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Growth and stability of surface chemical compounds in interaction between Be and (1010) Re surface

© E.V. Rut'kov, N.R. Gall

Ioffe Institute,
St. Petersburg, Russia

E-mail: rutkov@ms.ioffe.ru

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It is shown that the adsorption of Be on Re $(10\bar{1}0)$ in the temperature range of 850−950 K leads to the formation of specific adsorption states — surface chemical compounds (SC) of ReBe stoichiometry with a concentration of adsorbed N_{Be} atoms of $\sim 1.4 \cdot 10^{15}\,\mathrm{cm}^{-2}$. A multilayer film of beryllium (3−4 layers) is destroyed upon heating, and at 900 K all Be atoms leave the surface into the bulk of rhenium, except those that are part of the SC; atoms from the SC, in turn, actively dissolve at $T > 1050{-}1150$ K. This corresponds to a decrease in the activation energy of dissolution upon the formation of SC from about 3.3 to 2.7 eV. Thermal desorption of beryllium takes place only at $T > 2100$ K due to the emergence of Be atoms dissolved in the bulk of the metal onto the surface.

Keywords: beryllium, rhenium, surface chemical compounds, dissolution, thermal desorption

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1. Introduction

Interaction of s- and p-elements with the surface of high-melting metals is an interesting task from the scientific viewpoint and important from the practical viewpoint. It is at the junction of material physics, solid-state physics, physics of low-dimensional systems and physics of phase transitions [1]. A key issue here is the formation and role of surface chemical compounds — specific adsorption states arising upon interaction of p-elements with the surface, and drastically changing the properties of the given surface, particularly with regard to dissolution of atoms, i.e. their transition into the volume through a diffusion barrier [2] present on the surface. Their formation on external and internal surfaces (grain boundaries) to a large extent defines the differences in physical and chemical properties between conventional and ultra-pure materials [3].

Beryllium is one of the most promising elements for the aerospace industry, its alloys are widely used in metallurgy, instrument-making, defense industry [4,5]. Interaction of beryllium with refractory metals is important, since it characterizes alloys' stability, particularly under thermal loads, and their manufacturability.

From the physical and chemical viewpoint, beryllium is one of the most interesting elements that combine metallic conductivity, small atom size, a very high ionization potential (~ 9 eV), typical for non-metal atoms and negative electron affinity. This paper deals with high-temperature interaction of beryllium with the surface Re$(10\bar{1}0)$.

2. Experiment methods

The experiments were carried out in a ultrahigh-vacuum ($P \sim 10^{-10}$ Torr) electronic Auger spectrometer (EAS) of high resolution ($\Delta E/E \sim 0.1\%$) with a prismatic energy analyzer [6]. A primary electron beam with the energy of 1800 eV and current $\sim 5\,\mu$A irradiated the samples' working surface with the area of $1\,\mathrm{mm}^2$, from which Auger electrons were collected. A long distance (~ 74 mm) between the samples and the energy analyzer made it possible to obtain (without sensitivity losses) the Auger spectra from band samples heated up to 2500 K, which is often of fundamental importance for correct understating of high-temperature physical and chemical processes in the adsorbate-substrate system. To characterize the surface we used measurements of surface thermal ionization and thermionic emission.

Samples were thin rhenium ribbons sized $50 \times 1 \times 0.02$ mm, heated by direct passage of current. Impurities, mainly carbon, were removed from the ribbons by the standard procedure by successive heating of the ribbons in oxygen atmosphere at the pressure of $\sim 10^{-5}$ Torr and temperature of 1500 K and in ultra-high vacuum at 2500 K. After such cleaning, only Auger peaks of rhenium are recorded on the surface. Due to annealing, the rolling texture changes into recrystallization one, and the face $(10\bar{1}0)$ emerges to the surface. The degree of face orientation according to X-ray diffraction data was $\sim 99.5\%$. The work function of the surface was $e\varphi = 5.15$ eV, which corresponded to the face $(10\bar{1}0)$ [7]. The metal surface was homogeneous by work function, which resulted from the measurement of its value by the Richardson method and the method of surface ionization of Na atoms.

Beryllium was deposited by sublimation from Be-ribbons mounted on an iridium ribbon heated by direct passage of current and located at the distance of ~ 20 mm from the sample.

