

Short communication

Application of volumetric electric-spark dispersion for the fabrication of Ti–Zr–Ni hydrogen storage alloys

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Abstract

Results of X-ray and electrochemical analyses of properties of Ti–Zr–Ni powders obtained by the volumetric electric-spark dispersion method in water, alcohol, kerosene, liquid nitrogen and liquid argon are presented. The influence of working fluids and parameters of discharge pulses on the chemical composition, phase-structural state, electrochemical characteristics and electrical capacity of the obtained powders is considered. The effect of annealing in various media on the electrochemical properties of powders has been studied.

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1. Introduction

Active investigations are currently under way of Ti (Zr)-base alloys for the negative electrodes of Ni/MeH accumulators owing to high values of accumulated hydrogen volume for such alloys as compared, e.g. with Mm-base alloys [1–3]. Among these alloys, Ti–Zr–Ni alloys, which form Laves phase or a quasi-crystalline phase, are easily producible and relatively cheap [4,5]. The practical use of these alloys is prevented by the oxidation of the surface of particles on their mechanical dispersion, as a result of which a surface barrier to the incorporation of electrochemically generated hydrogen atoms into particles is formed. Introduction of V, Mn, Cr, Si, Co, Mo into alloys improves in principle the electrochemical characteristics of electrodes based on them [3,6,7], but their stability is nevertheless low; moreover, the technology for producing alloys becomes more complicated, and

their cost increases. A slight improvement of characteristics of electrodes based on these alloys can be attained by including Cu [8–10] and Ni [11] powders in the cathodic mass or by treating powders in a hot alkali [12], which decreases surface oxidation. A more efficient method for the oxidation protection of the surface is a plasma etching of alloy powders under vacuum followed by covering the surface with a thin layer of Pd [5], but this method is too labor-consuming and expensive. Thus, to produce an efficient negative electrode, based on Ti–Zr–Ni alloys, for Ni/MeH accumulator, it is necessary to greatly reduce the surface oxidation of alloy microparticles and to retain the bulk properties of the alloys.

The problem of producing fine powders of hydrogen-sorbing alloys to manufacture accumulator electrodes can be solved in principle by using so-called explosive methods, in which on very rapid heating of a limited amount of alloy, its microparticles detach, and on their cooling under predetermined conditions, powder particles with predetermined phase-structural state are formed. The spatial electric-spark

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dispersion (SESD) method is the most promising method of this class to date [13]. The method for the SESD of alloys consists in the formation of fast migrating multichannel sparks between starting-material granules, which are immersed in a low-conductivity working fluid. Under the action of thermodynamic, gas-dynamic and electromagnetodynamic forces, alloy microparticles detach from the granule and are ejected subsequently into the working fluid. Due to contact with the gas bubble that appears in this process and with the working fluid, rapid cooling and formation of disperse microparticles take place [14–18]. This makes it possible to produce multicomponent alloy powders in chemically inert liquids practically without change in chemical composition, to make the particle surface amorphous thanks to high cooling rates, and to activate particles during their production. The first feature of the method is valuable since the original alloys generally consist of three and more components, the ratio between which must be accurate within fractions of percent. Thanks to the second feature of the method, the corrosion resistance of powder particles increases. Finally, the method enables producing micron and submicron particles with extended surface. Depending on the conditions of carrying out the electric-spark dispersion process, the metal particles formed can partially or fully interact with the working solution. Therefore, the study of the effect of the conditions of carrying out the electric-spark dispersion process on the electrochemical properties of powders is a topical question.

The aim of our work was to examine the possibility of using the spatial electric-spark dispersion method to produce electrode materials for nickel-metal hydride accumulators.

