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Research Article

Effect of Liquid Ga on Metal Surfaces: Characterization of Morphology and Chemical Composition of Metals Heated in Liquid Ga

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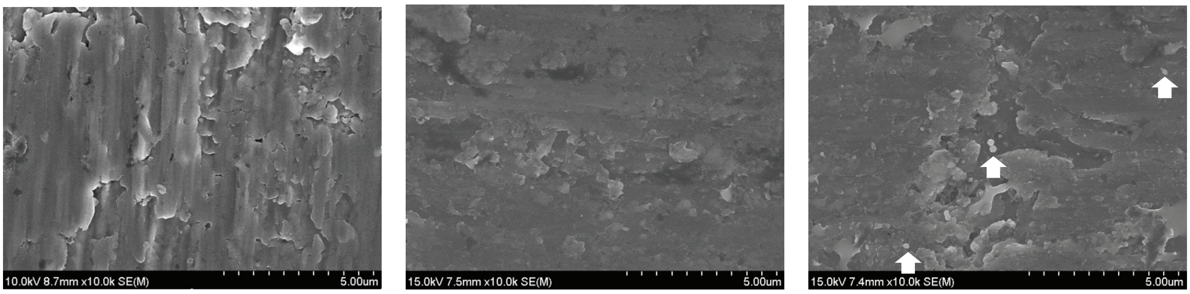
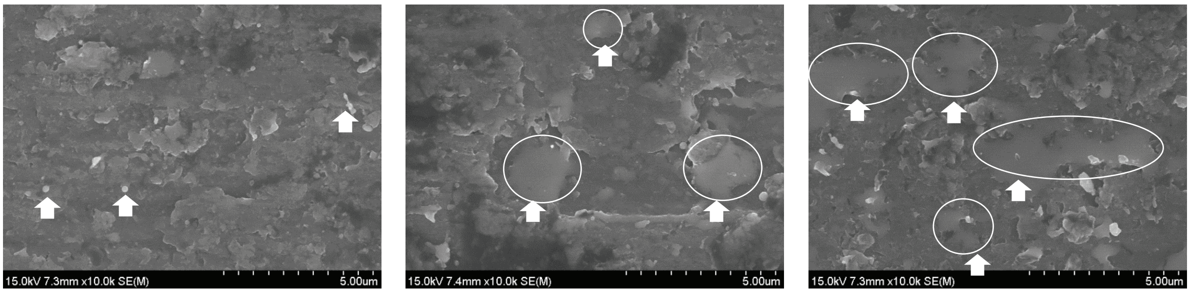
This study investigates the effect of liquid gallium (Ga) on metal foils made of titanium (Ti), niobium (Nb), and molybdenum (Mo). The Ti, Nb, and Mo foils were heated in liquid Ga at 120°C for a maximum of two weeks. After heating, the changes in the morphology and the chemical composition of the metal foils were analyzed by using a field emission scanning electron microscope, energy-dispersive X-ray spectrometer, X-ray diffractometer, and X-ray photoelectron spectrometer. The results of the analysis indicated that the Nb foil showed the minimum adhesion of liquid Ga to the surface while the maximum amount of liquid Ga was observed to adhere to the Ti foil. In addition, the Nb foil was oxidized and the Mo foil was reduced during the heating process. Considering these effects, we conclude that Mo may be used as an alternative encapsulation material for Ga in addition to Nb, which is used as the conventional encapsulation material, due to its chemical resistance against oxidation in hot liquid Ga.

1. Introduction

^{68}Ga has attracted great attention in such medical research areas as positron emission tomography (PET) because it decays mainly via positron emission and has a short half-life (~68 min) [1]. Therefore, the production of ^{68}Ge, the long-lived (half-life of ~288 days) parent radioisotope of ^{68}Ga, has become an important issue. ^{68}Ge can be produced by proton irradiation of a Ga target, or by alpha irradiation of a Zn target. However, the use of a Zn target induces difficulty in chemical processing after the irradiation because a third element (Zn) is involved, and, thus, the use of a Ga target has attracted additional research interest. Various forms of Ga, for example, Ga_2O [1], Ga_2O_3 [2], Ga_4Ni [3], and natural Ga [4] have been used for the production of ^{68}Ge by proton irradiation. Specifically, encapsulation is required when a natural Ga target is used because the natural Ga has relatively low melting point (~30°C) and is therefore easily liquefied by the temperature increase resulting from the bombardment of energetic protons. According to a report by Noriter et al., the maximum temperature produced in this process has been estimated to reach as high as 148°C in simulations under irradiation conditions of 29.5 MeV in proton energy and 250 μA in beam current [5]. When the encapsulation material is determined, its resistance to corrosion or embrittlement caused by liquid Ga is one of the most important criterion because the damage of encapsulation by liquid Ga during the proton irradiation can induce serious breakage of accelerator vacuum system. In this research, Ti and Mo were chosen as candidate encapsulation materials in addition to Nb, the conventional choice for the encapsulation of Ga [4] because of the following reasons: Ti, Mo, and Nb are known to have satisfactory resistance to attack by Ga at temperatures up to 400°C [6]. Moreover, Ti is known to resist embrittlement by liquid Ga [7]. In addition, Ti and Nb are widely used metals in the ^{18}O water target for ^{18}F production by proton irradiation because of their hardness and inertness [8], and Mo is used as a window material for the ^{124}Xe target in ^{123}I production by proton irradiation [9]. Therefore, we could conclude that Ti and Mo are suitable candidate materials to this paper. Furthermore, a temperature of 120°C was chosen for the experiments; in our institute, we plan to produce ^{68}Ge



