Orderings of the Crystal Structures of Elements after the Allotropic Transformation

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Abstract

In the previous report, it was shown that the crystal structures and solubility of elements in metals are distributed regularly on the thermal conductivity-Young's modulus diagram developed by the author. The elements of bcc structures lie on the straight line of the refractory metals and on the curve of alkali metals. The elements of fcc structures lie on the curve of fcc metals. The elements of hcp and miscellaneous structures are located elsewhere.

Many elements transform to other crystal structures at high temperatures. The orderings of the crystal structures after the allotropic transformations were examined. The elements which transform to bcc structures occupy the space between the straight line of refractory metals and the curve of alkali metals. The elements which transform to fcc structures after the allotropic transformations were Fe and Co, and some elements with low thermal conductivity including Mn.

The elements which transform to bcc structures show large solubility in bcc-structured matrix metals. In the same way, the elements which transform to fcc structures show large solubility in fcc-structured matrix metals.

Mn is located in the low thermal conductivity region on the TC-YM diagram, and undergoes multiple transformations. It shows large solubility in both bcc-structured and fcc-structured matrix metals.

Keywords - *Crystal structure; Allotropic transformation; Solubility; Thermal conductivity; Young's modulus*.

I. INTRODUCTION

The solid elements adopt various crystal structures. When the crystal structures are displayed on the periodic table, there seem some trends, but it is difficult to find the clear trends from it. The author has introduced a new diagram to explain the behaviors of elements, taking the thermal conductivity as the abscissa and the Young's modulus as the ordinate, which is referred to as the TC-YM diagram. The crystal structures of various elements show a significant distribution on the TC-YM diagram [1]. Specifically, the bcc-structured elements mostly lie on the straight line connecting V, Ta, Cr, Mo, and W, which can be called the straight line of refractory metals. Additionally, elements with fcc structures lie on a clear curve, which can be called the curve of fcc metals. Elements with hcp and other structures are distributed elsewhere.

But, there are many elements which transform to other crystal structures at high temperatures. The orderings of the crystal structures of elements after the allotropic transformation were studied here.

II. THE GENERAL TRENDS OF THE CRYSTAL STRUCTURES OF ELEMENTS

At first, the general trends of the crystal structures of elements are reviewed. Fig. 1 shows the distribution of the crystal structures of elements on the periodic table [2]. The alkali metals in the 1st group are all bcc-structured. But the alkali-earth metals show hcp, fcc, and bcc structures with increasing period. Totally, the elements show the agglomerations of the same crystal structures, but, they do not seem to have orderings.

Then, the crystal structures of elements were plotted on the TC-YM diagram with thermal conductivity on the abscissa and Young's modulus on the ordinate, as shown in Fig. 2. The bcc-structured elements mostly lie on a line connecting V, Ta, Cr, Mo, and W, which can be called the straight line of refractory metals. Niobium lies off the straight line of refractory metals, but connects to Ge and Si, which have diamond structures. Nb and Ge share non-closed-packed structures. Nb plays a role in bridging the refractory metals group to the diamond structure group containing Ge and Si.

Iron is located near the straight line of refractory metals. Additionally, elements with fcc structures lie on a clear curve, which can be called the curve of fcc metals. In contrast, bcc-structured alkali metals lie on a curve near the abscissa (the curve of alkali metals). Elements with hcp and other structures are distributed elsewhere. The elements with hcp structures Os, Re, Tc, and Ru form a circle in the upper part of the diagram. The elements with hcp structures Zn, Cd, and Mg form a triangle in the lower part of the

diagram. Lanthanides gather tightly in the low Young's modulus and low thermal conductivity region.

