Int. J. Electrochem. Sci., 9 **(2014)** 4352 - 4360

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Correlation Between Properties of Passive Film and Stress Corrosion Cracking of α-Ti in Methanol Solution

Zhi Qin[*], *Xiaolu Pang*, *Lijie Qiao*[*]

Corrosion and Protection Center, Key Laboratory for Environmental Fracture (MOE), University of Science and Technology Beijing, Beijing 100083, People's Republic of China
[*]E-mail: lqiao@ustb.edu.cn

Received: 1 April 2014 / *Accepted:* 4 May 2014 / *Published:* 19 May 2014

There is a close relationship between Stress corrosion cracking (SCC) mechanism and properties of passive film of pure titanium in methanol solution with water. A scratch test was conducted on the surface of titanium immersing in methanol solution with varying water content. The test showed water changed the mechanical properties of the passive film, until up to 0.2% water was added, which made the passive film stable. Moreover, water benefited the passivation capability of the titanium in methanol, and the passive film was weaker in the liquid than that in the air.

Keywords: Titanium; Passive films; Stress corrosion; Interfaces; Scratch.

1. INTRODUCTION

Stress corrosion cracking (SCC) of titanium and its alloys in methanol solution have been widely studied for a long time [1-4]. A passive film forms during SCC or natural corrosion of α-Ti which occurs under anodic dissolution in a methanol solution. Further studies find the correlation between the SCC susceptibility and the mechanical behavior of the passive film [5, 6]. The film-induced stress variation with electrical potential is consistent with α-Ti susceptibility to SCC; both film-induced stress and SCC susceptibility in the methanol solution are reduced by increasing water content in the methanol solution. A large passive film induced tensile stress is a necessary condition for SCC of α-Ti in the methanol solution. Moreover, the SCC susceptibility can be determined by the mechanical character: If the passive film can be easily broken, the metal would be more susceptible to SCC [7, 8].

Passive film forms and plays the following roles during SCC: First, passive film provides additional stress as a mechanical behavior. Film-induced or corrosion-induced stresses behave as additional mechanisms for the corrosion-enhanced dislocation emission and motion, in addition to the divacancies-enhanced dislocation climb. The film-induced stresses of metal brass [9], 310 stainless steel , α-Ti [10] and Ti3Al + Nb [11] can facilitate dislocation emission and motion during SCC by transmission electron microscopy. Secondly, the intact passive film can protect metal from the external environment. The SCC of most metals started with the breakdown of the surface film [12-19], such as stainless steel, carbon steel, Ti alloys, and α-brass. A reasonable assumption is made that the initiation of a crack nucleation starts at a defect in the passive film on stainless steel. And it is confirmed that methanol causes breakdown of the passive film on stressed Ti specimens. Obviously, there is a close correlation between the SCC susceptibility and the mechanical property of the passive film. As described above, a lot of work [5-7, 9, 20-24] has been done to reveal the relationship between the SCC susceptibility and the mechanical behavior of the passive film. More work should be done to build the association between the SCC susceptibility and the mechanical character of the passive film.

The scratch test was used to measure the thin, hard and well-adhering coatings from the 1980s [25]. During the scratching process, the linearly increased load drives an indenter tip over the surface to carry out a scratch. When the shear stress in the nearby film which induced by the linearly increased driven load on tip at the interface is sufficiently high, it induces adhesive failure at a critical load. Also scratch testing has been demonstrated in the literature to be useful in determining rates of metal dissolution, proton reduction, pitting potential, and oxide growth on many substrates including titanium [26].

According to the literature reports, the corrosion behavior and SCC property are governed by the stability of the passive film. A passive film is the key in protecting titanium from corrosion and stress corrosion cracking in methanol, and the ability of the stable film of titanium to regrow after film rupture is critical. So it is necessary to further reveal the SCC mechanism of α-Ti in the methanol solution. The present work contributes to the understanding of the SCC mechanism of pure titanium in methanol solutions by studying the role of water. In this paper, the mechanical character and the repassivation property of the passive film formed on pure titanium immersed in methanol solution without water, and with different water content were investigated by the scratching test.