(a) pristine (b) 1 day (c) 3 days



(d) 5 days (e) 9 days (f) 14 days

Figure 1: FESEM images of pristine Ti foil (a) and Ti foils heated in liquid Ga for 1 day (b), 3 days (c), 5 days (d), 9 days (e), and 14 days (f).

by proton irradiation with a <200 μA beam current, so we expect that the maximum temperature will not exceed 120°C. To investigate whether Ti and Mo can be used as alternative materials to Nb in the Ga target for ^{68}Ge production, we carried out heating experiments with Ti, Nb, and Mo foils in liquid Ga at 120°C and investigated the effect of liquid Ga on the morphology and chemical composition of those metals in this paper. The amount of residual Ga after heating and washing was also measured because fine separation between Ga and an encapsulation material is important in real application.

2. Experimental

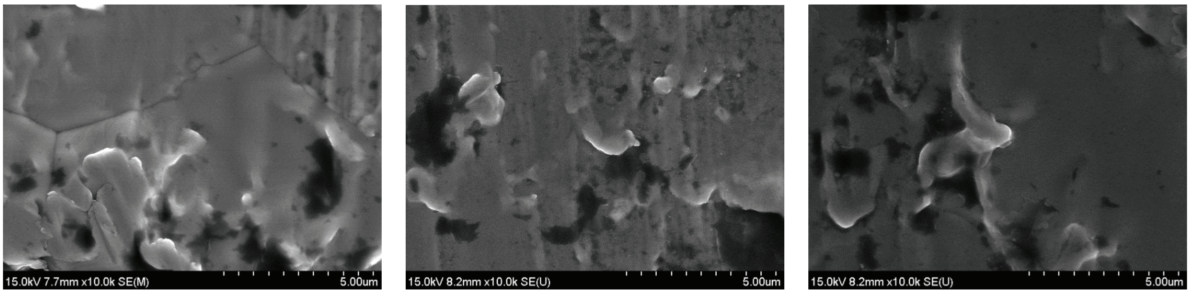
2.1. Material Preparation. Ga (Strategic Metal Investments, 99.9%) was melted by heating at a temperature slightly above its melting point (~40°C). Next, 2 mL of Ga was transferred to each of several vials (Thermo Scientific Reacti-Vial number 13223). Ti (Goodfellow, thickness: 0.075 mm, 99.6+%), Nb (Goodfellow, thickness: 0.1 mm, 99.9%), and Mo (Goodfellow, thickness: 0.05 mm, 99.9%) foils were cut into samples with sizes of 5 mm × 25 mm and dipped into the liquid Ga in the vials.

2.2. Heating Experiment. After the preparation of the vials containing liquid Ga and a sample of metal foils, the vials were placed on the heating device (Reacti-Therm Heating/Stirring Module, Thermo Scientific). The heating temperature was set to 120°C, and the heating time was varied from 1 day to 14 days (Figure S1) (see Supplementary Material available online at http://dx.doi.org/10.1155/2013/619682). After the heating experiments, the metal foils were taken out of the vials and carefully washed with ethanol several times to remove any residual Ga on the metal foil surfaces. After washing, the samples were put into a vacuum oven and then dried at 40°C for 2 hours.

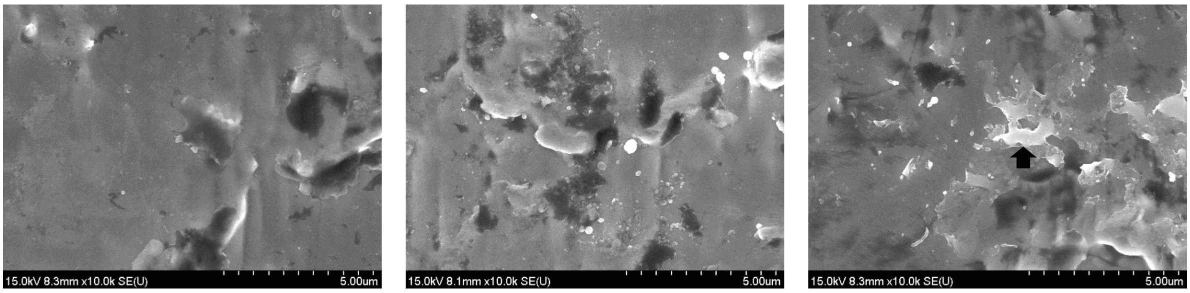
2.3. Characterization. The surface morphology of the metal foils heated in the liquid Ga was characterized with a field emission scanning electron microscope (FESEM, Hitachi S-4800). Energy dispersive X-ray spectroscopy (EDS) analysis was carried out using a FESEM (Nova230, FEI) instrument equipped with an energy-dispersive X-ray spectrometer. The chemical compositions of the pristine and heated metal foils were investigated by X-ray photoelectron spectroscopy (XPS) using an Mg and Al Kα X-ray source in a Sigma Probe (Thermo VG) spectrometer. The XPS spectra were curve fitted with a mixed Gaussian-Lorentzian shape using the XPSPEAK analysis software [10]. The Shirley function was used to remove the background prior to curve fitting. All of the XPS spectra were charge compensated to C 1s at 285.0 eV. The crystallinity of the pristine and heated metal foils was examined with an X-ray diffractometer (XRD, RIGAKU, D/MAX-2500).

