Office of Naval Research International Field Office

29. Zr-TM-Al Bulk Metallic Glass

Dr. Jun Kameda

July 17, 2003

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Contents:

Key Words: Bulk metallic glass (BMG), Combined ladle arc melting/squeeze casting (LASC) method, Hruby factor, Crystalline inclusion, Controlling of shear band structure, Fatigue properties

1. Summary

Dr. Yokoyama at Himeji Institute of Technology has recently invented a combined ladle arc melting/squeeze casting (LASC) method to fabricate bulk metallic glass (BMG) with improved mechanical properties. He traveled to Boston MA, Washington DC and Charlottesville VA under the Visitor Support Program (VSP) of the ONRIFO on December 1-12, 2002. The major objective was to seek U.S. collaborators for a NICOP proposal on BMG. He attended the MRS-Fall Meeting, visited with Dr. Pohanka, Director of Materials S & T Division (ONR 332) and Prof. Poon, University of Virginia, who is a project leader of Fe-based BMG program supported by the Defense Advanced Research Program Agency (DARPA). Dr. Yokoyama also gave an invited seminar at ONRIFO-Asia on April 14. Dr. K. Goretta, AOARD, and Dr. H-Y. Yu, AROFE have a strong interest in his BMG work. This report contains Yokoyama's presentation.

2. Background

BMG alloys have unique mechanical properties such as high strength and low modulus, which allow BMG to accommodate high elastic energy. It is empirically known that there are three conditions necessary for forming metallic glasses, i.e., negative heat of formation, large atom size difference and low liquidus temperature. The formability and phase stability of BMG alloys are related to the Hruby factor defined by $K_{gl} = (T_x - T_g)/(T_l - T_x)$ where T_g, T_l and T_x are the glass transition, liquidus and crystallization temperature. Among many BMG systems, Zr-TM-Al (transitional metals, TM = Cu, Ni, Co) alloys have better glass formability and phase stability of BMG and have widely been studied. Structural amorphous material projects are currently undergone to develop structural Fe-, Al- and Zr-based BMG alloys with the support of the Department of Navy, Airforce and Army.

3. Assessment

Yokoyama's group is attempting systematic studies on processing BMG in order to improve the mechanical properties under monotonic and cyclic loading, which are a critical issue for advancing its application. His recent work on fatigue properties of BMG is intriguing. This project deserves possible NICOP but he still is seeking U.S. partners for the NICOP.

4. Points of Contact

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Zr-TM-Al BMG

Himeji Institute of Technology
Yoshihiko Yokoyama

April 15, 2003

ONRIFO-Asia

Outline

- 1) Preparation Methods
- 2) Zr-Cu-Al Alloy System
- 3) Zr-Cu-Al-TM Alloy Systems
- 4) Zr-Cu-Ni-Al Alloy System
- 5) Controlling of Shear Bands Structure
- 6) Fatigue Properties of Zr-TM-Al BMG
- 7) Focus in Future

1) Preparation Methods

- 1-1) Purity of Materials

  low oxygen Zr (<45ppm)

- 1-2) Melting Process

  homogeneous mixing (alloying)

