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# Ni-rich precipitates in a lead bismuth eutectic loop

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A B S T R A C T

Solidified LBE was sampled from the specimens, electro-magnetic pump, filter, drain valve and oxygen sensor at the JAEA Lead Bismuth Loop-1 (JLBL-1) where the structural material was made of SS316. The concentration of Ni, Fe and Cr in LBE were analyzed by the Inductive Coupled Plasma atomic emission spectrometer. It was concluded that the solution of Ni into LBE was not saturated although the concentration of Fe and Cr almost achieved to the values in the literature. A needle-type structure appeared on the surface of solidified LBE inside the tube specimens. It was found to be Ni-rich precipitates by X-ray analyses (Field Emission Scanning Electron Microscope, FE-SEM). LBE samples collected from a circulating loop after discharging did not show the amount of impurities equivalent to the LBE bulk property.



## 1. Introduction

For an application of lead bismuth eutectics (LBE) to a spallation target system, there is an issue on materials at the beam window where high-energy proton beam will bombard [1]. From the point of view of avoiding brittle fracture due to irradiation damage, it is favorable to use austenitic stainless steels that behave in a ductile manner. LBE has a chemical property, which dissolves main elements of structural materials such as Fe, Cr and Ni in austenitic stainless steels [2]. A technical issue will be how to keep thermal-fluid and structural material performances. One of our concerns is that the mass transfer in the flowing system during a long operation time will affect LBE control and maintenance devices such as measurement sensors and a heat removal system.

Hitherto we have reported the experimental results on LBE flow rate insensitivity that the EMF output was decreased with increase of time by about 60%. Erosion–corrosion was occurred in flow profile disturbed regions [3,4]. Electrodes of EMF put in the flow channel of LBE were eroded [4]. Fe–Cr crystal precipitates were observed on the surface of lower temperature tube as well as on the filtering foils [4]. Zhang and Li analyzed corrosion and precipitation of Fe in JLBL-1 by non-isothermal kinematic model [5]. They could characterize precipitation property in the whole circulating line. If mass transfer due to corrosion and precipitation occurs massively, they may affect LBE flow control techniques. A stable flow rate of LBE is a primary requirement for operating such a system. It is important to avoid unexpected mass loss due to a local erosion–corrosion. Mass transfer from hot regions to cold ones will deposit Fe–Cr crystals on the surface of the heat removing tube and may change the heat transfer efficiency.

Sampling LBE from the loop was prepared for investigating elements dissolved from the steel by means of Inductively Coupled-Plasma techniques (ICP). The results will be reported on impurities of Ni as well as Fe and Cr. Ni-rich precipitates were found for the first time at JLBL-1. FE-SEM analyses will be reported.

## 2. JLBL-1 operations

The loop was made of the austenitic stainless steel, SS316, since electro-magnetic pump (EMP) needed non-magnetized materials. The flow diagram of the loop and the detail specification were already reported [3,4]. Fig. 1 shows a latest flow diagram of LBE with arrows indicating by IDs 1–9. Those are positions where solidified LBE samples were taken out. The loop was operated under a condition that temperature difference was 50 °C during first 6000 h and 100 °C during the following 3000 h. Throughout the operation, the maximum temperature was set to 450 °C in the circulating line between the heater and the cooler. The LBE flow rate was 5 L/min in a stationary condition, which was equal to 1 m/s in average velocity at the high temperature tube specimen with 10 mm in diameter, and 0.2 m/s at the lower temperature specimen with 24 mm in diameter. Flow rate was measured using an Electro-Magnetic Flowmeter (EMF). A total length of circulating line was about 15 m.