2. EXPERIMENTAL METHODS

All experiments were conducted using commercially pure titanium with the following composition: Ti 99.9wt. %, Fe 0.1wt. %, N 0.008wt. %, H 0.006wt. % obtained from rod. Before being used, the specimens were heat treated at 720 °C for 1 h in a vacuum furnace (less than 5 Pa pressure) and cooled therein. The sectioned sample was vacuum annealed to achieve a primarily α hexagonal close packed phase structure, and then electro polished in a mixture of 60 vol.% H_2SO_4, 25 vol.% HF, and 15 vol.% glycerin at approximately 30 V with a titanium cathode to remove the mechanically deformed layer.

Solutions of pure methanol, AR grade, without water, and with different water amounts of 0.1 vol. %, 0.2 vol. % and 1 vol. % were used.

The passive surfaces of the polished sample after immersion in the methanol solution with different water content for 3 h are scratched by CETR's Nano and Micro tribometer UMT-2. Each sample was scratched under two conditions respectively: in the air and in the liquid. The scratch distance for each test was set at 5 mm with a progressive loading method. The duration of 90 seconds was chosen to determine the critical load of the passive films.

During the scratch test, tangential force values, normal force values, and acoustic emission (AE) signals were acquired. At the same time, the anodic currents were monitored by the electrochemical station (CHI660D$_{412027}$). A standard three-electrode cell with 3 cm^2 working electrode exposed area was chosen to monitor the anodic currents, which had a platinum sheet as a counter electrode and a saturated silver-silver chloride (Ag-AgCl) electrode (A mature commercial, strict packaging electrode was chosen, in order to avoid additional water.) as the reference. Tests were carried out under automatic iR compensation (the solution resistance and the cell time constant were compensated for).

3. RESULTS

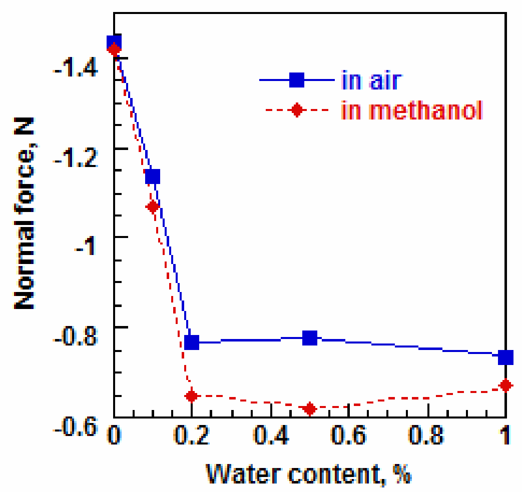

Figure 1. The critical normal force of the passive film vs. water content.

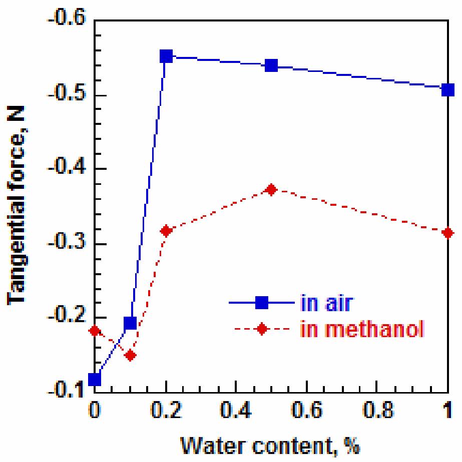

Figure 2. The critical tangential force of the passive film vs. water content.

Table 1. The critical values of the passive film breaking force with the corresponding varied water content.

Water content (%)	0	0.1	0.2	0.5	1	
Normal force （N）	-1.43	-1.14	-0.77	-0.78	-0.74	in air
	-1.42	-1.07	-0.65	-0.62	-0.67	under liquid
Tangential force (N)	-0.12	-0.19	-0.55	-0.54	-0.51	in air
	-0.18	-0.15	-0.32	-0.37	-0.32	under liquid

The critical load of the passive films, measured by the scratch test, which can be used as the parameters to describe the film failure, is listed in Table 1. In the case of a small amount of water (~0.2%), both normal force (F_N) and tangential force (F_T) tended to be stable when the passive film broke. The F_N decreased when water was added to methanol until the water content reached 0.2% in two cases (in the air and in the liquid). But the F_T performed in a different way: it increased with the water content until 0.2%. Variation of critical force with water is shown in Figure 1. and Figure 2. The values of both normal and tangential in the air are slightly greater than that in the liquid.

