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The Strengthening of Weight Heavy Alloys During Heat Treatment

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Abstract

The results of studies of W-Ni-Co-Fe experimental alloy, with chemical composition assuring a possibility of producing Ni-based supersaturated solid solution are presented. The alloy was prepared from tungsten, nickel, cobalt and iron powders which were first mixed then melted in a ceramic crucible where they slowly solidified in hydrogen atmosphere. Next specimens were cut from the casting and heated at a temperature 950°C. After solution treatment the specimens were water quenched and then aged for 20 h at a temperature 300°C. The specimens were subjected to microhardness measurements and structure investigations. The latter included both conventional metallography and SEM observations. Moreover, for some specimens X-ray diffractometry studies and TEM investigations were conducted. It was concluded that quenching lead to an increase of tungsten concentration in nickel matrix which was confirmed by Ni lattice parameter increase. Aging of supersaturated solid solution caused strengthening of the Ni-based matrix, which was proved by hardness measurements. The TEM observation did not yield explicit proofs that the precipitation process could be responsible for strengthening of the alloy.

Keywords: Precipitation hardening, Weight Heavy Alloys (WHA), Mechanical properties, Structure

1. Introduction

Tungsten heavy alloys (WHA) are materials considered as most promising replacement for depleted uranium which is by now used for the core of subcaliber projectiles [1, 2]. This is because of radiation of DU discovered in the region of war in former Yugoslavia. Because of specific microstructure consisting of tungsten grains, size of 30-40 μm, randomly distributed in Ni-base matrix, tungsten heavy alloys are called tungsten composites (fig.1). The efficiency of subcaliber projectiles follows from their high kinetic energy and this is why they are called sometimes Kinetic Penetrators – KE. The chemical composition of conventional WHA subcaliber cores of density of 17,5 Mg/m^3 is: 98 weight % of tungsten and the rest: Ni, Co and Fe. The iron with some amount of tungsten forms the matrix of the "tungsten composites". The rods from which the WHA cores are produced are prepared using liquid-phase sintering in hydrogen atmosphere. The microstructure and mechanical properties of WHA alloys depend on purpose. Thus, the WHA for antitank should exhibit very high strength and good toughness [3,4] while those appropriate for space objects, should be susceptible to frangible effect [5, 6]. The aim of this paper is the former alloy, for which we studied possibilities of strengthening using age hardening. The starting point for the investigations were results obtained by Edmonds [5] concerning precipitation during heat treatment of tungsten heavy alloys together with our preliminary observations concerning mechanical properties of these alloys during complex thermo-mechanical heat treatment including swaging aging in

vacuum furnace followed by quenching in water and subsequent aging at an elevated temperature.

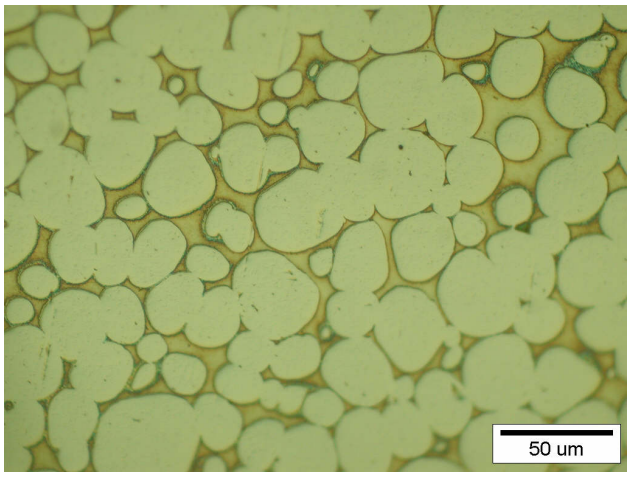


Fig. 1. The example of tungsten heavy alloy microstructure

As we can see from the Ni-W equilibrium diagram, the solubility of tungsten in nickel decreases with temperature decrease. This suggests that quenching should provide supersaturation Ni-solid solution with tungsten atoms, which is a necessary, although not sufficient condition for precipitation hardening. Therefore the aim of the studies was to investigate what is happening in the WHA matrix during its heat treatment including quenching and aging.

