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Effect of 0.3% Sc on microstructure, phase composition and hardening of Al−Ca−Si eutectic alloys

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Abstract: The phase composition, microstructure and hardening of aluminum-based experimental alloys containing 0.3% Sc, 0−14% Si and 0−10% Ca (mass fraction) were studied. The experimental study (electron microscopy, thermal analysis and hardness measurements) was combined with Thermo-Calc software simulation for the optimization of the alloy composition. It was determined that the maximum hardening corresponded to the annealing at 300−350 °C, which was due to the precipitation of Al_3Sc nanoparticles with their further coarsening. The alloys falling into the phase region (Al)+Al_4Ca+Al_2Si_2Ca have demonstrated a significant hardening effect. The ternary eutectic (Al)+Al_4Ca+Al_2Si_2Ca had a much finer microstructure as compared to the Al−Si eutectic, which suggests a possibility of reaching higher mechanical properties as compared to commercial alloys of the A356 type. Unlike commercial alloys of the A356 type, the model alloy does not require quenching, as hardening particles are formed in the course of annealing of castings.

Key words: Al−Ca−Si−Sc system alloy; eutectic; Al_3Sc nanoparticles; phase composition; microstructure; heat treatment; hardening

1 Introduction

Aluminum alloys of 3xx series hardened by heat treatment casting based on the silicon-containing eutectics are widely used for shaped castings [1,2]. A significant disadvantage of these alloys (in particular, the 356/357 type alloys) is the necessity for heat treatment as per T6 mode (including quenching) in order to achieve maximum hardening. On the other hand, it is known that using just annealing without quenching of wrought aluminum alloys, the comparable hardening can be obtained by the addition of scandium in the amount of about 0.3% (mass fraction) due to the formation of coherent Al_3Sc ($L1_2$) phase precipitates with a size less than 10 nm [3−7]. However, for Al−Si-based alloys, the addition of scandium does not allow to achieve a significant strengthening effect. The reason for this is that silicon leads to forming the ternary $AlSc_2Si_2$ phase during solidification [3,8], which further reduces the amount of Sc in (Al). The reduction of the scandium content in (Al) makes it impossible to form a sufficient amount of hardening nanoparticles of the Al_3Sc phase during annealing. To obtain a significant hardening effect in casting aluminum alloys by adding scandium, it seems reasonable to search for other aluminum-based eutectic systems.

According to Ref. [9], for the alloys based on the (Al)+Al_4Ca eutectic, the addition of 0.3% Sc allows to obtain almost the same effect of strengthening as in the binary alloys based on the Al−Sc system. Thus, the (Al)+Al_4Ca eutectic microstructure is substantially finer than that of the (Al)+Si eutectic. According to Refs. [10,11], in the ternary system Al−Ca−Si, there is a compound Al_2Si_2Ca, which is involved in three eutectic reactions. Among these eutectics, the ternary eutectic (Al)+Al_4Ca+Al_2Si_2Ca (612 °C, 7%−8% Ca and 0.8%−1.1% Si) has a finer microstructure than the binary eutectic (Al)+Al_4Ca. We believe that the alloys based on this ternary eutectic may have a good combination of various processing and mechanical properties. It should also be taken into account that in the alloys based on the Al−Si system, calcium is considered as a harmful impurity due to the microstructure of the ternary Al−Ca−Si system near the binary system Al−Si [1,2,12]. On the other hand, many publications considering

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calcium-containing magnesium alloys have appeared in recent years [13,14].

Given the above, we believe that the study of the microstructure, phase composition and hardening of the alloys based on the Al−Ca−Si−Sc system should be conducted. Taking into consideration the scarcity of information regarding the aluminium alloys with the addition of calcium, the main objectives of this work are as follows: 1) to study the phase composition of alloys based on the Al−Ca−Si−Sc system in an aluminum-rich corner at a constant content of 0.3% Sc (mass fraction) using experimental and computational methods; 2) to investigate the dependence of the Ca and Si contents and annealing mode on the effect of precipitation hardening by the formation of Al_3Sc nanoparticles; 3) to evaluate the mechanical and technological properties of the alloy based on the ternary eutectic (Al)+Al_4Ca+Al_2Si_2Ca.

