Hydrogenation of AB₅ and AB₂ metal hydride alloys studied by in situ x-ray diffraction

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Abstract

The evolution of lattice constants and abundances of metal (α) and metal hydride (β) phases during the hydrogenation process of an AB₅ alloy with a CaCu₅ crystal structure, an AB₂ alloy with a predominating C14 structure, and a C14/C15-mixed AB₂ alloy were reported. The preferred hydrogen insertion sites at different states of charge in both the α and β phases were studied based on the lattice parameter changes during hydrogenation. During the hydrogenation of the AB₅ alloy, the ratio between lattice parameters a and c (a/c ratio) in the α phase decreases, stabilizes, and then decreases again while that in the β phase decreases and then stabilizes. The trends in unit cell volume changes are increasing, plateauing, and increasing again in the α phase and increasing followed by plateauing in the β phase as the hydrogenation level increases. In the C14-predominant AB₂ alloy, the a/c ratio in the α phase increases at the beginning and then stabilizes while that in the β phase remains about the same and then increases during the addition of hydrogen. Moreover, the unit cell volume in the α phase increases slightly during hydrogenation, comparing to the increasing, decreasing, and then increasing trend in the β phase. In the C14/C15 mixed AB₂ alloy, hydrogenation of the C15 phase starts at the beginning and promotes the hydrogenation of the C14 phase. The

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C14 phase, as the main hydrogen storage phase, completes hydrogenation first compared to the C15 phase, which is about 50% hydrided at 1 MPa H₂.

Keywords: Hydrogen absorbing materials; Transition metal alloys; Hydrogenation; In situ X-ray diffraction

1. Introduction

Metal hydrides have been intensively investigated in recent years [1] in the applications of metal hydride air batteries [2], metal hydride Li-ion batteries [3], magnesium borohydride batteries [4] and thermo energy storage devices [5], and the most important Nickel-metal hydride (NiMH) battery [6-18] as an energy storage unit in portable electronics, hybrid electric vehicles, and alternative energy generation systems. The active material used in the negative electrode is an alloy capable of storing hydrogen repeatedly. Hydrogen enters and leaves the alloy during the charge and discharge of the battery, respectively. During the hydrogenation process, the inserted hydrogen expands the unit cell of the host alloy and occupies one of the interstitial sites in the lattice; and metal and hydrogen are in a two-component system with the α and β phases representing the host alloy with a small amount of diffused hydrogen randomly inserted and the metal hydride (MH) with a few vacancies unoccupied, respectively [19].

Research has been focused on improvements in the hydrogen storage capacity, cycle life and fast activation. As a traditionally-used metal alloy in commercialized NiMH batteries, AB₅ metal alloys are still the most extensively studied alloys. Efforts were focused on the optimization of the compositions [20], particle morphologies, size distributions [21], surface modification [22, 23] and surface oxides optimization [22] through variable preparation methods [24] in order to achieve a better compromise between degradation, kinetics and high capacity. The effects of hydride entropy and enthalpy, phase compositions on the hydrogen storage, and electrochemical performances have also been investigated [25]. Furthermore, phase formation mechanisms are also proposed for AB₅ metal alloy with certain compositions [21]. In addition to AB₅ metal alloys, different binary and ternary systems have also been investigated in the aspects of phase equilibria [26] and phase transitions during cycling [27], which include both Ti and Zr based AB₂ metal hydrides as well as a Mg-Ni amorphous/nanocrystalline system [28], to understand the critical factors of the electrochemical performances.

In order to further improve the hydrogen storage and cycle performance of these MH alloys, the understanding of hydrogen distribution during hydrogenation is very critical among all the decisive prerequisites. The crystal structures of the basic

