NEW MATERIALS—ATOM CLUSTERS

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ABSTRACT

When the size of materials themselves and/or their microstructures becomes smaller than the critical one, their behavior markedly changes. The mechanical and their related properties of materials are idealized when the microstructures take the size in the scale of 0.1μm. When the material becomes smaller than the "magic size" in the nanometer scale, the atomistic structure changes abruptly so that the behavior markedly changes just like a new material. These ultrafine materials are named "atom clusters". The magic size of atom clusters is determined by the long range interaction force among constitutive atoms, and closely related to the crystalline-amorphous transition of solid(s-Am). The magic size has been directly obtained by measuring the critical size at which the material behavior abruptly changes, e.g., those for amorphization, rapid sintering et al., on various materials.

The atomistic structure and behavior of the atom clusters are discussed based on the general rules of s-Am.

INTRODUCTION

Recently, it has been shown[1~3] that the material behavior markedly changes when the size of solid materials themselves and/or their microstructures decreases less than the critical one. For example, when the microstructures including individual grains take the size in the 0.1μm scale, the mechanical properties of materials become the ideal ones [1~3],because not only the heterogeneous deformation is effectively suppressed but also the hydrostatic stress is sufficiently induced by interaction among the microstructures. Figure 1 shows the size effect on the mechanical properties of materials. It is noted in Fig.1 that the flow stress abruptly increases when the stress concentration factor(K) is homogeneized to be K≃1 in all parts of a material. The value of K at the tip of a slip band is determined by the number of pile-up dislocations, and thus it increases to 10 or more in general when the material is plastically deformed. By overlapping long range interaction force among the deformed microstructures, K becomes unity when the structure size takes the scale of 0.1μm[3]. Therefore, the apparent flow stress increases more than 10 times, as shown in Fig.1. This type of size effect becomes more effective when deformation is carried out under low flow stresses or low strain rates, such as in fatigue and creep deformation, so-called super plasticity et al.[3]. In all composite materials, their mechanical properties and such related phenomena as stress corrosion et al. are also determined by this effect[3].

When the size decreases further to the scale of atom clusters whose size is 1∿20nm in diameter(Φ), the atomistic structure of materials also remarkably changes so that the new material behavior is expected to appear[4,5]. However, when the size becomes 1∿20nmΦ, which consists of 10^3∿10^5 atoms, the behavior of materials is just a black box at present, because this size range has not been investigated in detail in both the molecular science and the solid one. Namely, the size range has been too large in the molecular science, but too small in the solid science.

It was already reported by the author[4,5] that the crystalline-amorphous transition of solids(s-Am) is closely related to the atom clusters. Therefore, in the present paper, the black box mentioned above is investigated based on the experimental results of s-Am, and the atomistic structure and behavior of atom clusters is discussed.

NON-LINEAR COMPONENT OF MATERIAL BEHAVIOR

The material behavior consists of both the linear and non-linear components. A typical example of the linear component is the hard sphere model of atoms, and basic problems of solid state physics have been explained by using this model. On the other hand, in case the thermally activated phenomena are eliminated from discussion, the lattice distortion is a typical example of the non-linear component, and it results from the existence of the lattice defects in general. The lattice defects are generated or multiplied heterogeneously, and they are always interact cooperatively with each other. As a result, the non-linear component is remarkably increased by the aid of lattice defects, so that the materials become very structure sensitive.

The lattice distortion always causes the charge transfer among the constitutive atoms, so that both the shape and size of constitutive atoms are changed. Therefore, remarkable changes of the material behavior, such as mechanical, electric, electronic, magnetic and chemical ones, result from the lattice distortion. At present, theoretical calculation on details of the charge transfer is difficult to be carried out precisely, but the general rules have already been clarified on some of them phenomenologically as follows:

[A] Effect of mechanical force

Mechanical force causes the charge transfer among the constitutive atoms. A typical example of this effect is the charge transfer at the core of an edge dislocation, which occurs from the compression side to the expansion side[6], so that the lattice is locally ionized. This was explained experimentally by remarkable decrease of the flow stress when a superconducting crystal is kept below the transition temperature[7]. As a result of the charge transfer, the following facts can be expected to occur: (1) The atomic size decreases at the compression side and increases at the expansion one. (2) Ionic binding force is additionally applied between these both sides. This is one of the local molecularization. (3) A long range interaction force of the Coulomb type results from coupling of the unlike ionized regions.