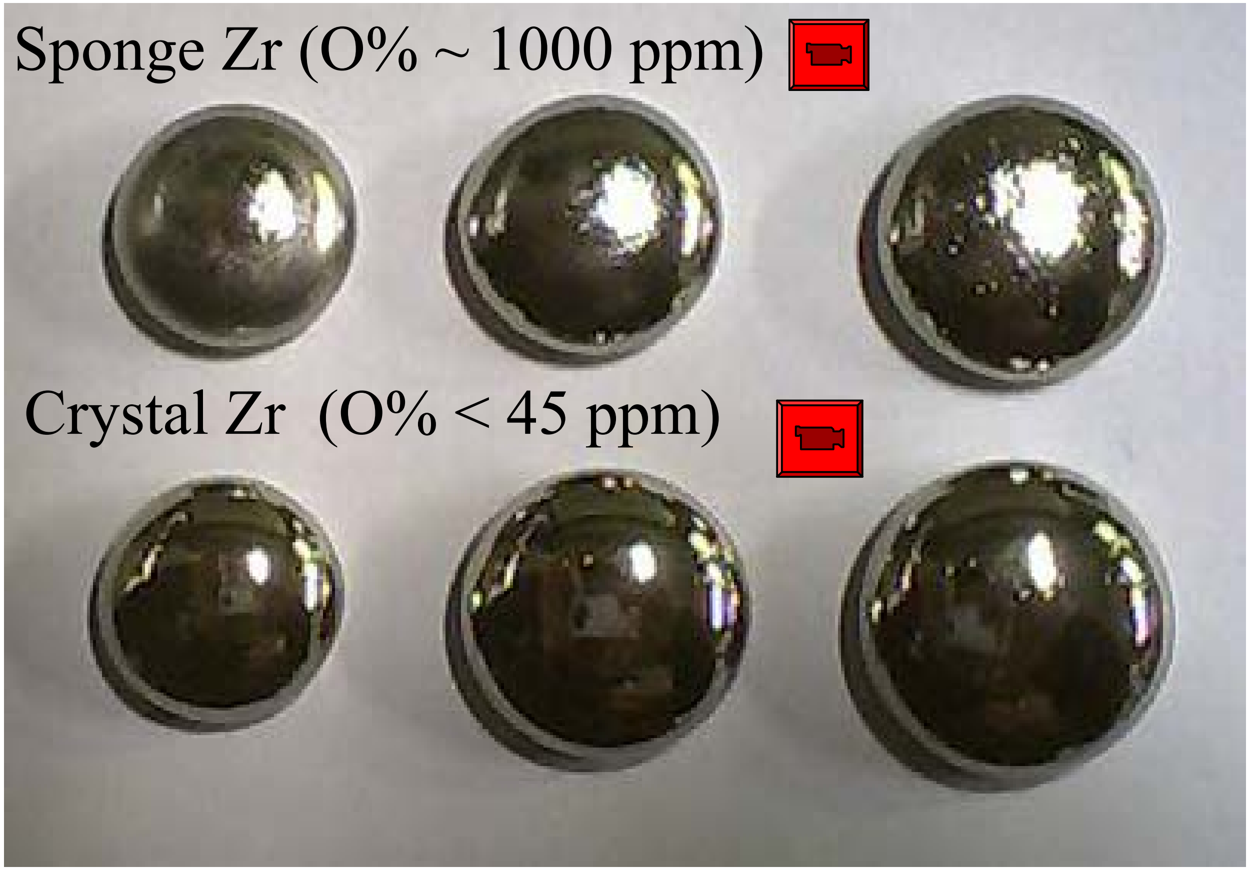
- 1-3) Casting Process

  complete melting state

- 1-4) Mechanical Finishing

  surface crystallization

1-1) Purity of Materials