binary/pseudo-binary MH, such as LaNi_5 [29], $(\text{Lu}_{0.4}\text{Y}_{0.6})\text{Mn}_2$ [30], La_2Ni_7 [31], Ce_2Ni_7 [32], $(\text{La,Mg})_2\text{Ni}_7$ [33], $\text{Ti}(\text{Ni, Cu})$ [34], Sm_2Co_7 [35], and YMgCo [36], are thoroughly studied. For example, Pan et al. [37] reported a metal hydride composed of a C14 Laves phase and a solid solution phase, in which the C14 Laves phase had good surface electrochemical activity for decomposing water when charging. The absorbed hydrogen was then fed to its neighboring V-based solid solution phase when the hydrogen content of this phase reached a high enough pressure. C14 Laves phase is considered to be a catalyst phase in this case. Except for the differences in the surface electrochemical activity, the LaNi_5 phase and the $(\text{La, Mg})\text{Ni}_3$ phase in the MH alloy have also been reported to have large differences in cell volume expansion, which causes a severe capacity degradation during cycling [38]. In addition, in-situ x-ray diffraction (XRD) has been employed in the cases of $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.4}\text{Co}_{2.5}\text{Si}_{0.1}$ [39], $\text{LaNi}_{4.7}\text{Sn}_{0.4}$ [40], $\text{Gd}_{0.5}\text{Y}_{0.5}\text{Ni}_{3.75}\text{Al}_{0.25}\text{Mg}$ [41], $\text{LaMg}_{11}\text{Ni}$ [42], and $\text{Ti}_{0.8}\text{V}_{0.05}\text{Cr}_{0.15}$ [43] to study the evolution of the α and β phases during hydrogenation in the alloys. However, similar studies on Laves phase-based AB_2 MH alloys with two possible structures (hexagonal C14 and face-centered-cubic C15) have not been reported previously. AB_2 alloys with higher hydrogen storage capacity are good candidates for NiMH batteries requiring higher specific energy. In fact, the first modern and commercially-built electric vehicle, the EV1 by General Motors, was powered by NiMH batteries with AB_2 MH alloy as the negative electrode active material. A study on the microstructures of multi-phase AB_2 MH alloys was investigated previously [44, 45]. The electrochemical contributions of the C14 and C15 phases were clarified in our earlier study as well [46]. The engineering of the C14/C15 ratio by composition design was also presented [47], which leaves the interaction of the C14 and C15 phases during hydrogenation the only unsolved puzzle in the area of applying AB_2 MH alloy as the negative electrode in NiMH battery. In this study, the lattice parameters, phase abundances, and preferred hydrogen insertion sites were investigated in a C14/C15 mixed phase AB_2 alloy. An AB_5 alloy and a C14-phase-predominated AB_2 alloy were also studied as comparisons.

2. Experimental setup

Three commercially-used MH alloys, Alloy A ($\text{La}_{10.5}\text{Ce}_{4.3}\text{Pr}_{0.5}\text{Nd}_{1.4}\text{Ni}_{64.3}\text{Co}_{5.0}\text{Mn}_{4.6}\text{Al}_{6.0}\text{Cu}_{3.2}\text{Zr}_{0.2}$ with a CaCu_5 structure), Alloy B ($\text{Ti}_{12}\text{Zr}_{21.5}\text{V}_{10}\text{Ni}_{37.7}\text{Mn}_{13.5}\text{Cr}_{4.5}\text{Al}_{0.5}\text{Sn}_{0.3}$ with a predominating C14 phase), and Alloy C ($\text{Ti}_{12}\text{Zr}_{21.5}\text{V}_{10}\text{Ni}_{40.2}\text{Mn}_{4.1}\text{Co}_{8.0}\text{Cr}_{3.5}\text{Al}_{0.4}\text{Sn}_{0.3}$, a C14/C15-mixed alloy), were prepared by arc melting under a continuous argon flow with a non-consumable tungsten electrode and a water-cooled copper tray. Microstructures of these three alloys were studied before by x-ray diffraction (XRD), scanning electron microscope and x-ray energy dispersive spectroscopy, and reported before [46, 48, 49]. Metals with purity greater than 99.9% were used to prepare the alloys according to the designed compositions. Before each arc melt experiment, a piece of sacrificial titanium was subjected to several melting-cooling cycles to reduce the residual oxygen concentration in the system. Each 10-g sample ingot was re-melted and flipped over several times to ensure uniformity in chemical composition throughout the ingot. PCT characteristics for each sample were measured using a Suzuki-Shokan multi-channel PCT system. Before the PCT analysis, each sample was first activated by performing two consecutive absorption/desorption cycles between room temperature and 300°C in hydrogen. The sample was then cooled to 30°C for isotherm measurements.

