2014 Spring

"Advanced Physical Metallurgy" - Bulk Metallic Glasses -

04.08.2014

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Contents for previous class



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2.5.2 Kinetics of Glass Formation

A. Homogeneous Nucleation rate, *I* (by David Turnbull)

$$I = \frac{k_{\rm n}}{\eta(T)} \exp\left[-\frac{b\alpha^{3}\beta}{T_{\rm r}(\Delta T_{\rm r})^{2}}\right]$$
(2.4)

where

b is a shape factor (= $16\pi/3$ for a spherical nucleus)

 k_n is a kinetic constant

 $\eta(T)$ is the shear viscosity of the liquid at temperature T

 $T_{\rm r}$ is the reduced temperature ($T_{\rm r} = T/T_{\rm l}$)

 $\Delta T_{\rm r}$ is the reduced supercooling ($\Delta T_{\rm r} = 1 - T_{\rm r}$)

 α and β are dimensionless parameters related, respectively, to the liquid/ solid interfacial energy (σ) and to the molar entropy of fusion, $\Delta S_{\rm f}$

Thus,

$$\alpha = \frac{\left(N_{\rm A}\overline{V}^2\right)^{1/3}\sigma}{\Delta H_{\rm f}} \qquad \beta = \frac{\Delta S_{\rm f}}{R}$$

where

 $N_{\rm A}$ is Avogadro's number \overline{V} is the molar volume of the crystal R is the universal gas constant

A. Homogeneous Nucleation rate, *I* (by David Turnbull)



- **1)** $\eta \uparrow$ (dense random packed structure) $\rightarrow I \downarrow$
- 2) For given T and η , $\alpha^{3}\beta$ \uparrow (σ solid interfacial E & $\Delta S_{f}\uparrow/\Delta H_{f}\downarrow$) $\rightarrow I\downarrow$
- 3) $\eta \sim T_{rg} (=T_g/T_l) \& \alpha^3 \beta \sim$ thermal stability of supercooled liquid * metallic melt의 경우 : $\alpha \beta^{1/3} \sim 0.5$

* if αβ^{1/3} > 0.9, 어떤 cooling 조건에서도 균일 핵생성으로는 결정화 안됨.
* if αβ^{1/3} ≤ 0.25, 결정화 막기 어려움.

B. Growth rate of a crystal from an undercooled liquid, U

$$U = \frac{10^2 f}{\eta} \left[1 - \exp\left(-\frac{\Delta T_{\rm r} \Delta H_{\rm f}}{RT}\right) \right]$$
(2.7)

where *f* represents the fraction of sites at the crystal surfaces where atomic attachment can occur (=1 for close-packed crystals and 0.2 ΔT_r for faceted crystals). Here also we can see that *U* decreases as η increases, and will thus contribute to increased glass formability.

- **1)** $\eta \uparrow$ (dense random packed structure) $\rightarrow U \downarrow$
- 2) For given T, $I \& U \sim \eta \rightarrow T_{rg}$ or $\alpha, \beta \uparrow \rightarrow GFA \uparrow$
- 3) Local ordering 혹은 segregation 같은 atomic rearrangement 통해 f 값↓
 → U↓

* metallic melt의 경우 : αβ^{1/3} ~ 0.5 / T_{rg} > 2/3 ~ high GFA

* Pure metal: $R_c \sim 10^{10-12}$ K/s, but if $T_{rg} = 0.5$, $R_c \sim 10^6$ K/s

Based on the treatment of Uhlmann [25], Davies [26] combined the values of I and U (calculated using Equations 2.4 and 2.7, respectively) with the Johnson–Mehl–Avrami treatment of transformation kinetics, and calculated the fraction of transformed phase x in time t, for small x, as