2. Experimental procedure

For the studies, the alloy W50Ni34Co6.6Fe9.4 was used. The alloy was obtained from a mixture of high purity component powders placed in a ceramic crucible and melted at a temperature 1450^{o}C in hydrogen atmosphere. The alloy was then subjected to 2h aging at a temperature 950^{o}C followed by rapid quenching in cold water. From the casting, the specimens 5mm thick were cut and isothermally aged for different time periods at a temperature 300^{o}C which was much lower than that typically applied in case of conventional WHA rods manufacturing. The specimens were subjected to hardness measurement and structure investigations. The latter included both transmission (TEM) and scanning electron microscopy (SEM) techniques. Moreover, EDX and X-ray diffractometry (XRD) methods were applied. The former was used for estimation of chemical composition of different phases and the latter for evaluation of the solid solution lattice parameter. The TEM observations were carried out on thin foils prepared using ion-beam technique. The specimens were first mechanically dimpled and then ion milled. Thin foils were observed in EM300 Philips EM electron microscope working at an acceleration voltage of 100kV. Both bright- and dark field techniques and also selected-area electron diffraction (SAD) [6,7] were used for gathering as much as possible data on the structure of material being studied. For SEM observation Leo 1530 electron microscope equipped with EDX stage for chemical analysis was used. The aim of XRD technique was to measure the lattice parameter of Ni-based solid solution after pouring, solution heat treatment and after 20h aging at a temperature 300^{o}C. X-ray studies were carried out in Philips diffractometer using CoKα radiation with wave length λ = 0.1542 nm and 2θ range of 130^{o}.

3. Results

3.1. Results of hardness measurements

In fig.2 the results of hardness tests as a function of aging at a temperature: 300^{o}C are depicted. As it is seen from the graph (fig. 2), the hardness increases very slowly with time and reaches approximately 318μHV after 32 hours aging. Although matrix hardness increased only by 10% approximately, compared to that after quenching, and is much lower than expected, the increase evidences some processes taking place in the material.

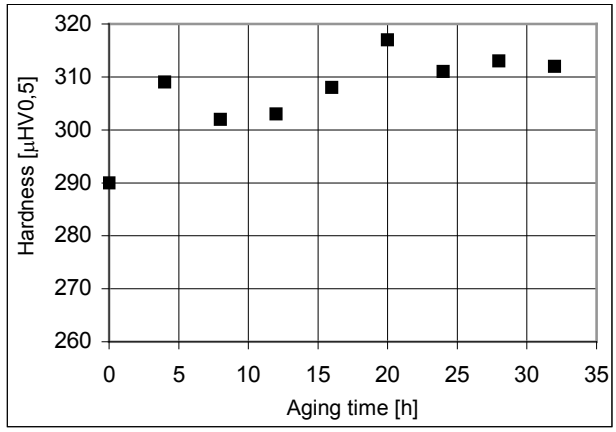


Fig. 2. The Vickers hardness as a function of aging time at a temperature 300^{o}C

3.2. Results of structure investigations

Metallography

Fig. 3 shows an example of typical microstructure of WHA after quenching. It is visible that is two-phase material. One phase (white) possesses dendrite morphology while the other (dark) is lamellar. The specific dendrite morphology suggests that it formed during solidification process. The latter phase occupies the interior of the dendrites, and the space between them being one of the eutectic. Metallography observations were limited to the microstructure after quenching only because this technique is too rough for observing precipitation on a scale which could be responsible for strengthening of the alloy.