Sample temperature was determined using an optical micropyrometer at $T \geq 1100$ K, while in the region of lower temperatures — by linear extrapolation of temperature dependence on ribbon heating current to room temperature. Uniformity of temperature for the sample central part (~ 40 mm) was not worse than ± 5 K.

Measurements were performed using the Auger peak of beryllium with the energy of $E = 104$ eV and Auger peaks of rhenium with the energies of $E = 161-176$ eV. Auger peaks of W with $E = 163$ eV, phosphorus with $E = 120$ eV, and silicon with $E = 92$ eV were also used for calibration.

3. Formation of beryllium surface compound on $(10\bar{1}0)$ Re

Figure 1 shows a change in intensity of Auger signals of Be (1) and Re (2) in Be deposition with constant flux onto Re$(10\bar{1}0)$ at $T = 900$ K. It is seen that the Auger signal of Be increases almost linearly in the beginning, and then increase slightly slows down and signal intensity at $t \geq 70$ s reaches saturation („plateau"). This intensity remains constant in the interval of $T = 900-1050$ K; it does not depend on density of Be atom flux, at least, in the flux interval $10^{12}-10^{14}$ at $\cdot$ cm^{-2} s^{-1}.

Similar curves have been previously observed for other elements (C, Si, P, O, S) on refractory metals (W, Re, Ta, Mo) [8], they correspond to the formation of surface compounds, usually MeX stoichiometry, where Me is the surface concentration of metal atoms in the upper monoatomic layer, X is the concentration of adsorbate atoms.

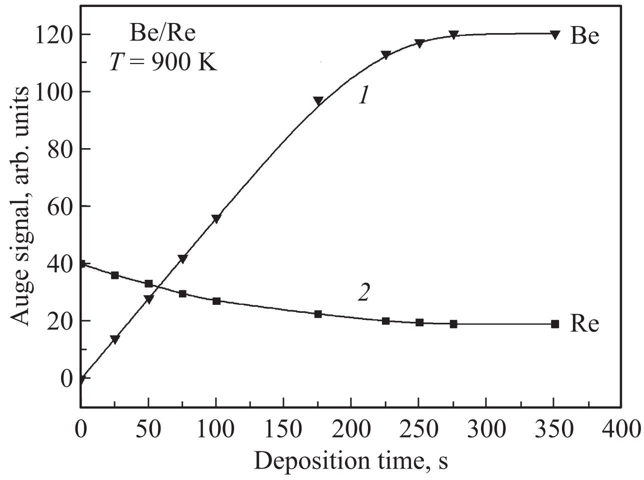

Figure 1. Change in intensity of Auger signals of beryllium (*1*) and rhenium (*2*) depending on time during beryllium adsorption on Re$(10\bar{1}0)$ at $T = 900$ K.

4. Determination of absolute beryllium concentration on the surface

Determination of absolute adsorbate concentration on the surface is rather a complicated task, since all spectroscopic methods are relative, while surface concentration references are absent due to the impossibility of their transfer through the atmosphere for placement in the instrument. The only way out is the use of references created in situ by known and reproducible procedures.

Rhenium is an element with a hexagonal densely-packed lattice, and its face $(10\bar{1}0)$, having a corrugated structure [9], is stable during texturing. This face is subject to reconstruction and is not very convenient for calibration. This difficulty was overcome by using an additional W ribbon, placed near the working one so that they could be successively positioned before entry in the energy analyzer. The face (100) with pronounced absorption centers is located on the surface of W that has a BCC structure.

Be was deposited on the tungsten surface at $T = 1100$ K for calibration. As with rhenium, the Auger signal of Be first increased linearly, and then signal intensity reaches saturation. The obtained plateau is stable in the interval of $T = 900-1150$ K; similar curves with exit to the „plateau" were also observed upon a change in tungsten ribbon temperature in the range of 900–1100 K; thereat, intensity of Auger signal of Be remained the same.

Apparently, similarly to other adsorbates, e.g., Si, P, S, C, O, that form surface compounds (SC) of the WSi, WP, WC stoichiometry etc. [8] with tungsten, beryllium also forms surface compounds with tungsten. In order to determine the absolute beryllium concentration in one experiment, after beryllium sputtering it was removed by thermal desorption at 2300 K, and phosphorus was deposited on the surface, which at $T = 1100$ K forms a surface compound of WP with the atom concentration of $P = 1 \cdot 10^{15}$ cm^{-2} [10].

