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面对等离子体壁材料中低 Z 元素的表面偏析

**SURFACE SEGREGATION OF LOW-Z ELEMENTS
ON PLASMA-FACING MATERIALS**



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钱家溥：研究员，聚变堆材料（系列）国际会议国际顾问委员会委员，中国核学会核材料学会专业委员会常务委员，核工业西南物理研究院聚变堆工艺与材料研究室主任。1960年毕业于清华大学核反应堆专业。

Qian Jiapu, Professor, member of International Adversary Committee for International Conferences on Fusion Reactor Materials, member of Standing Committee for Nuclear Materials Society, Chinese Nuclear Society, director of Fusion Technology & Materials Division, Southwestern Institute of Physics, CNNC. Graduated from Tsinghua University in 1960, majoring in nuclear reactor.

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钱家溥 刘翔

(核工业西南物理研究院, 成都)

摘 要

实验观察了三元合金 Al-Li-Mg 和二元合金 Cu-Be 中低 Z 元素 (如 Li 和 Be) 的表面偏析行为。采用了二次离子质谱仪 (SIMS) 和俄歇电子谱仪 (AES) 进行表面分析。Al-Li-Mg 合金的实验结果表明: 样品温度在 150℃ 到 300℃ 的范围内, 表面 Li 原子的浓度接近 100%, 这一结果可由 Gibbsian 偏析理论进行解释, 其中 Li 在样品表面的深度分布有一定程度的展宽, 这是由于刻蚀过程中高能氩 (Ar) 离子反冲植入所致。当样品温度超过 360℃ 时, 发现合金中的杂质元素 Be 开始在表面上偏析。为此, 作者采用 SIMS 和 AES 对 Cu-Be 合金进行了表面偏析研究。在位的 AES 分析表明: 样品升温过程中, Be 和 O 在合金表面富集, 考虑到 Be 和 O 的化学亲和作用, 偏析的根本动力来源于真空中的残余氧气。同时还对 Be 在合金表面的深度分布进行了测量。

SURFACE SEGREGATION OF LOW-Z ELEMENTS ON PLASMA-FACING MATERIALS

Qian Jiapu Liu Xiang

(SOUTHWESTERN INSTITUTE OF PHYSICS, CHENGDU)

ABSTRACT

Surface segregation behavior of low-Z elements, e. g. , lithium and beryllium on trinary alloy Al-Li-Mg and Binary alloy Cu-Be has been observed. The experiments were performed by means of Secondary Ion Mass Spectroscopy (SIMS) and Auger Electron Spectroscopy (AES). The experimental results of Al-Li-Mg alloy indicated that lithium concentration on the specimen surface reached approximately 100% in the temperature range of 150 to 300°C, which can be explained by Gibbsian segregation theory. The depth profile of Li showed that there was some broadening resulting from recoil implantation by high energy Ar ion bombardment. When the specimen temperature exceeded 360°C, beryllium, the impurity element in the alloy was found to segregate to the surface. For this reason, another experiment on surface segregation of Cu-Be alloy was carried out by SIMS and AES, the surface analysis utilizing in-situ AES analysis revealed that the surface was enriched by Be and O at elevated temperature, considering the chemical affinity of Be and O, the principal driving force of segregation was attributed to the oxygen partial pressure in the atmosphere. The depth profile of Be in the alloy was also investigated.