3. Results and Discussion

3.1. Surface Morphology. The surfaces of the Ti, Nb, and Mo foils were observed using FESEM. The surface of the pristine Ti foil appeared slightly rough, as shown in Figure 1(a). When the heating time of the Ti foil in the liquid Ga was increased, the amount of material adhered to the Ti foil was monotonically increased (Figures 1(b)–1(f)). The material that adhered to the surface of Ti foil was in the form of both nanoparticles with a size of several hundred nm

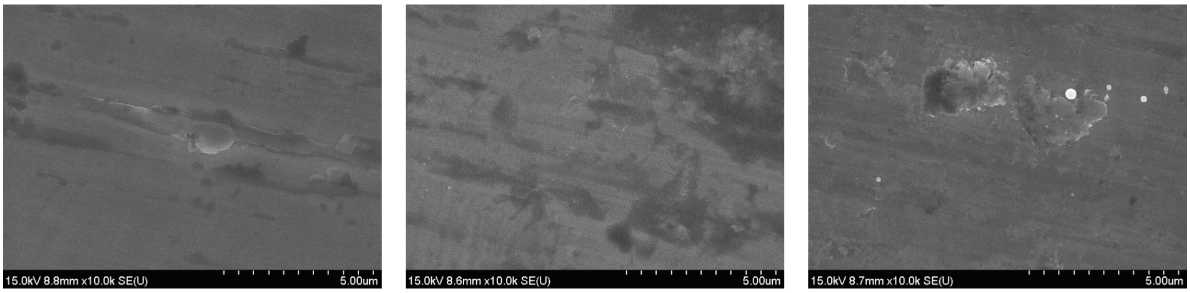


(a) Pristine (b) 1 day (c) 3 days

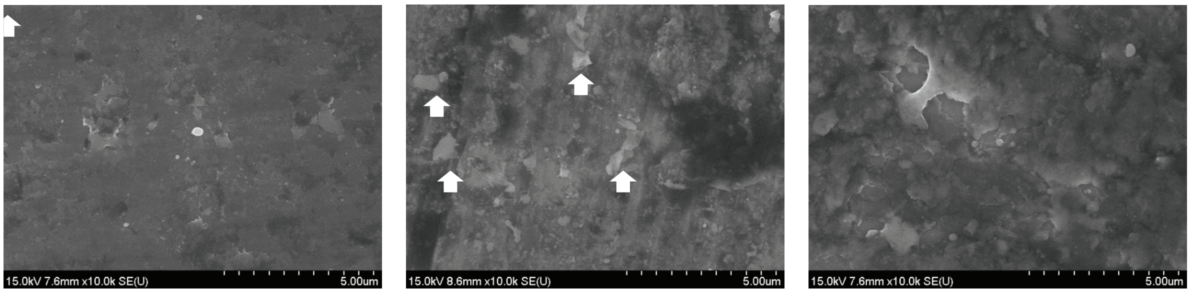


(d) 5 days (e) 9 days (f) 14 days

Figure 2: FESEM images of pristine Nb foil (a) and Nb foils heated in liquid Ga for 1 day (b), 3 days (c), 5 days (d), 9 days (e), and 14 days (f).