[B] Effect of the coordination number

As already reported[4], even in the case of inorganic materials, the interatomic distance(D) is a function of the coordination number(N) as in the case of organic materials proposed by Pauling[8], and can be expressed as

$$D=D_0 - \alpha \ln(n/N), \qquad (1)$$

where, D_0, n and α are the interatomic distance in the maximum coordination number, the number of valence electrons and an arbitrary constant.

The binding force at a boundary between two different crystals is an example of this effect. Here, the binding force(F) between two hard sphere atoms can be generally expressed by

$$F=-A/D^m + B/D^n , \qquad (2)$$

where, D, m , n and each of A and B are the interatomic distance, about 6,about 12, and an arbitrary constant, respectively. Furthermore, the binding force along the boundary is generally assumed to be propotional to the number of atom-couplings across the boundary. The number of the atom-couplings rapidly decreases with increasing misfit angle of the boundary, and thus the strength of a high-angle boundary should be decreased remarkably. Practically, however, the high pure polycrystal does not fracture along the boundary, but within either of both crystals. This means that F in eq.(2) rather increases as a whole along the boundary compared with those of individual crystals. In this problem, the effect of coordination number on the interatomic distance(D)is considered to play an important role,i.e., F remarkably increases locally with decreasing the coordination number of atoms on the boundary.

[C] Effect of Mass

1. *Effect of Cluster Size*
Both the atomistic structure and behavior of solid materials are a function of their size. When the size becomes smaller than the critical one, the behavior of materials remarkably changes to that of atom clusters. The critical size is named the "Magic Size"[5]. A typical example is s-Am, as will be mentioned later.

2. *Effect of the number of constitutive atoms*
It has been investigated[9] that both the binding force among atoms and the whole shape of an ultrafine block of material, i.e.,an atom cluster, become very sensitive to the total number of constitutive atoms in the block when the number of constitutive atoms on the surface becomes nearly equal to that of the interior. In the block, the shape of cluster frequently becomes rather stable when the number of constitutive atoms reaches a certain value. This value is called the "Magic Number"[9]. For example, the magic number in a carbon-atom cluster is 60 which takes a soccer-ball in shape, and its ionization potential is smaller than 5eV, as shown in Fig.2. When the number becomes smaller than 60, the shape changes from a circular one consisting of about 10 atoms to a linear-one consisting of several or less atoms. On the contrary, when the number increases to more than 60, the atomistic structure changes to a graphite structure. At the same time, the ionization potential changes from about 12eV to less than 5eV[9], as shown in Fig.2. These facts are considered to be closely related to eq.(1).

The non-linear component mentioned above is a function of the long range interaction force(LRF) among atoms. When two or more atoms in " the Periodic Table" are combined with each other, the group of atoms, i.e., a sort of atom cluster, shows special characters as a molecule. The number of constitutive atoms increases to the scale of about 10^2 , and then the group of atoms changes to a polymer. The number increases to the scale of about 10^4 , and then it changes to a protein, and so on. In these groups of atoms, LRF among the constitutive atoms always plays an important role. For example, when a protein is crystallized, each individual constitutive atom of the spiral atom-chains takes a definite site exactly with the corresponding long interatomic spacing. Furthermore, even in metallic crystals, there are many supper lattices, such as 9H, 18R et al., in which each individual solute atom also takes a definite site with the corresponding long interatomic spacing. These facts suggest that the behavior of materials will markedly change when the size of a group of atoms becomes the same as the affected range of LRF, which is a function of bonding mode and the binding strength, or less. This is the origin of the non-linear component in the behavior of atom clusters.

All of these three effects of non-linear component are closely related to the formation of non-equilibrium phases, especially s-Am, as will be mentioned later.

