

## Effects of Si and Ge Addition on the Al<sub>3</sub>Zr Precipitates in an Al-0.6mass%Zr Alloy

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### Abstract

Effects of Si and Ge addition on the formation of Al<sub>3</sub>Zr precipitates were investigated in a chill-cast Al-0.6mass%Zr alloy. Si and Ge addition to Al-Zr binary alloys reduced the amount of cellular reaction and resulted in an increased age-hardening. The crystal structure of the stable Al<sub>3</sub>Zr phase was also changed by the addition of Si or Ge from D0<sub>23</sub> to D0<sub>22</sub>. The KKR-Green function method with coherent potential approximation (CPA), one of the first principle calculations, revealed that the stability of D0<sub>23</sub> and D0<sub>22</sub> structures change when the Al sites of the two structures are substituted by Si or Ge.

### 1. Introduction

In aluminum alloys containing Zr, the fine spherical metastable Al<sub>3</sub>Zr with the L1<sub>2</sub> ordered structure which effectively retards recrystallization is formed. However, the amount of unfavourable cellular reaction of the L1<sub>2</sub> ordered Al<sub>3</sub>Zr is also increased by the high concentration of Zr. Si addition is well-known to suppress the cellular reaction and also change the crystal structure of the stable Al<sub>3</sub>Zr phase from D0<sub>23</sub> to D0<sub>22</sub> [1]. However, the mechanism of Si addition has not been clarified yet, although this might be explained by the interaction energies between atoms in alloys. Recently, the first principle calculations have been developed to evaluate interaction energies in solid. In the first principle calculations, total energy which is the sum total of occupied electronic orbital energies can be directly obtained and easily transferred to enthalpy. Therefore, the interaction energies are systematically derived from the total energies of ordered and disordered phases. In this work, we firstly investigated the effects of Ge addition, which is expected to similarly work to Si addition, on the formation of Al<sub>3</sub>Zr precipitates in an Al-0.6mass%Zr alloy. Then, the phase stability of the Al<sub>3</sub>Zr phases with Si and Ge were evaluated by using KKR-Green function method based on local density approximation. The similarity of Ge to Si well explained the reason why the stable Al<sub>3</sub>Zr phase is changed from D0<sub>23</sub> to D0<sub>22</sub>.

### 2. Experimental Procedure and Calculation Method

Alloy specimens of Al-0.6mass%Zr binary, Al-0.6mass%Zr-(0.2 and 0.4) mass%Si ternary and Al-0.6mass%Zr-(0.5, 1.0 and 2.0) mass%Ge ternary alloys were prepared by a chill-cast method. Small plate-shaped specimens were cut from these chill-cast materials

and subjected directly to various heat treatments. Micro Vickers hardness was measured to evaluate the effects of Si and Ge addition on the age-hardening behavior of the highly concentrated Al-Zr alloys. Precipitate microstructures were observed using an optical microscope, FE-SEM and TEM. The chemical compositions of precipitates were determined using an EDX analysis system attached to the TEM.

In this work, the phase stability of the Al<sub>3</sub>Zr phases with L1<sub>2</sub>, D0<sub>22</sub> and D0<sub>23</sub> structures estimated by using KKR-Green function with CPA (MACHIKANEYAMA2000) [2]. On evaluating the phase stability, the minimum of total energies was only considered and the effects of temperature and entropy were ignored. In addition, maximum angular momentum  $l_{max}$ , for the Green's function was chosen to be 2 because  $l_{max} = 2$  well evaluated the difference of total energies between each phase.

### 3. Results and Discussion

#### 3.1 Age Hardening Behavior

Micro Vickers hardness of the investigated alloys was measured during aging at temperatures between 673 and 773K. Figure 1 shows an example of the hardness curves at 673K. It is obvious that Ge addition accelerates the age-hardening and increases the peak hardness of Al-Zr alloys although such effects are less than those in the Si-added alloy.