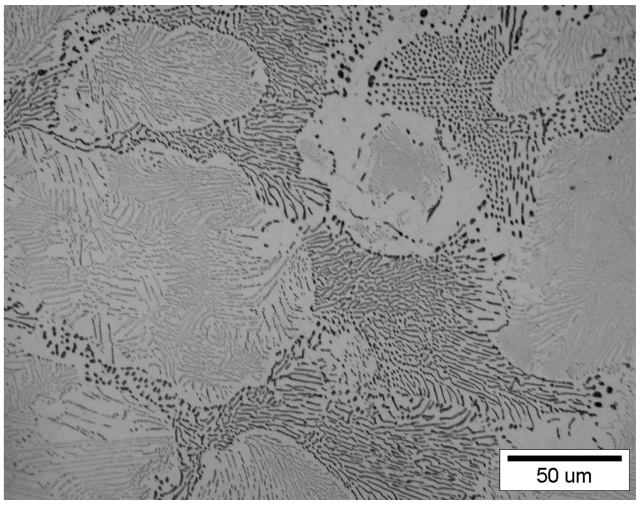


Fig. 3. The microstructure of WHA after solution treatment

SEM observations

In fig. 4 the microstructure of the alloy observed in BSE mode is presented. The microstructure is practically identical to that in fig. 3. The white-marked rectangle in fig. 4 shows the area from where the information on chemical composition was taken for case of a "mixed" region. To collect information concerning white and dark regions, similar procedures were used.

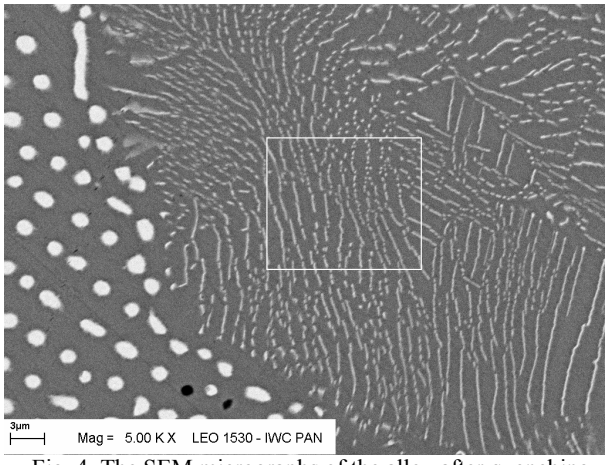


Fig. 4. The SEM micrographs of the alloy after quenching

The chemical composition of white and dark phases and that of the "mixed" region in the samples after pouring and at different time of aging at a temperature 300°C are given in table 1. As could be expected the white phase is rich in tungsten while the dark phase is Ni rich. This is not surprising when confronted with the electron scattering coefficients of tungsten and Ni.

Table 1.
The chemical composition of white and dark phases of the specimen after pouring, quenching and 20 and 36h aging at a temperature 300°C

State	Element	Chemical composition [at. %]		
		White	Dark	Mixed
As cast	Fe (K)	5,51	11,36	11,50
	Co (K)	6,4	14,95	15,22
	Ni (K)	23,76	58,10	56,07
	W (L)	64,26	15,59	17,22
Quenched	Fe (K)	7,18	11,46	1/,22
	Co (K)	8,97	14,54	15,26
	Ni (K)	31,31	57,53	56,69
	W (L)	52,24	**16,46**	17,83
Aged 20h T = 300°C	Fe (K)	5,6	11,74	12,58
	Co (K)	6,3	16,8	15,7
	Ni (K)	23,1	57,13	53,67
	W (L)	64,39	**14,24**	18,27
Aged 36h T = 300°C	Fe (K)	1,33	12,51	10,54
	Co (K)	4,07	16,24	15,24
	Ni (K)	10,52	56,44	55,99
	W (L)	84,08	14,81	18,24

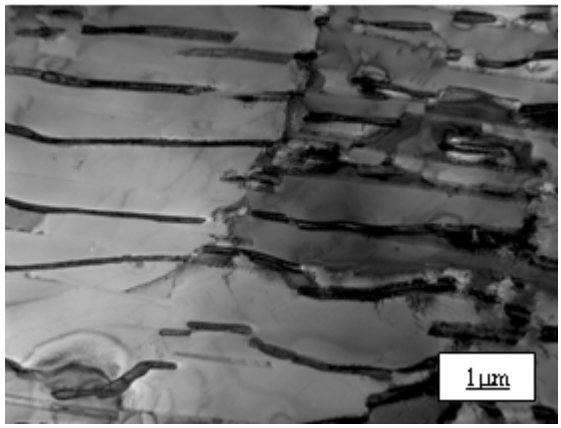
When comparing the values collected in table 1 for given phase at different stages we can see some differences. Although they are not very large, nevertheless they are large enough to be discovered. The most interesting ones are those concerning the concentration of tungsten in Ni, which is the lowest in alloy aged 20 hour at a temperature 300°C and equals 14,24 at. % and reach maximum after quenching approaching 16,46 at. %.