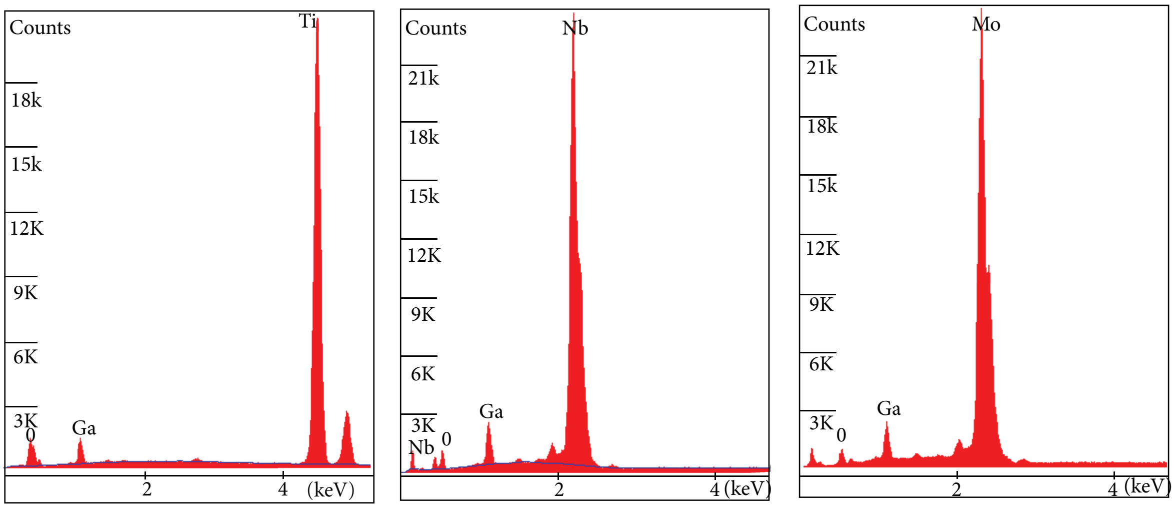
(a) Pristine (b) 1 day (c) 3 days



(d) 5 days (e) 9 days (f) 14 days

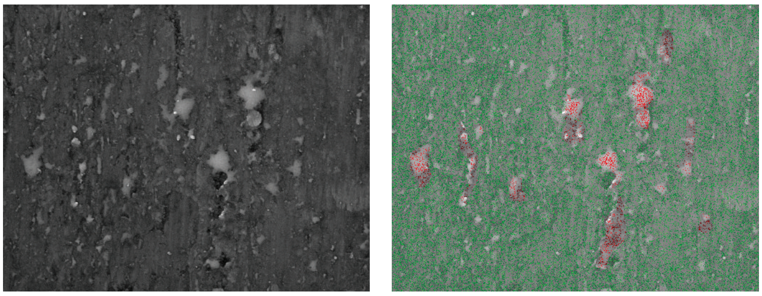
Figure 3: FESEM images of pristine Mo foil (a) and Mo foils heated in liquid Ga for 1 day (b), 3 days (c), 5 days (d), 9 days (e), and 14 days (f).

(see arrowed area in Figures 1(c) and 1(d)) and aggregates. Particularly, when the heating time was longer than nine days, lumps of aggregates with a size of several μm were easily observed on the Ti foil surface (see arrowed area in Figures 1(e) and 1(f)). In the case of the Nb foil, the amount of the adhered material also was monotonically increased as the heating time increased. However, the amount of material adhered to the Nb foils was significantly reduced compared with the Ti foils. When the heating time was increased up to three days, there was little material (in the form of either nanoparticles or aggregates) adhered to the Nb foil surface (Figures 2(a)–2(c)). After heating for more than five days, nanoparticles were found on the Nb foil surface, and the number of nanoparticles increased as the heating time was

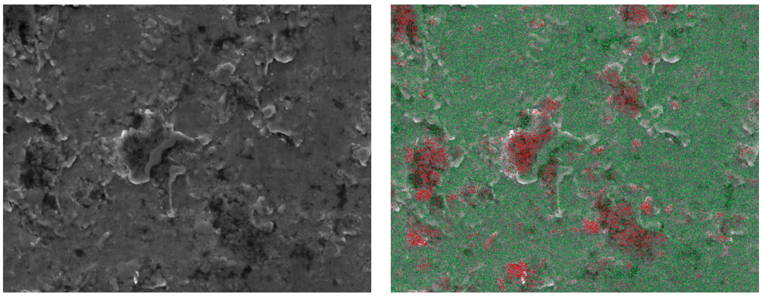


(a) (b) (c)

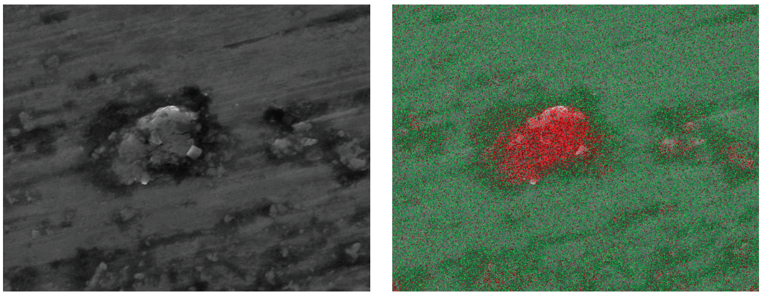
Figure 4: EDS peaks of Ti (a), Nb (b), and Mo (c) foils heated in the liquid Ga.