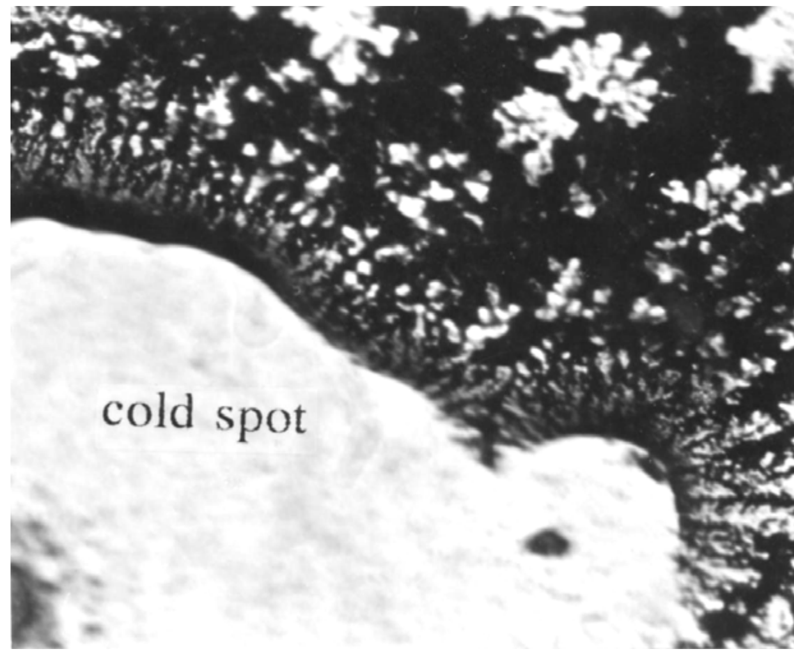


1-2) Melting Process

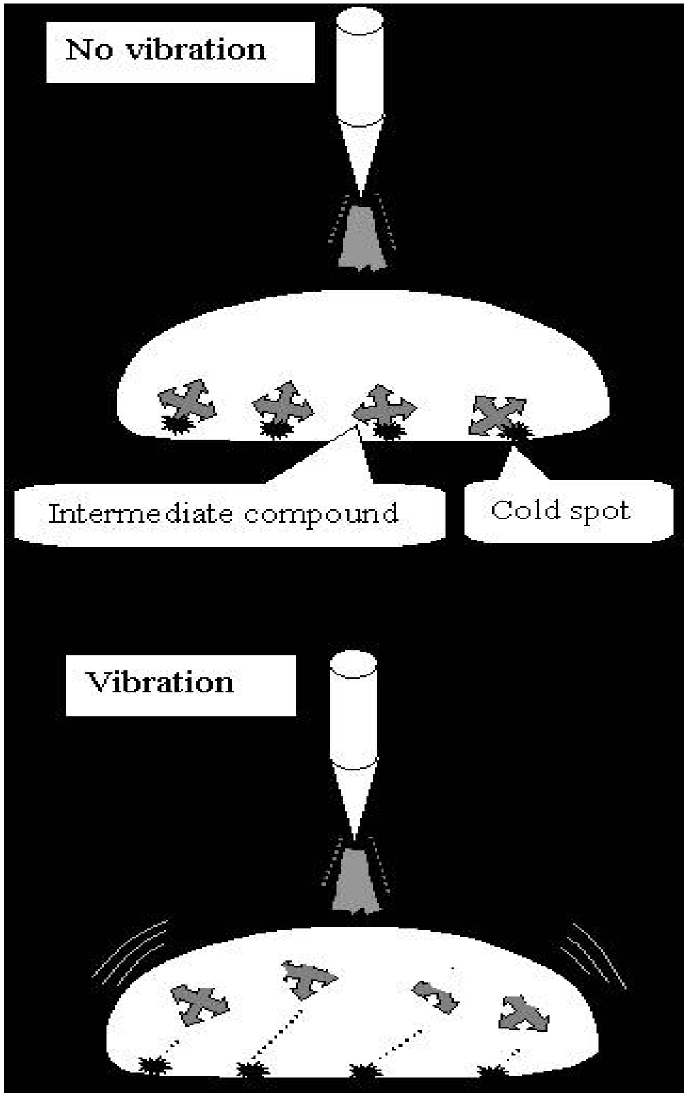
- Arc Melting Furnace
  difficult to obtain complete melting state