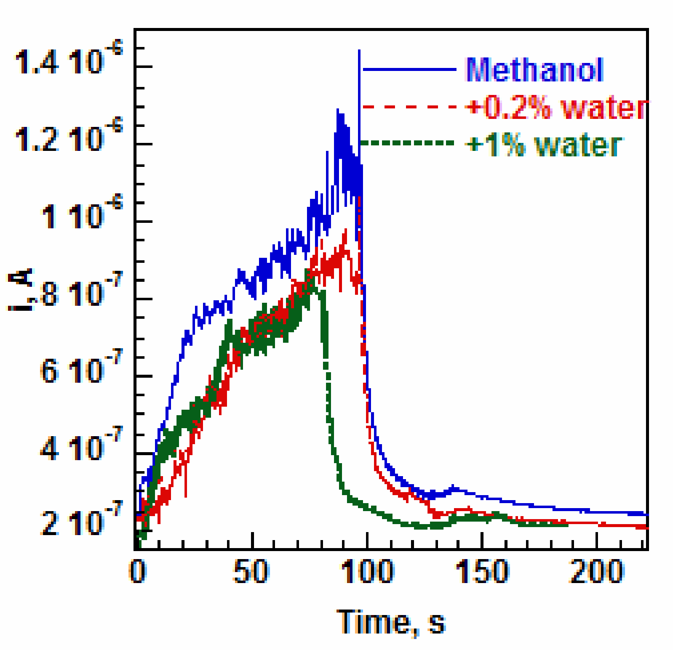

Figure 3. Current-time curves of titanium during scratching in methanol solution with different water content.

The current-time curves during the scratch in methanol solutions with different water content are shown in Figure 3. When the passive titanium is scratched in the methanol solutions, fresh Ti surface is reproduced and this will increase the anodic current due to the electrochemical dissolution. When scratching is completed, the current will rapidly decrease due to the repassivation of the new scratched surface. Therefore, the current-time curves could be used to evaluate the repassivation capability of titanium in the methanol solutions.

4. DISCUSSION

4.1. Mechanical character of the passive film

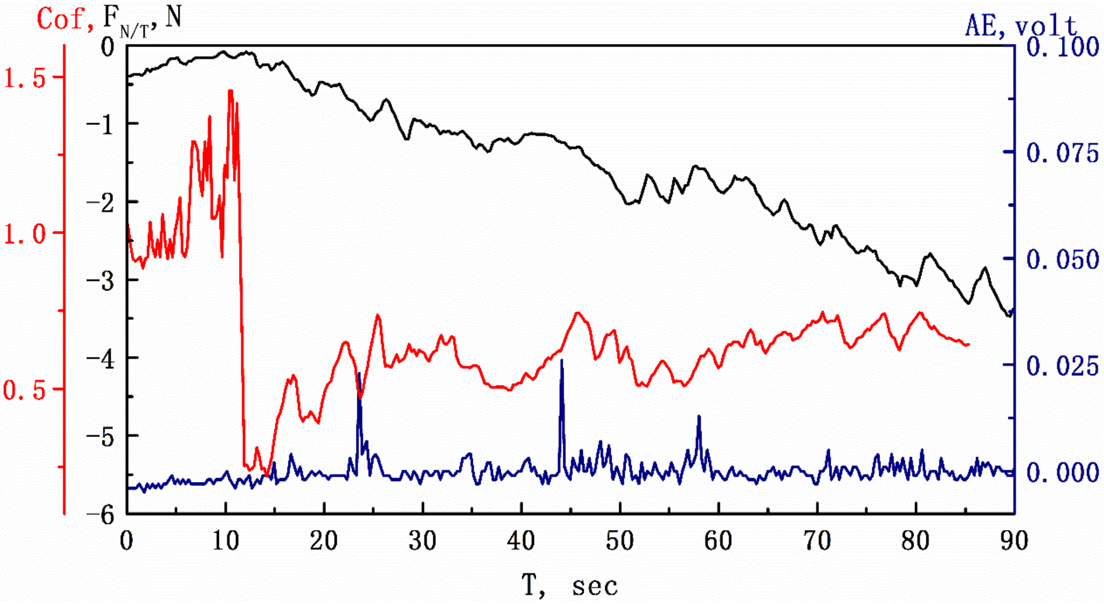

Figure 4. Schematic of scratch parameters: coefficient of friction (Cof), normal or tangential force ($F_{N/T}$) and acoustic emission (AE) vs. time (T).