2. Experimental

Alloy powders of the compositions $Ti_{45}Zr_{38}Ni_{17}$, $Ti_{51}Zr_{26}Ni_{19}Si_4$ and $Ti_{49}Zr_{25}Ni_{18}Si_8$ (at.%) produced by melting together individual components were investigated. The alloy powders were obtained by the SESD method in ethyl alcohol, distilled water, kerosene, liquid argon and liquid nitrogen and, for comparison, by mechanical dispersion in a ball mill (the average particle size in this case was 4–10 μm). The design of the discharge chamber in the SESD method (Fig. 1) permitted control of working fluid flow and ensured the conditions for the precipitation of powder. Alloy granules (No. (3) in Fig. 1) were loaded into the interelectrode space (IES) of the discharge chamber. The space length was controlled with special dielectric inserts (No. (4) in Fig. 1) with a step of 3 and 5 mm between 22 and 57 mm. Electrical pulses were transferred from the current source to the bed of granules by means of current leads (No. (8)) and electrodes (No. (9)). The granules were held over the reducing chamber, which is necessary for the prevention of turbulences in the working fluid stream, by means of a perforated dielectric bottom (No. (5)). The working fluid (No. (2)) was delivered under an excess pressure of 0.01–0.2 atm

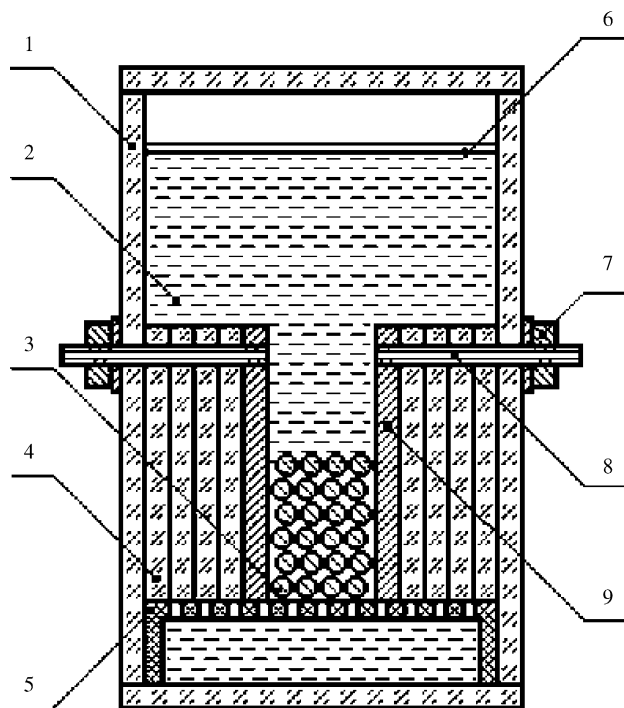


Fig. 1. Section of the discharge chamber: (1) casing; (2) working fluid; (3) alloy granules; (4) inserts for controlling the interelectrode space length; (5) perforated bottom; (6) rear wall of the chamber; (7) fastening of the current leads; (8) current leads; (9) nickel electrodes.

from below and carried away the erosion products at the top of the rear wall (No. (6)) into the settling chambers. The amplitude of discharge voltage between the nickel electrodes was varied between 200 and 600 V, the discharge pulse recurrence frequency was 5–300 Hz; the capacity of the electrical energy storage (capacitor) was varied between 10 and 50 μF , the inductance of the connecting cables was 0.5 or 1.5 μH , the height of the bed of original granules was 20–50 mm, and its length was 22–57 mm. Granules of 2–7 mm size were used. The discharge pulse length was in this case 15–800 μs , and the discharge current amplitude was 300–1350 A. The measurements of the electrical parameters were made by means of an S8–17 double-beam memory oscilloscope.

The suspension obtained after dispersion was dried. Then X-ray structure, optical and electrochemical investigations of powders were carried out. The X-ray structure investigations were carried out on a DRON-3.0 diffractometer using Fe $K\alpha$ radiation. To measure dispersity, optical and electron microscopy, as well as optical granulometry (Analyzette-22 laser granulometer made by the Fritsch company), were employed. A test for the evaluation of the electrochemical properties of the hydrogen-sorbing materials obtained was their use as the hydride electrode of a nickel-metal hydride accumulator. To carry out electrochemical investigations, electrodes, pressed on a nickel net, were prepared from alloy powders and fluoroplastic emulsion as a binder. The electrochemical characteristics of the alloys were stud-

ied in a mockup of nickel-metal hydride accumulator under galvanostatic conditions. A working electrolyte of the composition 7 M KOH + 1.5 M LiOH was used. When determining the electrical capacity of the electrodes, they were previously trained during six to nine charge–discharge cycles.