General Rules for the Solid Amorphization

As already reported[10,11], the author's group has succeeded to induce s-Am by electron irradiation effect, and this method is named electron irradiation induced(EII) method. Figure 3 shows s-Am in a Ni-50at%Ti alloy by EII-method, in which micographs(a),(b) and (c) show the start of s-Am, partly amorphized and completely amorphized states respectively. Each bright and dark spot in these micrographs represent an atom-chain whose direction is perpendicular to the specimen surface. Here, it should be noted in Fig.3 that the periodic array of spots can be observed in very limited regions. Namely, the periodic array of atom-chains is only observed in blocks whose size is larger than the critical one, i.e., the magic size, under which the material behavior is markedly changed. For example, the magic size of a Ni-50at%Ti alloy is about 3nmΦ, as seen in Fig.3(b). Using EII-method, the magic size can be easily and accuratly obtained in various materials, as seen in Figs.3 and 4. Figure 4 is an example showing s-Am in various intermetallic compounds of Al-Zr system. Open circles represent the phases which have shown s-Am by EII-method, and mark LQ indicates the composition range to induce amorphization by liquid-quenching method. It can be easily recognized that EII-method is superior to LQ-method in controlling conditions for amorphization. Thus, EII-method has been applied to examine the possibility of s-Am for more than 60 intermetallic compounds, and the general rules of s-Am have been investigated.

Table 1 is an example showing the relationships between s-Am of 26 intermatallic compounds and various factors which have been proposed up to date as the control factors of s-Am by many researchers. In Table 1, second and third columns show the minimum and maximum values of each corresponding factor in both solid amorphized and non-amorphized compounds, respectively, and each parenthesis shows an average value of 15 compounds in the former and 11 compounds in the latter,respectively. Here, the followings should be noted in Table 1:(a) Each factor does not show a good correlation with s-Am. (b) Only average values of electronegativity difference are narrowly correlated, and average values of both the atomic size difference and the extent of solubility are slightly correlated with s-Am.

These facts mean that there are other major factors for s-Am besides those listed in Table 1. These major factors have been investigated by the author based on the experimental results, and the general rules for s-Am were obtained [4,5,12] as follows:

Rule I: The material must be divided into small blocks whose size is smaller than the corresponding critical size. When the material consists of more than two phases or components, they must divide each other into the corresponding critical size each.

Rule II: At least one of the constitutive atoms must have two or more coordination numbers, i.e., more than two bonding modes, at the same time. Occurrence of amorphization becomes easy when different kinds of constitutive atoms take a large separation in the Periodic Table each other.

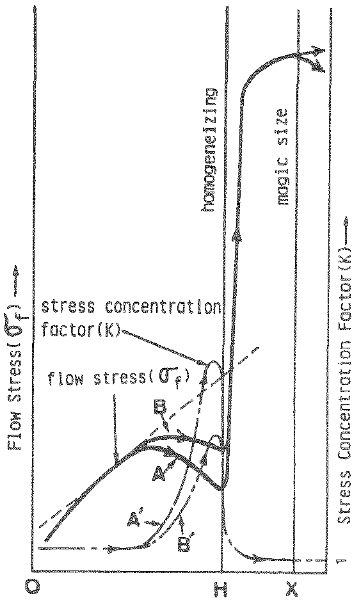


Figure 1. Size effect on the mechanical properties of materials.

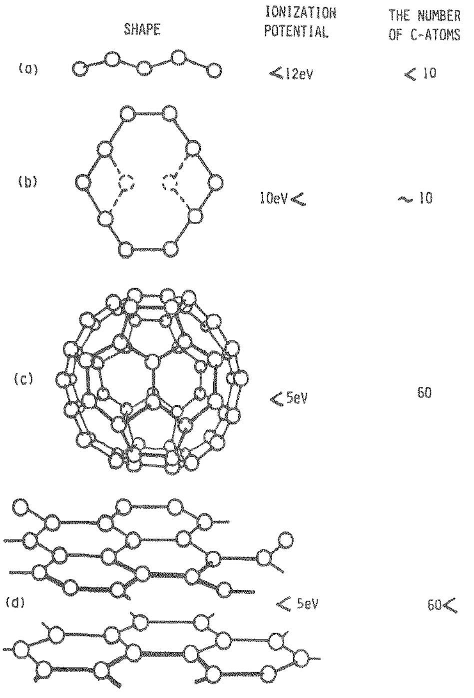


Figure 2. Shape and ionization potential of atom clusters as a function of the number of constitutive atoms(based on reference[9]).