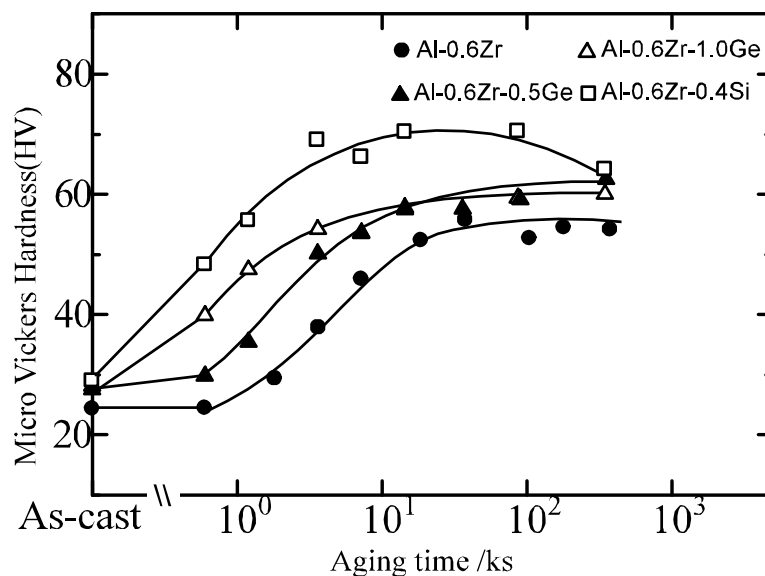


Figure 1: Isothermal aging curves of hardness for Al-0.6mass%Zr-Si and -Ge alloys with aged at 673K.

#### 3.2 Microstructure

The corresponding microstructures well explain the reason why the age-hardening is increased by Si and Ge addition. The suppression of cellular reaction is clearly observed in Figure 2 as shown by the decrease in areas of dark contrast, resulting in the formation of homogenous precipitates. Note that quite fine contrast of the homogenous precipitates is visible even in the optical micrographs of Si- and Ge-added alloys (Figure 2(b) and Figure 2(c)). Therefore, suppression of the cellular reaction seems to be caused by promotion of the homogenous precipitation which contributes to the acceleration of the age-hardening in Figure 1

### 3.3 Crystal Structure and Chemical Composition

In order to identify the crystal structure and chemical composition of the precipitates, TEM observation was performed for the Ge-added alloys. From the bright field images of Figure 3,  $L1_2$ - and  $D0_{22}$ -type  $Al_3Zr$  were found to co-exist; i.e. spherical and coherent  $L1_2$ -type  $Al_3Zr$  and semicoherent  $D0_{22}$ -type  $Al_3Zr$ . The crystallographic orientation between the  $D0_{22}$ -type  $Al_3Zr$  and the Al matrix was identified to be  $[100]_{D0_{22}}//[100]_{matrix}$ ,  $(001)_{D0_{22}}//[(001)_{matrix}$  from the corresponding diffraction pattern (Figure 3(c)). Furthermore, the EDX analysis revealed that the  $L1_2$ - and  $D0_{22}$ -type  $Al_3Zr$  contain Ge much higher than that in the Al matrix (Figure 4). By assuming that Ge substitutes the Al sites, the chemical compositions of precipitated particles were determined as listed in Table 1. Note that Ge addition to Al-Zr alloys was found to show the similar effect as Si addition on the precipitation behavior and the stability of  $Al_3Zr$  phases [1].