TEM observations

There is no question that TEM is the most adequate technique for studies of precipitation processes. This is not only because of the high magnification obtainable but also because high resolution this method. Moreover, TEM supplies not only information on size, morphology, and distribution of precipitates but also data on its crystallography structure. Those data can be obtained using selected area diffraction (SAD) and so called dark-field mode observations. However, it should be mentioned that TEM is no a direct method but needs the diffraction contrast to be assured. The specimen has to be tilted with respect to the electron beam in electron microscope to reach diffraction contrast which means that Bragg's conditions are met [7]. The preparation of thin foils for TEM is not easy and also very expensive. This was one of the reasons why only the specimens for selected heat treatment were selected for TEM observations.

Fig. 5 shows the most representative examples of the alloy structure after quenching. The first electron micrograph (fig. 5a) presents typical two-phase structure observed in bright-field while fig. 5c the same region observed in dark-field mode using electron spot marked in SAD pattern (fig. 5b). As follows from an analysis of all the information given in fig. 5, the spot used for dark-field micrograph (fig. 5c) represents lamellar precipitates which are light in dark-field electron micrograph (fig. 5c). According to the literature, these lamellar precipitates are almost pure tungsten [8].

a.



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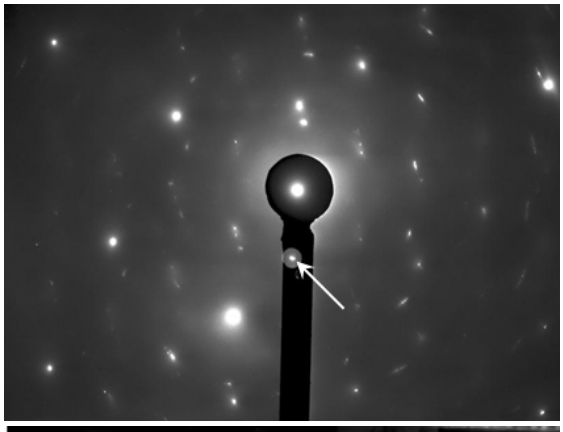

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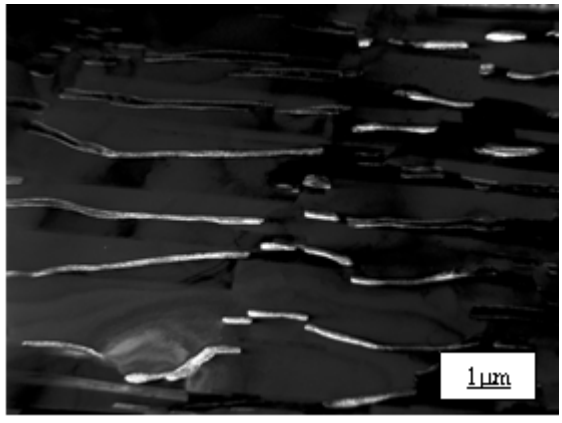
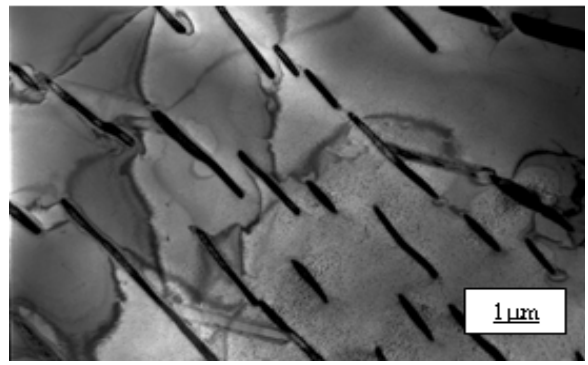


Fig. 5. The structure of alloy after solution heat treatment (quenching): a – bright-field electron micrograph, b – selected-area diffraction and c – dark-field electron micrograph

Fig. 6 shows the structure of alloy after 20 hours aging at the temperature 300°C. The structure looks very similar to that in fig. 5. The most outstanding difference is specific, much stronger contrast visible in fig. 6b and more pronounced in fig 6c which is a magnified picture of the central part of fig. 6.b. This specific contrast can be interpreted in a different manner. According to the theory of diffraction contrast [7], it may result from vacancy clusters, or it may represent radiation damage that formed during process of ion milling, or it may simply be very small coherent or semicoherent precipitates.

a.