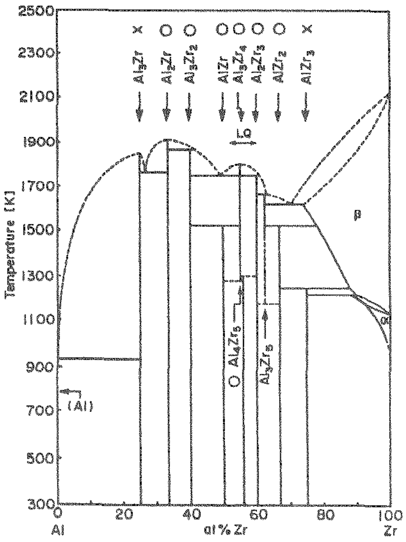


Figure 4. Crystalline → amorphous transition of Al-Zr alloys.

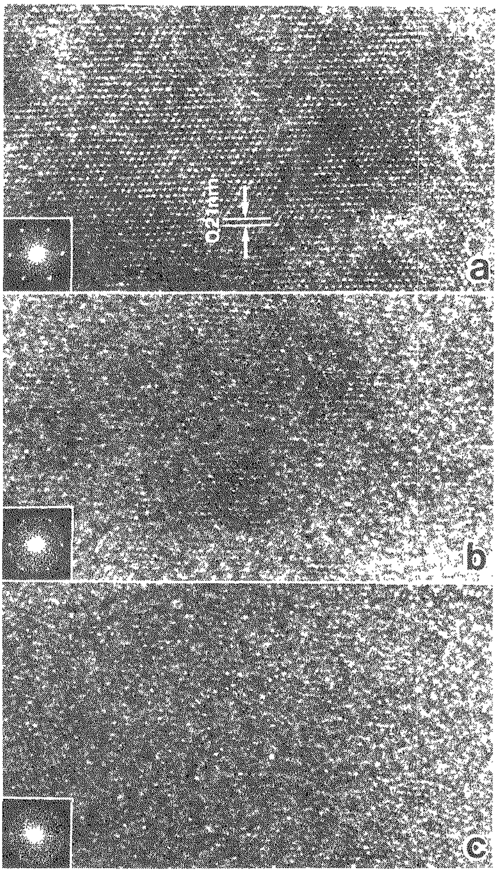


Figure 3. Solid amorphization induced by electron irradiation in a Ni-50at%Ti alloy.

Table 1
Correlation of physical properties between amorphized(Am) and non-amorphized(Non-Am) materials.

Parameter	Am	Non-Am
	min.- max.	min. - max.
Crystal structure	B_2 - Zr_7Ni_{10}	B_2 - DO_{24}
Transformation temperature(K)	713 - 1700 (1399)	1143 - 2208 (1659)
Atomic size ratio	1.12 - 1.28 (1.178)	1.02 - 1.18 (1.129)
Electronegativity difference	0.1 - 0.4 (0.233)	0 - 0.3 (0.181)
Extent of solubility(at%)	None - 8 (2.153)	None - 14 (3.989)

(   ) show an average value of intermetallic compounds used for each parameter.

Table 2
Effect of bonding mode on the magic size. Here, isolated and embedded atom clusters are named neo-molecules and embryonic blocks respectively.

Magic size(nmφ)		Bonding mode of materials
Isolated	Embedded	
20 - 10	8 - 4	Metallic and ionic bonding
10 - 5	5 - 3	Intermetallic compounds
5 - 2	3 - 1	Covalent and diamond bonding

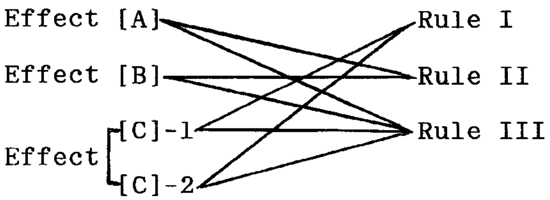
TABLE 3
Effect of environments on the condition of atom clusters.

Atom clusters
- Neo-molecules: Isolated atom clusters surrounding with free surfaces in vacuum or gases. Their surface energy is large in general.
- Embryonic blocks: Embedded atom clusters surrounding with interfaces in liquids or solids. They have small surface energies in general.

