

limited resources at Unlimited Capabilities

-new ideas, processes & materials will allow a good and can provide a brilliant future-

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Abstract— Any modern society considers sustainability, saving resources and increasing performance every day and our all future will be ruled by materials as never before. Based on general materials limitation, goal (a) is "making more with less" and since materials consumption contradicts with such limited resources, goal (b) is recycling. Along with the clear understanding, that there is no waste on this planet but material, both induce to advanced materials processing with the utilization of larger surface and finer structures leading to nanostructures.

High kinetic processing has been proven as a major route for reducing materials' grain size in large volume at economic manufacturing and cost capability as well as the "nanostructure-making-equipment", the Simoloyer[®] is well-known including technology and key advantages.

Zentallium[®], the super-light-weight material at half titanium cost approaching pressing and sintering after hot extruded semi-finished material is on the market. Zentallium[®] represents grain size stabilized aluminum utilizing carbon nanotubes.

The globally first public bridge by Zoz/Dyckerhoff high performance cement at high strength, virtually endless durability and enormous CO₂-emission savings has been set up in Germany in November 2012. Second demonstrator has followed in June 2013 (heritage balustrade at ZCS Siegen - 12 tons) and the first product from the shelf came up early 2015.

Other materials manufacturing results are Nanostructured Ferritic Alloys (next gen. ODS, Zoz/GE), Hydrolium[®]/H₂Tank2Go[®] including vehicles (Zoz ZEV-fleet & H₂-OnAir+ - Zoz/HZG/Airbus et al.), advanced Zn-flake coatings (anti-corrosive material, Zoz, RFS) and even battery cathodes (phosphate systems Mn and Fe, ZoLiBat[®]) as well as a novel processing route of generating high quality rubber from the roots of dandelion plant (Zoz, Fraunhofer & Continental).

Keywords - Simoloyer[®], High Kinetic Processing, Zentallium[®], FuturZement, Hydrogen-storage

I. INTRODUCTION

Today and for the future, mankind is obliged to think about what will happen if there is not enough material and if there are not enough resources anymore. Therefore the importance of ultimate and utmost complete recycling and recovery does also include wastes of the past as well as the corresponding suitability of any new product before launched in the market.

The only other possibility of generating more (resources) is increasing performance of all processing, application and materials.

Recycling & Performance are the key issues for achieving sustainability.

Looking at materials, advanced performance can be achieved by increasing the materials function that describes the relation of invested material vs. achievable utilization over volume and time. Since the materials function is mostly depending on materials surface, increasing effective surface is the goal to be achieved by decreasing the unit-size/scale.

Nanomaterials are materials which are produced and applied on a small scale and show enhanced and unique properties compared to comparable materials which are not nanosized [1]. They offer lots of opportunities. Nanostructured materials are modified on the atomic scale. This results in a change of the material's surface-near solid state properties [2].

Nanostructured materials provide a grain size <100nm resulting in a large surface of grain boundaries, virtually a large inner surface. Nanostructures can also represent e. g. a micron-scale matrix with nano-scale phases for generating enhanced properties or other combinations.

Nanostructures can be manufactured in large volume at economic level and insofar contribute significantly to the overall goal of "making more with less".

One of the most practicable and insofar

economic routes to obtain useful nanostructures is the High Kinetic Processing technique (HKP) performed by Simoloyer[®].

II. HIGH KINETIC PROCESSING IN THE SIMOLOYER[®]

HKP is a synonym for well known processes Mechanical Alloying (MA), High Energy Milling (HEM) and Reactive Milling (RM) at higher energetic level.

MA has been described by repeated deformation, fracture and cold welding of powder particles by highly energetic collisions of grinding media [3,4]. Such process can allow the synthesis of novel materials with enhanced or even new properties that cannot be synthesized by conventional techniques due to chemical, physical or thermodynamic barriers.

HEM and RM follow the same principle with a focus on creating reactive surfaces and enabling chemical and physical reactions [3,4]. They differ in the target of processing and in energy that is transferred into the material.

Compared to the well-known/conventional "milling" devices, HKP in the Simoloyer[®] provides a significantly higher kinetic energy impact and energy impact efficiency [3,4].

Simoloyer[®] is basically representing a high energy horizontal rotary ball mill where the definition "mill" does not perfectly but nearest meets the proper definition [5].