INTRODUCTION

It is well known that the high Z impurity in fusion plasma is very harmful and impurity control is necessary for fusion devices. The low Z coating has ever been proved experimentally to exist the advantage to prevent the high Z impurity from coming the plasma. But a number of problems associated with the interface occur as a result of thermal shock and build-up of implanted hydrogen and helium. Meanwhile, the lifetime of the coating is also limited by factors relating to redeposition and mechanical integrity of the coating. It is therefore desirable to keep the initial coating as thin as possible, limit substrate sputtering, and provide a mean of replenishing the low Z material at locations where it preferentially eroded. Several suggestions have been put forward for this purpose. Taking advantage of self-sustained low-Z coating of Al-Li and Cu-Li alloys^[1,2], these kinds of alloys are suggested as a Tokamak first wall and limiter materials. A number of researches on experiment and theory have been carried out in the nearly ten years^[3,4]. A ternary alloy Al-Li-Mg that has better property on strength and conductivity has been developed. Its surface segregation is described in present paper. Since the surface segregation of impurity element beryllium in the alloy was found, on the other hand, beryllium is now seriously considered as a plasma-facing material because of its low-Z, favorable thermo-mechanical properties and expected low tritium retention, a beryllium contained alloy Cu-Be was developed and the surface segregation of beryllium was studied.

1 SURFACE SEGREGATION OF Al-Li-Mg ALLOY

1.1 Experiment

The experiment was performed by means of secondary ion mass spectroscopy (SIMS). The specimen material was a ternary alloy Al-Li-Mg, in which the atomic concentration of Al, Li and Mg was about 92%, 4% and 4%, respectively. Be is an impurity element whose content is estimated less than 0.05 wt. %. The size of the specimen was 10 mm × 10 mm × 2 mm. All of the specimens were polished mechanically and cleaned supersonically before putting into SIMS. The SIMS used in this experiment was LAS 2000, made in France. The primary ions in the SIMS were Ar⁺ and the specimen was mounted on the specimen holder, which can be heated up to 500°C if necessary. The

thermocouples show the holder temperature and the temperature of the specimen can be determined by the calibrating curve measured in advance. Ar ion beam incident angle was 45° to the normal of the specimen surface and there was not any secondary electron suppresser in front of the specimen. The ultra-high vacuum system of the SIMS maintained the vacuum in the specimen room better than 10^{-6} Pa during experiment.

In order to record the signals of varied elements on the specimen surface simultaneously, the scans were multiplexed so that the secondary ion peaks of various mass-number were sampled sequentially. The scan rate was varied from a few seconds to several ten seconds. The scan range of mass-number in the most experiment was 1 to 40.

1.2 Results and discussion

Al-Li-Mg alloy specimen mounted on the holder in SIMS was heated slowly from room temperature. The power applied to the holder heater was enhanced step by step so that the specimen can be heated to a temperature and maintained at this temperature for a time and then to be heated to the other higher temperature. When the specimen reached a fixed temperature and maintained at this temperature, the Ar^+ ion source was turned on to scan the specimen surface several times, meanwhile the secondary ion spectra were recorded, and then the ion source was turned off. About 20 minutes later the Ar ion source was turned on again until the secondary ion spectra recorded in two adjacent times were approximately same. When these scans were finished, the specimen was heated to the next higher temperature and maintained at this temperature, the measure process at this temperature was just as same as described at previous lower temperature. The typical heating process is shown in Fig. 1. At beginning the Li secondary ion signal increased sharply with temperature rising. At 80°C the Li^+ signal was 3 times that at room temperature. When the specimen just reached a higher temperature and started maintaining at this temperature, Li^+ signal even increases with time before equilibrium. When the specimen temperature rose up to 156°C , the Li^+ signal reached the maximum value, which was 5 times greater than the value at RT. Besides, although magnesium atoms were as many as lithium atoms in the alloy, but no considerable Mg signal has been observed in the experiment. A little increase of Mg^+ signal was observed only during the temperature range from RT to 80°C and then dropped back to the value as nearly same as that at RT. The

Li⁺ signal between about 150~300°C maintained at the maximum and the Al⁺ signal decreased so quickly that between 200°C and 300°C, the Al⁺ signal could even be considered as zero comparing with Li⁺ signal. It means that a complete Li enrichment layer has formed on the surface of the specimen and the Li concentration was nearly 100% in this temperature range. When the temperature was over 360°C, an interesting new phenomenon occurred : the Li⁺ signal dropped rapidly while the Be⁺ signal appeared and rose linearly with temperature rising. In this case, impurity element Be was able to diffuse through the matrix and Li enrichment layer and reached the overlayer of the specimen surface. Of course, both lithium and beryllium are candidate low Z coating materials, so the Be enrichment at the high temperature does not affect the feasibility of using the alloy as the first wall material. On the contrary, the enrichment of beryllium on the surface of this alloy is expected, for beryllium has an advantage over carbon materials as plasma-facing materials, the latter have been widely tested in the present Tokamak machines. On the other hand, it is impossible that the Al-Li-Mg alloy would be used at so high temperature.