## 3. Experiments

Commercial lead bismuth solder bars were used for circulation at JLBL-1. Table 1 shows chemical compositions of nominal and measurement values. The measurement values indicate that Fe

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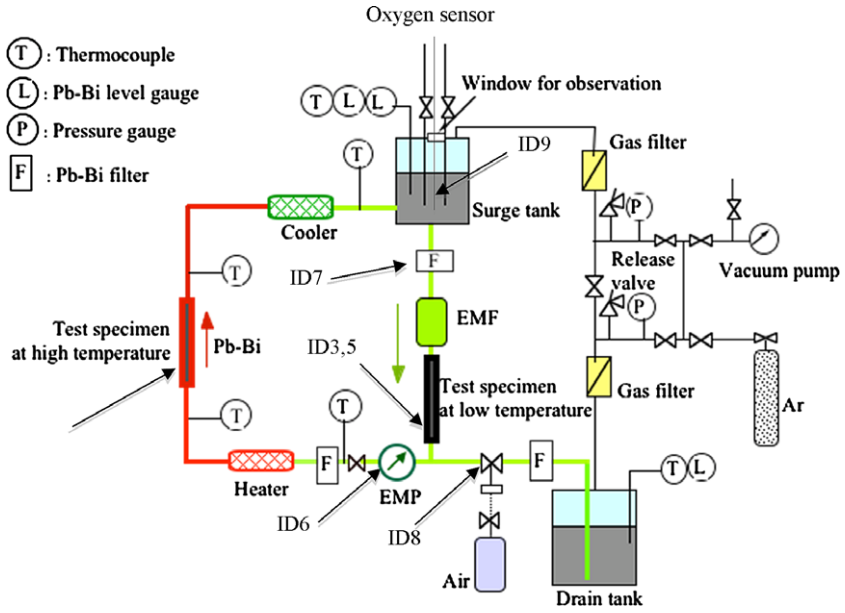



**Fig. 1.** Flow diagram of JLBL-1 and LBE sampled positions are indicated by ID1–ID9.

**Table 1**
Impurities in the lead bismuth solder (mass%).

| Elements | Bi | Pb | Sb | Cu | Zn | Fe | Al | As | Cd | Sn |
|---|---|---|---|---|---|---|---|---|---|---|
| Nominal | 54.5–56.5 | BAL | <0.12 | <0.05 | <0.002 | <0.02 | <0.002 | <0.03 | <0.002 | <0.25 |
| Measurement | 55.85 | BAL | 0.0011 | 0.0003 | 0.0001 | 0.0024 | 0.0001 | 0.0006 | <0.0000 | 0.0048 |

was included before usage in the loop as impurities. A portion of LBE was sampled from the test specimen at high temperatures (IDs 1, 2 and 4), the test specimen at low temperatures (IDs 3 and 5), the electro-magnetic pump (ID 6), the lead bismuth filter (ID 7), the drain valve (ID 8) located between the drain tank and the EMP, and the oxygen sensor (ID 9) submerged in the surge tank at times of 3000 h, 6000 h or 9000 h as described in Table 2. The loop operation was interrupted at a period of 3000 h and the specimen was exchanged. Temperature at the drain valve was kept to 300 °C during operation period, which was kept at the lowest temperature among them.

For the measurement of Fe, Cr and Ni in LBE, an Inductive Coupled Plasma atomic emission spectrometer (ICP, ULTIMA2) was used for analyses. Emission spectrums are 259.940, 267.716 and 231.604 nm for Fe, Cr and Ni, respectively. Nitride and hydrochloric acids were used to make a solution from the samples. In addition, alkali fluxes, $Na_2CO_3$ and $H_3BO_3$, were also used in order to melt solid residuals remained in the solution. Standard materials were prepared for calibrating quantities of each element. A usage of alkali fluxes coincided with Fe and Cr rich LBE.

We have also inspected the LBE samples detached from the JLBL-1 loop, after the last 3000 h operation. It was found that needle-type precipitates existed on the surface of solidified LBE inside the tube specimens as shown in Fig. 2. A size is tens micron meters in width and over hundreds micron meters in length, for example. They existed not only at the low temperature part of the loop, but also at the high temperature parts.

In order to investigate precipitated elements by X-ray analyzer, we used the focused ion beam (FIB) technique to make a LBE free sample. The surface of precipitates was covered with residual LBE. Fig. 3 explains how to cut a specified sample from LBE bulk volume taken at the low temperature part. As a solidified LBE is