Rule III; The interatomic distance (D) between adjacent atoms is a function of the coordination number , and expressed by eq.(1). Here, it is considered that the number of valence electrons(n) per atom has a tendency to increase with decreasing the coordination number(N). As a result, the binding force sufficiently increases with decreasing interatomic distance so that each constitutive atom does not migrate a long distance below a certain temperature, i.e., the amorphization temperature.

These general rules are realized in any amorphization methods such as liquid quenching, spattering, particle irradiation, chemical amorphization, mechanical alloying et al.[12]. Namely, these rules are the general rules for the amorphization of materials.

Here, the following points should be noted in these general rules: (a) All of the three effects of non-linear component in the material behavior are connected with these general rules as follows:



(b) Most of the factors listed in Table 1 are also correlated to s-Am of the materials which satisfy these general rules. For example, when the general rules are satisfied, occurrence of s-Am becomes easy in crystals with large unit cells,i.e., complex atomistic structures.

In the general rules, it is emphasized that the periodic array of atoms is loosed from the periphery region when the crystal size becomes smaller than the critical one[4,5,12], as seen in Fig.3. This critical size exactly corresponds to the magic size.

MAGIC SIZE OF ATOM CLUSTERS

As mentioned already, the magic size can be obtained directly by EII-method. Table 2 shows the magic sizes of materials as a function of the bonding mode. Furthermore, there are two kinds of atom clusters ,i.e.,the Neo-Molecules and the Embryonic Blocks, depending on the surrounding conditions, as shown in Table 3. These two kinds of atom clusters are listed separately in Table 2. Most magic sizes of the embryonic blocks were directly measured by EII- method, and the other were estimated by comparing the bonding mode of unknown-materials with those of known-ones. On the other hand, most magic size of neo-molecules in Table 2 were also directly obtained from their critical size at which sintering speed abruptly increases, and the other were also estimated from the bonding

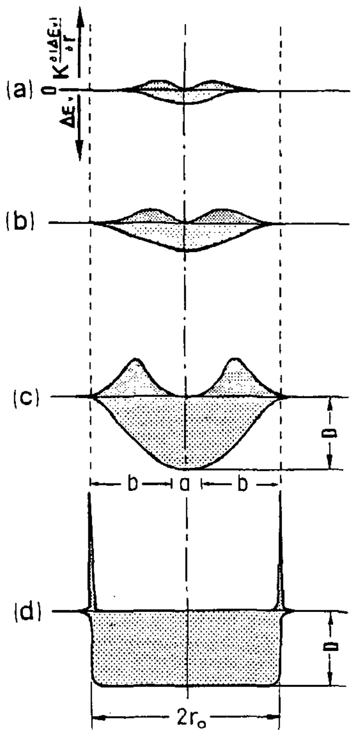


Figure 5. Lip-shape model showing relationships between the volume free energy difference and the surface energy of an atom cluster as a function of the atomistic structure of cluster.

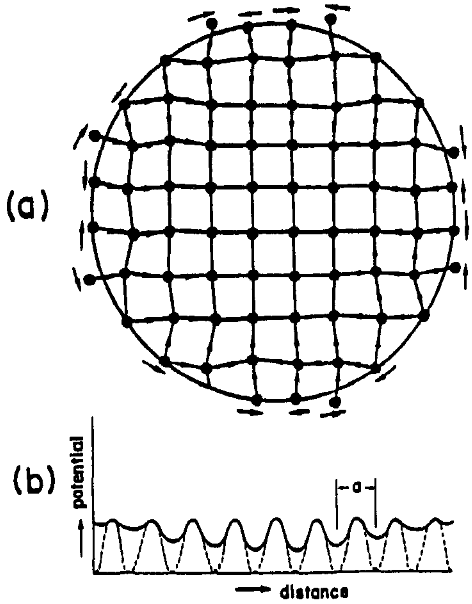


Figure 6. Atomistic structure(a) and the corresponding potential(b) among the atom-chains in an atom cluster.