(a) Ti

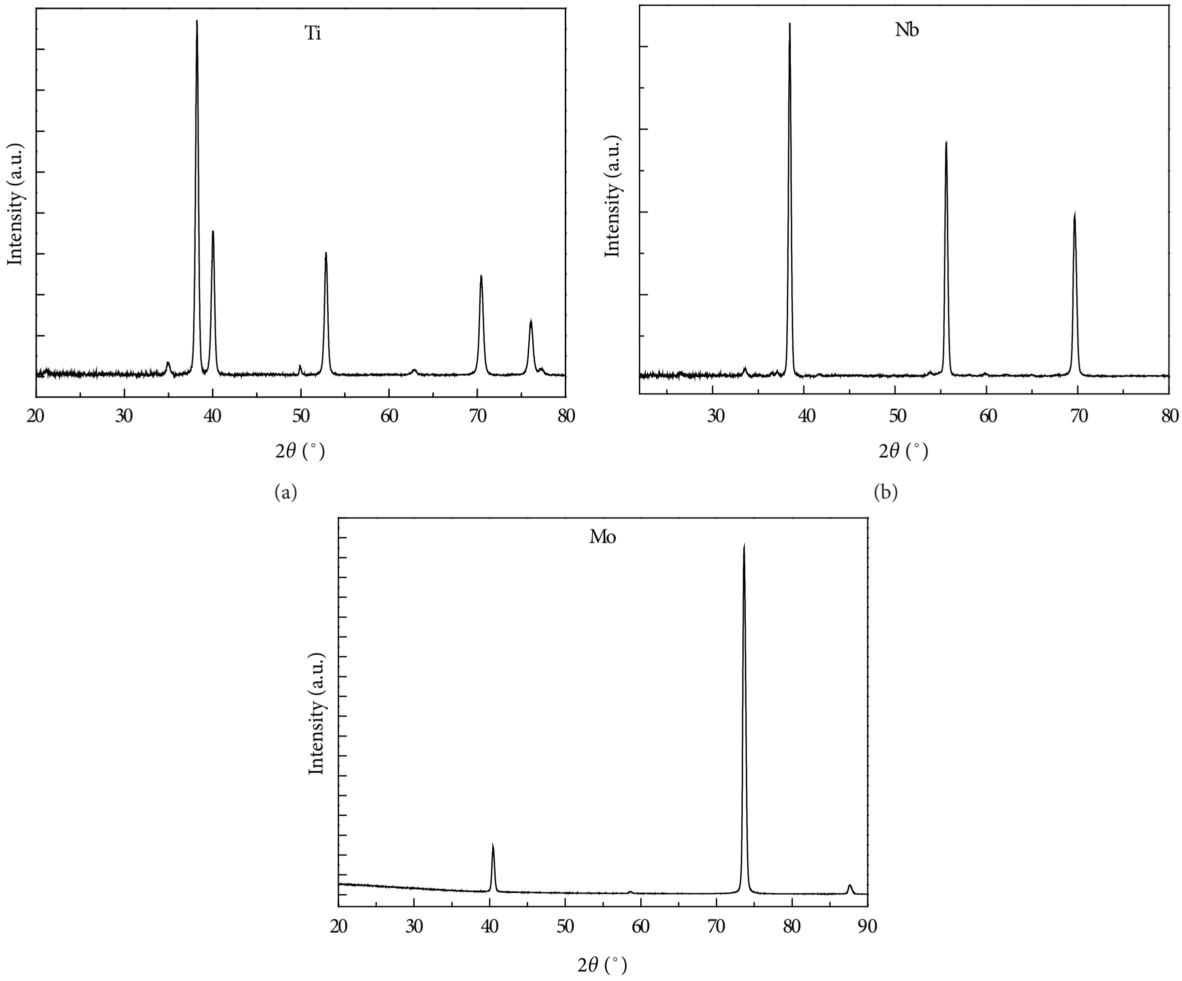


(b) Nb



(c) Mo

Figure 5: FESEM images and corresponding EDS mapping data of Ti (a), Nb (b), and Mo (c) foils heated in liquid Ga.



(a)

(b)

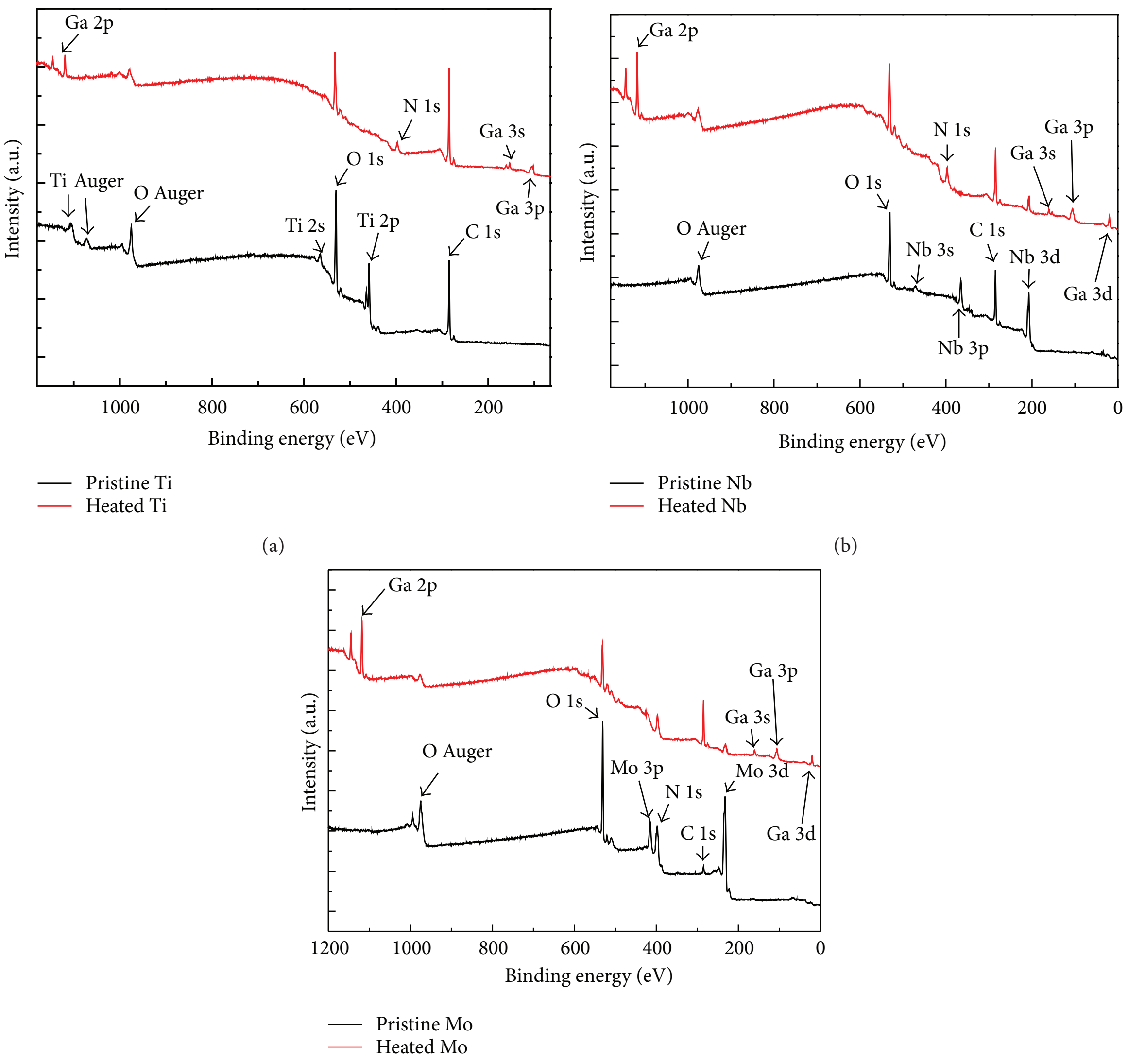
(c)