3. Results and discussion

The alloy powders obtained by mechanical dispersion had an average particle size of 60–100 μm . After SEDS, the particles of alloy powders were spherical in shape and had a wide size distribution. It should be noted that in most cases, two particle fractions were observed: submicron particles and particles of about 0.1–10 μm size. The ratio of the volume fractions of the submicron and micron fractions varied depending on the type of working fluid and discharge process characteristics. The characteristic particle size of the fine fraction was 0.02–0.5 μm . The particle size of the coarse fractions ranged between 0.5 and 20 μm depending on different factors. The coarsest powders (5–15 μm) have been obtained in liquid argon, slightly finer powders (0.1–10 μm) in distilled water, still finer powders in kerosene, then in liquid nitrogen (0.05–2 μm), and the finest powders have been obtained in ethyl alcohol (0.01–1 μm).

On the other hand, the parameters of discharge pulses (voltage amplitude, length, pulse power) also affected the particle size of the powders obtained. For instance, to reduce the average particle size, it is necessary to increase the pulse amplitude and to decrease the voltage. Increasing the pulse length (to 500 μs) and reducing the voltage amplitude (to 70–80 V) made for larger particle size of the powder obtained. It was this combination of parameters that contributed to the retention of Laves phase in the powders obtained.

The structural state and phase composition of the powders obtained by the SEDS method depended not only on the composition of the original alloy, but also on many technological factors: dielectric medium, energy and length of discharge pulses, their amplitude, shape and recurrence frequency. Fig. 2 shows fragments of the diffractogram of the Ti–Ni–Zr alloy in the initial state (diffractogram 1), after its electrolytic hydrogenation (diffractogram 2), and of the alloy produced by the SEDS method in ethanol (diffractogram 3). It is seen from Fig. 2 that in the diffractograms of massive samples, there are only lines due to Laves phase, and in the diffractograms of samples after their dispersion there are also lines due to tightly bound hydrides. In the diffractograms of powders dispersed in ethanol, there are also lines due to zirconium oxide. It is also seen from this figure that the powder diffractogram has a smaller number of lines, but they are greatly broadened and shifted towards smaller angles as compared with the initial state. This indicates that the dispersion of the materials under investigation affects greatly their structural state. The reasons of this structural change of powders

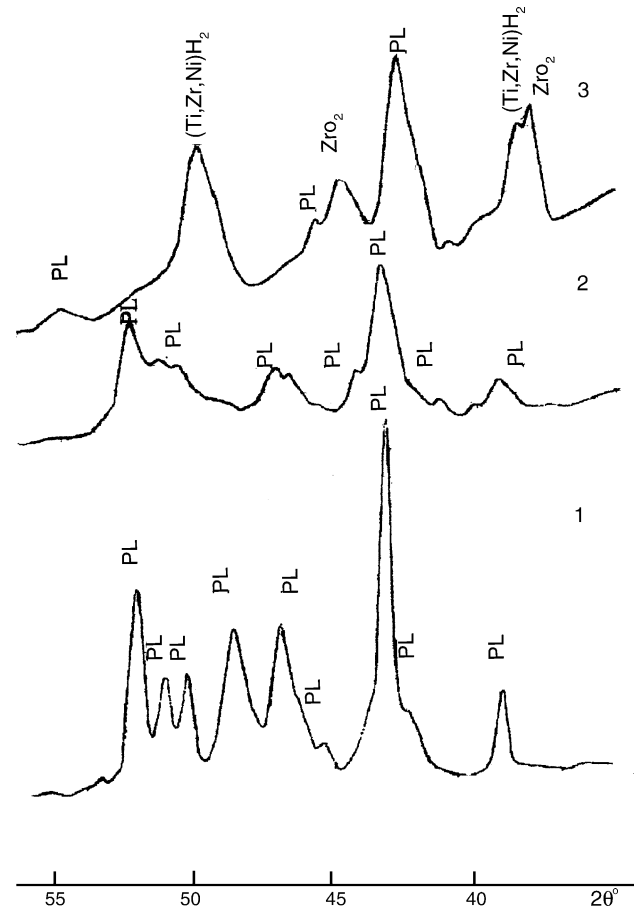


Fig. 2. Fragment of diffractograms of the $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ alloy in the initial state (1), after electrolytic hydrogenation (2) and of powder obtained by the SEDS method in ethanol (3); LP: Laves phase.