Milling/grinding is understood as a process to reduce the particle size of solids such as granules or powders. HKP is understood as a process to primarily reduce the grain size of solids e. g. granules or powders. Reduction of particle size at HKP can be a primary goal e. g. for materials with a very high hardness. On the contrary, also a growth in particle size can be the target e. g. manufacturing ductile metal flakes (DMF) from fine powder dust.

The kinetic impact can be described by the maximum relative velocity (MRV) of (grinding)media. HKP in the Simoloyer[®] today can reach 18 m/s compared to <6m/s in conventional (milling) processes at high (energetic) efficiency >50% compared to <5% [6] at conventional ball- rod- or shaker-milling insofar confirming the simple understanding of kinetic energy equation (Eq. 1).

$$E_2 = \frac{1}{2}mv^2 \quad (1)$$

Since HKP describes a process based on collision rather than of shear and friction interaction of (grinding)media, consequently HKP also allows a process at a low level of contamination caused by the processing (milling) tools. This is also favored by shorter processing times resulting in a higher energetic impact level.

Table 1 compares the Simoloyer with other devices in use for MA, HEM and RM with respect to capacity, impact and provided energy.

Table 1 Devices in use for MA, HEM and RM [3,4]

device	Simoloyer [®]	Shaker Mill	Planetary ball mill	Attritor [®]	Drum(ball)-mill
max. diameter [m]	0.9	0.08	0.2	1	3
max. total volume [l]	900	0.2	8	1,000	20,000
MRV [m/s]	16/18	4-5 (4.2)	5	4.5-5.1	< 5
specific energy [kW/l]	1.1(-3)	-	-	0.1-(0.75)	0.01-0.03
scaling up	yes	no	no	yes	yes

^a. Simoloyer[®] is a brand of Zoz GmbH, Germany, Attritor[®] is a brand of Union Process, USA

III. THE SIMOLOYER[®]

The Simoloyer[®] is the HKP device, patent-protected and responsible for numerous inventions in materials and processing [7].

Advanced process control is provided by the Maltoz[®]-control software allowing patented Cycle Operation particularly for ductile materials composites exhibiting critical milling behavior (CMB) countering agglomeration tendency.

Advanced processing is provided by patented air-lock systems including dead-zone free processing, charging and discharging under vacuum/inert gas at elevated as well as undercooled temperature. The Simoloyer[®] is technically scalable from lab-scale to industrial in batch, semi-continuous and auto-batch operation mode (carrier gas). Processing tools are available in stainless steel/Stellite[®], WC-Co and Si₃N₄.



Fig. 1. Simoloyer[®] CM01-21m laboratory scale with air-lock (a); Simoloyer[®] CM081m (back) and CM201m in front (b); CM201m-s1, semi-continuous operation mode (c) and Simoloyer[®] CM100-s2, auto-batch operation mode.

The Simoloyer[®] is the commercial device for synthesizing advanced/new materials e.g. far away from thermal equilibrium or at conventional immiscibility of components. By structural design, important materials' properties can be influenced, grain size tremendously reduced and also chemical reactions can be performed under solvent-free clean condition by solid state synthesis and at 100% yield. Up to 900 tonnes p. a. and per unit can be manufactured.

IV. APPLICATIONS IN HIGHLIGHTS

A. Super-light-weight: Zentallium[®]

Zentallium[®] is the Al-CNT composite which is lighter than aluminum and as strong as steel. At a tensile strength of 700MPa, the specific strength is exceeding that from Ti-6-4 at about half of the materials cost and significantly higher than that of stainless steel (Fig. 5).

Basically, the Al 5083 is grain-refined to nanoscale utilizing the Simoloyer[®] at strictly closed condition and ultimate cycle operation processing. In situ and air-locked, the carbon nanotube (CNT) sponges are dissolved and alloyed into the Al-matrix on nanoscale.