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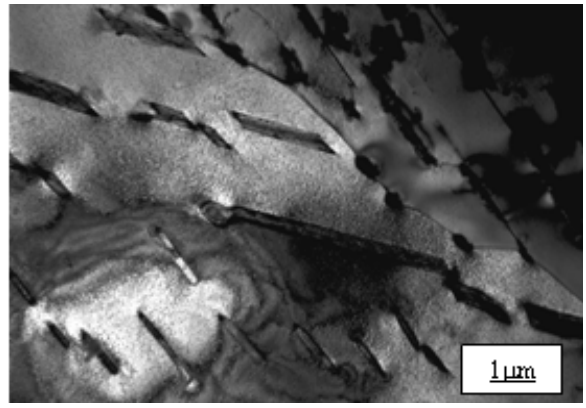

c.

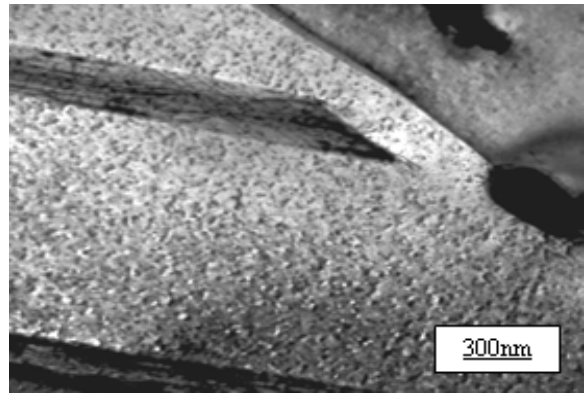

Fig. 6. The TEM micrographs of the model alloy structure after 20h aging at 300°C : a – bright field, b – dark field electron micrograph taken from the matrix electron diffraction spot c – magnified central part of electron micrograph in fig.5b

However, we were not able to resolve this question. We tend to suspect that the latter possibly is indeed the case because no such strong contrast was observed in alloy after solution heat treatment, although all specimens were prepared in exactly the same manner.

X-ray diffraction

The results of X-ray diffraction investigations are given in table 2 where we put the values calculated on the basis of diffractograms using the peaks 2θ located behind 90 degree. As follows from table 2, lattice constant of Ni(W) supersaturated solid solution, $a_0^{sup.}$, is substantially larger than the equilibrium one which can be represented by the lattice parameter after aging at a temperature 300°C which is very close to that obtained for the alloy in as cast.

Table 2.
The results of X-ray investigations

Phase	Lattice type	Lattice constant $a_0^{calculated}$		
		As cast	Solution heat treated (quenched)	Aged 20 hours at T = 300°C
Ni(W) solid solution	FCC	0.359934	0.360203	0.359806
Tungsten	BCC	0.316506	0.316560	0.315956

Taking take into account the values of Ni, Ni(W) saturated, and Ni(W) supersaturated solutions lattice parameters which equals: 0.35169 nm, 0.35985 nm, and 0.36020 nm respectively, the concentration of tungsten in supersaturated solid solution after quenching was calculated. According to Ni-W binary equilibrium diagram [10] the maximum solubility of tungsten in nickel-based saturated solid solution equals 31 weight % (16 atomic %). Assuming that the lattice parameter Ni(W) saturated solid solution is represented by the value obtained for the alloy after 20 hours aging at 300°C, we calculated the coefficient representing the influence of W concentration on Ni lattice parameter change. As follows from our calculations based on Vegard's law, the water quenching of a solution heat treated alloy leads to increase of tungsten concentration in nickel up to 32,5 weight % which equals 16,8 atomic %. This is in agreement with maximum solubility of tungsten in nickel at a temperature 900°C, applied for solution heat treatment.

4. Discussion

The WHA alloys are very attractive materials not only for military applications. It is obvious that the designer needs materials which are stronger and stronger. As was stated at the beginning, the strengthening of WHA is usually achieved by rotary swaging allowing up to 60% cold working. It is natural to look for other methods which could increase the strength without fracture toughness decrease. A study of Ni-W equilibrium diagram shows the decrease of maximum solubility of tungsten in nickel with temperature decrease [10]. Moreover, intermetallic phases may form in this system. The question is, if any of them form precipitates which may be obstacles for moving dislocations.