Figure 6: XRD peaks of Ti (a), Nb (b), and Mo (c) foils heated in liquid Ga.

increased, as shown in Figures 2(d) and 2(e). Aggregates were also observed when the heating time was increased to 14 days (see arrowed area in Figure 2(f)). In the case of the Mo foil, the amount of adhered material was monotonically increased as the heating time increased, similar to the case of Ti and Nb (Figure 3). The amount of the adhered material was relatively abundant compared with that of Nb. In addition, the adhesion material in this case appeared mainly in the form of micro/nanoparticles (see arrowed area in Figure 3(e)) while the adhesion material was mainly in the form of aggregates for the Ti foil.

3.2. EDS Analysis. To identify the materials that adhered on the metal foil surfaces, the samples were analyzed using EDS. The EDS peaks measured from the Ti, Nb, and Mo foils after heating in the liquid Ga are shown in Figure 4. All samples exhibited peaks of the elements that compose the pristine foils: Ga peaks with intensities much smaller than those of the former peaks (Ti, Nb, and Mo), and small oxygen (O) peaks that possibly originated from the metal foil surfaces that were oxidized naturally or via the heating process. In addition, elemental mapping of the Ti, Nb, and Mo foils heated in liquid Ga was performed. Figure 5 displays the FESEM images showing the attached Ga on the metal foil surfaces and the corresponding EDS elemental mapping data (green: metal foil, red: attached Ga). This result revealed that a relatively small amount of Ga was attached to the metal surfaces by heating in the liquid Ga. According to the result of the EDS element analysis, the proportion of Ga was only a few weight percent for the Mo and Nb foils while much larger amount of Ga was attached to the Ti foil (Table S1). The Nb foil showed the minimum adhesion of Ga while the Ti foil exhibited the maximum adhesion of Ga.

3.3. XRD and XPS Analysis. To clarify whether Ga was either physically attached or chemically bonded on the metal foil surfaces, XRD and XPS data were collected and analyzed. The XRD peaks measured from the Ti foil heated in liquid Ga are shown in Figure 6(a). The peaks were centered at 34.94°, 38.21°, 40.03°, 52.83°, 62.83°, 70.44°, 76.03°, and 77.32°, corresponding to the (100), (002), (101), (102), (110), (103), (112), and (201) planes of pure Ti, respectively. However, no XRD Ga peaks were found. This result indicates that heating in liquid Ga at 120°C for two weeks did not affect the Ti foils,



(a)

(b)

(c)

Figure 7: XPS survey spectra of Ti (a), Nb (b), and Mo (c) foils before and after heating in the liquid Ga.

and the amount of Ga that adhered to the Ti foils was too small to be detected by XRD. The Nb and Mo foils exhibited XRD peaks with the same behavior. For the Nb foil, the XRD peaks were centered at 38.44°, 55.59°, and 69.66°, corresponding to the (110), (200), and (211) planes of pure Nb, respectively (Figure 6(b)). Similarly, the XRD peaks of Mo were centered at 40.42°, 58.58°, 73.61°, and 87.59°, corresponding to the (110), (200), (211), and (220) planes of pure Mo (Figure 6(c)).

The chemical composition changes in the metal foil surfaces were investigated using X-ray photoelectron spectroscopy (XPS). The XPS survey spectra of the Ti, Nb, and Mo foils heated in the liquid Ga are shown in Figure 7. All of the pristine metal foils exhibited their characteristic peaks, a C 1s peak that possibly resulted from a surface contaminant, and the O peaks that most likely resulted from a natural oxidation. However, all of the XPS peaks of Ti (such as the Ti 2s, 2p, and Auger peaks) disappeared while the Ga peaks (such as the 2p, 3s, and 3p peaks) appeared after heating in the liquid Ga (Figure 7(a)). The change in survey spectra of the Ti foil may result from the formation of a thin Ga layer (> a few nm) on the Ti foil surface after the heating in the liquid Ga because these XPS signals originate from the material surface at a depth of only a few nm [11, 12], while the conventional XRD is able to gather data at a depth of several μm from the material surface due to the difference in the energy of the X-ray radiation. In the case of the Nb and Mo foils, only the small 3d peaks of Nb and Mo remained, and the Ga peaks appeared after heating in the liquid Ga (Figures 7(b) and 7(c)). It appears that Ga layer which adhered to the Ti foils was relatively thicker than that of the Nb and Mo foils.