**Table 2**
Impurities of Fe, Cr and Ni in solidified lead bismuth eutectics.

| ID | Sample position | Sample weight (g) | Elapsed time (h) | Operation temperature (°C) | Used acid flux (s) | Used alkali fluxes | Fe mass (%) | Cr mass (%) | Ni mass (%) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | High temperature specimen | 2.48 | 3000 | 450 | $HNO_3$ HCl | | 0.023 | 0.0008 | 0.0090 |
| 2 | High temperature specimen | 1.00 | 6000 | 450 | $HNO_3$ | | 0.0047 | 0.0025 | 0.031 |
| 3 | Low temperature specimen | 1.82 | 9000 | 350–400 | $HNO_3$, HCl | $Na_2CO_3$, $H_3BO_3$ | 0.10 | 0.021 | 0.014 |
| 4 | High temperature specimen | 1.30 | 9000 | 450 | $HNO_3$ | | 0.0032 | 0.0022 | 0.0069 |
| 5 | Low temperature specimen | 1.00 | 9000 | 350–400 | $HNO_3$, HCl | $Na_2CO_3$, $H_3BO_3$ | 1.03 | 0.23 | 0.011 |
| 6 | Electro-magnetic pump core | 1.16 | 3000 | 420 | $HNO_3$, HCl | $Na_2CO_3$, $H_3BO_3$ | 58.4 | 11.9 | 0.094 |
| 7 | Filter | 1.70 | 6000 | 400 | $HNO_3$ | | 0.015 | 0.0010 | 0.021 |
| 8 | Drain valve | 0.78 | 3000 | 300 | $HNO_3$ | | 0.087 | 0.0045 | 0.0093 |
| 9 | Oxygen sensor | 0.87 | 3000 | 400 | $HNO_3$, HCl | $Na_2CO_3$, $H_3BO_3$ | 0.047 | 0.64 | 0.020 |

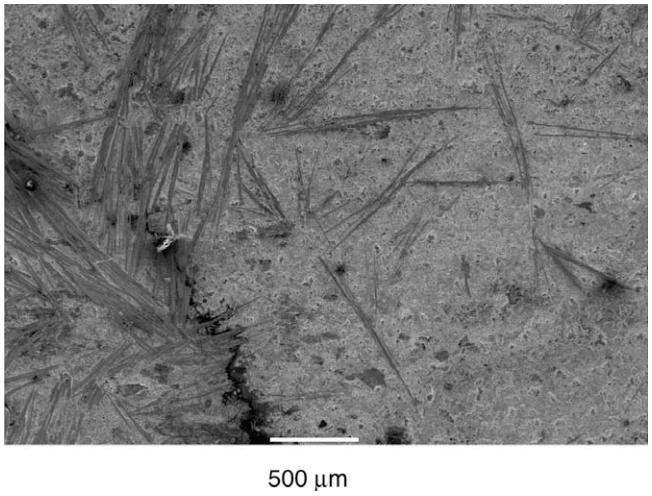



**Fig. 2.** Precipitates on the surface of solidified LBE in the tube specimen.

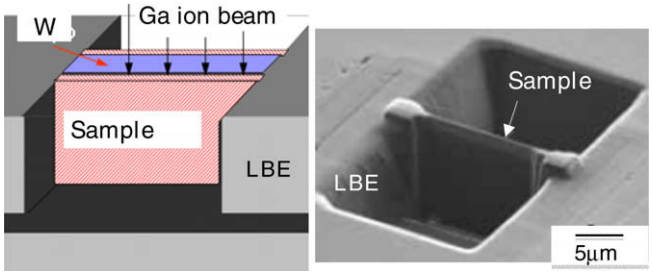



**Fig. 3.** Focused Ga ion beam processing to prepare analyzing sample taken from LBE. Deposition layer of W makes LBE hard. Thin sample can be shaped without disturbing cut line due to heat expansion.

soft, a LBE sample can be easily deformed by heat deposition by Ga ion beam processing. Tungsten was used as deposition to make a hard shell on the surface of LBE. Then Ga ion beam was processed to make cutting. A thickness of final product is estimated to be sub-micron meter. Macroscopic features were observed by laser microscope (KEYENCE-VK8500). X-ray analyses were done by FE-SEM (HITACHI-4800).