It follows from the atlas of intensities of chemical elements' Auger spectra for the case of electronic Auger spectroscopy [11] that phosphorus $\sim$ is in 2.05 times better „felt" by the EAS method than beryllium, while direct comparison of intensities is justified, since adsorbate atoms in both cases are located strictly on the surface and the Auger signal is not screened. In the experiment, intensity of Auger signal of phosphorus ($E = 120$ eV) is 2.1 times higher than that of beryllium ($E = 104$ eV) on the corresponding „plateau". It means that, apparently, the concentrations of P and Be atoms on W(I00) in surface compounds are identical, and, consequently, beryllium on tungsten forms a SC of the WBe type, where $N_{\mathrm{Be}} = 1 \cdot 10^{15}$ at/cm^2.

For greater confidence, the experiment for calibration of the SC of Be with W(I00) was repeated, with obtaining of a WSi SC on the same ribbon, using the method previously described in [12]. Direct comparison of the intensities I_{Si} ($E = 92\,\mathrm{eV}$) and I_{Be} has yielded the value of $I_{\mathrm{Si}}/I_{\mathrm{Be}} = 3.4 \pm 0.2$, which agrees well with the same value from the elements' spectra atlas $I_{\mathrm{Si}}/I_{\mathrm{Be}} = 3.5$ [11], which confirms the above-mentioned calibration.

Comparison of the intensities of Auger signals of Be from the WBe SC and from the SC of beryllium on rhenium in one experiment has showed that beryllium concentration on rhenium in the SC $N_{\mathrm{Be}} = 1.4 \cdot 10^{15}\,\mathrm{at/cm^2}$; since the concentration of rhenium atoms on the edge $(10\bar{1}0)$ in the first layer is $N_{\mathrm{Re}} = 1.35 \cdot 10^{15}\,\mathrm{at/cm^2}$ [9], stoichiometry of the compound corresponds to ReBe.

5. Thermal stability of beryllium films on the rhenium surface

Let us consider thermal stability of the SC of beryllium with rhenium. Figure 2 shows the change in intensity of the Auger signal of Be during annealing of the ReBe SC. The SC was formed by adsorption at 950 K, as described above. Then the sample was successively heated, with the interval of 100 K, and kept at each T for 20 s. It can be seen that the compound starts actively disintegrating at $T > 1000\,\mathrm{K}$, and at $T = 1250\,\mathrm{K}$ the surface is completely free from beryllium, while intensity of the Re Auger signal restored to the former value.

Figure 3 shows the kinetics of decrease of intensity of the Be Auger signal at its withdrawal from the surface of $\mathrm{Re}(10\bar{1}0)$ at $T = 1200\,\mathrm{K}$. The curve has a monotonous nature and in the first approximation is approximated by the exponent, which shows a constant activation energy of the process that ensures withdrawal of Be atoms from the surface; this process is thermal desorption or dissolution in the bulk, i.e. concentration dependence of $E = f(N_{\mathrm{Be}})$ is very weak. By using the known expression for life times of adatoms on the surface $\tau = \tau_0 \exp(E/kT)$ [9], and taking $\tau_0 = 10^{-13}\,\mathrm{s}$ [13], we can estimate the value of bonding energy E for Be adatoms with $\mathrm{Re}(10\bar{1}0)$: $E = 3.3\,\mathrm{eV}$.

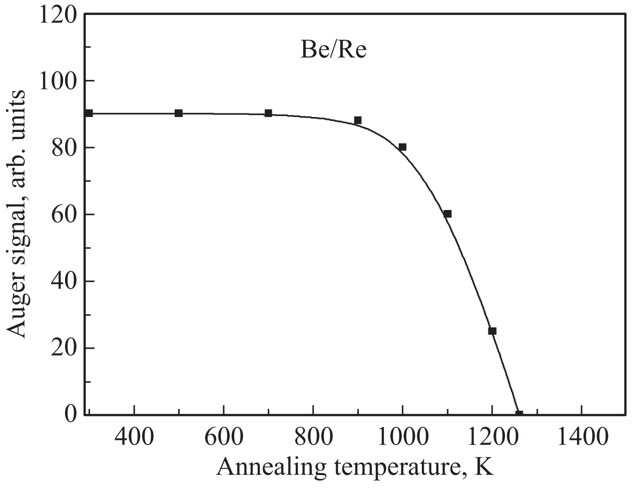

Figure 2. Change in intensity of the Auger signal of beryllium vs. temperature during annealing of the ReBe surface compound. Annealing time at each temperature point is 20 s.