The Ga 2p peaks of the Ti, Nb, and Mo foils were all centered at ~1118 and ~1145 eV, corresponding, respectively, to the typical $2p_{3/2}$ and $2p_{1/2}$ peaks of pure Ga (see Figure S2). This result showed that the Ga is only physically attached

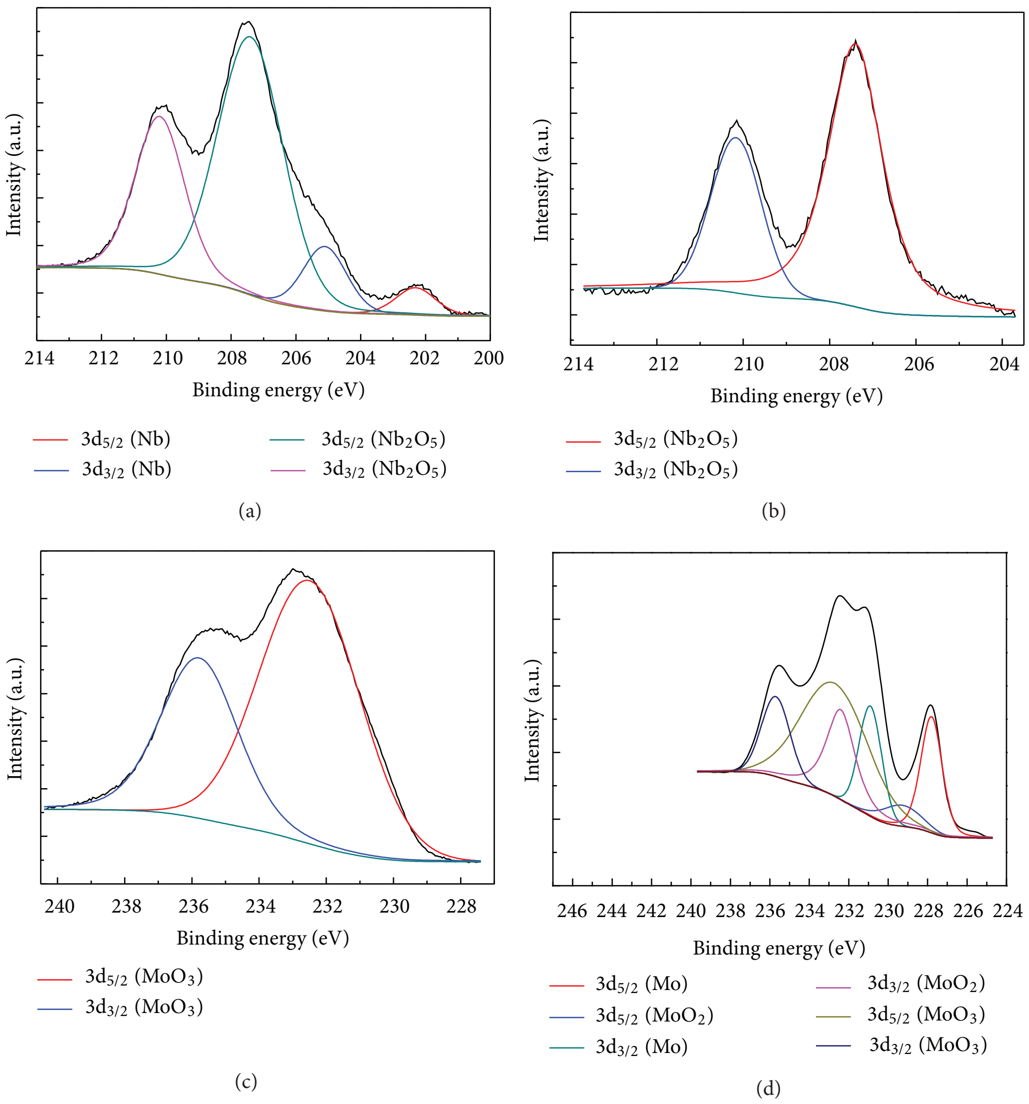


Figure 8: 3d peaks of pristine Nb foil (a), Nb foil heated in the liquid Ga (b), pristine Mo foil (c), and Mo foil heated in liquid Ga (d).

to the metal foil surfaces, with no evidence of any chemical bonding.