A native oxide film can be yield on the surface of titanium when exposed to the environment. The passive film protects mental from damaging, and the mechanical characters of the passive film are related to the metal properties such as SCC susceptibility. Scratch testing is one of the most practical way to evaluate the mechanical characters of the surface film. The tangential force values, normal force values, coefficient of friction and acoustic emission (AE) signals can be acquired from the scratch test, as the schematic shown in Figure 4. All these parameters change during the scratching process: a spherical indenter tip slides over the surface of the sample at an incremental normal load. The tangential force increases with the progressive load (the normal force). The fast shift of the coefficient of friction is due to the tip contacts to substrate. Acoustic emission sensors is insensitive to mechanical vibration frequencies of the instrument, so the failure of the passive film can be distinguished from the sudden change spot of the AE signals. For scratch tests, there is neither standard test procedure nor perfect methodology to associate the mechanical characters of passive film and the SCC property. However, this ‘semi quantitative’ work has long been trying to make such effects combining with the former studies [5-7] which are about associating the properties of passive film and the SCC sensitivity, as an extension of the studies of the properties of passive film, to make the system more integrated.

The critical force in different directions represent different aspects of film failure. In the case described in Figure 1., the shift of the coefficient of friction precedes the sudden change spot of the AE signals, therefore the critical normal force at the shift spot is ascribed to film fracture; the critical tangential force at the first isolated high peaks of the AE signals is responsible for delaminating of the interface between the passive film and the substrate. Such hard film/ soft substrate system follows this phenomenon well. The passive film of titanium formed in pure methanol without water, and in methanol with water consist mainly of TiO_2. The elastic modulus of TiO_2 is 300 GPa, and that of Ti is 100 GPa. The elastic modulus ratio of film and the substrate is less than 4, so the passive film on titanium belongs to the hard film/ soft substrate system.

The extent of consistency of the change of F_N and the change of the break load of the passive film in the same condition [7] reduces by adding more water to the methanol solution (Figure 1.), due to the thickness of passive film decreased with the increasing water content [27]. On the contrary, F_T is raised by adding water (Figure 2.).

It is a general idea that small amounts of moisture contained in the methanol can inhibit the SCC of titanium, and the more water the less susceptible. For titanium SCC in methanol, if the passive film is stronger, the susceptibility to SCC is less. F_N and F_T represent the force which passive film can endure in the direction perpendicular and parallel to the surface respectively. By comprehending above two views, a reasonable inference can be made: the ability of the passive film to resist the force parallel to the surface is the dominant role of passive film in protecting titanium from being attacked by methanol solution.

4.2. Repassivation property of the fresh surface

Table 2. The starting current and the maximum current during scratching in methanol solution with varied water content.

H_2O, %	i_s, A	i_m, A
0	2.43E-07	1.44E-06
0.1	2.38E-07	1.29E-06
0.2	2.26E-07	9.84E-07
0.5	2.08E-07	8.99E-07
1	1.87E-07	8.70E-07

In order to further understand the effect of water in methanol on the passivation progress, the real-time current in methanol with varied water content was monitored during the scratch progress (as shown in Figure 3.). The rise and the rapid drop of the anodic current are due to the electrochemical dissolution of new Ti surface by scratch and the repassivation of the scratched surface respectively. There is much fluctuation in the current during the scratch progress observed in the current-time curves. This kind of oscillation is attributed to the competition between film formation and dissolution. The starting current (i_s) and the maximum current (i_m) in methanol solutions are given in Table 2. The starting current and ending current are with similar values in the steady state before the scratch. However, the increase of the current (i_m - i_s) is decreased by adding water significantly (as shown in

Figure 5.). The sample in methanol without water shows the maximum increment of the current. Then the increment of the current dropped with the adding water. The increment did not level off until the water content reached 0.2%. The value of the current due to the exchange rate of the charge [28]. For the same metal titanium, the greater current represents the electrochemical reaction is more intense. The increment of the current indicates that water reduces the rate of the electrochemical reaction on the fresh Ti surface. When scratching is completed, the current will rapidly decrease due to the repassivation of the fresh surface. Under the same experimental conditions, the current is recovered earlier to the initial state in the methanol solution with more water, which also illustrates that water in the environment improves the passive ability of titanium. Moreover, using a straight line to connect the initial current and steady current after scratching in the current-time curve, the area between the current curve and the straight line can be acquired. The area is approximately proportional to the total amount of titanium dissolution. The increase of the current during scratch could be depressed by repassivation of scratched surface because the low speed present work is used. Nevertheless, the result clearly demonstrates the benefit of water to the passivation behavior of pure titanium in methanol solution.