2 Experimental

The main objects of the experimental study were the four alloys based on the Al−Ca−Si−Sc system with the addition of 0.3% Sc (Table 1). The melting was conducted in an electric resistance furnace in clay−graphite crucibles. All the alloys (1 kg in mass) were prepared based on high purity aluminum (99.99%). Calcium and scandium were added in the form of master alloys (Al−18%Ca and Al−2%Sc correspondingly) and silicon was added as a pure element. The melt was poured into a graphite mould at 800 °C to produce flat castings with 15 mm × 30 mm × 180 mm in size (the cooling rate during solidification was about 10 K/s). The actual chemical composition of the alloys obtained by a spectral analysis is given in Table 1. The heat treatment of the castings was carried out in a muffle electric furnace using step cycles in the range from 200 to 550 °C (Table 2). The Brunell hardness was determined in a DuraVision−20/200/250 hardness testing machine. The hardness values are given as arithmetic mean values from at least 5 single hardness measurements for at least 3 samples. The hot rolling was carried out by the 260 laboratory camp.

Table 1 Actual chemical composition of experimental alloys

No.	Mass fraction (mole fraction)/%[1]			
	Ca	Si	Sc	Al
1	3.30 (2.26)	14.80 (14.48)	0.27 (0.016)	Bal.
2	4.08 (2.79)	4.25 (4.15)	0.29 (0.18)	Bal.
3	9.90 (6.91)	4.80 (4.78)	0.30 (0.19)	Bal.
4	6.00 (4.13)	0.64 (0.63)	0.29 (0.18)	Bal.

[1] Content of each impurity does not exceed 0.01% in mass fraction

The microstructure was examined by means of transmission electron microscope (TEM, JEM−2100) and scanning electron microscope (SEM, TESCAN VEGA 3) and by electron microprobe analysis (EMPA, OXFORD AZtec). The samples were cut from the castings, ground and polished using standard procedures. Mechanical polishing (Struers Labopol−5) with further etching using Keller's reagent was applied. Thin foils for transmission electron microscopy (TEM) were prepared by ion thinning with a PIPS (precision ion polishing system, Gatan) machine and studied at 160 kV. To calculate the phase composition, the Thermo-Calc software (TTAL5 database [15]) was used.

3 Results and discussion

The contents of Ca and Si in the experimental alloys (Table 1) were chosen based on the results of the Al−Ca−Si phase diagram calculations. The feature of this ternary system is a vast area of primary crystallization of the Al_2Si_2Ca compound (Fig. 1(a)). As shown in the vertical section which was calculated at 90% Al (Fig. 1(b)), a small addition of Ca (a few hundredths of a percent) in binary Al−Si alloys dramatically increases the liquidus temperature (T_L). From Fig. 1(b), it also follows

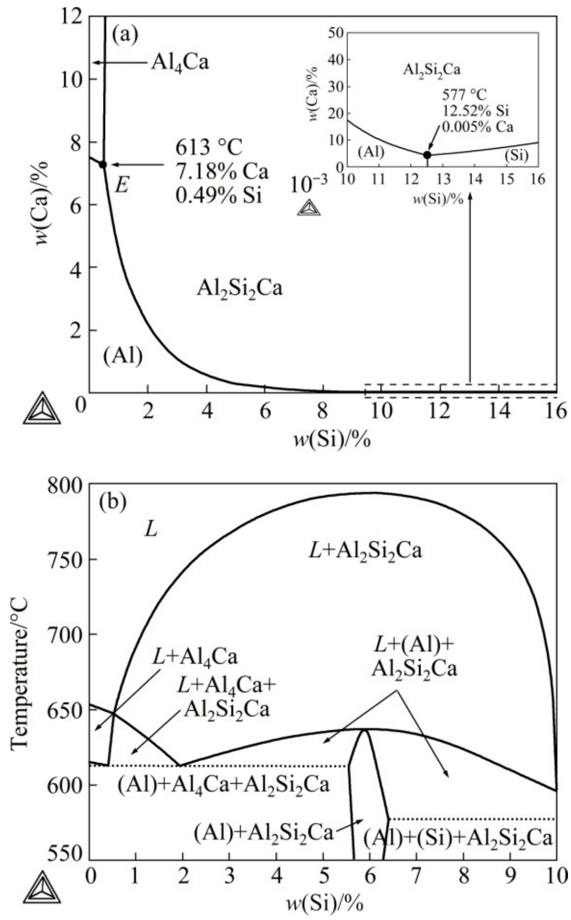

Fig. 1 Phase diagram of Al−Ca−Si: (a) Liquidus projection; (b) Vertical section at 90% Al