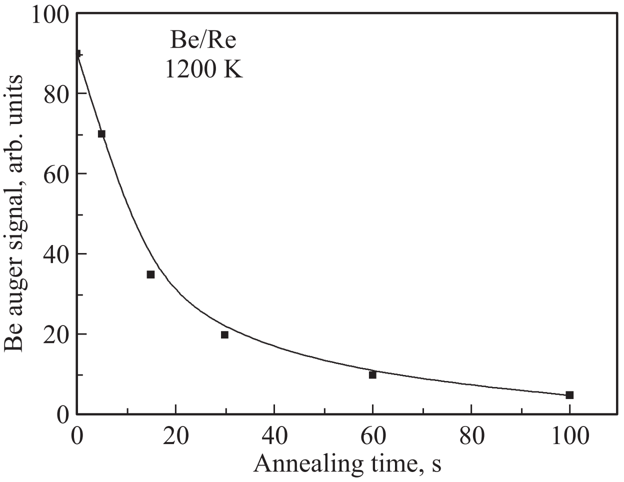

Figure 3. Change in intensity of the Auger signal of beryllium vs. time during annealing of the ReBe surface compound at $T = 1200\,\mathrm{K}$.

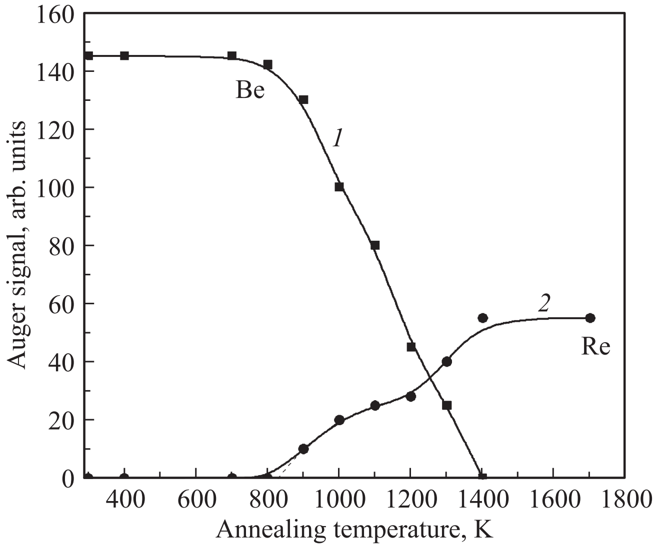

Figure 4. Change in intensity of the Auger signal of beryllium (*1*) and rhenium (*2*) vs. temperature of annealing of a beryllium film having the thickness of 3–4 layers formed by Be deposition at 300 K. Annealing time at each temperature point is 20 s.

Figure 4 shows a change in intensity of the Auger signal of Be (*1*) and Re (*2*) during annealing of a beryllium film having the thickness of 3–4 layers, formed at $T = 300\,\mathrm{K}$; beryllium Auger spectrum from such a film with a high resolution is shown in Fig. 5 (spectrum *1*). A beryllium film having the thickness of 4 layers almost completely screens the rhenium Auger signal, which means its continuity and, apparently, a growth mechanism close to the layer-by-layer one.