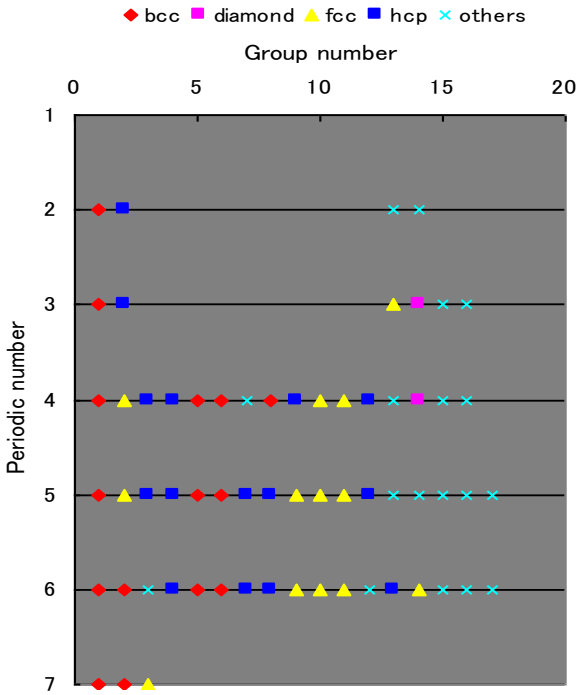

Fig. 1: Crystal Structures of Elements on the Periodic Table

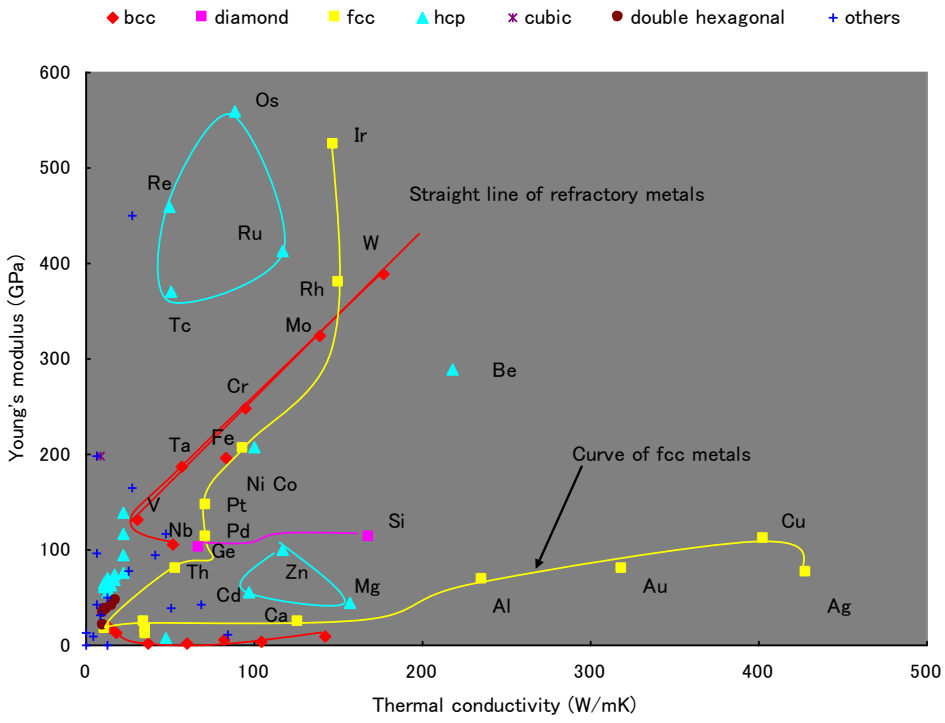

Fig. 2: Crystal Structures of Elements on the TC-YM Diagram

Fig. 3 shows the distribution of crystal structures for elements of low Young's modulus and low thermal conductivity. The lanthanides are distributed across a wide Young's modulus at low thermal conductivity [3]. The lower Young's modulus elements include La, Ce, Pr, Nd and Pm, which adopt double hexagonal structures. The higher Young's modulus elements include Gd, Tb, Dy, Ho, Er, Tm and Lu, which adopt hcp structures. Sm is a transient element and lies between these groups, adopting a rhombohedral structure.

Eu and Yb do not follow this trend, and are instead located at much lower Young's modulus. Eu lies at lower Young's modulus and lower thermal conductivity, and on the extension of the curve of alkali metals. The curve of alkali metals contains Na, K, Li, Rb and Cs, trending from high to low thermal conductivity. The alkaline earth metal Ba lies on the extension of the curve of alkali metals. Eu lies on this extension line after Ba. This is why Eu adopts a bcc structure, and does not follow the trend of the other lanthanides. This is why Ba adopts a bcc structure, and does not follow the trend of the alkaline earth metals.

Yb is located at low Young's modulus but slightly higher thermal conductivity than Eu. It is located near Pb, which lies on the curve of fcc metals. The curve of fcc metals proceeds from Ag (right-most side) through Cu, Au, Al, Ca, Pb, Th, Pd, Pt, Ni, and Rh, and ends at Ir, as shown in Figure 2. Yb and Sr are located near Pb and the curve of fcc metals. This is why Yb adopts a fcc structure and does not follow the trend of the lanthanides. This is why Sr adopts a fcc structure and does not follow the trend of the alkaline earth metals.

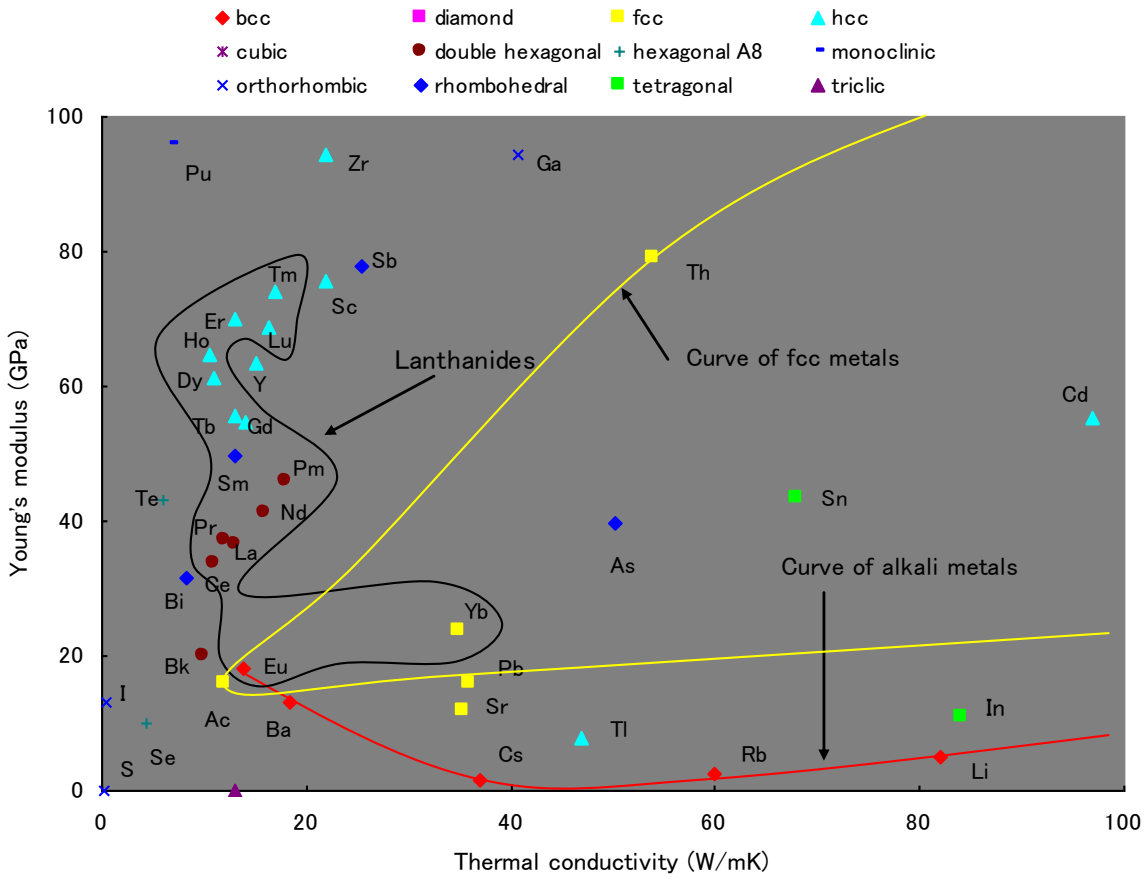

Fig. 3: Crystal Structures of Low Young's Modulus and Low Thermal Conductivity Elements on the TC-YM Diagram

Many of these elements transform to other crystal structures at high temperatures. Whether the orderings in the crystal structures of elements still exist after the allotropic transformation was studied as follows [4-8].