may be not only the conditions of their preparation (heating of the alloy to high temperatures and high cooling rate of particles), but also high fineness of particles and saturation of particles by interstitial impurities, which are formed as a result of the interaction of particles with the cooling medium. Such interstitial impurities may be primarily hydrogen and oxygen. This follows from comparison of the diffractogram of a massive alloy sample electrolytically saturated with hydrogen (diffractogram 2 in Fig. 2) with the diffractogram of powders prepared by the SEDS method (diffractogram 3). It can be seen that the lines due to hydrogen-saturated massive samples are broadened, no lines due to tightly bound hydrides are observed, and that some lines are shifted just as this was observed in the case of powders. An X-ray phase analysis of powders obtained in water and ethanol showed the presence oxides and hydrides. The powders obtained in ethanol exhibited lines due to hydride $(\text{TiNiZr})\text{H}_2$. The phase composition of the powders obtained in water differed greatly from that of massive alloy: the powder diffractogram contained only lines due to original metal oxides. The powders obtained in kerosene contained mainly complex hydrides, which had the same symmetry (fcc) but different lattice parameters. Only the powders obtained in cryogenic liquids

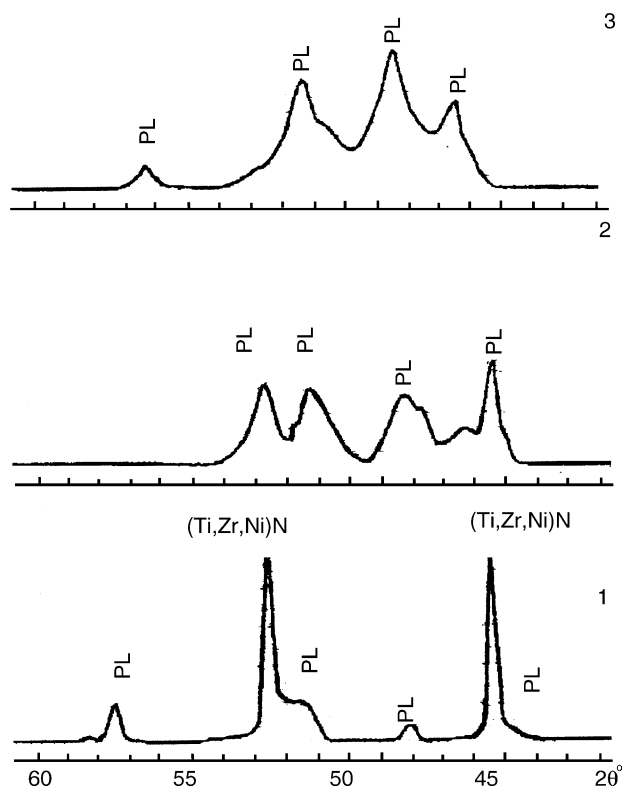


Fig. 3. Fragments of diffractograms of $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ alloy powders obtained in liquid nitrogen (1) and in liquid argon (2 and 3): (1 and 2) $U_m = 450$ V, $\tau_n = 15$ μs , $C = 10$ μF ; (3) $U_m = 450$ V, $\tau_n = 30$ μs , $C = 50$ μF .

contained no appreciable amount of products of the interaction of alloy granules with the liquid surrounding them. Typical diffractograms for these powders are shown in Fig. 3. In the diffractograms of the powders obtained in liquid argon (diffractograms 2 and 3) there are only the lines corresponding to Laves phase. Increasing the capacity of the working capacitor resulted in a broadening of peaks (diffractogram 3), which was due to an increase in powder fineness. In the diffractograms of the fine powders obtained in liquid nitrogen, there are lines due to the complex nitride (TiZrNi)N in addition to the lines corresponding to Laves phase (Fig. 3, diffractogram 1).