The film deposited at room temperature was annealed in the experiment successively with the interval of 100 K,

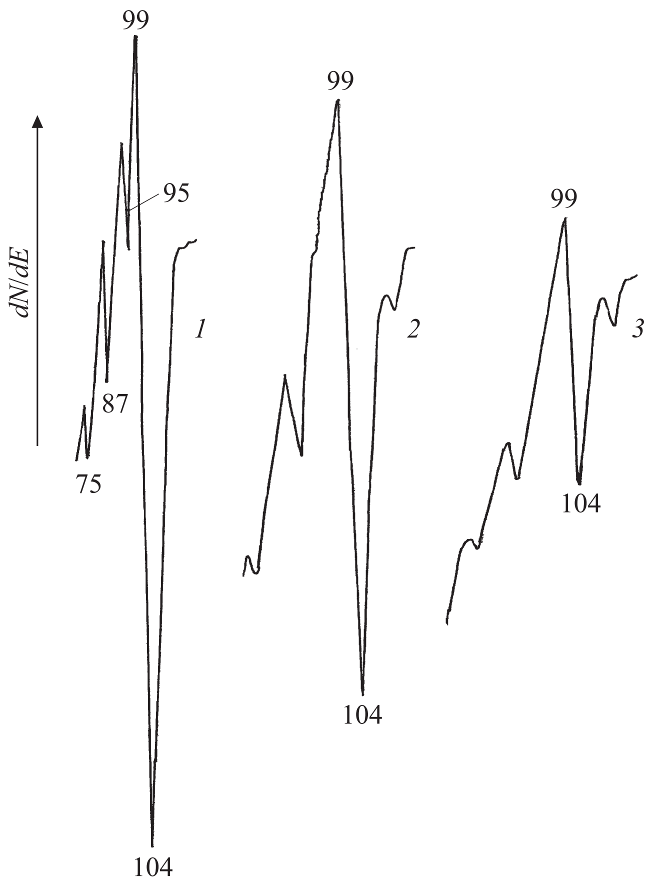

Figure 5. Auger spectra for a thick (3–4 layers) Be film on Re($10\bar{1}0$), formed at 300 K (*1*); after film annealing for 20 s: at 1350 K (*2*), and at 1450 K (*3*).

each time maintained at a constant temperature for 20 s. It can be seen that film destruction starts at $T \geq 800$ K: intensity of the Auger signal of Be with temperature rise decreases considerably, the Auger peak of rhenium becomes observable. At 1400 K beryllium disappears from the rhenium surface, at the same T the rhenium Auger signal restores to its initial value, which means surface cleanness.

It should be noted that upon transition of the thick Be film to the SC state, the Be Auger signal undergoes certain changes, in particular, the peaks with the energies of 95 and 87 eV disappear (see Fig. 5). At concentrations below the one typical for SC, the shape of the high-resolution Auger signal remains constant, which means invariability of its chemical form on the surface (Fig. 5, spectra *2* and *3*).

It is interesting to compare the curve in Fig. 4 with the curve shown in Fig. 3 and characterizing the withdrawal of beryllium from the surface from the SC. Firstly, decrease of intensity of the beryllium Auger signal from a multilayer film begins at lower T than in the case of SC; secondly, final beryllium removal from the surface takes place at higher temperatures.

6. Desorption or dissolution of Be

To describe the physics of the process correctly, it must be determined whether there is thermal desorption of beryllium from the surface in the experiments described above or whether it dissolves in in the bulk of substrate. We have performed special experiments for this purpose: an additional ribbon tape was installed (it was similar to the working one) so that its surface faced the sample's working surface. Besides, a special beryllium ribbon was installed to assess the possibility of direct sublimation of Be atoms.

Several hung pieces of Be ribbon having the thickness of 20 μm and width of 1 mm were placed on the auxiliary rhenium ribbon, the ribbon was heated, and the state of the working ribbon's surface was monitored by means of EAS. Direct observation of hung Be pieces through an optical micropyrometer has showed that at $T \approx 1300-1400$ K the hung pieces have disappeared, and darker regions have formed in their place, i.e. regions with a slightly lower greyness coefficient, apparently as a result of metallic beryllium decomposition and diffusion of its atoms into the rhenium bulk, probably with the formation of bulk beryllide. Beryllium desorption began at $T = 2100-2200$ K and beryllium traces started appearing on the working ribbon's surface. At $T \approx 2300$ K, flux density of beryllium on the working ribbon's surface was about $10^{12}\,\mathrm{at}\cdot\mathrm{cm}^{-2}\mathrm{s}^{-1}$, which, taking into account the geometrical arrangement of ribbons, corresponds to the density of a desorbing flux from the auxiliary rhenium ribbon at the level of $10^{13}-10^{14}\,\mathrm{at}\cdot\mathrm{cm}^{-2}\mathrm{s}^{-1}$.