C.
$$x = \frac{1}{3}\pi I U^3 t^4$$
 (2.8)

Substituting the values of *I* and *U* in Equation 2.8, the time needed to achieve a small fraction of crystals from the melt was calculated as

$$t \approx \frac{9.3 \eta a_o^2 x}{kT f^3 \overline{N}_v} \left[\frac{\exp\left(\frac{1.07}{\Delta T_r^2 T_r^3}\right)}{\left\{1 - \exp\left(-\frac{\Delta H_f \Delta T_r}{RT}\right)\right\}^3} \right]^{1/4}$$
(2.9)

where

 a_{o} is the mean atomic diameter

 \overline{N}_{v} is the average volume concentration of atoms, and all the other parameters have the same meaning, as described earlier

A time-temperature-transformation (T-T-T) curve was then computed by calculating the time, *t*, as a function of T_r , to transform to a barely detectable fraction of crystal, which was arbitrarily taken to be $x = 10^{-6}$.

Nucleation and Growth Rates – Poor Glass Formers



- Strong overlap of growth and nucleation rates
- Nucleation rate is high
- Growth rate is high
- Both are high at the same temperature

Nucleation and Growth Rates – Good Glass Formers



TTT curves and the critical cooling rate, R_c





FIGURE 2.3

Time-temperature-transformation (T-T-T) curves (solid lines) and the corresponding continuous cooling transformation curves (dashed lines) for the formation of a small volume fraction for pure metal Ni, and Au₇₈Ge₁₄Si₈, Pd₈₂Si₁₈, and Pd₇₈Cu₆Si₁₆ alloys.

2.6 Methods to Synthesize Metallic Glasses

2.6.1 Vapor-state Processes: expensive & slow, electronic & magnetic applications

- A. Thermal Evaporation Surface coating
 - Thermal evaporation is a common method for thin film deposition.
 - The source material is evaporated from a source by heating in a vacuum.
 - The evaporated material is then condensed on the substrate.





Heating : resistance heating (Joule effect)

First Amorphous Metals: evaporation method

Über nichtleitende Metallmodifikationen¹)

Von Johannes Kramer

(Mit 8 Figuren)

Das metallische Leitvermögen wird bekanntlich auf das Vorhandensein freibeweglicher Elektronen und damit auch ortsgebundener positiver Ionen zurückgeführt. Da nun ein nichtionisierter Metalldampf ein vollkommener Nichtleiter ist, so liegt die Vermutung nahe, daß es bei Kondensation eines solchen Dampfes gelingen müßte, nichtleitende Schichten zu erhalten, wenn Wechselwirkungen zwischen den regellos aufeinandergepackten Atomen vermieden werden könnten. Man hätte es dann mit einem Gebilde zu tun, das als völlig amorph anzusehen wäre und in seiner Konstitution am ehesten einem hochkomprimierten Gase entspräche.



Sb metal \rightarrow Bi, Ga, and Sn-Bi alloys



Fig. 1. Zerstäubungsapparatur

J. Kramer Nonconducting modifications of metals. Ann. Physik (Berlin, Germany) 19, 37 (1934)

What is Sputtering?

Surface coating

- B. Sputtering is a common method for thin film deposition.
- Process whereby atoms are ejected from a solid target material due to bombardment of the target by energetic particles.
- Ejected atoms are deposited on the substrate, form thin film.

Ref. http://en.wikipedia.org/wiki/Sputtering

Vacuum : evaporated particles can travel directly to the substrate



Radio Frequency Sputtering



✓ DC vs RF

	DC Sputter	RF Sputter
Deposition rate	faster	slower
Inert Gas Pressure	Higher	lower
Dep.material	Metal	Metal, Insulator, oxide
ETC		Improve plasma handling.

Controlling Temperature of Chuck Cooling rate of the thin film can be modulated.

Some of materials can formed to amorphous state.