## 4. Results

Fig. 4 shows results of ICP analyses. Unused LBE had already contained 0.0024 wt% of Fe. ICP analyses indicated that the concentrations of Fe ranged from this value to a several tens wt%. The

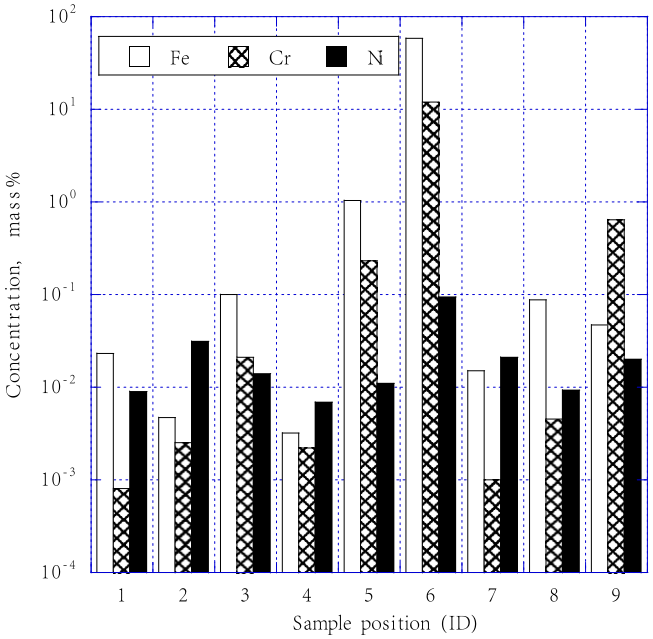
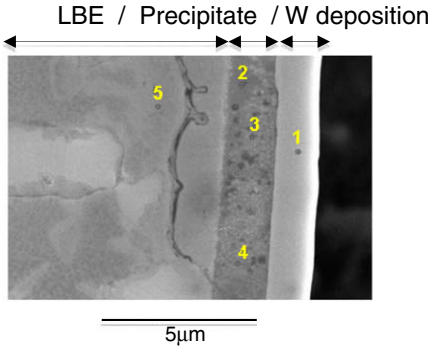



**Fig. 4.** Results of ICP analyses. IDs 1, 2 and 4: specimen at the high temperature, IDs 3 and 5: specimen at the low temperature, ID6: EMP core, ID7: filter, ID8: drain valve, ID9: oxygen sensor in surge tank.




| ID/Element | Ni | Pb | Bi |
|---|---|---|---|
| 2 | 65.53 | 22.51 | 11.96 |
| 3 | 56.36 | 26.59 | 17.04 |
| 4 | 51.36 | 29.44 | 19.20 |
| 5 | 0.00 | 67.90 | 32.10 |

**Fig. 6.** A SEM micrograph showing the cross-section of a LBE sample prepared with the FIB technique and the positions for the EDX analysis. ID1 indicates W deposition. Unit is atomic%.

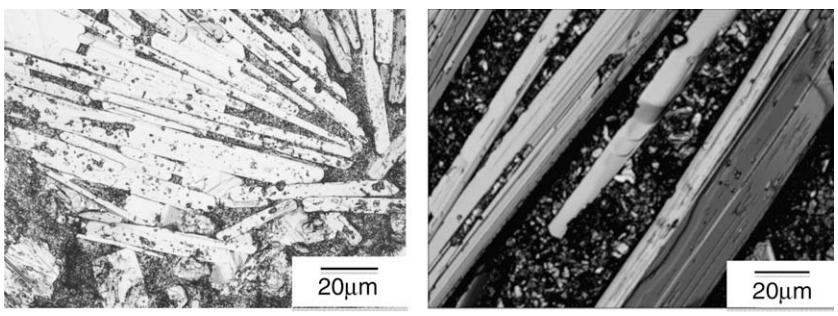



**Fig. 5.** Needle-type thin precipitates on the surface of residual LBE at low temperature part (left) and at the high temperature part (right). Both were observed using a laser microscope.

sample showing a several tens wt% of Fe in the LBE corresponds to that, which was sampled from the core channel of EMP, for it contained Fe–Cr precipitates [4]. Concentration of Ni ranged from 0.008 wt% at the high temperature specimen to 0.1 wt% at EMP.

Fig. 5 shows precipitates observed using a laser microscope at the low temperature part (left) and at the high temperature part (right). It appeared that precipitates in the left figure were crowded and smaller than that in the right figure. Both precipitates, however, look similar and have a needle-like shape.