III. ELEMENTS WHICH ADOPT BCC STRUCTURES AFTER THE ALLOTROPIC TRANSFORMATION

Fig. 4 shows the elements of genuine bcc structures and those which adopt bcc structures after the allotropic transformation.

A. *Ti, Zr And Lanthanides Transform to Bcc Structures At High Temperature*

Ti, Zr and the lanthanides lie between the straight line of refractory metals and the curve of alkali metals. These elements have hcp structures because they fall within the hcp region. But most transform to bcc structures at high temperature, because they are affected by the refractory metals and bcc alkali metals. In general, elements with bcc structures can potentially lie anywhere from W (top of straight line of refractory metals) to Na (right-most end of curve of alkali metals). Elements with bcc structures do not exist elsewhere in the diagram.

B. *Refractory Metals of High Melting Temperature And Alkali Metals of Low Melting Temperature Have Bcc Structures*

The transformation of Ti, Zr and the lanthanides into bcc structure at high temperature indicate that bcc is a stable structure at high temperature. The melting temperature of the elements decreases for elements lower on the diagram. The Young's modulus is large and the binding force is strong for the refractory metals, so their bcc structure is stable down to low temperatures. Consequently, they have bcc structures at all temperatures. For Ti, Zr and the lanthanides, the Young's modulus and binding force are mid-range; therefore the bcc structure is unstable at low temperature. Consequently, these elements adopt other structures at low temperature.

For the alkali metals, the Young's modulus is small, the binding force is weak, and the melting temperature is low. Thus, room temperature is a high relative temperature for alkali metals, so they adopt bcc structures at room temperature. Na and Li adopt hcp structures at very low temperatures.

C. *Several Hcp Elements Do Not Transform To Bcc Structures At High Temperature*

The elements with the highest Young's moduli include Os, Re, Tc, and Ru. They adopt hcp structures and do not transform into bcc structures, because they are located away from the bcc metal region in Figure 2. Elements with low Young's moduli and mid-range thermal conductivities include Zn, Cd and Mg. They adopt hcp structures and do not transform into bcc structures, because they are located away from the bcc metal region in Figure 2.

D. *Alkaline earth metals adopt various crystal structures.*

The alkaline earth metals adopt various crystal structures, despite their belonging to the same group in the periodic table. Be and Mg adopt hcp structures, because they are located in the region in Figure 2 outside of the bcc and fcc regions. Be transforms to a bcc structure at high temperature, because it is located near the straight line of refractory metals. Ca adopts a fcc structure, because it is located on the curve of fcc metals. Ca transforms to a bcc structure at high temperature, because it is located near the curve of alkali metals. Sr adopts a fcc structure, because it is located on the line of fcc metals. Sr transforms to a hcp structure and then a bcc structure at high temperature, because it is located near hcp Tl and the line of alkali metals. Ba adopts a bcc structure, because it is located on the extension of the line of alkali metals. Ra adopts a bcc structure and has the same thermal conductivity as Ba, but its Young's modulus is unknown. It can be speculated that it is the same as that of Ba.

It is found from Fig. 4 that the elements which adopt bcc structures after the allotropic transformation connect the refractory metals group and alkali metals group.

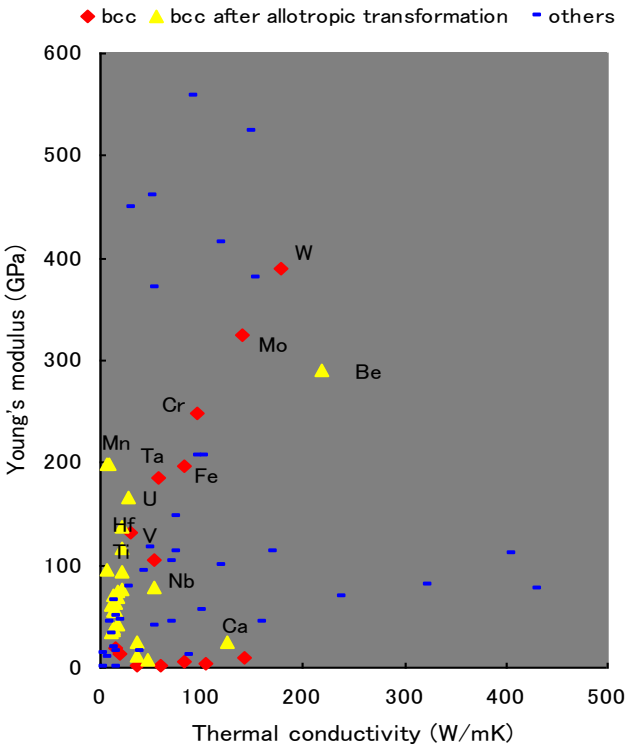

Fig. 4: Elements of Genuine Bcc Structures and those of Bcc Structures After The Allotropic Transformation on the TC-YM Diagram

IV. ELEMENTS WHICH ADOPT FCC STRUCTURES AFTER THE ALLOTROPIC TRANSFORMATION

Fig. 5 shows the distribution of elements of genuine fcc structures and those of fcc structures after the allotropic transformation on the TC-YM diagram.