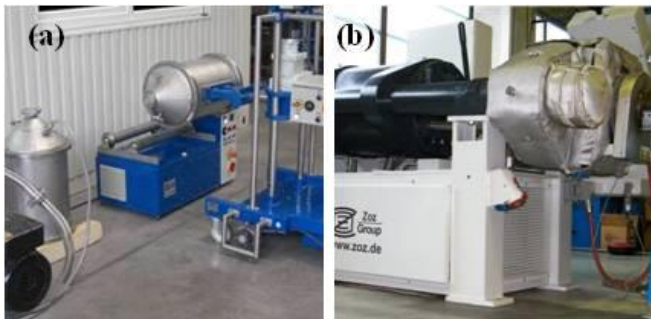


Fig. 2. Passivation of Zentallium[®] powder after Simoloyer[®]-processing and hot extrusion at ZTC

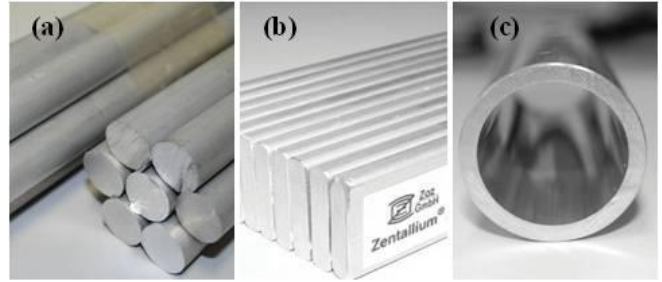


Fig. 3. Hot-extruded bars D15mm, rods 20/5mm, tube 30x3mm (semi-finished)

After a passivation step (Fig. 2a) of the highly reactive composite powder, Zentallium[®] is consolidated by hot extrusion (Fig. 2b) into different semi finished products (Fig. 3a-c). The CNTs during this manufacturing step are hindering the structural re-growth after severe grain-refinement. Zentallium[®]-powder can also be pressed and sintered, however, so far only hot-extruded semi-finished products bars D15, rods 20/5 (Fig. 3a-b) are available at Zoz from which finished products (Fig. 4b-c) are processed by common machining at weight-saving rates >60% compared to steel.

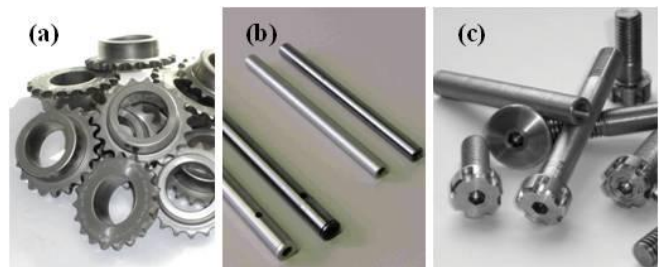


Fig. 4. Zentallium[®] finished gear parts (pressed & sintered), helicopter shafts & bicycle screws (made from Zentallium[®] bars)

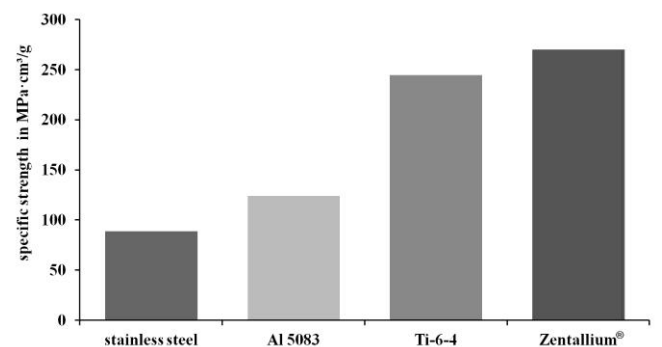


Fig. 5. Specific strength of stainless steel, Al- and Ti-alloys and Zentallium[®]

Zentallium[®] obtains its high strength according to nano-scale crystallites following the Hall-Petch-relation [8-10]. Zoz received the

Materialica Award 2010/Germany for some structural parts by Zentallium®.

B. High Performance Cement/Concrete: FuturZement/FuturBeton

FuturZement and the resulting FuturBeton represent nanostructured cement res. concrete at outstanding performance, economics and environmental friendly impact. FuturBeton is 3-4 times stronger (~140MPa) than ordinary concrete (OPCC) exhibiting very high early strength (~45MPa after 1 day) at superior durability and substantial CO₂-emission saving (20%). The total absorption costs (TAC, Germany 2012) based on a single Simoloyer® CM900, leading to about 43,000 tons FuturBeton p. a. is resulting into additional cost of 10 USD per ton of super-concrete.