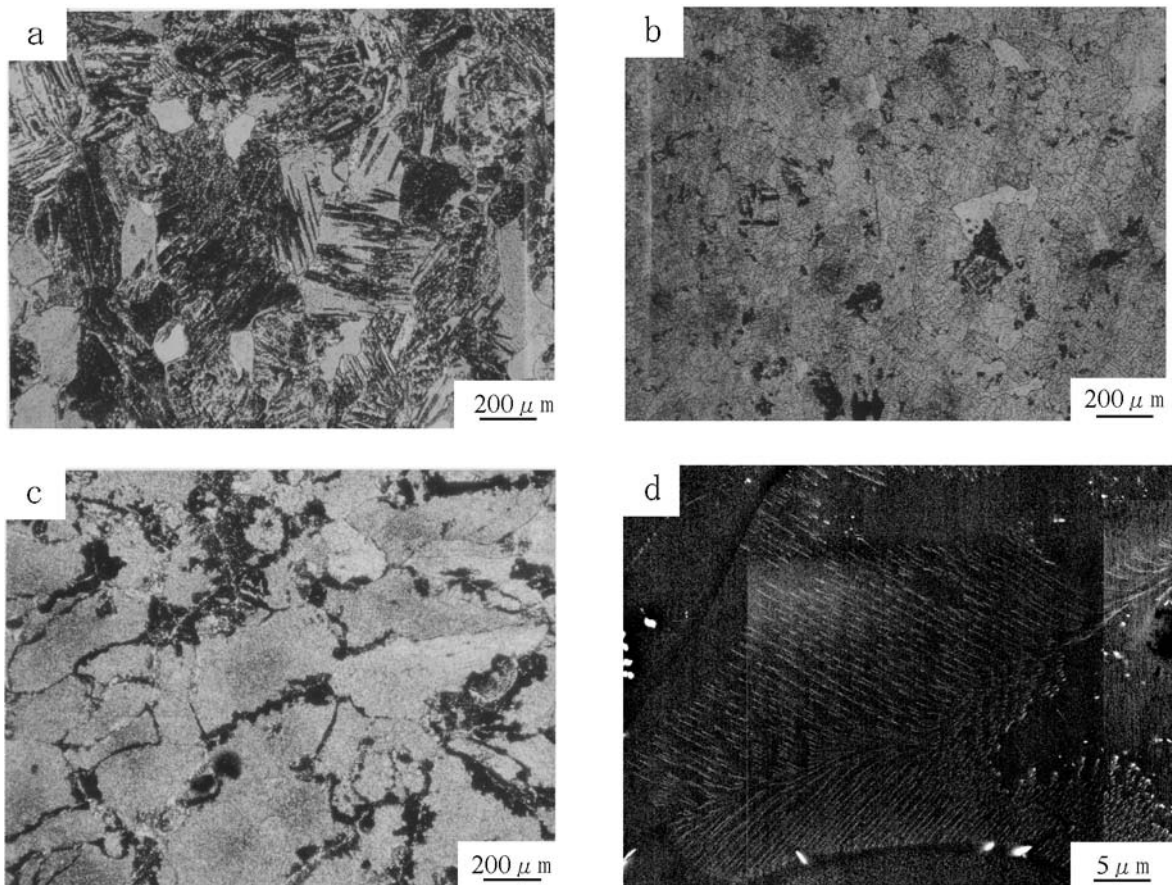


Figure 2: Optical micrographs of (a) Al-0.6mass%Zr, (b) Al-0.6mass%Zr-0.2mass%Si and (c) Al-0.6mass%Zr-2.0mass%Ge alloys aged at 773K for 86.4ks. The dark contrast shows the cellular reaction areas. (d) high magnification of the dark contrast areas of Al-0.6mass%Zr alloy aged at 773K for 86.4ks obtained by FE-SEM.

### 3.4 Calculation of the Phase Stability of $Al_3Zr$ Phases

The calculation results of equilibrium lattice constant of  $a$  and  $c/a$  ratio for  $Al_3Zr$  phases are listed in Table 2. The corresponding structural energy - lattice parameter curves proved that the minimum phase stability of each  $Al_3Zr$  phase is obtained at the equilibrium lattice constant. By comparing the phase stability, furthermore, the minimum total energy was obtained for the  $D0_{23}$  structure (Figure 5). This indicates that the calculation well reproduced the experiment data within a small amount of errors as shown in Table 2. As for the effects of Si and Ge addition on the phase stability of  $Al_3Zr$  phases, all possibilities of the substitutions of Si and Ge to Al or Zr sites were considered. Figure 6 shows an example of structural energy - lattice parameter curves for  $(Al_{0.72}, Si_{0.28})_3Zr$  and

(Al<sub>0.84</sub>,Ge<sub>0.16</sub>)<sub>3</sub>Zr. The D0<sub>22</sub>-type Al<sub>3</sub>Zr was found to be most stable if Si and Ge substitute the Al sites. On the other hand, the curves for Al<sub>3</sub>(Zr<sub>0.56</sub>,Si<sub>0.44</sub>) and Al<sub>3</sub>(Zr<sub>0.68</sub>,Ge<sub>0.32</sub>) in Figure 4 indicate that the D0<sub>22</sub> structure is no longer estimated as the most stable phase although Si and Ge slightly change the stability of Al<sub>3</sub>Zr phases. Note that chemical compositions in Figure 6 and Figure 7 were calculated from the EDX analysis results in Figure 3 and reported results [1]. From the calculated results, therefore, it was concluded that Si and Ge addition is attributed to the formation of the most stable D0<sub>22</sub>-type of Al<sub>3</sub>Zr phase, if Si and Ge substitute the Al-sites of Al<sub>3</sub>Zr phases.