A. Fe And Co Transform to Fcc Structures at High Temperatures

Fe, Ni and Co lie in close proximity from left to right, near the straight line of refractory metals. Ni is a genuine fcc structure, so lies on the curve of fcc metals. Fe lies slightly to the left of Ni, and nearer the straight line of refractory metals. Consequently, Fe has a bcc structure at room temperature, and a fcc structure at high temperature, following the crystal structure of nearby Ni. Co lies slightly to the right of Ni in the hcp region, so has a hcp structure at room temperature. However, it transforms to a fcc structure at high temperature, following the crystal structure of nearby Ni.

The order Fe–Ni–Co on the diagram explains some of these elements crystallography, despite Fe–Co–Ni being their order in the periodic table.

B. Some Elements with Low Thermal Conductivity Transform to Fcc Structures

As shown in Fig. 5, elements which adopt fcc structures after the allotropic transformation are fewer than those which adopt bcc structure after the allotropic transformation. It is remarkable that the elements of low thermal conductivity Mn, Pu, Ce, and La are included. It is also remarkable that they transform to fcc structures at medium temperatures and do to bcc structures at higher temperatures.

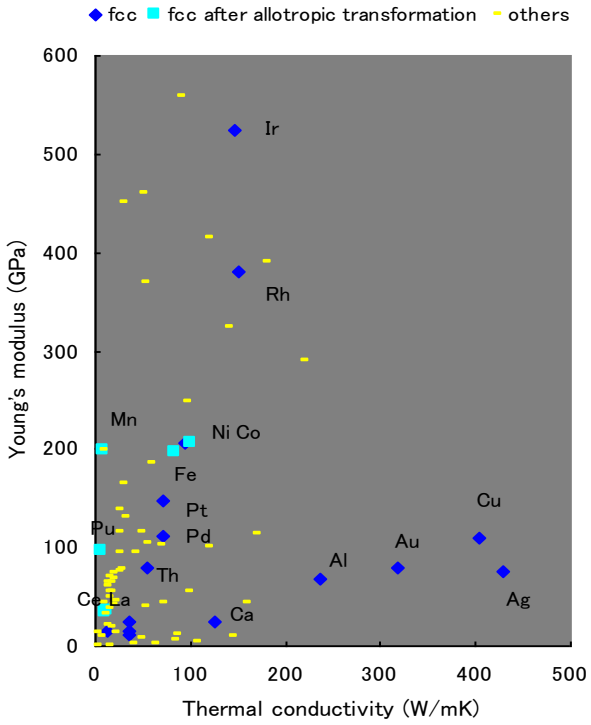

Fig. 5: Elements of Genuine Fcc Structures and those of Fcc Structures After the Allotropic Transformation on the TC-YM Diagram

V. THE ELEMENTS WHICH ADOPT MULTIPLE PHASES

There are some elements which transform to other phases more than twice. Mn transforms from cubic (A12) to cubic (A13), fcc, and bcc. Np and U do from orthorhombic to tetragonal, and bcc. Pu does from monoclinic to orthorhombic, fcc, and bcc. La and Ce do from double hexagonal to fcc and bcc. Sr does from fcc to hcp and bcc. They are shown in Fig. 6. They are all the elements of low thermal conductivity. Np and Mn are very close to each other.

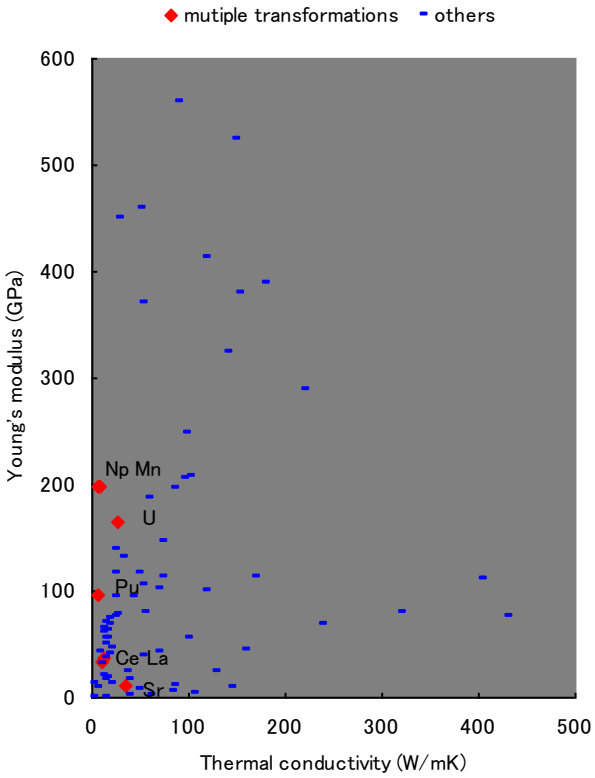

Fig. 6: Elements of Multiple Transformations on the TC-YM Diagram

VI. DISCUSSION

From mentioned above, it was found that the elements which transform to bcc structures play a role in bridging the refractory metals group to the alkali metals group. It was also found that the elements which transform to fcc structures are Fe and Co in the proximity of Ni and Mn, Pu, La, and Ce lie in the low thermal conductivity region. . The elements Mn, Pu, La, and Ce undergo multiple transformations, namely transform further to bcc structures at higher temperatures.

How the crystal structures of elements after the allotropic transformation affect the solubility of elements in metals was studied here [2][9].

A. Solubility of elements in metals of bcc structures

Fig. 7shows the distribution of solubility of elements in α-Fe on the TC-YM diagram. The solubility of elements varies with temperature, therefore, the maximum solubility in the α-phase was adopted as the solubility in α-Fe. The figures in the legend show the range of solubility in mol percent.