The quasi in-situ XRD studies were conducted using a Philips *X'Pert Pro* X-ray diffractometer. To produce the negative electrode, the alloy powder (around 30 to 40 mg) was pressed onto the center of a piece of nickel mesh ($1 \times 1 \text{ cm}^2$) with a Carver auto hydraulic press at a pressure of 26 tons for 30 seconds. Nickel leads were spot-welded to both the negative and positive electrodes and connected to the Arbin cycler. As shown in Fig. 1, the negative electrode was then assembled with over-capacity $\text{Ni}(\text{OH})_2$ positive electrodes with a grafted polypropylene/polyethylene separator in between. The cell was then sealed in and held together by a polyether ether ketone (PEEK) bag ($1.5 \times 2 \text{ cm}^2$) with the nickel leads exiting through the edge of the bag. 30 wt.% KOH electrolyte was injected into the PEEK bag through the holes where the leads exit. After the holes were heat-sealed by a heat sealer, the cell was then mounted in a sample holder with the negative electrode facing up to the incident x-ray pathway. The capacity of the negative electrode was first measured and used to determine the charge rate for the in-situ XRD

studies. After the first discharge to 0.9 V at the rate of C/10, the first XRD measurement was taken and marked as 0% state of charge (SOC). The cell was then charged to each target SOC with a C/10 rate followed by an XRD measurement.

3. Results and discussion

3.1 Gaseous phase study

Gaseous phase hydrogen storage properties of the three as-prepared alloys were studied by PCT characterizations. The PCT isotherms measured at 30°C for these three alloys are shown in Fig. 2. While the isotherm of Alloy A (AB_5) shows a clear plateau between 0.2 and 1.0 wt.% of hydrogen, the isotherms of Alloys B and C (both AB_2) are more slanted due to their more disordered crystal structures/composition. The hysteresis between absorption and desorption isotherms of Alloys A and B are smaller than that of Alloy C, indicating a lower energy barrier for the lattice distortion during hydrogenation. The remaining hydrogen levels in Alloys A and B after desorbing at 1 kPa are lower than that of Alloy C, indicating an incomplete dehydrogenation in Alloy C. The maximum hydrogen storage capacities for Alloys A, B, and C roughly correspond to $AB_5H_{5.5}$, AB_2H_3 , and AB_2H_2 , respectively. The electrochemical properties of these three alloys can be found in our earlier publications [46, 48, 49].

3.2 XRD analysis of AB_5 alloy with a $CaCu_5$ structure

Quasi in-situ XRD studies were performed on the three MH alloys at different SOC in order to analyze the changes in lattice parameters and phase abundance during the charging process. XRD patterns of Alloy A at 0, 20, 40, 60, 80, and 100% SOC are plotted in Fig. 3. The diffraction peaks at 44.65° and 52.05° are from the nickel mesh substrate in the negative electrode. Both the metal (M, or α) and MH (β) phases exhibit a hexagonal crystal structure similar to $CaCu_5$. While the intensity of the peaks of the MH phase (solid circle symbols) increase, the peaks of the metal phase (open circle symbols) show a gradual reduction in intensity with the increase in SOC due to the gradual phase