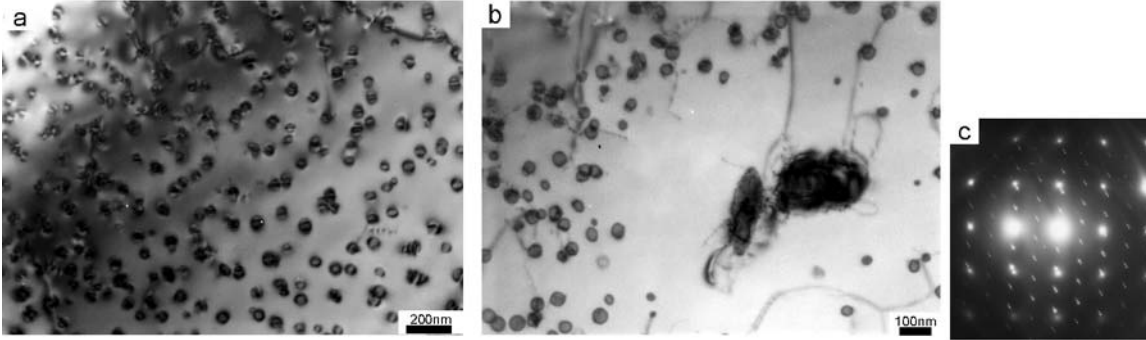


Figure 3: Transmission electron micrographs of Al-0.6mass%Zr-2.0mass%Ge alloys aged at 773K for 345.6ks showing (a) spherical L1<sub>2</sub>-type Al<sub>3</sub>Zr and (b) D0<sub>22</sub>-type Al<sub>3</sub>Zr with (c) the diffraction pattern from D0<sub>22</sub>-type Al<sub>3</sub>Zr.

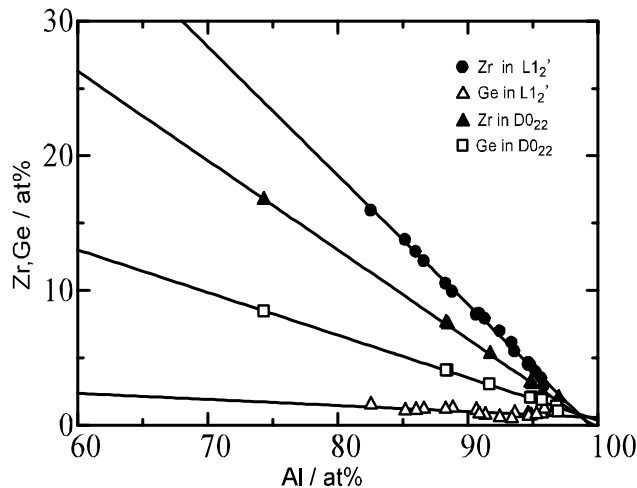


Figure 4: EDX analysis data from L1<sub>2</sub>- and D0<sub>22</sub>-type Al<sub>3</sub>Zr precipitates in Al-0.6mass%Zr-2.0mass%Ge alloys aged at 773K for 345.6ks.

Table 1: Chemical compositions of Al<sub>3</sub>Zr phases and matrix for the Al-0.6mass%Zr-2.0mass%Ge alloys aged at 773K for 345.6ks (at%).

Al <sub>3</sub> Zr	Al	Ge	Zr
L1 <sub>2</sub> -type Al <sub>3</sub> Zr	72.7	3.3	25.0
D0 <sub>22</sub> -type Al <sub>3</sub> Zr	62.6	12.4	25.0
Matrix	99.2	0.7	0.1

Table 2: The calculation and experimental results of equilibrium lattice constant of a and c/a ratio for L1<sub>2</sub>- and D0<sub>23</sub>-type Al<sub>3</sub>Zr in Al-Zr binary system [3]. The experimental values of D0<sub>22</sub>-type Al<sub>3</sub>Zr also listed from Al-Zr-V system [4].