It is interesting that, despite the relatively small beryllium sublimation heat, 3.25 eV [5], its direct sputtering from the Be ribbon is inefficient: any significant flux is observed only at $T = 1500$ K, at which the ribbon burns out quickly. Apparently, this is due to the presence of high-melting and semi-volatile oxide BeO on the beryllium surface.

7. Discussion of results

As demonstrated in our papers [8,10,12], the SC formation is related to the fact that the surface of metals, in particular Re, have centers with different values of chemical bond with the adsorbate. The centers with a strong bond are occupied in the first place. Concentration of such centers on Re($10\bar{1}0$) is equal to the atom concentration in the first layer and is $N = 1.35 \cdot 10^{15}\,\mathrm{at/cm}^2$. Only after their occupation, the newly arriving atoms start either dissolving in the metal bulk (Si, C) or desorbing (S, P, O) [8,10]. The situation is, apparently, similar in case of Be. At intermediate temperatures (900–1000 K), all the arriving atoms remain on the surface and form a ReBe SC. The newly arriving Be atoms dissolve in the metal bulk.

Upon thermal degradation of the multilayer film, all strongly bound centers remain occupied, while the excessive Be atoms dissolve in the volume at a lower $T \sim 800$ K, which corresponds to the activation energy of $E \sim 2.7$ eV.

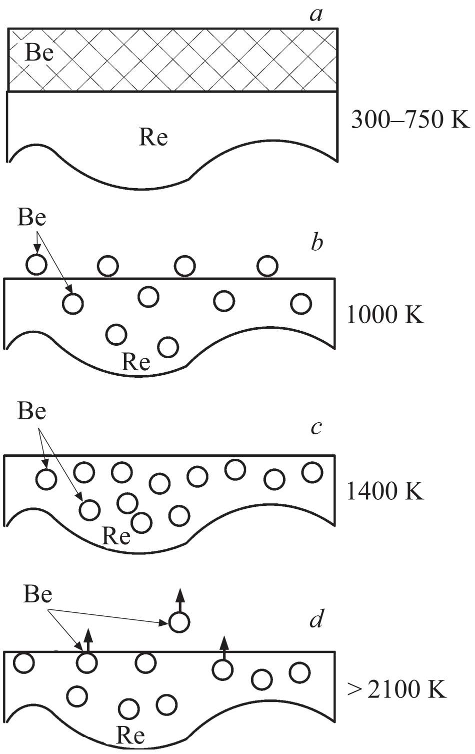

Figure 6. Scheme of processes taking place during thermal annealing of the Be film on the rhenium surface: a — 300 K, b — 1000 K, c — 1400 K, d — > 2100 K.

Beryllium atoms from the SC also, most likely, do not desorb, but are dissolved in the volume, which is proved by very high thermal desorption temperatures observed in the experiment. It is interesting that differences in the chemical state of Be atoms in the SC and in the multilayer film are also seen in the shape of the high-resolution Auger spectra, as observed previously for silicon and carbon on many substrates.

Let us illustrate the physics of thermal processes taking place on the surface and in the rhenium bulk with involvement of beryllium atoms (Fig. 6). The multilayer film at $T > 800$ K breaks down due to the withdrawal of Be atoms into the bulk, and only the SC remains on the surface (Figs. 6, a and 6, b), at $T > 1400$ all the Be atoms are in the dissolved state in the rhenium bulk. At $T > 2100$ K, Be atoms start coming out to the surface and thermally desorbing from it (Fig. 6, d).

8. Conclusion

The Be — rhenium surface system, unlike the previously studied Si — Re surface and Si — W surface systems, demonstrates its unexpected features. As with many other adsorbates, Be forms a surface compound with stoichiometry close to BeRe, thereat, the chemical state of Be atoms in this compound differs from the bulk Be, while the dissolution activation energy abruptly decreases upon filling of the given adsorption state. However, unlike many other adsorbates, beryllium atoms that form a surface compound with BeRe stoichiometry, do not desorb from the surface but dissolve in the bulk at $T > 950-1250$ K, while thermal desorption takes place only at very high $T > 2100$ K.

Conflict of interest

The authors declare that they have no conflict of interest.

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