Fig. 6 presents results of X-ray analyses of cross section of sampled LBE including a precipitated thin plate. W is the deposition material. Atomic percentage of Ni, Bi and Pb at points 2, 3 and 4 ranged from 52% to 66%, 12% to 19% and 23% to 29%, respectively. It is found that precipitates are Ni-rich with Bi and Pb in addition. The LBE behind the precipitates consists of just Pb and Bi and the atomic ratio between Pb and Bi is not constant in the residual solidified LBE. Fig. 7 shows X-ray energy spectrum measured at points 2–4 as indicated in Fig. 6.

## 5. Discussion

It is expected that impurities will increase with increase of operation time for the case of total volume in LBE. Because corrosion–erosion process dissolves structural materials into LBE, the

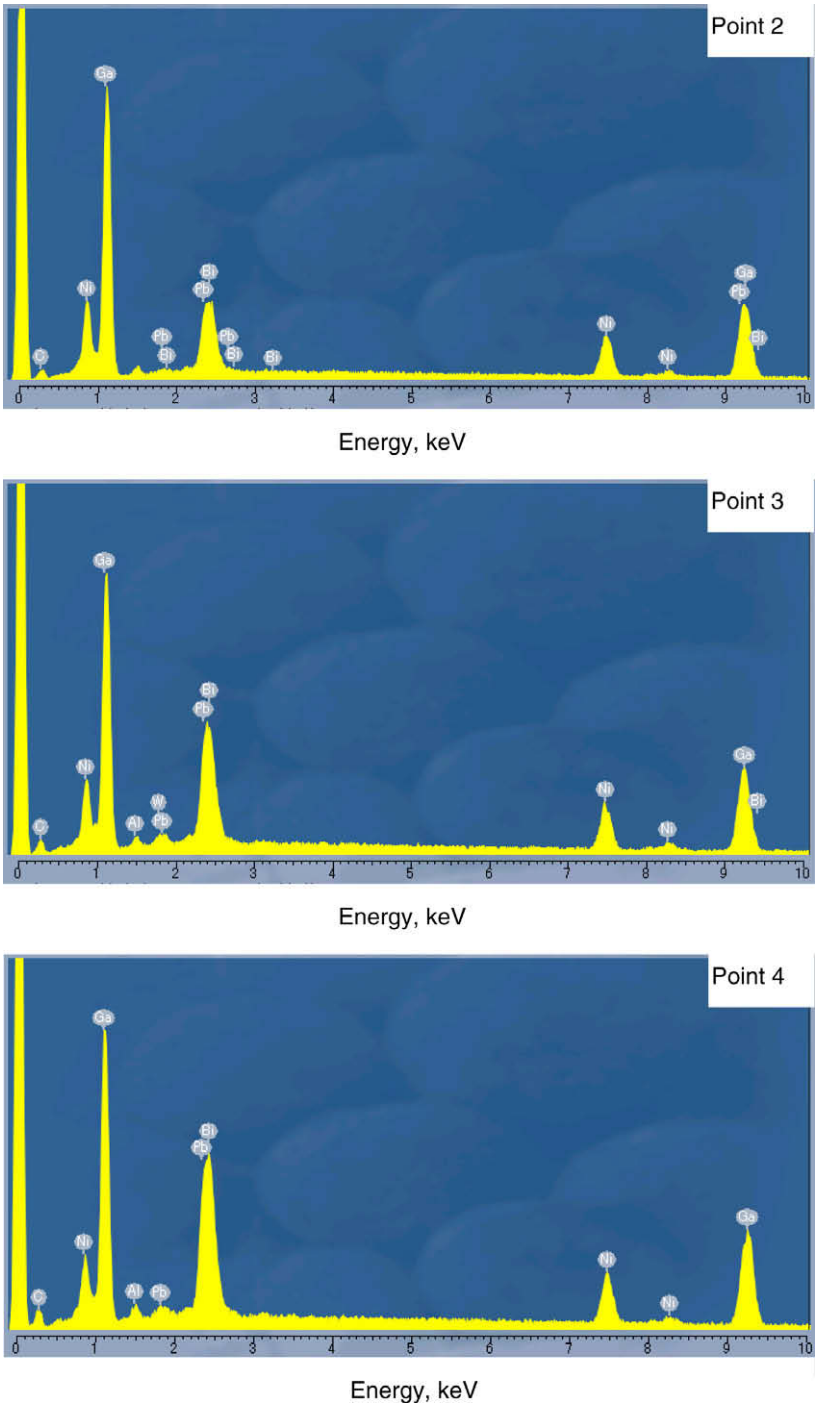



**Fig. 7.** X-ray analyses of LBE sample at points 2–4. Position is shown in Fig. 6.

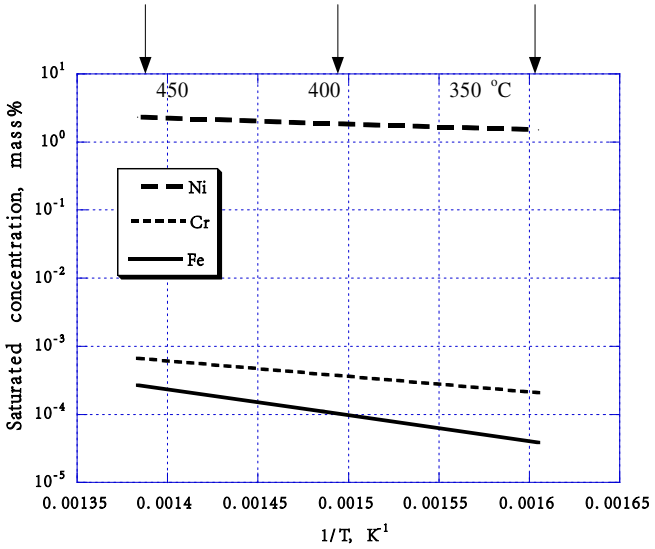



**Fig. 8.** Saturated concentration of Ni, Cr and Fe in LBE vs. temperature [6].

amount of solution of foreign elements increases and forms precipitates or slug. A question is whether the solidified LBE samples collected from a circulating loop after discharging show the amount of impurities equivalent to that in LBE before testing. Fig. 8 shows saturated concentration of Ni, Cr and Fe in LBE [6]. Solubility of Ni is higher than that of Fe and Cr, and to be a couple of mass% in the temperature range of 350–450 °C. Fig. 4, however, showed that Ni concentration was below 0.1 wt%. In addition, Ni-rich precipitates were found not only at the high temperature part but also at the low temperature part, and on the surface of residual LBE. This was not a case for Fe–Cr precipitates. Fe–Cr precipitates were only found at low temperature part. The driven force of Fe–Cr precipitates was concluded to be a difference of saturated concentration at different temperatures [4], although the precipitation rate is not clear. If precipitation rate were so fast