Al <sub>3</sub> Zr	L1 <sub>2</sub>	D0 <sub>22</sub>	D0 <sub>23</sub>
calculate a/nm	0.406	0.390	0.398
calculate c/a	1.0	2.3	4.3
experiment a/nm	0.405	0.391	0.400
experiment c/a	1.000	2.250	4.330

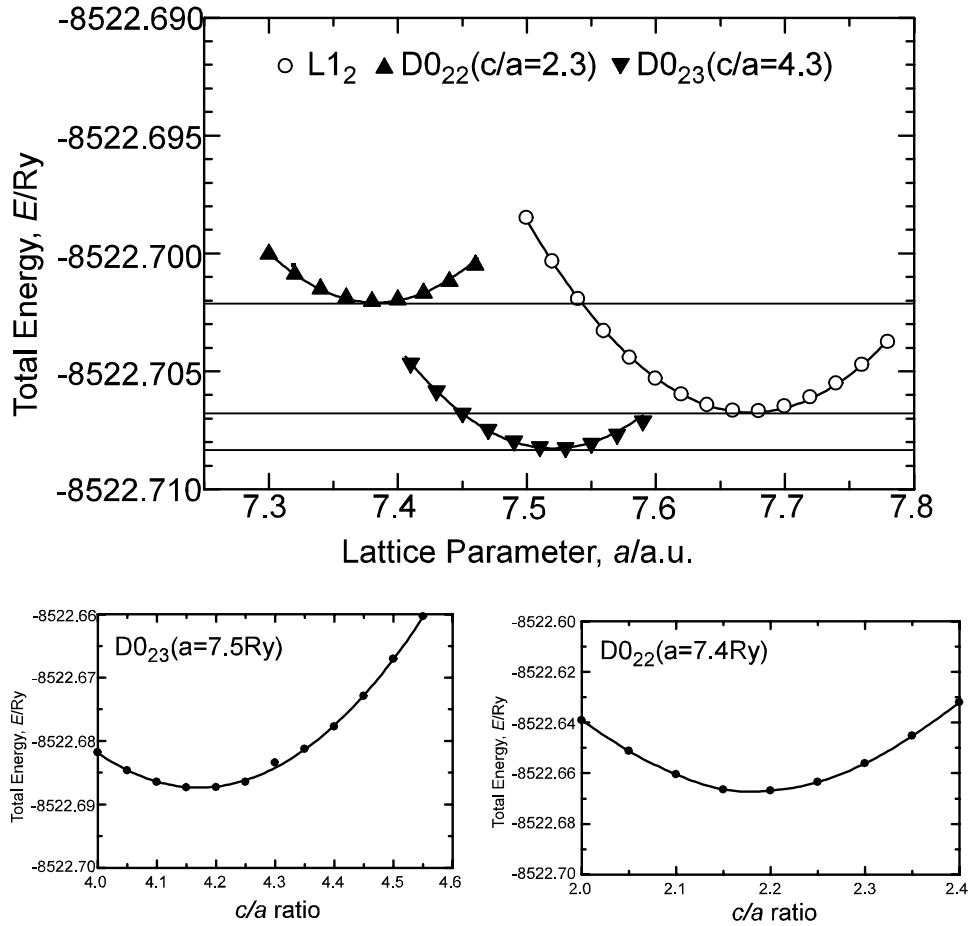


Figure 5: Structural energy-lattice parameter curves for L1<sub>2</sub>-, D0<sub>22</sub>- and D0<sub>23</sub>-type Al<sub>3</sub>Zr phases obtained by the KKR-Green function method. 1 a.u. converts into 0.0529nm.