The Simoloyer® is utilized in a semi-continuous processing mode (Fig. 1c) to super-activate ground granulated blast furnace slag (GGBS). HKP does increase the basically very low hydraulicity of GGBS to a level, where HKP-GGBS can react without any further activators and is replacing 30% of Ordinary Portland Cement (OPC). Due to the continuous processing, the super-activation on nanoscale takes a few seconds at a significantly increased processing kinetic level [11-14].

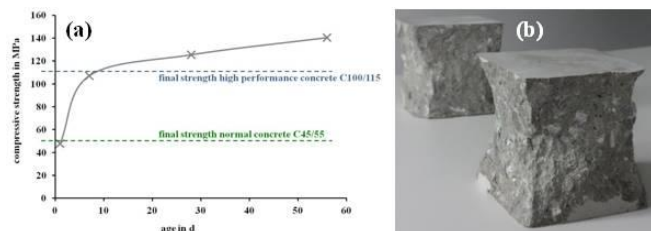


Fig. 6. Compressive strength of FuturBeton vs. ordinary concrete (OPCC) and high performance concrete (HPC) and "used" ASTM test-cubes (b)



Fig. 7. Bridge Rosenthal at Olpe/Germany

HKP-GGBS is then mixed with 70% OPC at high intensity resulting into FuturZement that is further processed to FuturBeton at practically conventional conditions. The resulting advanced construction material provides a significantly denser packing and fined porosity which means that water / moisture virtually cannot penetrate any longer or at least far less resulting in a significant improvement of durability against diffusion of aggressive media that can destroy concrete.

The CO₂ emission saving of 20% is achieved by substitution of clinker/OPC. Additional CO₂-savings can be claimed due to the high durability and high strength because of less materials consumption and less maintenance or replacing of corroded parts. Thus FuturZement and FuturBeton are highly economic and ecologic.

With FuturBeton, construction-industry can build more faster, sleeker, higher, cost-effective, durable and more environmentally friendly with better surface and less steel.

C. Energy Storage: H₂ solid state absorber, H2Tank2Go®, IronBird, P2G2F®, BAS-SM

H2Tank2Go® represents the "click'n-go" Hydrogen-tank cartridge system containing rechargeable nanostructured RT-MH Hydrolium® powder (Fig. 08a) that is developed for a clean, reliable, fast, mass-capable and cost-effective solid state hydrogen storage future utilizing given infrastructures such as vending machines (Fig. 8b), home-depot and home delivery. The H₂-capacity of 2-4 wt-% of the <1l tanks is >50g operating at <10bar at a lifetime >20years.



Fig. 8. H2Tank2Go® loaded with Hydrolium® (dark powder) (a), H2Tank2Go® at a tank vending machine (b), IronBird/Stromkoffer in the trunk of a Zoz-ZEV vehicle (c) and solar-aircraft Icare II (IFB) shall learn to fly on H₂ (d)

The *IronBird/Stromkoffer* (IronBird is the Airbus definition of the Zoz-Stromkoffer to be translated as power-box) represents the light-weight, cost-effective on-board energy platform carrying 6 H2Tank2Go® and 2 small PEMFC (fuel cells) focusing on both, H₂-repowering of

battery ZEVs in ground transportation (Fig. 8c) as well as range extending the Icare II solar glider (IFB, H2-OnAir) in aviation (Fig. 8d).

The systematic of *Power-to-Gas-to Fuel* (P2G2F[®]) was nominated for the German Environmental Award 2013 and describes Hydrogen generation from renewable energies, solid state storage, vending-like distribution and consumption in transportation - rethinking mobility for tomorrow's world.



Fig. 9. H₂-tank system B4S-SM complex metal hydrides (a) and HZG@ZTC (b).

B4S-SM is the world-wide first semi-commercial borohydride solid-state storage tank based on complex metal hydride (LiBH₄ & MgH₂) and has just been introduced in June 2016 by Zoz and Helmholtz-Centre Geesthacht (HZG) in Germany (Fig. 9). Resulting from the EU-project BOR4STORE [15], the reactive hydride composite material (RHC) is synthesized under extremely closed & clean condition in a Simoloyer[®] CM100 in auto-batch processing at the HZG-Hydrogen Technology Centre at ZTC in Olpe.