that the addition of Si up to 0.8% in the Al−Ca alloys should not increase T_L. At the content of Si up to 0.5%, the Al_2Si_2Ca compound must be formed only via the eutectic reaction: L→(Al)+Al_4Ca+Al_2Si_2Ca. Alloys 1−3 with compositions listed in Table 1 are located in the areas where the primary crystals of the Al_2Si_2Ca phase must be present. Alloy 4 (its composition was assumed as the optimal) is located near the ternary eutectic (point E in Fig. 1(a)) which corresponds to the reaction L→(Al)+Al_4Ca+Al_2Si_2Ca. Alloys 3 and 4 fall exactly into this three-phase region. Alloys 1 and 2 are in the other three-phase region: (Al)+(Si)+Al_2Si_2Ca.

Table 2 Annealing regimes of experimental alloys

Designation	Annealing regime	Designation	Annealing regime
S200	200 °C, 3 h	S400	S350+(400 °C, 3 h)
S250	S200+ (250 °C, 3 h)	S450	S400+ (450 °C, 3 h)
S300	S250+ (300 °C, 3 h)	S500	S450+ (500 °C, 3 h)
S350	S300+ (350 °C, 3 h)	S550	S500+ (550 °C, 3 h)

Vertical sections of quaternary system calculated at 0.3% Sc are shown in Fig. 2. In accordance with Fig. 2(a), the equilibrium solidification of the Al−6%Ca−0.6%Si−0.3%Sc alloy proceeded via the following reactions: initially the appearance of the Al_3Sc phase primary crystals at 650 °C, then the successive formation of the binary L→(Al)+Al_3Sc, ternary (L→(Al)+Al_2Si_2Ca+Al_3Sc) and quaternary (L→(Al)+Al_4Ca+Al_2Si_2Ca+Al_3Sc) eutectics. The calculation shows that the temperature of the final eutectic reaction is 613 °C at the contents of 7.12% Ca, 0.48% Si and 0.16% Sc. However, in accordance with the results presented in Ref. [9], it can be expected that in real conditions, all scandium may enter in (Al) during solidification. The results of EPMA have confirmed this assumption. The vertical section calculated at 0.3% Sc and 10% Si (Fig. 2(b)) also shows the presence of quaternary eutectic, with the temperature (577 °C) and composition being very close to the binary eutectic in the Al−Si system (in particular, the Ca content is less than 0.05%).

It was found that the microstructure of the hypereutectic alloys 1−3, as predicted by thermodynamic calculations (Fig. 1), contains significant amounts of primary crystals, which have the form of polyhedrons. According to the EMPA analysis (Table 3), compositions of these crystals in all three alloys are close to the Al_2Si_2Ca compound formula. Scandium in these crystals has not been identified. On the other hand, in alloys 1 and 2, the primary crystals of the Sc-containing phase in the form of polyhedrons were also detected.