The negative electrodes based on alloy powders produced by mechanical dispersion possessed as a rule low specific characteristics (the discharge capacity, Q_d , was 15–25 mAh g^{-1}). The electrodes based on powders produced

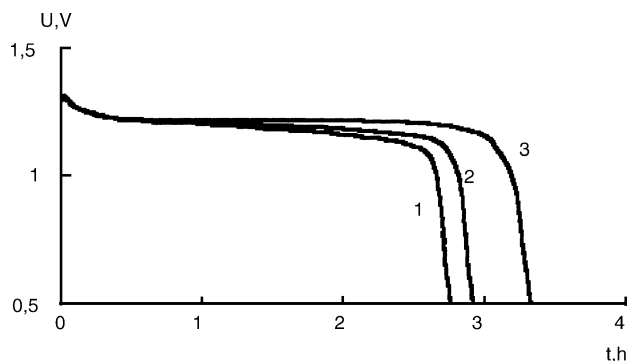


Fig. 4. Discharge curves for electrodes based on Ti–Zr–Ni alloy powders obtained by the SESD method in ethyl alcohol. Mass of powders: 0.25 g, discharge current: 14 mA. (Curve 1) $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$, (curve 2) $\text{Ti}_{51}\text{Zr}_{26}\text{Ni}_{19}\text{Si}_4$ and (curve 3) $\text{Ti}_{49}\text{Zr}_{25}\text{Ni}_{18}\text{Si}_8$.

by the SESD method in distilled water and kerosene did not have satisfactory discharge capacity values either and were of no practical interest. The best electrochemical characteristics were obtained after dispersing alloys in rectified ethyl alcohol and in cryogenic liquids (nitrogen and argon). Fig. 4 (curve 1) shows a discharge curve for an electrode made of Ti–Zr–Ni alloy powder obtained in ethyl alcohol. It has been found that when using ethyl alcohol for Ti–Zr–Ni electrode, a specific discharge capacity of $C_d = 150$ mAh g^{-1} and an efficiency of $\eta = 53\%$ ($\eta = Q_d/Q_c$, where Q_d and Q_c are the electric charge passed during the discharging and charging of the electrode, respectively) can be achieved. Addition of several percent Si to such an alloy (Fig. 4, curves 2 and 3) increased the operating efficiency of the electrode based on it. For the powders of such alloys dispersed in ethyl alcohol, the maximum value of discharge capacity was $C_d = 160$ – 170 mAh g^{-1} .

Table 1 presents conditions for producing disperse $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ particles in cryogenic liquids and electrochemical properties of electrodes made on the basis of the powders obtained. The highest value of discharge capacity and discharge efficiency was shown by the electrodes made of Ti–Zr–Ni powders obtained in liquid nitrogen (200 mAh g^{-1} and 67%, respectively), which is of practical interest. Relatively coarse powders (ca. 15 μm) obtained in liquid argon at peak values of discharge pulse voltage of up to 100 V allowed us to reduce the self-discharge time to 280 h (the capacity decreasing by 20%). The specific discharge capacity was in this case 170–185 mAh g^{-1} , which is an acceptable

Table 1

Parameters of the process for producing $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ particles dispersed by the SESD method in cryogenic liquids and electrochemical properties of these particles

Pulse voltage amplitude, U_m (V)	Discharge current amplitude, I_m (A)	Discharge pulse length, τ_u (μs)	Capacity of the working capacitor, C (μF)	Cryogenic liquid	Number of charge cycles	Specific discharge capacity, C_d (mAh g^{-1})	Discharge efficiency, η (%)
400–450	400	–	50	Nitrogen	8	200	67
75	600	500	300	Argon	9	175	50
100	430	63	50	Argon	9	170	40
200	600	50	50	Argon	8	85	34