In other experiment, a specimen was heated quickly to 436°C and maintained for a while in the SIMS without any ion beam scanning and switched off the heater then. When the specimen was cooled to RT (about 10 hours later), the Ar⁺ beam was switched on and the depth profile of the lithium,

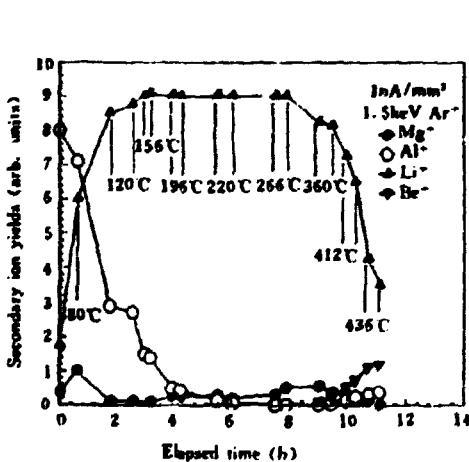


Fig. 1 Secondary ion yields of the Al-Li-Mg alloy during a heating sequence from RT to 436°C

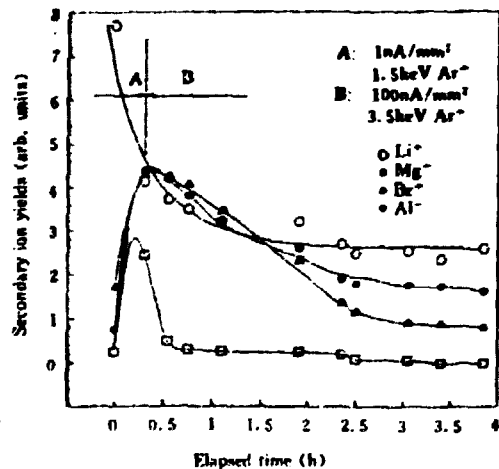


Fig. 2 Secondary ion depth profile of Al-Li-Mg alloy at room temperature after a cooling sequence from 436°C

aluminum, beryllium and magnesium were recorded very quickly. The results are given in Fig. 2. In the first 20 minutes the energy and current of etching Ar^+ were 1.5 keV and 1 nA/mm², respectively. The Li^+ signal decayed rapidly and Al^+ and Be^+ signals rose sharply. After that, the energy and current density of Ar^+ were changed to 3.5 keV and 100 nA/mm², respectively. Fig. 2 indicates that the lithium depth profile is that of classical diffusion with subsurface solute depletion as expected for Gibbsian segregation effect. The Li-enriched region showed some broadening, which possibly resulted from recoil implantation of Li by the primary Ar ions of relatively high energy. It is also showed in Fig. 2 that beryllium enrichment is mainly in the subsurface region. After removing away several uppermost atom layers, both Li^+ and Be^+ signals decayed slowly.