Chuck temp

Surface coating



Surface coating

- PECVD (Plasma Enhanced CVD)
- LPCVD (Low Pressure CVD)
- APCVD (Atmospheric Pressure CVD)
- UHVCVD (Ultra-high vacuum CVD)
- DLICVD (Direct liquid injection CVD)
- AACVD (Aerosol-assisted CVD)
- MPCVD (Microwave Plasma CVD)
- ALCVD (Atomic Layer CVD)

Laser CVD

Formation of Amorphous Thin Film Surface

Surface coating

Calculation of Diffusion Length



Formation of amorphous

Surface coating

- Amorphous forming ability is depends on diffusion length
- ✤ Diffusion length $\propto \sqrt{Dt}$
- Deposit process is commonly forming amorphous because of low temperature and rapid growth rate
- CVD process is progressed at little high temperature, so metal do not forming amorphous generally



2.6.2 Liquid-state Processes : Rapid Solidification Process (RSP) 10⁵⁻⁶ K/s most ideal way to obtain metallic glasses, especially the bulk variety



Glass formation : stabilizing the liquid phase

First metallic glass (Au₈₀Si₂₀) produced by splat quenching at Caltech by Pol Duwez in 1960.



2.6.2 Liquid-state Processes

B. Brief Definition of Melt Spinning

A jet of liquid metal is ejected from a nozzle and impinges on the surface of a rotating substrate, where a thin layer is formed from a melt puddle and rapidly solidifies as a continuous ribbon.

Free Jet Melt spinning (FJMS) Planar Flow Melt spinning (PFMS) **Example (PFMS, Siemens) Outside of Wheel** Inside of Wheel Gas Pressure Crucible Crucible Induction coil ias Nozzle Contact zone ressure Ribbon product Melt Strip (+) 0 Rotation Copper disk Wheel Substrate (a)

Several Types of Melt Spinning Method

• Melt-spinning method

Thin film



Surface coating





Basic Concept of Electrolytic Deposition С.

Electroplating is a plating process in which metal ions in a solution are moved by an electric field to coat an electrode. The process uses electrical current to reduce cations of a desired material from a solution and coat a conductive object with a thin layer of the material, such as a metal. Electroplating is primarily used for depositing a layer of material to bestow a desired property (e.g., abrasion and wear resistance, corrosion protection, lubricity, aesthetic qualities, etc.) to a surface that otherwise lacks that property. Another application uses electroplating to build up thickness on undersized parts. However, the limited size of the product formed in one experiment puts a limitation on the usefulness of this technique to produce large quantities of metallic glasses



2.6.2 Liquid-state Processes

C. Electro-deposition Methods It was in 1950, for the first time, that Brenner et al. [38] reported the formation of an amorphous phase in electro-deposited Ni–P alloys containing >10 at.% P. The amorphous nature of the deposit was inferred from the presence of only one broad diffuse peak in the XRD pattern. These alloys have a very high hardness and consequently these are used as wear- and corrosion-resistant coatings [39].

U. S. Department of Commerce National Bureau of Standards Research Paper RP2061 Volume 44, January 1950

Part of the Journal of Research of the National Bureau of Standards

Electrodeposition of Alloys of Phosphorus with Nickel or Cobalt

By Abner Brenner, Dwight E. Couch, and Eugenia Kellogg Williams

Alloys containing nickel or cobalt and as much as 15 percent of phosphorus have been electrodeposited from solutions containing phosphites. The alloys are hard and may be further hardened by heat-treating at 400° C. The high-phosphorus nickel alloy is more resistant to attack by hydrochloric acid than pure nickel deposits. The high-phosphorus alloys are bright as deposited, but their reflectivities are lower than those of buffed coatings of pure nickel.

Powder

Gas Atomization



D. Components of Atomizer





Mechanical Metallurgy & Advanced Materials Processing Laboratory

A. Mechanical alloying/milling

: MA/ MM performed in a high-energy ball mill such as a shaker mill or planetary mill will also induce severe plastic deformation in metals. During milling, particles are fractured and cold welded together, resulting in large deformation.

Schematic Diagram of Mechanical Alloying Process





A. Mechanical alloying/milling

The milled powder particles experience heavy plastic <u>deformation</u> leading to the generation of a variety of crystal defects such as dislocations, grain boundaries, and stacking faults. These defects <u>raise the</u> <u>free energy of the crystalline system to a level higher than that of a hypo-</u> thetical amorphous phase, and consequently, the crystalline phase becomes <u>destabilized and an amorphous phase forms [41,42]</u>.