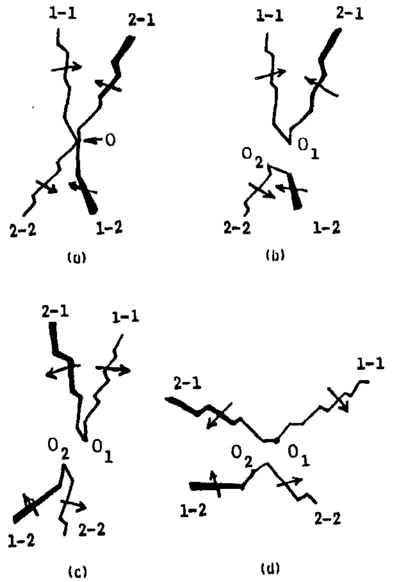


Figure 7. Interaction between two zigzag atom-chains during deformation of an neo-molecule.

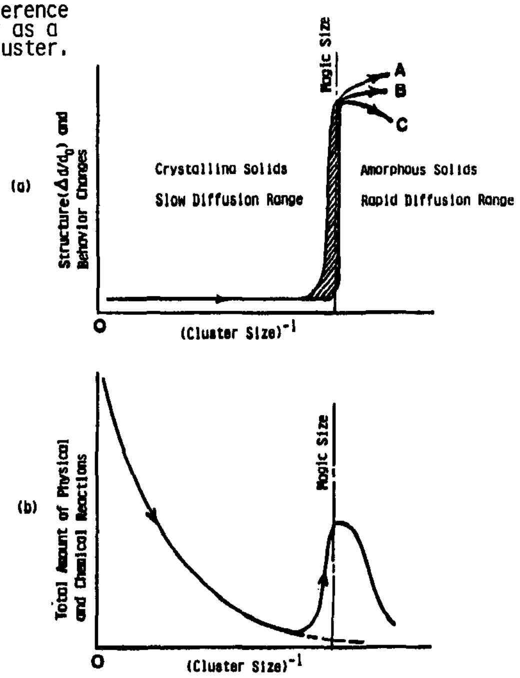


Figure 8. Size effect on behavior of materials. Behavior remarkably changes at the magic size.

mode difference in the same way. Here, it is noted that the magic size corresponds to the size at which materials behavior remarkably changes, but that the magic size is not necessarily correlated with s-Am. Namely, all of the general rules must be satisfied for s-Am even when the material is smaller than the magic size. Otherwise, large displacement of lattice atoms hardly occurs in crystalline materials with close-packed structures. It is also noted in Table 2 that the magic size in each group decreases with increasing degree of the covalent bonding and with decreasing coordination number. For example, the magic size of neo-molecules takes a value of 15 ∿ 20nmΦ for f.c.c metals and alloys, and 10 ∿ 15nmΦ for b.c.c. metals and alloys. Furthermore, the magic size of neo-molecules is ∿18nmΦ for Al_2O_3 and 3 ∿ 5nmΦ for TiC and SiC. For embryonic blocks, it is ∿2nmΦ for Si and ∿1nmΦ for diamond, respectively. Furthermore, the metallic and ionic materials show almost the same magic size in Table 2. This fact suggests that the affected range of LRF becomes almost the same in these two bonding modes, because the magic size corresponds to the affected range of LRF, as already reported[4,5].

ATOM CLUSTERS AND CRYSTAL NUCLEATION

Crystal nucleation is one of the important phenomena in materials science, but details of its mechanism have not been verified yet in spite of numerous theoretical and experimental studies. Based on the experimental results obtained by in situ experiment with high voltage electron microscopes [4,13, 14], it is concluded that the crystal nucleation is just the reverse process of s-Am of crystalline materials[4, 5,12]. From this point of view, the author already proposed "Lip-Shape Model"[4] for the nucleation and s-Am of crystalline materials. Figure 5 is the lip-shape model showing the size effect on the crystal periodicity of atoms within an atom cluster. In crystal nucleation, the following facts have been clarified experimentally[13, 14] and theoretically[4, 5]: (1)Both the specific volume free energy difference between the block and the surrounding matrix and the specific surface energy are functions of the block size. (2)The latter is always controlled by the former so that the latter should be smaller than an absolute value of the former in order to make crystal nucleation. (3) When the crystal size becomes smaller than the magic size or the degree of crystallization is decreased in the crystal whose size is the magic one, the crystal changes to an atom cluster. (4)Variable range of new functional behavior is propotional to the total density of energy states of atoms, i.e., the entropy of an atom cluster, which is expressed by the integrated volume of lower-lip in range *b* of the cluster. Namely, it takes the maximum value when range *a* is just vanished in Fig.5(c).