The elements near Fe and on the straight line of refractory metals Cr and V show 100 pct solubility. The elements on the straight line of refractory metals have the same bcc structure as α-Fe. However, the elements Mo and W far from Fe show small solubility, although they are located on the straight line of refractory metals. The elements Mo, Be, Si, Zn, and Ga surrounding the elements Cr and V of 100 pct solubility show the next largest solubility. The farther elements show small solubility or no solubility.

Among the elements of multiple transformations, only Mn shows solubility in α-Fe.

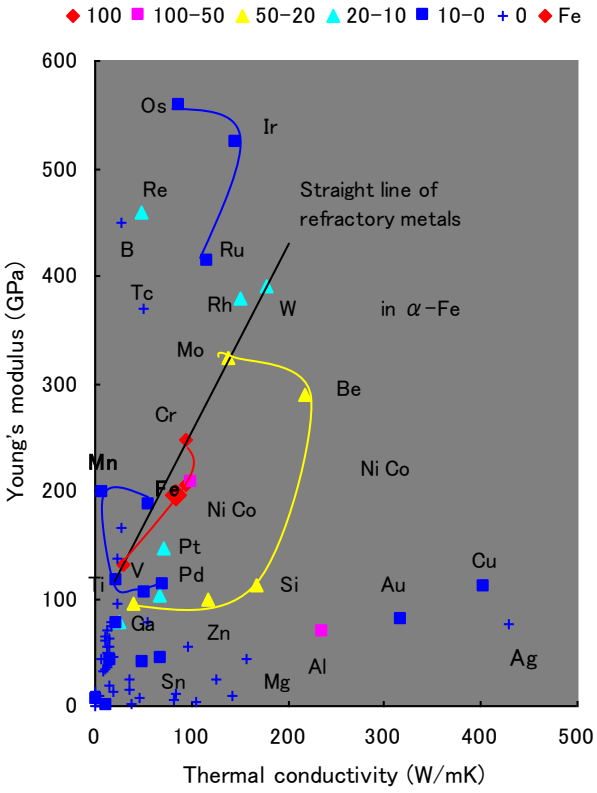

Fig. 7: Solubility of Elements in A-Fe on the TC-YM Diagram

Fig. 8 shows the distribution of solubility of elements in Mo on the TC-YM diagram. Mo is located at the upper part of the straight line of refractory metals. All of the elements on the straight of refractory metals W, Cr, Ta and V show 100 pct solubility. Ti which transforms to bcc at high temperature and Nb of genuine bcc structure also show 100 pct solubility. The elements of multiple transformations Mn and U show medium solubility.

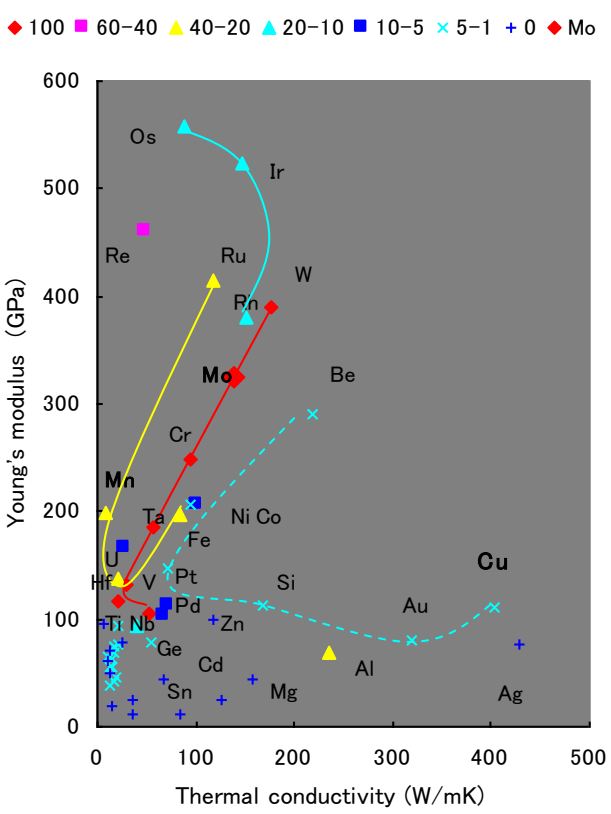

Fig. 8: Solubility Of Elements In Mo On The TC-YM Diagram

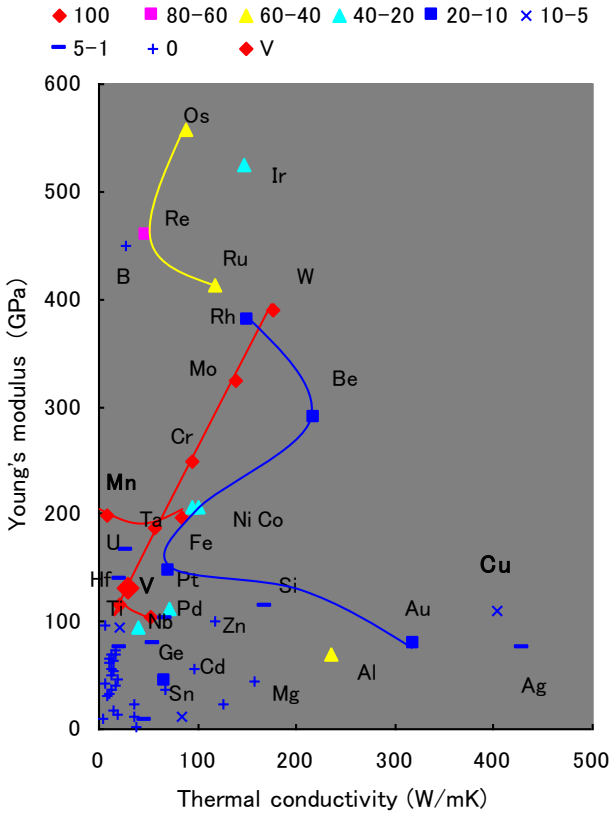

Fig.9: Solubility Of Elements In V On The TC-YM Diagram

Fig. 9 shows the distribution of solubility of elements in V on the TC-YM diagram. V is located at the lowest end of the straight line of refractory metals. All of the elements on the straight of refractory metals W, Mo, Cr, and Ta show 100 pct solubility. Ti which transforms to bcc at high temperature and Nb of genuine bcc structure also show 100 pct solubility. The element of multiple transformations Mn also shows 100 pct solubility, while U shows small solubility.