The first report of the formation of an amorphous phase by mechanical milling was in a Y–Co intermetallic compound [43] and that by mechanical alloying in a Ni–Nb powder blend [44]. Subsequently, amorphous phases have been formed in a number of binary, ternary, and higher-order systems by this method. Unlike in RSP methods, the conditions for the formation of an amorphous phase by mechanical alloying/milling seem to be quite different. For example, amorphous phases are formed, not necessarily near eutectic compositions, and in a much wider composition range. The nature and transformation behavior of the amorphous phases formed by mechanical alloying/milling also appear to be different from those formed by RSP.

A. Mechanical alloying/milling

Amorphization during Mechanical Alloying



Magnesium Technology Innovation Center

B. Hydrogen-induced Amorphization

- Yeh et al. [45] reported the formation of an amorphous metal hydride Zr₃RhH_{5.5} by <u>a reaction of hydrogen with a metastable crystalline Zr₃Rh compound at sufficiently low temperatures (< about 200°C). A similar amorphous hydride phase was also reported to form when the amorphous Zr₃Rh alloy obtained in a glassy state was also reacted with hydrogen.</u>
- Aoki [46] has reported that hydrogen-induced amorphization is possible in many binary metal compounds.

C. Multilayer Amorphization

- An amorphous phase was found to form when thin metal films (10–50 nm in thickness) of La and Au were allowed to interdiffuse at relatively low temperatures (50°C–100°C). Similar to the case of hydrogen-induced amorphization, here also the large asymmetry in the diffusion coefficients of the two elements was found to be responsible for the formation of the amorphous phase [47]. Since then, a large number of cases where multilayer amorphization occurs have been reported.
- **Ex)** cold rolling of thin foils of Ni and Zr, and then annealing them at a low temperature.

Solid-State Diffusional Amorphization

- Alternate layers of crystalline metallic films ('diffusion couples') interdiffuse under isothermal conditions, with the eventual amorphization of the entire multilayer.
- Couple: late transition metal with early transition metal ex. Au-La, Au-Zr, Au-Y, Cu-Zr, Cu-Er, Ni-Er, Ni-Ti, Ni-Hf, Fe-Zr, Co-Zr, Ni-Zr
- ✓ Low temperature annealing below the crystallization temperature (the nucleation or growth of crystalline phases cannot occur)

* Diffusion in multiple binary system



Solid-State Diffusional Amorphization

Schematic Diagram



(A) Direct nucleation of the amorphous phase

(B) Substantial mutual dissolution of the parent metals leading to unstable solid solutions

Two Main Attributes

 A strong thermodynamic driving force

i.e. a large negative heat of mixing



Diffusional asymmetry

i.e. one element diffuses anomalously fast in the other, but not vice versa



D. Pressure-induced Amorphization

• Alloys in the systems Cd–Sb, Zn–Sb, and Al–Ge were subjected to high pressures when they <u>formed unstable crystalline phases and then decayed in a</u> <u>short time to amorphous phases [50]</u>. An amorphous phase was also found to form in Cu–12–17 at.% Sn alloys when they were heated to high temperatures in a confined pressure, and turning off the power suddenly.

e. Amorphization by Irradiation

A number of intermetallics, for example, NiTi, Zr₃Al, Cu₄Ti₃, CuTi₂, FeTi, etc., have been amorphized by irradiation with high-energy electrons, heavy ions, or fission fragments [18]. It is only intermetallics, and not solid solutions, that have been amorphized this way. Several different criteria have been proposed for this purpose, which include low temperature, high doses, high dose rates, intermetallics with an extremely narrow homogeneity range, permanently ordered compounds (i.e., intermetallics which are ordered up to the melting temperature and do not show an order–disorder transformation), which also have high-ordering energies, destruction of long-range order by irradiation, etc. Fecht and Johnson [52] have analyzed the fundamental issues involved in the amorphization of intermetallics by irradiation methods.