enough to produce crystals in the cooling process, it would arise Fe–Cr precipitates not only at low temperature part but also at high temperature part. It can be assumed that Ni-rich precipitates formed on the surface of residual LBE during a cooling period, although the precipitation rate is not known for question for such a Ni-rich structure. Slug is an alternative source for Ni-rich precipitates found at the high and low temperature parts. Slug can either float at the highest position of free surface or flow with main LBE. When LBE is discharged, slug will adhere on the surface of flow channels. In the surge tank LBE flow is stagnant near the free surface, because circulating tube is connected near the bottom side. It is possible that impurities of light species locate near surface and gives a concentration higher than average LBE.

In the literature, crystal structure of a binary alloy of Ni and Bi were reported [7]: $NiBi_3$ exists in a form of soft needles and suggests being orthorhombic over 75 atomic% of Bi. X-ray analyses indicate the atomic% of each element as shown in Fig. 6. The ratio of Bi to Ni differs from the value range reported in the literature. Excess Ni atoms can be assumed to be located randomly in interstitial positions, because the atom diameter of Ni is so differ from that of Bi. NiBi is an alternative from the point of view of measured ratio of Bi–Ni. Further investigations are needed to confirm such a crystalline structure.

## 6. Conclusions

A needle-type structure existed on the surface of solidified LBE inside the tube specimens was found to be Ni-rich precipitate. A solution of Ni into LBE was not saturated although those of Fe and Cr almost achieved to the values reported by IPPE [6]. Samples collected from solidified LBE on the surface at different positions of the circulating loop after discharging show that the accumulation of impurities are different from that of the LBE bulk.

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