Fig. 10 shows the distribution of solubility of elements in β-Ti on the TC-YM diagram. Ti is located on the extension line of the straight line of refractory metals and near V. Ti adopts bcc structure at high temperature. All of the elements on the straight of refractory metals W, Mo, Cr, Ta, and V show 100 pct solubility. Nb of genuine bcc structure also shows 100 pct solubility. The elements which adopt bcc structures at high temperatures Hf, Zr, and Sc also show 100 pct solubility.

The element of multiple transformation U also shows 100 pct solubility, while Mn shows medium solubility. It is because U is nearer Ti than Mn.

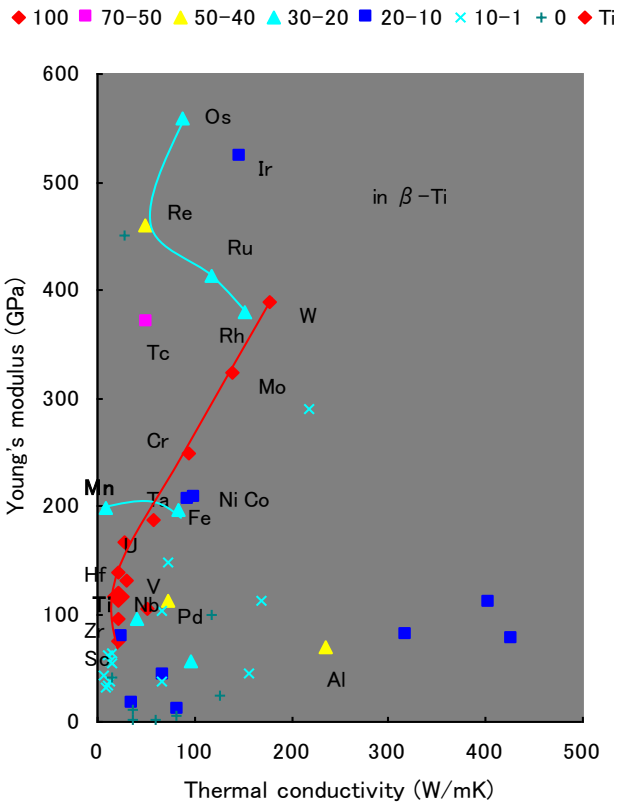

Fig. 10: Solubility Of Elements In B-Ti On The TC-YM Diagram

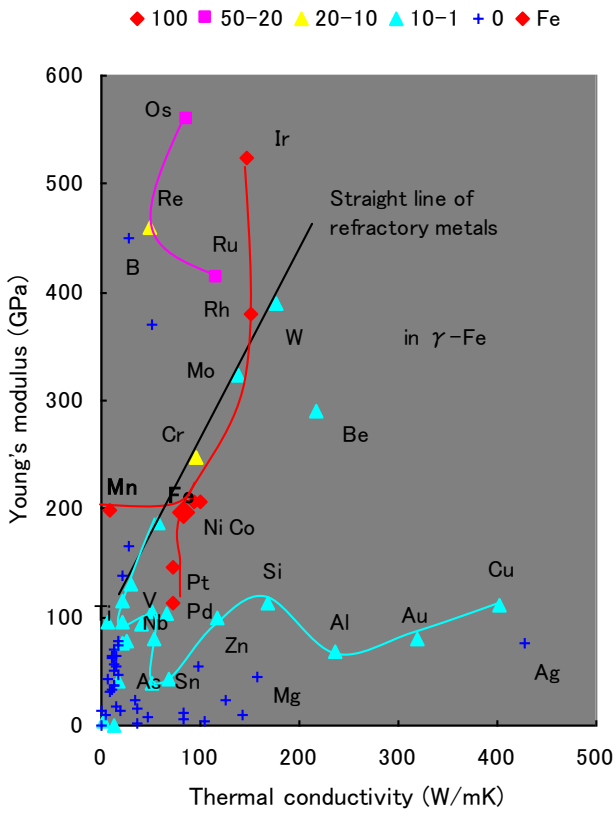

Fig. 11: Solubility Of Elements In Γ-Fe On The TC-YM Diagram

B. Solubility of elements in metals of fcc structures

Fig. 11 shows the distribution of solubility of elements in γ-Fe on the TC-YM diagram. Elements of 100 pct solubility lie on the curve of fcc metals and are relatively near Fe. They have the same fcc structure as γ-Fe. The other fcc elements of lower Young's modulus, Cu, Au, and Al, and those of other crystal structures and of similar Young's modulus, Si, Zn, Sn, As, Th, Ga, Zr, Pu, Ti, , and V, show small solubility.

In this case, Mn shows 100 pct solubility, while U shows no solubility. It is proved that Mn behaves also as a fcc-structured element. U shows no fcc structure in its multiple transformations, therefore, it shows less solubility in fcc-structured metals.

Fig. 12 shows the distribution of solubility of elements in Ni on the TC-YM diagram. Most of the elements on the curve of fcc metals Cu, Au, Pd, Pt, Rh, and Ir, and the elements near Ni (Fe and Co) show 100 pct solubility.

