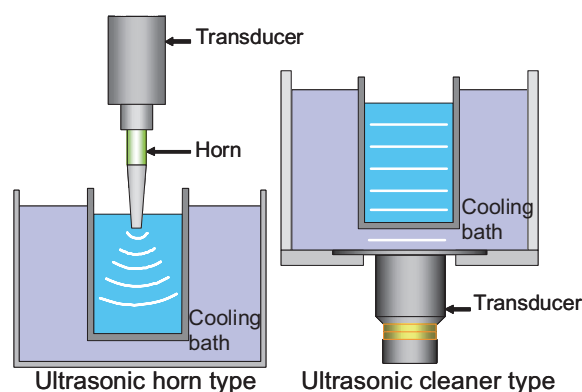


Fig.1. Two representative apparatus in sonochemistry.

spectroscopy (Hamamatsu C8801-01), the detector of which was an intensified charge coupled device (ICCD). The behavior of cavitation bubbles was observed using a CCD camera with a backlight of stroboscopic flash pulse of 90 ns.⁹⁾

3. Results and Discussion

Figure 2 shows photographs of MBSL by an ultrasonic horn at 20 kHz in 1 M Na₂SO₄ sulfuric acid. The ultrasonic power was increased from (a) to (c), although all the powers shown here were in the very low range relative to the full range. It is seen that orange emission can be seen in larger area at the lower power.

Figure 3 shows photographs of the behaviors of cavitation bubbles corresponding to Fig. 2. In Fig. 3 (c), there were many bubbles moving down violently below the horn, but MBSL was observed only in the small region near the horn tip as shown in Fig. 2 (c), where orange emission was hardly observed. In horn-type reactors, higher power than (c) is normally used, where sodium atom emission bubbles may hardly contribute to chemical reactions.

Figure 4 shows photographs of MBSL in an ultrasonic cleaner at 40 kHz. In contrast to Fig. 2, orange emissions are observed between blue-white emissions in a laminar structure. In the previous paper, we confirmed that orange emissions occur between pressure nodes and antinodes in a standing wave field.⁵⁾ From the results in Figs. 2 and 4, it is inferred that orange emissions may occur relatively low pressure regions in the both cases.

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The corresponding MBSL spectra in the ultrasonic horn and cleaner are shown in **Figs. 5 and 6**, respectively. In Fig. 5, the measurement positions of the spectra are the blue-white emission region close to the horn tip in Fig. 2(a): Low Cont, the orange emission region far from the horn tip in Fig. 2(b): Mid Na, and the blue-white emission region close to the horn tip in Fig. 2(c): High. In the corresponding spectrum to Fig. 2(c), the spectrum intensity decreases, in spite of higher ultrasonic power. The emission area also decreases. From the stroboscopic observation, bubbles below the horn tip in (c) were very crowded, although the image was not shown here. In Fig. 6, the measurement positions of the spectra are the blue-white emission region: Stw Cont, and the orange emission region: Stw Na. From the comparison between Figs. 5 and 6, there seems to be no significant difference between them.

In the horn type reactor, sodium atom emission was observed only in the very low ultrasonic power range, where people may not use an ultrasonic horn normally. At higher power, MBSL shows only featureless spectrum. This tendency is similar to that in excited argon atom emission during MBSL in sulfuric acid.¹⁰⁾ The condition of cavitation bubbles with alkali-atom emissions in a horn type reactor may similar to that in ultrasonic cleaner.

4. Conclusion

Sodium atom emission in the sulfuric acid solution during MBSL by the ultrasonic horn was observed only in the very low ultrasonic power range relative to the normally using range. The spectra and bubble behaviors with the sodium atom emissions in the ultrasonic horn and cleaner were not significantly different.

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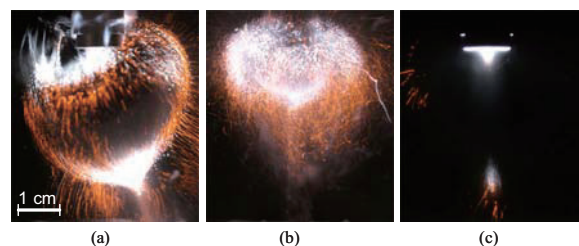


Fig. 2. MBSL in 1 M Na_2SO_4 sulfuric acid solution under Ar by an ultrasonic horn. The ultrasonic power was increased from (a) to (c).

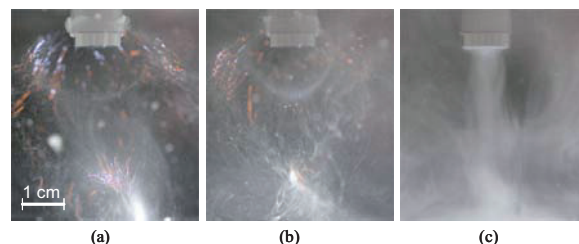


Fig.3. Cavitation behaviors corresponding to Fig. 2.

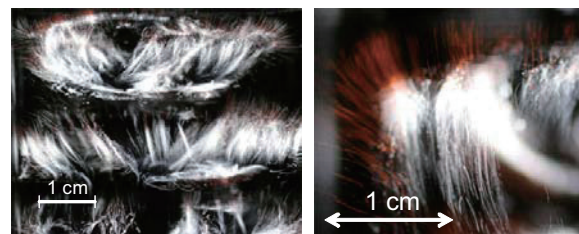


Fig.4. MBSL in 1 M Na_2SO_4 sulfuric acid solution under Ar in an ultrasonic cleaning bath at 40 kHz. The right photo is the magnification of the left one.

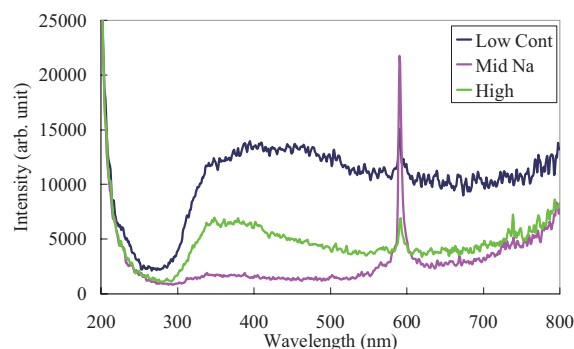


Fig.5. Corresponding MBSL spectra by the ultrasonic horn.

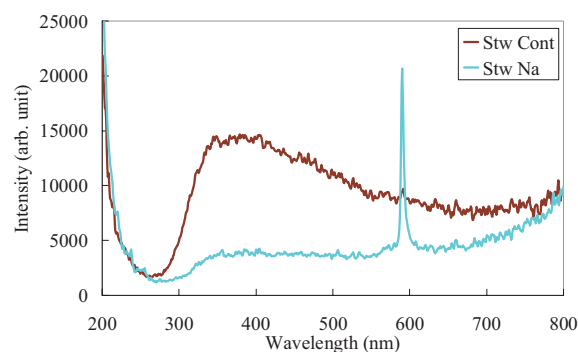


Fig.6. Corresponding MBSL spectra in the ultrasonic cleaning bath.