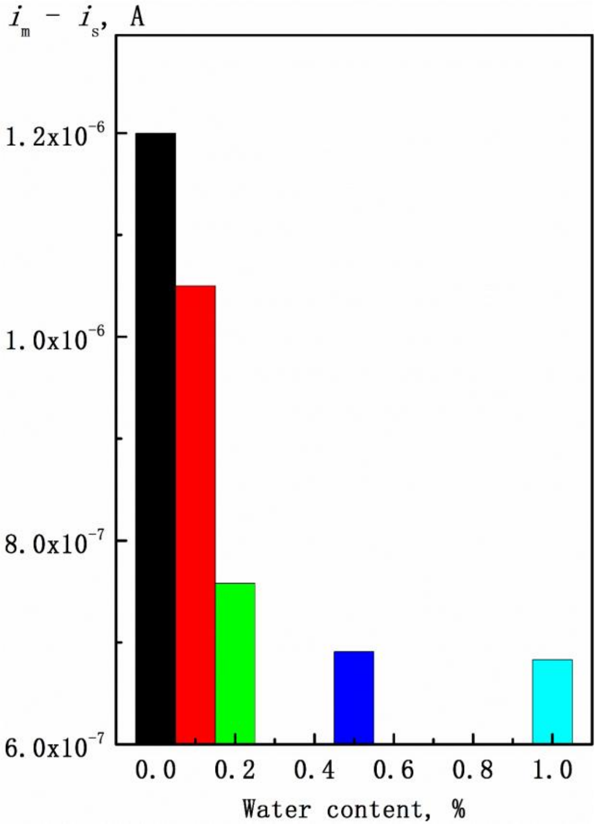

Figure 5. The increase of the current (i_m - i_s) vs. time (T).

The combination of titanium atom and oxygen atom is stable, and it is easy for stronger poly molecules to adsorb substance. Since the polarity of methanol is less than water which is more easily to absorb and more preferential to react with titanium. Water molecules contain unique chemical bond which can be inserted: O-H. The main product of Ti reacted with water is TiO_2, and the reaction is as follows:

$$Ti+2H_2O \rightarrow TiO_2 + 4H^+ + 4e^- \quad (1)$$

Compared with water, methanol molecules are much more complicated. There are C-H, C-O, and O-H bonds which belong to methanol molecules. And all of them can be inserted with the Ti ion [29]. The favorable path to insert the methanol molecule is to insert the O-H bond due to the chemical reactivity order: O-H>C-O>C-H. So $Ti(OCH_3)_x$ is one of the products of Ti reacted with methanol, following the reaction:

$$Ti + xCH_3OH \rightarrow Ti(OCH_3)_x + xH^+ + xe^- \quad (2)$$

Methoxides can be hydrolyzed by water. When adding water into the methanol, reaction follows the hydrolysis:

$$Ti(OCH_3)_x + H_2O = Ti(OH)(OCH_3)_{x-1} + CH_3OH \quad (3)$$

The combination of reaction 2 and 3 affirms that water prevents the reaction between titanium and methanol. The results above demonstrate that 0.2% is the critical water content to stop the dissolution of the titanium in methanol.

5. CONCLUSIONS

The mechanical character of the passive film is formed on pure titanium immersed in methanol solution without water, and phenomena with different water content were studied using the scratch test detected by the acoustic emission signal. At the same time, the repassivation ability was evaluated by the electrochemical tests. The passive film plays an important role in the stress corrosion cracking process of titanium in methanol solution. In order to further reveal the SCC mechanism with the passive film of pure titanium in methanol, the following conclusions are obtained:

1. The passive film of pure titanium is weaker in the liquid than in the air no matter the film is generated in methanol solution with any water content.
2. The ability of the passive film to resist the force parallel to the surface is the dominant role of passive film in protecting titanium from being attacked by methanol solution.
3. The critical value of water content to produce stable and protective passive film on pure titanium in methanol is 0.2%.
4. Water dose not only change the mechanical properties of the passive film generated on titanium in methanol, but also benefits the passivation capability of the titanium with improved corrosion resistance.