To investigate the effect of Ar^+ bombardment on surface segregation, another specimen was put into the SIMS and bombarded by Ar^+ continuously during all of heating and cooling process, meanwhile the secondary ion signals were also recorded continuously. The energy and current density of Ar^+ beam were 2 keV and 10.5 nA/mm², respectively. The results of the experiment indicated that the Li^+ signal maintained the maximum in the temperature range of 160 to 270 °C and then dropped rapidly, while the Be^+ signal started to appear at 280 °C and rose with increasing temperature. Comparing with Fig. 1, it can be found that the temperature at which Be^+ signal started to appear were lower. It maybe shows that the defects induced by Ar^+ ion bombardment accelerate the segregation process of beryllium. When the specimen temperature rose to 360 °C, the heater was turned off and the temperature started to decrease. Because of continuous etching the Be^+ signal still increased gradually and exceed the Li^+ signal. In this case, it seems that the Be enrichment mainly occurred in the subsurface region of the specimen. After the specimen cooled to RT, the depth profile curves were recorded and the results were shown in Fig. 3. An approximate depth scale in the figure was obtained assuming a sputtering yield corresponding to that of pure aluminum. The Li^+ signal dropped rapidly in about 11 nm of thickness and Al^+ signal rose quickly in the same thickness. Then the Li^+ and Al^+ signals varied gradually in the thickness of about 40 nm. The Be enrichment region is wider than one of Li and reached maximum value at about 11 nm of depth. It is also shows that Be-enriched region was mainly in the subsurface of the specimen while Li-enriched region

was in the uppermost layer. The damage profile for 2 keV Ar⁺ ion incidence on aluminum specimen surface covered by one monolayer of lithium was calculated by TRIM. Calculation showed that the Ar ion projected range was about 10 nm. It can be found that the Be-enriched width is consistent with the Ar ion range and the Li-enriched layer is broadening which shows that recoil implantation also happened in this case.

On Ar⁺ ions irradiation, the surface segregation of beryllium can be explained by the theory of irradiation-induced segregation^[5,6], but how to explain the segregation of beryllium on the surface of Al-Li-Mg alloy without ions irradiation seems necessary to be resolved. In order to make this problem clear, a Cu-Be alloy was chosen to study the surface segregation of beryllium.

2 SURFACE SEGREGATION OF Cu-Be ALLOY

2.1 Surface segregation studied by SIMS

Similar to the experimental process described above, the alloy specimen Cu-12 at. % Be was installed on sample holder in vacuum chamber by transmission mechanism and the specimen temperature was changed from RT to 550°C step by step, on every temperature value set up, such as 100°C or 200°C, the secondary ion signals of the specimen were scanning until no any obvious change was observed, it showed that the thermal balance had formed in the specimen, then the secondary ion signals were recorded. The time of thermal balance that the specimen reached was about 10 minutes to 60 minutes determined by various temperature values. The secondary ion yield ratio Be⁺/

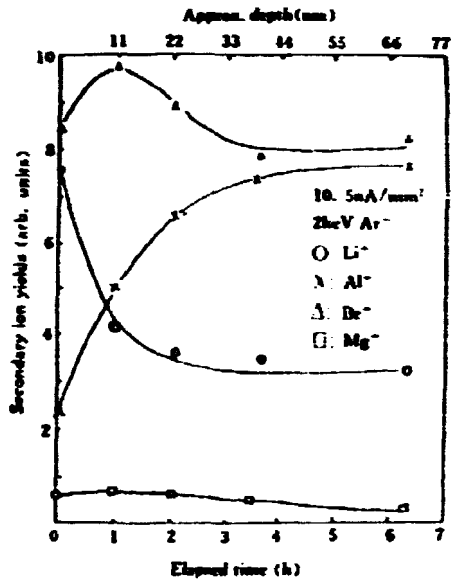


Fig. 3 Secondary ion depth profile of Al-Li-Mg alloy at room temperature after heating and cooling, between RT and 360°C, during this process, the specimen was Ar ions irradiated continuously

Cu^+ changed with temperature was indicated in Fig. 4. From Fig. 4, it can be seen that the surface concentration ratio $C_{\text{Be}}/C_{\text{Cu}}$ increased with the rising of the specimen temperature, which implied that Be enriched on the surface during annealing, namely surface segregation of Be had occurred.