shifting from metal to MH as proton inserting into the occupation sites gradually during charging. Lattice constants, a/c ratios, and unit cell volumes calculated by Jade 9 software are listed in Table 1. Phase abundance at each SOC is also listed in Table 1. The measured abundance of the MH phase is slightly lower than the corresponding target SOC value since some hydrogen may escape from the alloy during the XRD measurement. The a/c ratio and unit cell volume as functions of SOC are plotted in Fig. 4. It should be noted that data from the α phase at 100% SOC was removed due to the large magnitudes of errors based on its small abundance (6%). As shown in Table 1, lattice parameters a and c of the α phase increase at different rates when SOC increases initially. The differences between the increasing rates of a and c are depicted by the evolution of the a/c ratio in Fig. 4. The CaCu_5 structure is composed of alternating AB₂ and B₃ layers along the c -axis. In this structure, the hydrogen occupation sites are either at the basal plane (AB₂ layer) or half-plane (B₃ layer) (see Fig. 1b in [50]). With the decreasing, stabilized, and decreasing trend of the a/c ratio, it can be concluded that the diffused hydrogen first fills the octahedral site (3f) at the half-plane ($z = \frac{1}{2}c$), causing a more rapid increase in c compared to that in a and a decrease in a/c ratio; during the plateau region of the a/c ratio curve, the octahedral (4h and 12n) and tetrahedral sites (12o) near the basal plane ($z = 0$) are filled by hydrogen atoms, resulting in a similar increase in rate in a to that in c ; finally, the remaining tetrahedral site (6m) at the half-plane (see Fig. 3 in [51]), which was not available earlier due to the squeeze from the occupied 3f site at the same plane, are filled since most of the 4h, 12n, and 12o sites are occupied, leading to a decline in a/c ratio. This result is in agreement with the heat of solution of interstitial sites calculated by the first-principle electronic structure [52]. The evolution of a/c ratio as shown in Fig. 4 suggests that the filling of occupation site finishes with those near the half-plane (decreasing a/c ratio) first and follow by these near the basal plane (unchanged a/c ratio). About 3% lattice volume expansion was induced within both the α and β phases, while a much larger volume expansion of about 24% happened during the phase transition from α phase to β phase.

3.3 XRD analysis of AB₂ alloy with a predominating C14 structure

XRD patterns of Alloy B at 0, 20, 40, 60, 80, and 100% SOC are plotted in Fig. 5. Alloy B, when prepared by arc melting, is mainly composed of a C14 phase (> 95%). The Ni peaks at 44.25° and 51.75° are from the nickel mesh substrate in the negative electrode. The open circle and solid circle symbols represent peaks from the metal (α) and MH (β) phases of the C14 main phase, respectively. As SOC increases, the peak intensities of the pristine metal phase reduce gradually while those of the MH phase increase gradually due to the phase shifting from metal to MH phase. Phase abundances, lattice constants, a/c ratios, and unit cell volumes were calculated by the Jade 9 software and listed in Table 2. The calculated phase abundances of the metal and MH phases are comparable to the corresponding target SOC value within experimental errors; except for at 100% SOC which can be attributed to the escape of hydrogen during XRD testing. Similar to the CaCu_5 crystal structure, C14 is made from alternating A2B (at basal plane) and B3 layers (at half-plane) along the c -axis. Possible hydrogen occupation sites in the C14 structure are at the half-plane, close to the half-plane, and close to the basal plane (see Fig. 1a in [50]). The evolutions of the a/c ratio and unit cell volume in both metal and MH phases as functions of SOC are plotted in Fig. 6 and summarized in Table 2. Lattice constant a of metal increases as SOC initially increases due to the hydrogen diffusion into the half-plane since insertion of hydrogen into any other planes will increase the lattice constant c . Insertion of hydrogen in the half-plane also reduces lattice parameter c , which is the result from the re-adjustment of unit cell. The a/c ratio in the α phase stays constant when $\text{SOC} > 20\%$, which is similar to that in the β phase when $\text{SOC} < 60\%$. This can be explained by the fact that the preferred hydrogen occupation sites during this hydrogenation period are not on the half-plane. As SOC increases to above 60%, the a/c ratio in the β phase increases again, indicating that in the later stage of SOC the hydrogen occupies the sites at the half-plane, which causes the increase in lattice constant a . The unit cell volume increases slightly in the α phase with the introduction of hydrogen. In the β phase, the unit cell volume increases when $\text{SOC} < 40\%$ and $\text{SOC} > 80\%$. The abnormal unit cell volume decrease of MH at SOC ranging from 40 to 80% is due to the decrease in c , which needs to be further analyzed.