B4S achieves a gravimetric H₂-density of almost 10 wt-% !! fully reversible in the H₂-storage powder where the theoretical value is even higher at 18.3 wt-%.

In this respect, novel and advanced in-tank-storage and absorber materials are the objective of the ongoing HySCORE-project [16]. The availability of low cost PEM electrodes is the goal of the ongoing project LOCOPEM [17] and in case of success will be essential for the economics of the IronBird.

D. Anti-corrosion: Ductile Metal Flakes & ZFP Coating

HKP/Simoloyer[®] can be utilized for the rapid manufacturing of all kind of ductile metal flakes powder [18,19]. Virtually by means of the "HEM-effect" at high kinetic energy impact, processing can be up to 1.000 times faster [20] than in the conventional route (classic ball milling or stamping). By the "MA-effect", a whole range of alloys can be *in situ* synthesized e. g. a zinc flake

becomes brighter if a small fraction of Al-powder is added into the process.

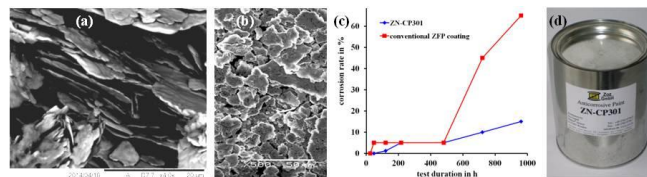


Fig. 10. HKP-ZFP (Zinc-Flake by Simoloyer[®]), SEM (a), corresponding Zn-lamellar layer (b) corrosion rate of ZN-CP301 vs. conventional ZFP coating at salt spray test (c) and a product can of anticorrosive paint ZN-CP301 (d).

Zoz in this field is focusing on ZFP coatings (ZFP = zinc-flake pigments) where the advanced flake manufacturing leads to both, outstanding cost-efficiency and far higher corrosion protection than conventional flake-based products. Since by HKP the flake is processed not in solvents but under dry condition with small fractions of polymer process controlling and dispersing agents, the result is highly flexible and highly economic and also environmentally friendly at a remarkable saving of volatile organic compounds (VOC). Processing times are ranging in minutes rather in hours and days [21] resulting in a high manufacturing capability of up to 1.000 tons p. a. ZFP in a single Simoloyer[®] CM900 unit.

In order to bringing this HKP-ZFP to the market, appropriate binder systems have been developed for manufacturing ZFP-lacquer systems resulting in the resin based ZN-CP301 anticorrosive coating (Fig. 10d). Figure 10a shows the Zn-flake after rapid manufacturing by HKP/Simoloyer[®], Figure 10b a corresponding Zn-lamellar layer and Figure 10c the corrosion rate of ZN-CP301 in comparison to a conventional ZFP coating at outstanding and far superior performance with respect to long term stability in salt spray according to ISO 7253. E. g. after 950h, the corrosion rate of the ZN-CP301 product is >4 times lower!

After this technical-economic success, the ongoing development of HKP-ZFP to stable water-dispersible pigments is expected to lead to an innovation at highest economical and ecological importance. Previous results are promising and shall break a path to a future with water-based efficient high performance stir-in ZFP-lacquers for industrial, trade and Do-It-Yourself utilization.

E. ODS/NFA-manufacturing

One of the most exclusive application fields of the Simoloyer[®] is represented by Oxide Dispersion Strengthened alloys (ODS) and lately also by Nanostructured Ferritic Alloys (NFA) that may be described as a next gen. ODS at further advanced dispersoids by quality, scale, density and by their location in the matrix.

Common ODS alloys (e. g. Plansee PM2000 [22,23]) provide advanced mechanical and/or structural properties such as high tensile and creep strength at elevated temperatures mainly in Al-, Fe- and Ni-based materials in power generation, aerospace and automotive. NFAs, exhibiting a dense dispersion of finer oxides (NFs sub 10nm) are developed for particular demands in nuclear fission and fusion technology such as advanced irradiation damage- and/or corrosion-resistance and high accident tolerance [24].

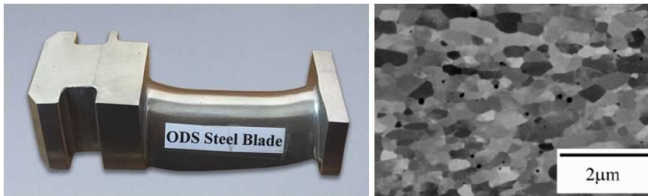


Fig. 11. Turbine blade from ODS steel (picture taken from Zoz-ARCI Center, India) and BSE SEM image of 14 YWT [18].