In order to study the concentration profile in surface layer of the specimen, after the specimen reached thermal balance at 550°C , the heater was switched off. When the specimen cooled at RT, an Ar ion gun, whose energy is 2 keV and flux density is 10 nA/mm^2 , was used to bombard the specimen surface, meanwhile, the secondary ion signals were recorded. The secondary ion yield ratio Be^+/Cu^+ changed with sputtering time was showed in Fig. 5. Taking the sputtering yield of copper by Ar ions as 4, the erosion velocity can be estimated at 0.2 to 0.3 nm/s. From Fig. 5, the ratio Be^+/Cu^+ was nearly no change in the primary 30 s and then decreased rapidly. Therefore, the thickness of beryllium segregation layer can be estimated at 6 to 10 nm. Considering that the sputtering yield of beryllium was about one third of that of copper, the thickness of beryllium segregation layer should be approximately estimated at 5 nm, which close corresponding to the results made by AES described in next section.

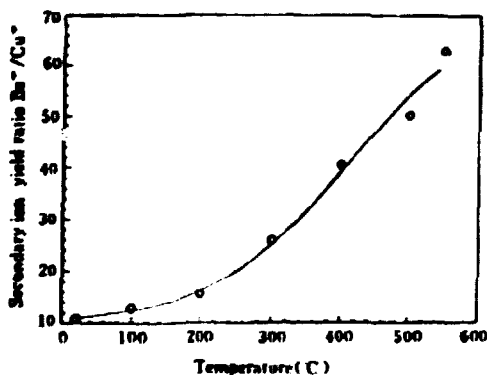


Fig. 4 Change of secondary ion yield ratio Be^+/Cu^+ with specimen temperature

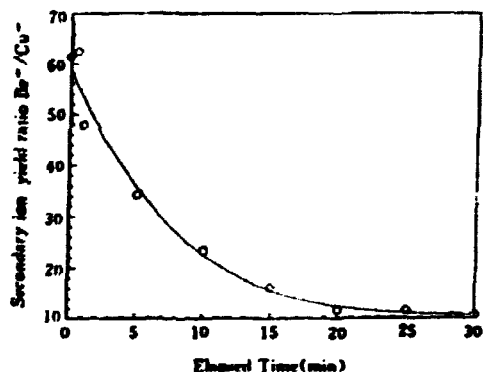


Fig. 5 Secondary ion depth profile at room temperature after a cooling sequence from 550°C

2.2 Surface segregation studied by a in-situ AES analysis

The experimental apparatus was shown in Fig.6, the details of it have been described in the previous paper^[7]. But briefly speaking, it is composed of a vacuum vessel whose ultimate pressure is below $1 \times 10^{-6} \text{ Pa}$. The vessel is separated by the specimen into two parts; the upstream side is evacuated by a

turbomolecular pump backed by a rotary pump, and the downstream side by a sputter ion pump. It is also equipped with two ion guns, one in each part, and an in-situ Auger electron spectrometer utilizing a 3 keV electron beam.

The specimen employed in the present study was a Cu-Be alloy containing about 12 at. % Be which was manufactured by NGK Insulators, Ltd. The major bulk impurity was cobalt (Co) whose content was less than 0.2 wt. %. The thickness of the specimen was 0.135 mm and the specimen was electrochemically polished in a solution of phosphoric acid (H_3PO_4). AES analysis was occasionally performed on the upstream side surface to monitor its chemical compositions.

From Fig. 7 (a) through Fig. 7 (e), the AES spectra of the alloy surface under various conditions are shown. The surface just after the bake out of the vacuum chamber is shown in Fig. 7 (a), where relatively

large concentration of carbon (C) is observed. However, C can be rapidly removed when the sample is annealed in vacuum at 700°C, which is shown in Fig. 7 (b). The surface contains only Be and oxygen. Obviously, they form in beryllium oxide (BeO). Considering the bulk composition, it can be said that surface segregation of Be took place. On the other hand, when the specimen cooled down to RT from 700°C and was bombarded by 3 keV Ar^+ ions with a flux density of $1 \times 10^{17} Ar m^{-2}s^{-1}$, the signal of Cu starts to appear after one hour of bombardment, see Fig. 7 (c). No further change in the surface composition can be observed after more than five hours of continuous Ar^+ ion bombardment, the AES spectrum of which is shown in Fig. 7 (d). After that, the specimen was heated to a temperature of 300°C, its surface composition was indicated in Fig. 7 (e). In addition, from Fig. 7 (d), another peak emerges at