3.4 XRD analysis of C14/C15-mixed AB_2 alloy

XRD patterns of Alloy C at 0, 20, 40, 60, 80, and 100% SOC are plotted in Fig. 7. According to a previous study, Alloy C consists of 32% C14 and 67% C15 in the main phase and about 1% of other Zr_xNi_y -related secondary phase [46]. Both C14 and C15 are Laves phases with an AB_2 stoichiometry but different stacking sequences of the same repeating asymmetric units: hexagonal C14 consisted of A-B-A-B stacking along the $\langle 0\ 0\ 1 \rangle$ direction and face-centered-cubic C15 consisted of A-B-C-A-B-C stacking along the $\langle 1\ 1\ 1 \rangle$ direction. Another hexagonal Laves phase, C36, has a stacking sequence of A-B-A-C-A-B-A-C along $\langle 0\ 0\ 1 \rangle$ and may also be present in Alloy C. However, all major XRD peaks of the C36 phase overlap with those of C14 due to the similarity between the two phases. Consequently, C36 cannot be distinguished from C14 by XRD analysis. Moreover, based on transmission electron microscopy analysis, it has been reported that other phases with even longer repetitive sequences are possible but rarely seen [44, 52, 53]. Therefore, only the C14 and C15 phases are focused on in the current study. As shown in Fig. 7, the C15 peaks coincide with the C14 peaks completely at 36.35° and 42.95° . Moreover, the Ni peak from the nickel mesh substrate at about 44.5° overlaps with one of the C14 peaks. The only separate C14 peak, at about 39.4° , is used to identify the change in C14 phase abundance. As SOC increases, the corresponding C14 MH peak (at 38.05°) reaches close to its maximum peak intensity at a low SOC, which indicates that it is easier for the C14 phase to be fully hydrided compared to the C15 phase. The abundances of both C14 and C15 before and after hydrogenation are plotted as functions of SOC in Fig. 8. At the end of hydrogenation (100% SOC), the C14 phase is completely hydrided while about half of the C15 phase is hydrided. This explains the relatively low capacity of Alloy C compared to that of Alloy B in the pressure range of our PCT apparatus (0.001 to 1 MPa) as seen from the PCT isotherms in Fig. 2. This result is in agreement with a previous report [53], in which it is concluded that the C15 phase has a higher average electron density due to its higher Ni-content, which contributes to the higher plateau pressure and better catalytic nature [46, 54]. Song et al. [55] also reported the easier electrochemical activation trend with increasing C15 phase abundance in AB_2 alloys. The proposed mechanism herein is that at the beginning of the hydrogenation process, a small amount of C15 (catalytic phase) is initially hydrided, which acts as a

catalyst for the hydrogenation of C14 (storage phase). Consequently, the C14 phase easily reaches full hydrogenation at an early SOC stage due to the acceleration from catalysis (hydrided C15 phase), which lowers the hydrogenation energy barriers. Only after the C14 phase, with a lower plateau pressure, is fully hydrided, can the bulk C15 phase be hydrided. In the gaseous phase, the relatively low storage capacity of Alloy C, compared to C14-predominant Alloy B (0.93 vs. 1.54 wt.%), can be attributed to the incomplete C15 hydrogenation. However, in the electrochemical environment, the plateau pressure of the C15 phase could be reduced due to the synergetic effects among various phases (similar to the case of ZrNi₅-series of alloys in [56]), which causes the drastic increase in capacity from gaseous phase measurement (249 mAh g⁻¹ with conversion of 1 wt.% = 268 mAh g⁻¹) to electrochemical measurement (335 mAh g⁻¹ [46]).

4. Conclusions

The hydrogenation process of three metal hydride alloys was studied by a novel quasi in-situ XRD technique. In a CaCu₅-structured AB₅ alloy, the unit cell volume increases in both the α and β phases from both the increasing lattice constants a and c , but c increases faster due to the more preferred hydrogen insertions along the c -axis. In a C14-predominant AB₂ alloy, while the introduction of hydrogen increases lattice constant a greatly with a slightly decreasing c at both SOC < 20% in the α phase and SOC > 60% in the β phase due to the preferable sites at the half-plane, both lattice constants increase at about the same rate in the range when the hydrogen starts to occupy other sites. In a C14/C15-mixed AB₂ alloy, a small amount of the C15 phase, with a higher plateau pressure hydrides at the very beginning of charging, serves as a catalyst for the C14 phase hydrogenation. Next, the C14 phase is fully hydrogenated and then the main body of C15 phase starts to be hydrided. In the gaseous phase (up to 1 MPa H₂), the hydrogenation of the C14 phase is almost complete while that of the C15 phase is only about halfway done.

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Figure Captions

Fig. 1

Schematic of in-situ XRD setup.