In this case also, Mn shows 100 pct solubility, while U shows small solubility. It is proved again that Mn behaves as a fcc-structured element.

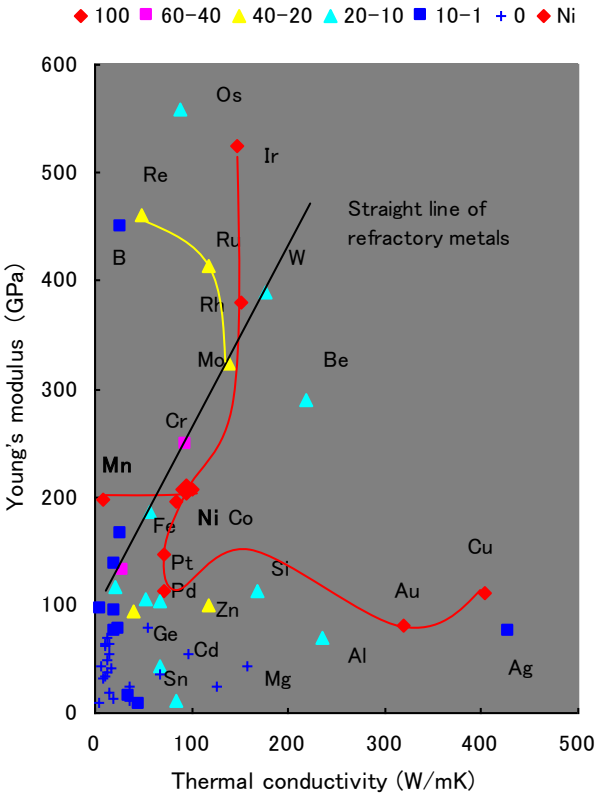

Fig. 12: Solubility of Elements in Ni on the TC-YM Diagram

Fig. 13 shows the distribution of solubility of elements in Cu on the TC-YM diagram. Cu is located nearly at the right-most end of the curve of fcc metals. Most of the elements on the curve of fcc metals Cu, Au, Pd, Pt, Ni, and Rh show 100 pct solubility. The elements Fe, Co, and Ir do not show 100 pct solubility in contrast to the case of Ni. It is because Cu is farther from these elements than Ni on the TC-YM diagram.

In this case also, Mn shows 100 pct solubility, while U shows no solubility. It is proved again that Mn behaves as a fcc-structured element.

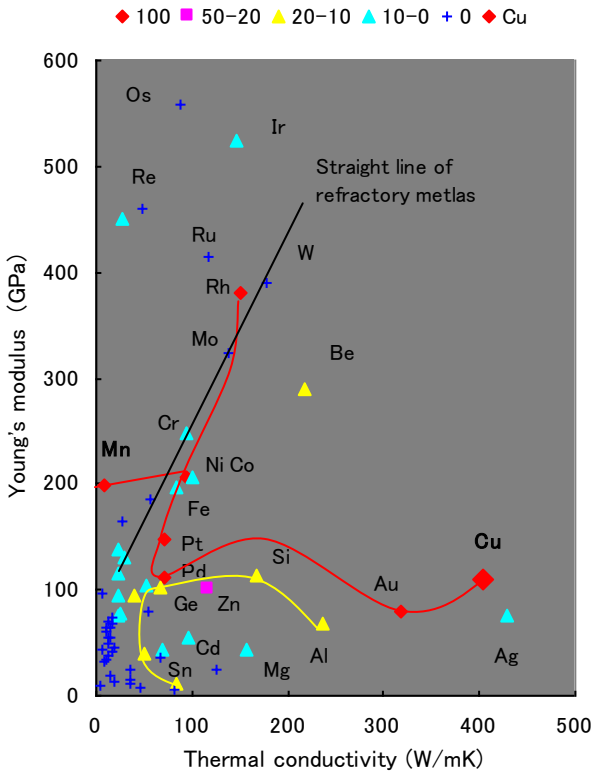

Fig. 13: Solubility of Elements in Cu on The TC-YM Diagram

Fig. 14 shows the distribution of solubility of elements in Al on the TC-YM diagram. Al is located nearly at the middle of the curve of fcc metals. Al shows low thermal conductivity and low Young's modulus, consequently, it has small capacity to dissolve other elements. It dissolves only the elements in the neighborhood to the limited degree.

Nevertheless, in this case also, Mn shows some solubility, while U shows no solubility. It is proved again that Mn behaves as a fcc-structured element.