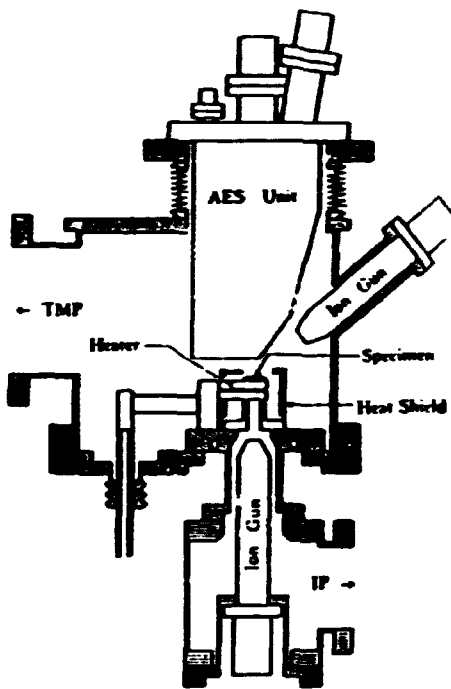


Fig. 6 A schematic layout of the permeation measuring apparatus incorporating an in-situ AES analyzer

slightly higher energy (105 eV, indicated by an arrow) than the initial Be peak (95 eV). This may be assigned to an elemental Be^[8], which implies that a fraction of BeO may have been reduced to Be after prolonged bombardment. The details of the change in the surface composition due to Ar⁺ bombardment are summarized in Fig. 8.

According to the phenomenological bond breaking theory^[9,10], segregation of Be is not expected, for there is little difference in the heats of sublimation between Cu and Be; i. e., they're 3.49 eV (336 kJ/mol) and 3.32 eV (320 kJ/mol), respectively^[11]. Meanwhile, the heat of sublimation of Al is 3.39 eV (327 kJ/mol). segregation of Be from Al based alloy is also not expected. In fact, no segregation has been reported for Al-Be alloys^[12]. However, one may realize that there is a considerable difference between the two metals in the free energy of formation of oxides; these are -207 kJ/mol for CuO and -1048 kJ/mol for BeO, respectively, on the basis of 1 mol of O₂ at 600°C^[13]. The relation of free energy of formation for CuO and BeO with temperature is shown in Fig. 9. Hence, there is no question that Be at the outermost layer is in the form of BeO, and that the principal driving force of the segregation is the oxygen partial pressure in the atmosphere.

Concerning Fig. 8, due to uncertainties in the sensitivity factor of Auger

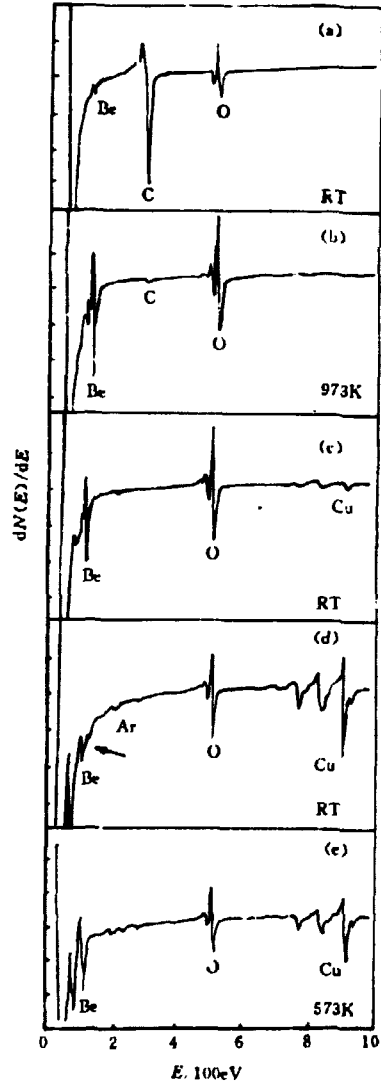


Fig. 7 Auger electron spectra of the surface of a Cu-Be alloy (a) after bake-out; (b) Annealed in vacuum at 700°C for 5 h; (c) after 1 h of Ar ions sputtering; (d) after 5 h of Ar⁺ sputtering, and (e) annealed at 300°C for enough time again