Preparation of amorphous materials by irradiation Two kinds of irradiation effects

• Laser/electron irradiation:

Small area melting \rightarrow cooling \rightarrow amorphous layer/crystalline



• Neutron and heavy ion irradiation:

Atomic displacement \rightarrow recovery \rightarrow amorphous phase

> Mechanism of irradiation amorphization:

- The kinetic knock-off of atoms from their lattice positions
- Very high temperature is expected in a very small volume during a short time (ps), which causes melting of material in a local small point.

> Two opposing radiation-induced processes can be operative:

- **Radiation-induced chemical disordering** of atoms on lattice sites will tend to promote amorphization;
- Radiation-induced defect migration will tend to restore ordering.
- ➡ The irradiation be <u>carried out at sufficiently low temperature</u> to suppress the defect migration.

방사선 결함: 고에너지 입자와 재료의 충돌에 의한 결함

▶ 고에너지 입자 충돌에 의해 발생되는 가장 기본적인 결함 : Vacancy & Interstitial (Frenkel pair)



20keV Fe displacement cascade in bcc Fe at 600K

http://www.youtube.com/watch?v=0btHd_8JFV4

* A primary knock-on atom (PKA) displaces neighbouring atoms, resulting in <u>an atomic displacement</u> <u>cascade</u>, leading to formation of point defects and defect clusters of vacancies and interstitial atoms.

Seeger et al., Proc. Symp. Radiat. Damage Solids React. 1 (1962) 101-1056.

방사선 결함: 고에너지 입자와 재료의 충돌에 의한 결함



S. Zinkle, Defects, deformation and damage in structural materials, 2012

Sample Preparation : Surface Damage

Ion beam induced amorphous formation in Silicon (100)



Y.W. Kim, Metals and Materials International, 7, 499 (2001)

The schematic diagram of High Energy Electron beam accelerator



The making method of amorphous materials by Irradiation



Electron beam irradiation is heating the mixture of powder.

✤ The temperature of substrate is so low that surface is super-cooling.



Surface : Amorphous alloy

Surface gloss, Hardness, corrosion resistance,

Substrate : Cu(or Ti, Fe) alloy

Ductility, limited size of amorphous materials,

It is possible to make mass production and reduce weight

f. Severe Plastic Deformation : Intense deformation at low temperatures (SPD methods)



Schematic diagrams showing the (a) equal channel angular pressing (ECAP) and (b) high-pressure torsion (HPT) processes.

HPT process: Equivalent strain induced on sample



HPT: severe plastic deformation, but Inhomogeneous process

f. Severe Plastic Deformation : Intense deformation at low temperatures (SPD methods)

• The SPD methods have some advantages over other methods in <u>synthesiz-</u> ing ultrafine-grained materials. Firstly, ultrafine-grained materials with highangle grain boundaries could be synthesized. Secondly, the samples are dense and there is no porosity in them since they have not been produced by the consolidation of powders. Thirdly, the grain size is fairly uniform throughout the structure. Lastly, the technique may be applied directly to commercial cast metals.

• However, the limitations of this technique are that the minimum grain size is not very small (typically it is about 200–300nm), and that amorphous phases or other metastable phases have not been synthesized frequently. But, these methods are very useful in producing bulk ultrafine-grained materials.

The methods of SPD described above have two drawbacks. Firstly, forming machines with large load capacities and expensive dies are required. Secondly, the productivity is relatively low.

g- Accumulative Roll Bonding (ARB process)

: 2 sheets of the same material are stacked, heated (to below the recrystallization temperature), and rolled, bonding the 2 sheets together. This sheet is cut in half, the 2 halves are stacked, and the process is repeated several times. Compared to other SPD processes, ARB has the benefit that it does not require specialized equipment. However, the surfaces to be joined must be well cleaned before rolling to ensure good bonding.