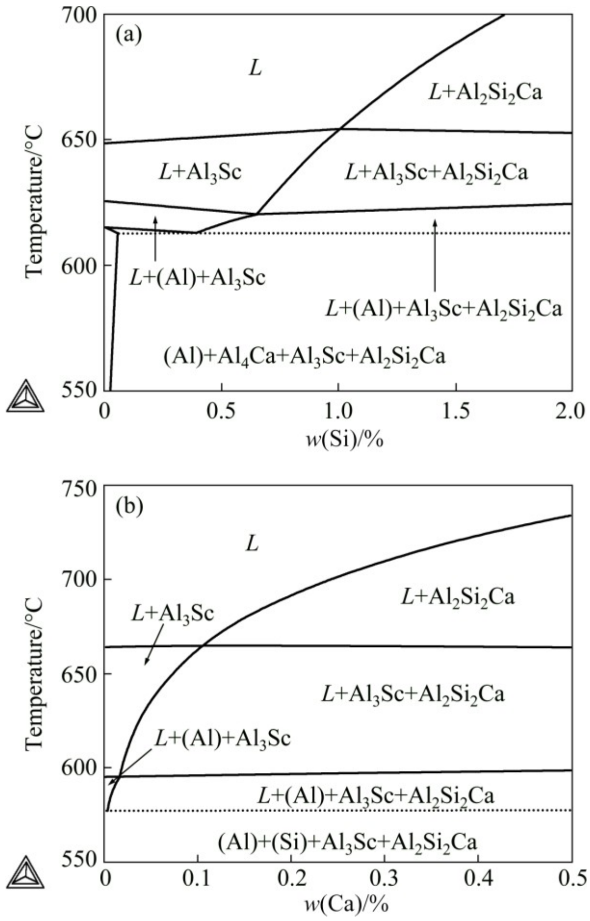

Fig. 2 Vertical sections of Al−Ca−Si−Sc system at 0.3%Sc: (a) At 6% Ca; (b) At 10% Si

Table 3 Average compositions of Al_2Si_2Ca primary crystals in annealed (S500) alloys 1−3

Alloy No.	Mass fraction (mole fraction)/%			
	Al	Si	Ca	Sc
1	36.64 (40.86)	36.14 (38.72)	27.09 (20.34)	0.12 (0.08)
2	36.63 (40.79)	36.56 (39.12)	26.63 (19.97)	0.18 (0.12)
3	36.50 (40.70)	36.36 (38.95)	27.04 (20.29)	0.11 (0.08)

According to Fig. 3(a), the ternary eutectic in alloy 4 has a highly fine microstructure (the size of the dendritic branches less than 0.2 μm). It is known that the fineness of the eutectic microstructure in the as-cast state determines, to a great extent, its capability to change its form during heat treatment [2,16]. The study on the influence of an annealing temperature (with 3 h holding) on the morphology of the eutectic constituents detects the first symptoms of fragmentation at 450 °C. With an increase in the temperature, the changes become detectible at the resolution of optical microscope. At 500 °C, almost all Al_4Ca and Al_2Si_2Ca particles take a globular form, but their sizes remain submicron (Fig. 3(b)). At the maximum tested temperature of annealing (550 °C), the microstructure becomes much

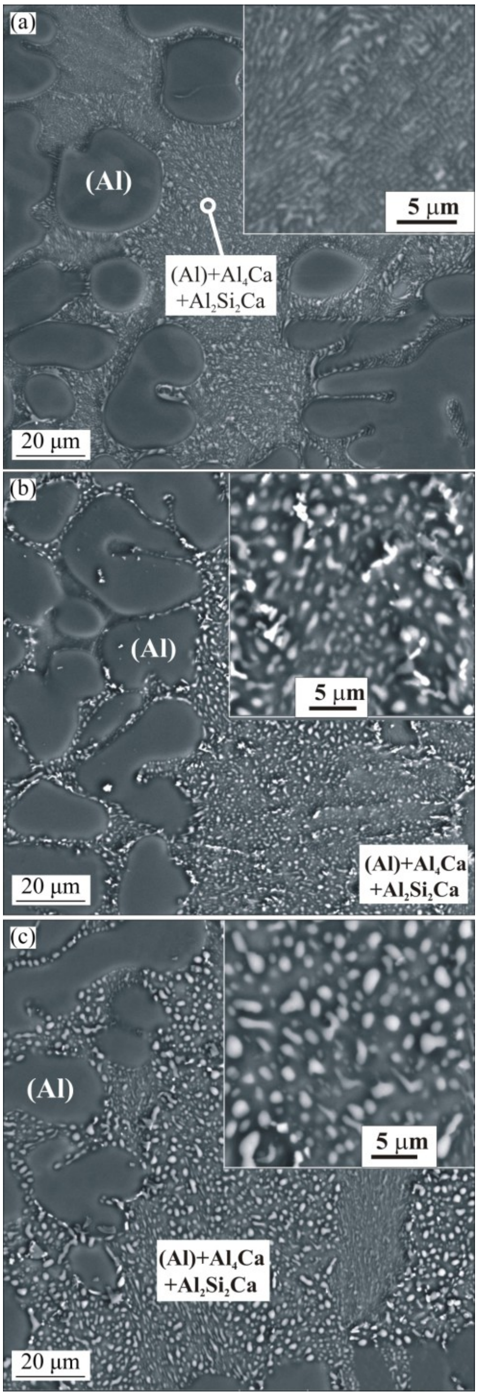

Fig. 3 SEM images of eutectic (Al)+Al_4Ca+Al_2Si_2Ca in alloy 4: (a) As-cast; (b) S500; (c) S550

coarser, the size of some particles reaches 5 μm (Fig. 3(c)).