The most determining parameters, dispersion and refining are achieved by HKP. The virtually forced solubility of the dispersoid in the metal matrix requires an ultimate high energy transfer into the powder material leading to full dissolution of the starting oxide material creating homogenous network dispersion after consolidation. Same ultimate is a consequent clean handling particularly a clean atmosphere and low contamination during loading, processing and unloading at a full materials yield.

As of the above, the Simoloyer[®] is practically the globally exclusively applied device / technique. When it comes to semi-industrial or industrial manufacturing, the Simoloyer[®] represents the only known processing solution where the manufacturing of hundreds of kilos under such conditions has been proven since 2014 [25]. This also included 50 kg of a 14YWT Nanostructured Ferritic Alloy FCRD NFA-1 [26] with an oxide scale of 1-4 nm at defined crystal lattice position with a high dislocation density, a superior irradiation damage resistance and a

remarkable thermal stability of the dispersed oxides even after 19.000 hours (792 days) at 1.000°C ending with the summary question/proposal: "do NFA`s represent the "omega" nuclear structural material ?!" [26].

F. Extending limited resources: Taraxagum[™]

Taraxagum[™] is a brand of the Continental Tires Germany GmbH representing auto-tires made with natural rubber from dandelion. To date the conventional cultivation of natural rubber is utilizing the rubber tree (*Hevea brasiliensis*) mainly in the so-called "rubber belt" up to 30 degrees north and south of the equator. The continuously increasing demand of rubber processing industries as well as the fact, that newly planted rubber trees only after 7-10 years are bringing up a first return along with a global environmental understanding is challenging to finding alternative sources preferably to grow outside the "rubber belt".



Fig. 12. Continental-Expo with Taraxagum[™] auto-tire at the OZ-16 Nanostructure Symposium at Wenden/Germany (left) and ZTC at Olpe/Germany, location of the rubber extraction facility, plant-photo not allowed.

For Zoz and Zoz- processing technology expertise, the dandelion-rubber as a promising alternative became a goal several years back. Starting with a top-secret cooperation with the Fraunhofer Institute for Molecular Biology and Applied Ecology - IME at Münster/Germany this resulted in the Fraunhofer-IME Dandelion Rubber Extraction Facility under the roof of ZTC at Olpe. The semi-industrial manufacturing unit started processing container-loads in 2016. These Fraunhofer-activities are practically funded by Continental, technical details are confidential.

G. Energy Storage: Li-Ion-3rd generation cathodes and battery ZoLiBat[®]

ZoLiBat[®] is representing advanced cathode material for 3rd gen. Li-Ion batteries and a battery series itself. In this field Zoz is a) equipment supplier (LithiumFerroPhosphate = LFP) and materials co-developer and equipment supplier (LithiumManganesePhosphate = LMP) for the

phosphate systems that are doped by HKP on nanoscale. On the anode side so far only preliminary work on a nanostructured Si-matrix is done. The ZoLiBat[®] as a battery answers the political demand of availability of a domestic high performance state of the art electrochemical energy storage system.



Fig. 13. Pouch-cell ZoLiBat[®] (LMP) and ZoLiBat[®]-battery pack (14 cells).



Fig. 14. isigo[®]1.0-ZLB with 1 and longo[®]1.0-ZLB for 4 ZoLiBat[®]-battery packs.



Fig. 15. LMP-cathode material made with Zoz-Simoloyer[®], HPL>DOW-Kokam.

The ZoLiBat[®] cathode material/technology provides a high efficient nanostructured LFP- and LMP-electrode material offering a high structural stability due to the strong P-O-bonding. High C-rates allow fast charging and the nano-phosphates result at a low inner resistance R_i staying low over the entire lifetime, high currents can be achieved. Low toxicity and good thermal and electrical cycle-stability are very important benefits. The absence of cobalt offers a significant cost-

advantage at high scaling effects. Scaling is not intended to be done at Zoz, likewise all advanced materials manufactured are basically/originally demonstrators for the advanced HKP technology.

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