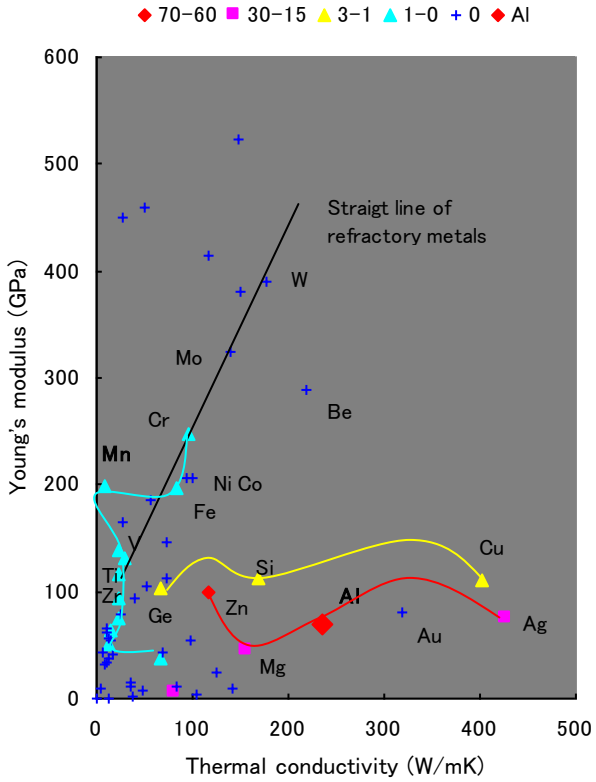

Fig. 14: Solubility of Elements in Al on the TC-YM Diagram

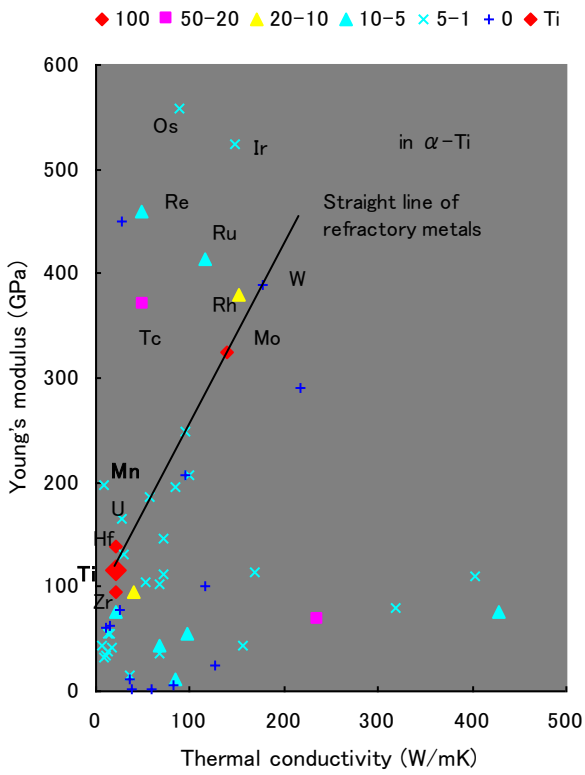

Fig. 15: Solubility of Elements in A-Ti on the TC-YM Diagram

C. Solubility of elements in metals except for bcc and fcc structures

Fig. 15 shows the distribution of solubility of elements in α-Ti on the TC-YM diagram. The elements, Hf and Zr, with the same hcp structure as α-Ti show 100 pct solubility.

Mn and U show small solubility, probably because they have no hcp structures in their allotropic transformations.

Fig. 16 shows the distribution of solubility of elements in Zn on the TC-YM diagram. Zn shows a hcp structure, low thermal conductivity and low Young's modulus, therefore, Zn has small capacity to dissolve other elements.

Only the elements in the neighborhood show some solubility. Nevertheless, Mn shows small solubility in Zn.

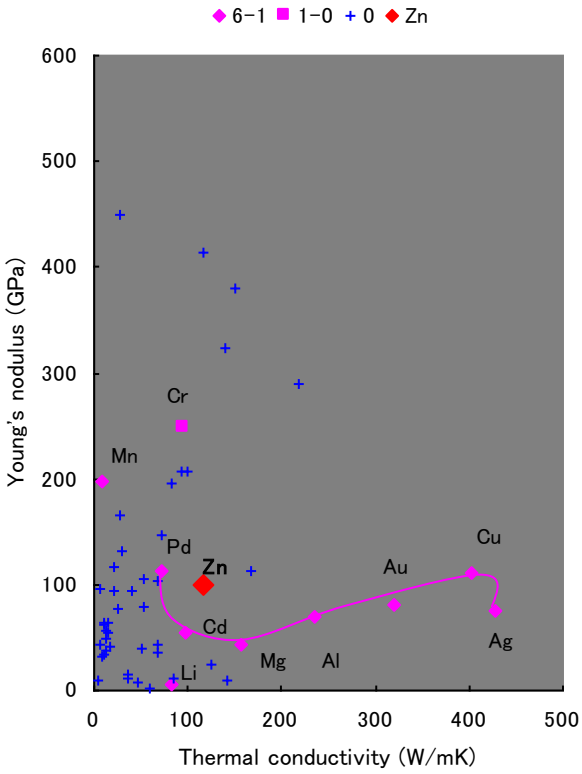

Fig. 16: Solubility of Elements in Zn on the TC-YM Diagram

In this way, Mn has versatility in crystal structures and solubility behaviors. It stems from its unique location on the TC-YM diagram. Its very low thermal conductivity looses the bonding of the lattice and makes it easy to transform to other crystal structures. (Its melting point is relatively low. [10]) As a result, Mn dissolves into both bcc-structured metals and fcc-structured metals to a large extent. Mn could be referred to as "the amphibious element".

VII. CONCLUSIONS

The orderings in the crystal structures after the allotropic transformations were found. The elements lying between the lowest end of the straight line of refractory metals and the curve of alkali metals tend to transform to bcc structures.

The bcc structure can be thought as the high temperature phase of elements. For refractory metals, their bcc structures are stable down to low temperature, because their binding forces are strong. For Ti, Zr and lanthanide, the bcc structure is unstable at low temperature. Consequently, these elements adopt other structures at low temperature. Room temperature is a high relative temperature for alkali metals, so they adopt bcc structures at room temperature.

The elements Fe and Co near Ni, and the elements with low thermal conductivity Mn, Pu, Ce, and La transform to fcc structures.

The elements with low thermal conductivity Np, Mn, U, Pu, Ce, La, and Sr show multiple transformations which transform from the original crystal structures to fcc and finally to bcc structures.

As to the effects of the allotropic transformations of the alloying elements on the solubility in metals, the conclusions obtained in the previous study that the same crystal structure as the matrix metal and the location near the matrix metal are necessary conditions were confirmed to be valid also in the elements which undergo allotropic transformations.

The elements which transform to bcc structures show large solubility in bcc-structured matrix metals. In the same way, the elements which transform to fcc structures show large solubility in fcc-structured matrix metals.

Mn is located in the low thermal conductivity region on the TC-YM diagram, and undergoes multiple transformations. It shows large solubility in both bcc-structured and fcc-structured matrix metals.

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