The experimentally determined contents of Ca and Si in the eutectic (Table 4) are close to the calculated results. It should be noted that the Sc content in the (Al) primary crystals and eutectic (Al)+Al_4Ca+Al_2Si_2Ca is approximately the same and is close to its content in the alloy.

Figure 4(a) shows the hardness change of the experimental alloys during annealing. In alloys 3 and 4

Table 4 Average composition of aluminum solid solution and eutectic in as-cast alloy 4

Structural constituent	Mass fraction (mole fraction)/%			
	Al	Si	Ca	Sc
(Al)	99.60 (99.76)	<0.01 (<0.01)	0.10 (0.07)	0.29 (0.17)
(Al)+Al_4Ca+ Al_2Si_2Ca	90.95 (93.49)	1.04 (1.03)	7.65 (5.29)	0.31 (0.19)

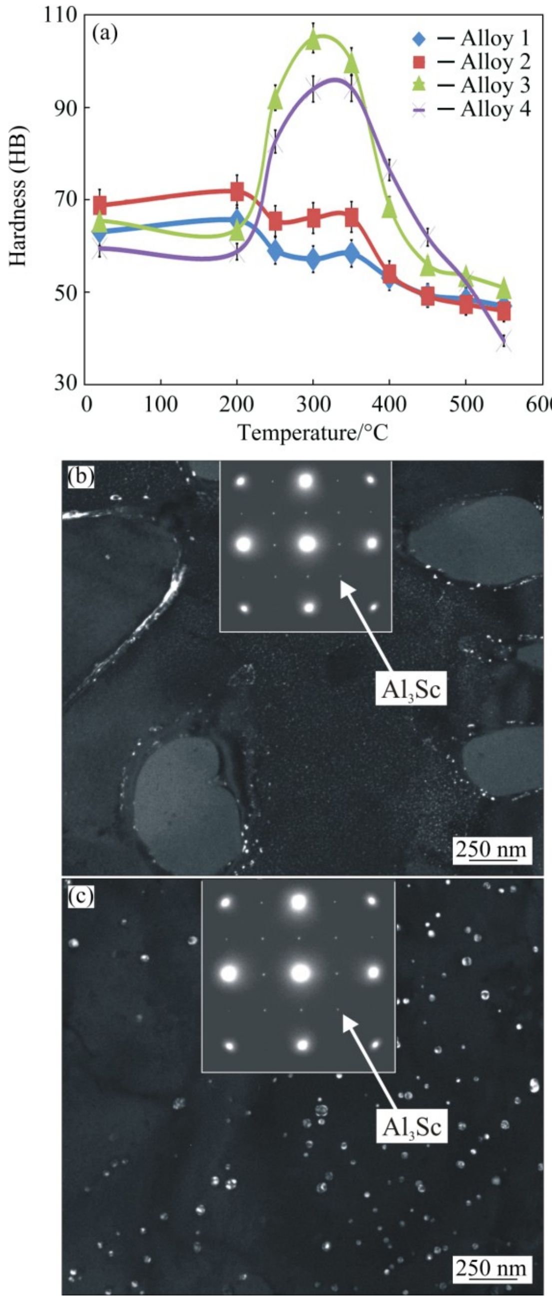

Fig. 4 Effect of annealing temperature on hardness (a) and TEM (dark field) microstructures of experimental alloys in S300 (b) and S450 (c) modes

whose compositions fall into the phase region (Al)+ Al_4Ca+Al_2Si_2Ca, the level of hardening (about HB 40) is comparable to the hardening of the binary alloy Al−0.3%Sc [3,8]. The maximum hardness is achieved in