Some earlier results [9] and described above shows that solid solution heat treatment with immediate water quenching leads to supersaturation of nickel-based solid solution with tungsten which is documented in fig. 7 although the supersaturation is 1,5 weight % only. Low-temperature aging lead to decomposition of supersaturated Ni(W) solid solution (fig. 7). This process causes some hardness increase but it is much smaller than we expected.

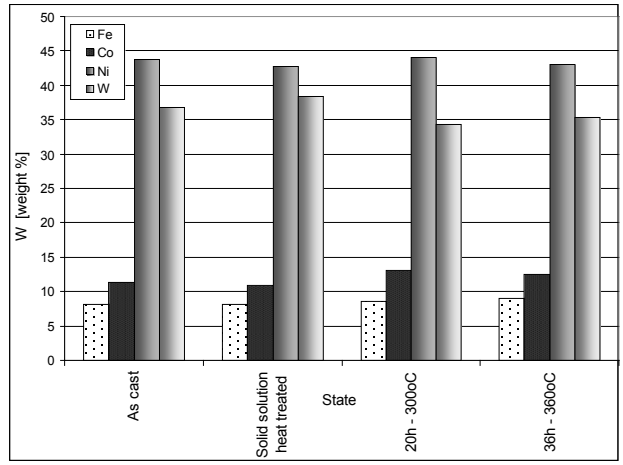

Fig. 7. The changes of Ni, W, Co, and Fe concentration in the matrix after casting, solid solution heat treatment, and aging 20h and 36h at a temperature 300°C

The TEM observations provide some indications of precipitation process but these are not explicit since very similar contrast on TEM micrographs may by obtained in case of vacancy clusters or very small dislocation loops [6]. The hypothetic particles, which could be e.g. Ni_4W precipitates, were too small to give explicit answer to the question, what is responsible for specific contrast on fig. 6c? On the other hand, there is the information in the literature on Ni_4W intermetallic phase (compound) obtained in nickel-based superalloy used for directionally solidified gas turbine blades [11]. This phase, denoted as β-Ni_4W phase, was observed as small particles 50-100 nm of size has body-centered tetragonal (BCT) lattice. Similar type ordered Ni_4W phase was observed by Kinegetsu at all in Ni-16.6at.%W alloy [12] and also Jones and coworkers [13]. According to SAD patterns analysis presented in this paper, β-Ni_4W was identified in Ni(W) matrix to, although this phase appears as a lamellas rather than small precipitates which could be responsible for precipitation hardening. Then, the question arise - what is happening with tungsten atoms trapped in supersaturated Ni(W) solid solution during aging? As follows from table 1 and fig. 7, the maximum content of tungsten in Ni in solution treated WHA, decrease after aging. It is obvious that tungsten atoms have to "push" into Ni(W) matrix but because limited solubility W in Ni saturated solid solution should precipitate in form particles. Looking into Ni-W equilibrium phase diagram the most probable phase which could precipitate is Ni_4W phase. It's forming is preferred not only because thermodynamic point o view but also because formation of Ni_4W phase is easier from diffusion point of view than NiW or NiW_2 intermetallic phases.

5. Conclusions

On the basis of the results and their analysis presented above following conclusions can be proposed:

1. Solution heat treatment including 2 hours aging at a temperature 950^{o}C followed with water quenching causes formation of supersaturation of Ni-based solid solution where the W concentration exceed equilibrium value.
2. Aging of supersaturated Ni(W) matrix at a temperature 300^{o}C causes the strengthening of the NiW alloy with time of aging which is demonstrated by 10% increase of hardness.
3. Aging at a temperature 300^{o}C leads to decrease of W concentration in Ni-based matrix which was proved by EDX and X-Ray method results.
4. Although no explicit evidence of precipitation processes were observed the authors suggest that specific contrast visible in TEM micrograph may be caused by very fine particles.
5. The relative small strengthening effect with increase of aging time may result from lack of coherency between precipitates and Ni(W) matrix.

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