This work is a tentative study to continue the previous SCC mechanism with the passive film generated on pure titanium in methanol. However, only the semi quantitative experimental results were obtained for lack of a perfect method.

ACKNOWLEDGEMENTS
The author would want to thank the support from the National Nature Science Foundation of China under Grand No. 51201011 and the Specialized Research Fund for the Doctoral Program of Higher Education 20110006120024.

References

1. J. R. Ambrose and J. Kruger, *Corros Sci*, 8(1968), 119.
2. M. Levy and D. W. Seitz Jr, *Corros Sci*, 9(1969), 341.
3. D. N. Fager, *Corros Sci*, 10(1970), 175.
4. D. J. Simbi and J. C. Scully, *Corros Sci*, 34(1993), 1743.
5. X. Z. Guo, K. W. Gao, W. Y. Chu, and L. J. Qiao, *Mater Sci Eng, A*, 346(2003), 1.
6. H. Lu, K. W. Gao, L. J. Qiao, Y. B. Wang, and W. Y. Chu, *Corros*, 56(2000), 1112.
7. Z. Qin, X. Pang, Y. Yan, L. Qiao, H. T. Tran, and A. A. Volinsky, *Corros Sci*, 78(2014), 287.
8. Y. Yao, L. J. Qiao, and A. A. Volinsky, *Corros Sci*, 53(2011), 2679.
9. X. Z. Guo, K. W. Gao, L. J. Qiao, and W. Y. Chu, *Metall. Mater. Trans. A*, 32(2001), 1309.
10. K. W. Gao, W. Y. Chu, B. Gu, T. C. Zhang, and L. J. Qiao, *Corros*, 56(2000), 515.
11. K. W. Gao, W. Y. Chu, Y. B. Wang, and C. M. Hsiao, *Scripta Mater*, 36(1997), 259.
12. S. A. Fernández and M. G. Alvarez, *Corros Sci*, 53(2011), 82.
13. M. G. Alvarez, P. Lapitz, S. A. Fernández, and J. R. Galvele, *Corros Sci*, 47(2005), 1643.
14. X. Y. Lou, D. Yang, and P. M. Singh, *J Electrochem Soc*, 157(2010), 86.
15. G. Sanderson and J. C. Scully, *Corros Sci*, 8(1968), 541.
16. Q. Yang and J. L. Luo, *Electrochim Acta*, 46(2001), 851.
17. S. Toshio, *Corros Sci*, 49(2007), 20.
18. Z. Szklarska-Smialowska, *Corros Sci*, 44(2002), 1143.
19. X. S. Du, Y. J. Su, C. Zhang, J. X. Li, L. J. Qiao, W. Y. Chu, W. G. Chen, Q. S. Zhang, and D. X. Liu, *Corros Sci*, 69(2013), 302.
20. H. Lu, H. Gao, L. Qiao, and W. Chu, *J Mater Sci Technol*, 17(2000), 413.
21. X. Z. Guo, K. W. Gao, L. J. Qiao, and W. Y. Chu, *Corros Sci*, 44(2002), 2367.
22. X. S. Du, Y. J. Su, J. X. Li, L. J. Qiao, and W. Y. Chu, *Corros Sci*, 60(2012), 69.
23. X. J. Guo, K. W. Gao, L. J. Qiao, and W. Y. Chu, *Corros Sci*, 44(2002), 2367.
24. K. W. Gao, W. Y. Chu, H. L. Li, Y. P. Liu, and L. J. Qiao, *Mater Sci Eng, A*, 371(2004), 51.
25. A. J. Perry, *Thin Solid Films*, 107(1983), 167.
26. D. Kolman and J. Scully, *J Electrochem Soc*, 143(1996), 1847.
27. Z. Qin, X. Pang, L. Qiao, M. Khodayari, and A. A. Volinsky, *Appl Surf Sci*, 303(2014), 282.
28. I. u. Toor, *Int J Electrochem Sci*, 9(2014), 2737.
29. B. C. Guo, K. P. Kerns, and A. W. Castleman, *J phys chem*, 96(1992), 4879.