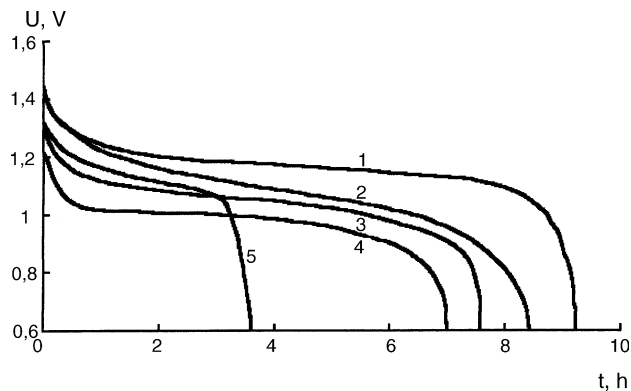


Fig. 5. Electrochemical characteristics of a $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ alloy powder obtained by the SESD method in liquid Ar (curves 1, 2 and 5) and ethyl alcohol (curves 3 and 4) after annealing in Ar (curves 1 and 3), under vacuum (curves 2 and 4) and in hydrogen (curve 5). Powder mass: 0.5 g, discharge current: 11 mA.

characteristic. Finer powders, which were obtained in liquid argon at a voltage with an amplitude of 200 V and higher, did not have electrochemical characteristics, which is due to a change in their phase composition during dispersion. The results obtained show the SESD method to be the most efficient method for producing alloy powders for the negative electrode of Ni/MeH accumulator by the use of inert oxygen-free dielectric liquids, in which making the surface amorphous does not involve simultaneous formation of surface oxides.

To improve the electrode characteristics, experiments on annealing the powders obtained in gaseous argon, hydrogen and under vacuum have been made. The powders obtained in liquid argon and annealed in gaseous argon at $T=900^\circ\text{C}$ during $t=30$ min showed the best results (Fig. 5, curve 1). As follows from Fig. 5 (curve 2), vacuum annealing was second in efficiency; hydrogen annealing (Fig. 5, curve 5) showed the worst results. It has been found from an X-ray structure analysis of these powders that there is no change in phase composition after annealing, though some line narrowing indicated sintering of the powder and an increase in grain size. Annealing of powders, obtained in alcohol, in gaseous argon at $T=900^\circ\text{C}$ during 30 min also led to an increase in discharge capacity (Fig. 5, curve 3), and the self-discharge time increased to 70–80 h. The results of an X-ray structure analysis showed that the relative intensity of the lines corresponding to oxides increased probably owing to the destruction of some complex hydrides which contained oxygen. Note that the powder annealing temperature had a considerable effect on electrode characteristics. For instance, the powders annealed at $T=800^\circ\text{C}$ did not change their electrochemical properties, whereas the electrochemical properties of electrodes based on powders annealed at $T=970^\circ\text{C}$ deteriorated sharply. It should also be noted that during the cycling of electrodes, the value of discharge capacity also increased (Fig. 6), which may be due to a change in both surface and bulk properties of microparticles during their hydrogenation.

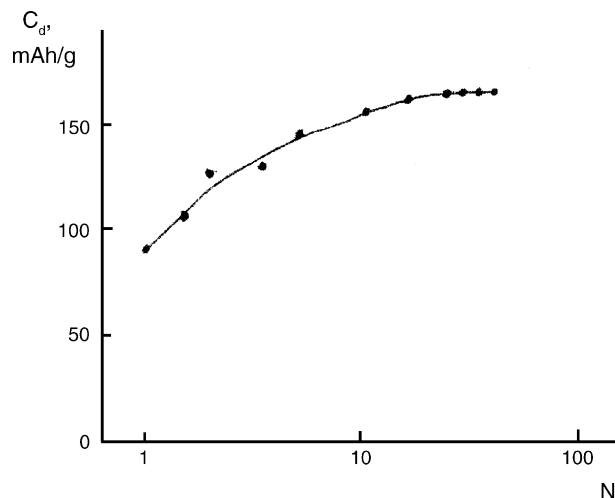


Fig. 6. Specific capacity C_d as a function of the number of cycles (N) for a negative electrode based on the $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ alloy dispersed in liquid argon.

4. Conclusions

Thus, the investigations carried by us showed the SESD of Ti–Ni–Zr alloy granules to be a promising method for producing metal alloy powders for the negative electrode of nickel-metal hydride accumulator. This dispersion method has a considerable effect on the surface of alloy microparticles, as a result of which its oxidation decreases, and the accumulation of electrochemically active forms of bound hydrogen in the bulk of particles is enhanced.

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