However, a chemical change in the metal foil surfaces was observed. For the Ti foil, further analysis could not be carried out because all of the Ti peaks disappeared after heating in the liquid Ga. Detailed analysis of 3d spectra was performed for Nb and Mo. As shown in Figure 8(a), the 3d peak of the pristine Nb could be deconvoluted into four peaks centered at 202.3, 205.1, 207.4, and 210.2 eV, corresponding to the $3d_{5/2}$ and $3d_{3/2}$ peaks of pure Nb, and the $3d_{5/2}$ and $3d_{3/2}$ peaks of Nb_2O_5, respectively. This result means that the surface of the Nb foil consisted of pure Nb and its natural oxide. In contrast, the two peaks centered at 202.3 and 205.1 eV disappeared, and only two other peaks centered at 207.4 and 210.2 eV remained after the heating in the liquid Ga, which implies that the material was transformed into a fully oxidized surface (Figure 8(b)). On the other hand, the 3d peak of the pristine Mo could be deconvoluted into two peaks centered at 232.7 and 235.8 eV, respectively, corresponding to the $3d_{5/2}$ and $3d_{3/2}$ peaks of MoO_3, which is one of the oxide forms of Mo (Figure 8(c)). Interestingly, the Mo foil surface appeared to be reduced after heating in liquid Ga. After heating in the liquid Ga, the shape of the Mo 3d peak became more complicated, as shown in Figure 8(d). The peak could be deconvoluted into six peaks including the former two peaks and peaks centered at 227.8, 229.3, 230.9, and 232.5 eV, corresponding to the $3d_{5/2}$ peak of pure Mo and MoO_2 and the $3d_{3/2}$ peaks of pure Mo and MoO_2, respectively. This result indicated that a portion of the Mo(VI) was reduced to Mo(0) or Mo(IV).

4. Conclusions

This work investigated the effect of liquid Ga on Ti, Nb, and Mo foils at temperatures higher than the melting point of Ga. After the metal foils were heated in the liquid Ga at 120°C, a small amount of Ga remained on the metal foil surfaces even after several washing steps. Among the metal foils used in this study, the Nb foil showed the minimum adhesion of Ga while the Ti foil exhibited the maximum adhesion of Ga. From the perspective of separation of Ga from the metal foils, we can conclude that Nb is the most attractive material among the three tested. In contrast, from the perspective of the chemical composition change, the Nb foil surfaces appeared to be oxidized after heating in the liquid Ga while the Mo foil surfaces were reduced. In conclusion, the conventional Nb encapsulation material of Ga exhibited the least Ga adhesion, a superior property, but Mo also could be used as the encapsulation material for Ga due to its chemical resistance against oxidation during the heating, even though a relatively larger amount of Ga was observed to adhere to its surface compared with Nb.

Acknowledgment

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References

[1] C. Naidoo, T. N. van der Walt, and H. G. Raubenheimer, "Cyclotron production of ^{68}Ge with a Ga_2O target," *Journal of Radioanalytical and Nuclear Chemistry*, vol. 253, no. 2, pp. 221–225, 2002.

[2] P. J. Pao, D. J. Silvester, and S. L. Waters, "A new method for the preparation of ^{68}Ga-generators following proton bombardment of gallium oxide targets," *Journal of Radioanalytical Chemistry*, vol. 64, no. 1-2, pp. 267–272, 1981.

[3] C. Loc'h, B. Maziere, D. Comar, and R. Knipper, "A new preparation of germanium 68," *International Journal of Applied Radiation and Isotopes*, vol. 33, no. 4, pp. 267–270, 1982.

[4] G. E. Meinken, S. Kurczak, L. F. Mausner, K. L. Kolsky, and S. C. Srivastava, "Production of high specific activity ^{68}Ge at Brookhaven National Laboratory," *Journal of Radioanalytical and Nuclear Chemistry*, vol. 263, no. 2, pp. 553–557, 2005.

[5] F. M. Noriter, M. E. Fassbender, M. Dejohn et al., "Targetry at the LANL 100 MeV isotope production facility: lessons learned from facility commissioning," in *Americas Nuclear Energy Symposium*, LA-UR-04-6421, October 2004.

[6] L. R. Kelman, W. D. Wilkinson, and F. L. Yaggee, "Resistance of materials to attack by liquid metals," Argonne National Laboratory Report ANL-4417, 1950.

[7] M. H. Kamdar, "Embrittlement by liquid metals," *Progress in Materials Science*, vol. 15, no. 4, pp. 289–374, 1973.

[8] M. S. Berridge, K. W. Voelker, and B. Bennington, "High-yield, low-pressure [^{18}O] water targets of titanium and niobium for F-18 production on MC-17 cyclotrons," *Applied Radiation and Isotopes*, vol. 57, no. 3, pp. 303–308, 2002.

[9] L. C. A. Sumiya and V. Sciani, "Evaluation of irradiation parameters of enriched ^{124}Xe target for ^{123}I production in cyclotrons," *Applied Radiation and Isotopes*, vol. 66, no. 10, pp. 1337–1340, 2008.

[10] R. W. M. Kwok, "XPS Peak Fitting Program for WIN95/98 XPSPEAK version 4.1," 2000.

[11] C. Y. Tang, Y. N. Kwon, and J. O. Leckie, "Probing the nano- and micro-scales of reverse osmosis membranes—a comprehensive characterization of physiochemical properties of uncoated and coated membranes by XPS, TEM, ATR-FTIR, and streaming potential measurements," *Journal of Membrane Science*, vol. 287, no. 1, pp. 146–156, 2007.

[12] B. Berini, N. Keller, Y. Dumont et al., "Reversible phase transformation of $LaNiO_{3-x}$ thin films studied in situ by spectroscopic ellipsometry," *Physical Review B*, vol. 76, no. 20, Article ID 205417, 9 pages, 2007.