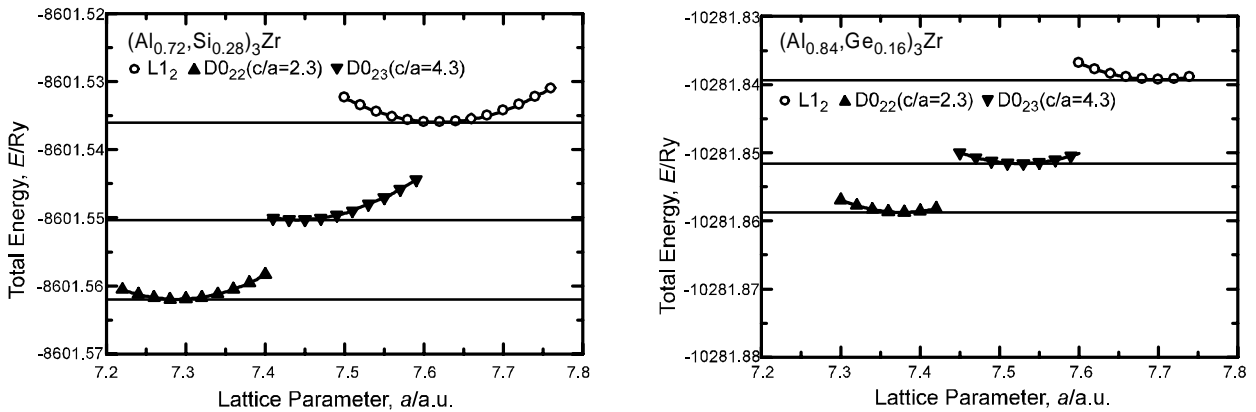


Figure 6: Structural energy-lattice parameter curves for L1<sub>2</sub>-, D0<sub>22</sub>- and D0<sub>23</sub>-type Al<sub>3</sub>Zr phases with Si and Ge. Note that composition of (Al<sub>0.84</sub>, Ge<sub>0.16</sub>)<sub>3</sub>Zr was determined from EDX analysis results in Figure 3 by assuming that Ge substituted Al sites. (Al<sub>0.72</sub>, Si<sub>0.28</sub>)<sub>3</sub>Zr is a reported composition in ref.[1].

#### 4. Conclusions

- (1) Ge addition to an Al-0.6mass%Zr alloy increased the hardness during aging and significantly inhibited cellular reaction similar to Si addition.
- (2) EDX analysis revealed that both of the metastable L1<sub>2</sub>-type Al<sub>3</sub>Zr and subsequent D0<sub>22</sub>-type Al<sub>3</sub>Zr contain Si and Ge.
- (3) KKR-Green function method well reproduced not only the phase stability of the Al<sub>3</sub>Zr phases but also the effects of Si and Ge on the stability of the phases. From

the calculated results, it was found that Si and Ge substitute the Al-sites in the  $\text{Al}_3\text{Zr}$  phases.

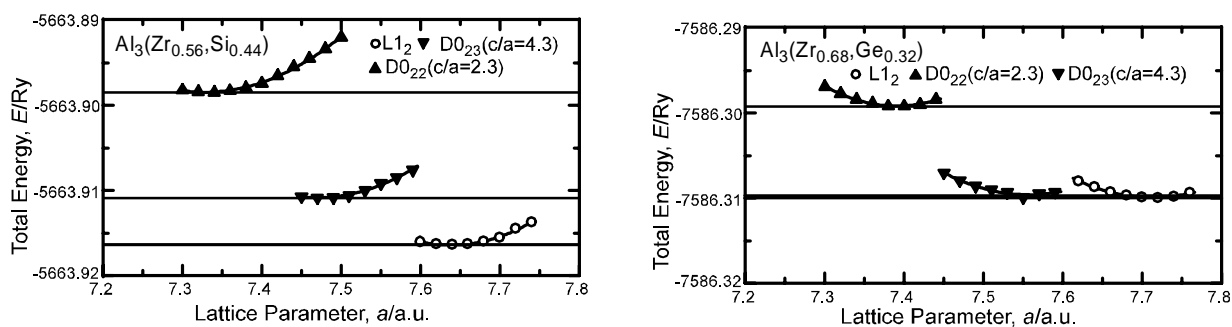


Figure 7: Structural energy-lattice parameter curves for  $L1_2$ -,  $D0_{22}$ - and  $D0_{23}$ -type  $\text{Al}_3\text{Zr}$  phases with Si and Ge. Note that composition of  $\text{Al}_3(\text{Zr}_{0.68}, \text{Ge}_{0.32})$  was determined from EDX analysis results in Figure 3 by assuming that Ge substituted Zr sites. Similarly the composition of  $\text{Al}_3(\text{Zr}_{0.56}, \text{Si}_{0.44})$  was determined from the composition of  $(\text{Al}_{0.72}, \text{Si}_{0.28})_3\text{Zr}$  in ref.[1] by assuming that Si substituted Zr sites.

## References

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