Fig. 2

PCT isotherms measured at 30°C for Alloy A (AB_5), Alloy B (C14-predominant AB_2), and Alloy C (C14/C15-mixed AB_2). Open and solid symbols are for absorption and desorption curves, respectively.

Fig. 3

XRD patterns using $Cu-K_\alpha$ as the radiation source for Alloy A (AB_5) measured at 0% (a), 20% (b), 40% (c), 60% (d), 80% (e), and 100% SOC (f). Metal (M, or α) and MH (β) phases are in open and solid symbols, respectively. Ni signature is from the Ni mesh substrate.

Fig. 4

Lattice constant ratio (a/c) and $CaCu_5$ unit cell volume as functions of SOC for both M (α) and MH (β) phases in Alloy A (AB_5).

Fig. 5

XRD patterns using $Cu-K_\alpha$ as the radiation source for Alloy B (C14 AB_2) measured at 0% (a), 20% (b), 40% (c), 60% (d), 80% (e), and 100% SOC (f). M (α) and MH (β) phases are in open and solid symbols, respectively. Ni signature is from the Ni mesh substrate.

Fig. 6

Lattice constant ratio (a/c) and C14 unit cell volume as functions of SOC for both M (α) and MH (β) phases in Alloy B (C14-predominant-AB₂).

Fig. 7

XRD patterns using Cu-K α as the radiation source for Alloy C (C14/C15-mixed AB₂) measured at 0% (a), 20% (b), 40% (c), 60% (d), 80% (e), and 100% SOC (f). M (α) and MH (β) phases are in open and solid symbols, respectively. Ni signature is from the Ni mesh substrate.

Fig. 8

Phase abundances as functions of SOC for both M (α) and MH (β) of C14 and C15 phases in Alloy C (C14/C15-mixed AB₂).

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Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

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Fig. 7

Fig. 8

Table 1 Lattice constants, ratio, unit cell volume, and measured abundance in metal and hydride phases at different states of charge for Alloy A.

SOC	Metal (α phase)					Hydride (β phase)				
	a (Å)	c (Å)	a/c	Vol. (Å ³)	Abundance	a (Å)	c (Å)	a/c	Vol. (Å ³)	Abundance
0%	4.98	4.01	1.24	86.2	99.2(0.0)%	NA	NA	NA	NA	0.8(0.0)%
20%	4.99	4.07	1.23	87.7	77.8(3.3)%	5.25	4.37	1.20	104.4	22.2(1.9)%
40%	4.99	4.09	1.22	88.3	71.1(4.0)%	5.24	4.40	1.19	104.9	28.9(2.3)%
60%	4.99	4.09	1.22	88.4	66.7(4.3)%	5.22	4.48	1.17	105.8	33.3(4.2)%
80%	4.97	4.18	1.19	89.5	30.4(3.7)%	5.23	4.51	1.16	106.8	69.6(3.7)%
100%	5.19	4.09	1.27	95.3	6.2(0.7)%	5.24	4.51	1.16	107.0	93.8(5.5)%

Table 2 Lattice constants, ratio, unit cell volume, and abundance in metal and hydride phases at different states of charge for Alloy B.

SOC	Metal (α phase)					Hydride (β phase)				
	a (Å)	c (Å)	a/c	Vol. (Å ³)	Abundance (tolerance)	a (Å)	c (Å)	a/c	Vol. (Å ³)	Abundance (tolerance)
0%	4.95	8.09	0.612	171.8	98.8(1.5)%	NA	NA	NA	NA	1.2(0.0)%
20%	4.98	8.06	0.617	172.8	75.2(4.5)%	5.28	8.72	0.606	210.8	24.8(3.5)%
40%	4.98	8.06	0.618	173.0	56.5(5.2)%	5.30	8.73	0.607	212.0	43.5(6.2)%
60%	4.97	8.06	0.617	172.6	40.1(4.1)%	5.26	8.67	0.607	207.7	59.9(4.1)%
80%	4.97	8.06	0.617	172.6	19.6(3.3)%	5.26	8.60	0.611	205.9	80.1(5.7)%
100%	4.98	8.06	0.618	173.1	17.9(2.0)%	5.29	8.64	0.613	209.5	82.1(6.8)%