S300 and S350 modes (Table 2). Hardening in these alloys is due to the formation of the Al_3Sc nanoparticles, as shown in Fig. 4(b). These nanoparticles form in the process of annealing from supersaturated aluminium solid solution (Al). On the other hand, at higher temperatures the hardness decreases due to coarsening of precipitates Al_3Sc (Fig. 4(c)), as well as due to fragmentation and spheroidization of the eutectic intermetallics (Figs. 4(b) and (c)). In the alloys 1 and 2 whose compositions fall into the phase region (Al)+(Si)+Al_2Si_2Ca, the hardening is virtually absent. This is connected with a low content of scandium in (Al) (less than 0.1%).

The alloys based on the ternary eutectic (Al)+Al_4Ca+Al_2Si_2Ca show the combination of the high castability (due to the narrow temperature range of solidification) and ability to plastically deform with a significant degree of compression. Moreover, the high deformability can be available even for alloys with a high volume fraction of the eutectic intermetallics (more than 20%, volume fraction), because after annealing at high temperatures, these intermetallic compounds acquire a globular shape. It was exemplified by the (Al)+Al_8Cu_4Ce eutectic [17]. Determination of the casting properties of alloy 4 shows that its fluidity and hot cracking resistance are close to those of the standard alloy 356 [1,2,16]. This suggests that the experimental model alloy can be used to obtain castings with a complex shape.

To evaluate the deformability by hot rolling, alloy 4 was also used. The initial state of the alloy before rolling was S500, which provided the microstructure with globular eutectic particles intermetallics (Fig. 3(b)). The hot rolling was conducted at 450 °C. The total degree of reduction is 50% which is a proof of sufficient reserve of plasticity. After rolling, the hardness increases from HB 58 to HB 72, which is an indicator of the recrystallization processes incompletion. There are no significant changes in the microstructure of the deformed specimens, only slight elongation in the deformation direction of the aluminum solid solution branches and eutectic colonies.

Thus, using the studied results of alloy 4 based on the (Al)+Al_4Ca+Al_2Si_2Ca eutectic, the principal possibility to create technologically universal eutectic composites type alloys, which allow to obtain both shaped castings and deformed intermediates, was demonstrated.

4 Conclusions

The phase compositions of aluminum alloys of the Al−Ca−Si−Sc system, containing 0.3% Sc, were studied using computational and experimental methods. It is shown that only phases of the binary systems (Al_4Ca, Al_3Sc and (Si)) and the ternary compound Al_2Si_2Ca may be in equilibrium with the aluminium solid solution. It was determined that the maximum hardening corresponded to the annealing at 300−350 °C, which was due to the precipitation of Al_3Sc nanoparticles with their further coarsening. It is shown that the (Al)+Al_4Ca+Al_2Si_2Ca eutectic has a fine structure, and after annealing above 450 °C, the eutectic compounds may acquire a globular shape. The structure with uniformly distributed compounds (reinforcing phases) in the aluminum solid solution (matrix) is the basis for the creation of the so-called natural composites produced by conventional casting.

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添加 0.3%Sc 对 Al−Ca−Si 共晶合金显微组织、相组成及硬化性能的影响

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摘　要：研究含 0.3% Sc、0−14% Si 和 0−10% Ca 铝基合金的相组成、显微组织和硬化性能。采用实验研究包括扫描电镜、热分析和硬度测试与 Thermo-Calc 软件模拟相结合的方法对合金的组成进行优化。结果表明，经 300~500 °C 退火处理后合金的硬化效果最好，这是由于 Al_3Sc 纳米颗粒的析出及其进一步粗化。成分在 (Al)+Al_4Ca+Al_2Si_2Ca 相区的合金呈现明显的硬化效应。三元共晶合金(Al)+Al_4Ca+Al_2Si_2Ca 比 Al−Si 共晶合金的显微组织细得多，这表明实验合金相对于 A356 系列工业合金具有更高的力学性能。与 A356 系列合金不同，实验合金不需要淬火处理，因为在其铸件的退火过程中形成了硬化粒子。

关键词：Al−Ca−Si−Sc 系列合金；共晶；Al_3Sc 纳米颗粒；相组成；显微组织；热处理；硬化

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