electron peaks, it may not strictly reflect the actual concentration profile. However, it can be seen that the relative intensity of Be is nearly constant between 0 and 4000 s, then followed by a transient region where the concentration of Be is observed to decrease gradually. Hence, if one takes the time interval of 0 to 4000 s in Fig. 8 as representing the oxide, and further assumes that at room temperature segregation rate is negligible, then one obtains the value of about 4 nm for the thickness of the oxidized layer. In the above estimation, TRIM code was employed to estimate the physical sputtering yield of BeO by Ar^+ [14].

3 CONCLUSIONS

The surface segregation of low-Z elements, Li and Be on alloys Al-Li-Mg and Cu-Be was studied by SIMS and AES. The segregation of Li on Al-Li-Mg alloy shows that the concentration of Li on the alloy surface is about 100% in the temperature range of 150~300°C; the depth profile indicates that Li enriches on the outermost several atoms layers and Be on the subsurface. On Ar ions irradiation, the depth profile of Be in Al-Li-Mg alloy specimen is close corresponding to Ar ions projected range, which can be explained by irradiation-induced segregation. However, the surface segregation of impurity Be on the Al-Li-Mg alloy during specimen annealing does not expected according

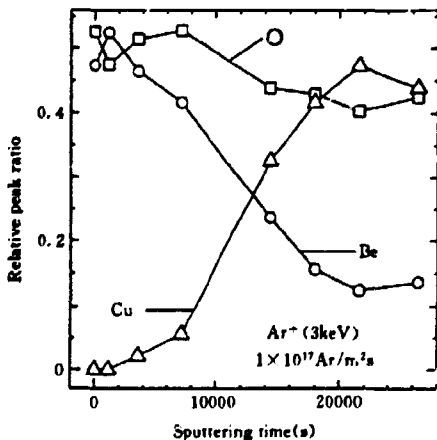


Fig. 8 Depth profile of the surface of a Cu-Be alloy employed in the present study which was determined by combining Ar^+ bombardment and AES analysis

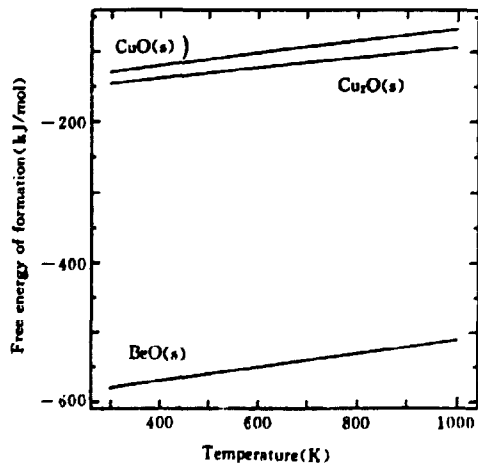


Fig. 9 Free energy of formation for various beryllium and copper oxide compounds on the surface

to Gibbs segregation theory, for this reason, the surface segregation of Cu-Be alloy was studied; experimental results indicated that the segregation of Be on both Al-Li-Mg and Cu-Be alloys can be explained by oxygen chemisorption effect. The depth profile of Be in the alloy surface was also measured, and the thickness of beryllium oxide is estimated about 4 nm.

Since lithium and beryllium are both benefit metal elements for plasma-facing materials in fusion apparatus, in the meantime, aluminum and copper alloys are also the candidates for first wall materials, the present work will offer a constructive suggestion on the possible applications of self-sustained low-Z coating in fusion reactor materials.

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