ATOMISTIC STRUCTURE AND BEHAVIOR OF ATOM CLUSTERS

According to the results mentioned above, the atomistic structure of an atom cluster can be estimated, as shown in Fig.6 [4,5,12]. It is noted in Fig.6 that the atomistic structure is a function of both the distance from the surface and the directions within the cluster. Namely, deviation of each atom from the periodic position takes the maximum amount as a whole at the periphery of the atom cluster, and decreases as the position approaches the center region. Furthermore,constitutive atoms form the atom-chains of zigzag shape along the radial direction, but atomic reconstruction occurs along the tangential direction of the atom cluster[4,5, 12]. As a result, the bonding potential among the atom-chains becomes quite shallow, as shown with a solid curve in the lower figure of Fig.6, so that the atom-chains easily move relatively. When these atom-chains intersect with each other during movement, the effect of coordination number in Rule III for the amorphization plays an important role, as shown in Fig.7. In Fig.7(a), when two atom-chains cross each other at point O, the coordination number increases at point O, so that the binding force of atoms around point O decreases by eq.(1). Thus, combination of these atom-chains is switched from (1-1)-(1-2) and (2-1)-(2-2) to (1-1)-O-(2-1) and (2-2)-O-(1-2), as seen in Fig.7(b). After that, these segments of atom-chains, e.g., (2-1)-O_1 ,(1-1)-O_1 ,(2-2)-O_2 and (1-2)-O_2 , easily move each other and take various positions successively, as shown in Figs.7(c) and (d). This process frequently occurs at every part of the atom-chains, so that atom-chains easily move as a whole within an atom cluster. This is a reason why, a neo-molecule can easily deformed like a liquid drop by an extremely small applied force in spite of the strong binding force along the zigzag atom-chains.

The amorphous solids generally consist of more than two different phases. In such a case, each embryonic block,i.e., an embedded atom cluster, is surrounded with embryonic blocks of another phase so that the interfacial energies of these embryonic blocks remarkably decrease[12]. As a result, the constitutive atoms of different phases are strongly combined with each other through the interfaces, as mentioned already on the binding force of boundaries, and thus mobility of the atom-chains in each block is strictly restricted. Therefore, the strength of such amorphous solids markedly increases in general even when they consist of atom clusters.

The special behavior of atom clusters, such as rapid sintering even at sub-zero temperatures and easy shape-change like liquid drops at very low temperatures, can be recognized from their atomistic structure mentioned above.

Figure 8 is schematic illustrations showing the behavior of atom clusters. Curves A,B and C in Fig.8(a) show behavior change of each individual neo-molecule, including the atomistic structure change, as a function of block size. For example, the atomistic structure follows curve A in general, i.e., the difference in interatomic distance generally increases abruptly at the magic size and then its changing rate decreases like curve A. Deformation and diffusion phenomena of the atom clusters are a function of the atomistic structure, and thus these phenomena rapidly and easily occur just like interaction among liquid drops. Namely, mechanical twinning, transformation and plastic or viscous deformation easily occur within each individual neo-molecule even at very low temperatures. Sintering and alloying among the atom clusters also rapidly occur even at sub-zero tmperatures and also even when atomic size ratio is extremly large.

Besides these diffusion phenomena, most of the material behavior, which are closely related to the atomistic structure and/or the band structure of electrons, are also markedly changed when the size becomes smaller than the magic one. Embryonic blocks also do not show any resistance for movement of magnetic domain walls when their magic size is smaller than the width of walls, as in the case of amorphous materials. Furthermore, in case the material behavior is a function of the entropy of an atom cluster, it follows curve C.

Figure 8(b) show the same size effect on the total amount of physical, e.g., mechanical polishing et al., and chemical, e.g., catalytic et al., reactions of a group of neo-molecules. The total amount in this case is determined by a product of the activity of each individual atom cluster and the density of atom clusters, and it also increases markedly at the magic size.

The results mentioned above are some examples showing behavior of both types of atom clusters. Their behavior is quite different from those of bulk materials, so that the atom clusters can be reasonably called "new materials" showing new types of functional behavior.

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