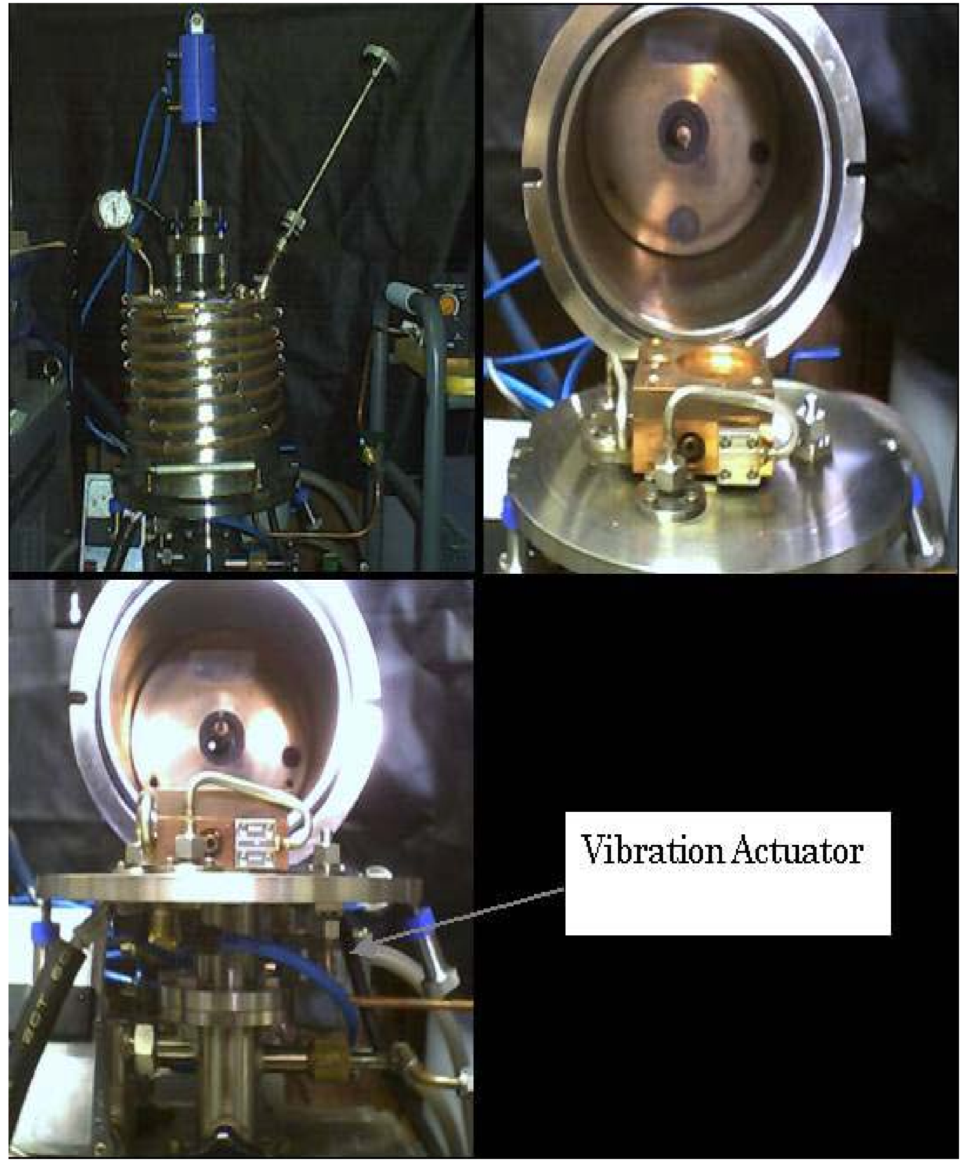
Cold Spot : Spring of Free Nuclei

Bottom : ~~complete melting~~



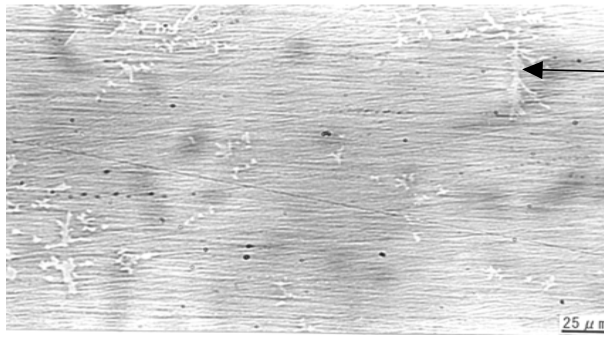
- Vibration…


No vibration
Intermediate compound
Cold spot
Vibration


Vibration Actuator

Crystalline inclusions

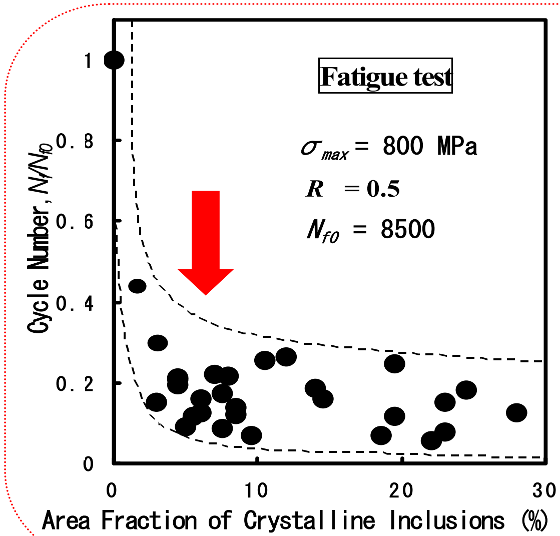
$Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk amorphous alloy

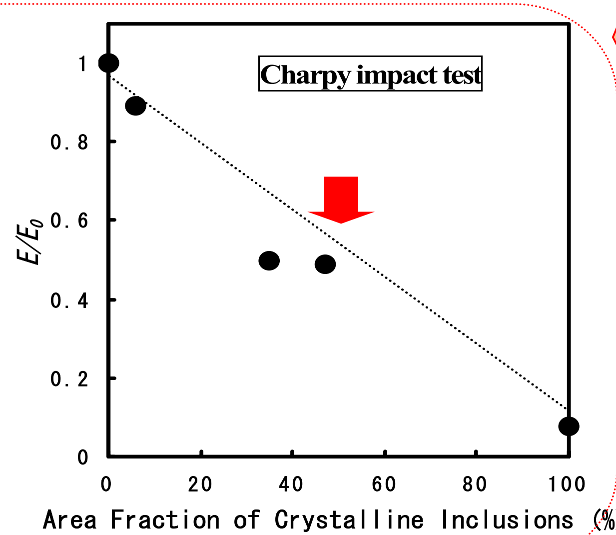


$Zr_{51}Cu_{29}Al_{20}$ (τ_3)

Crystallization enhanced by oxygen !!

The effect of crystalline inclusi



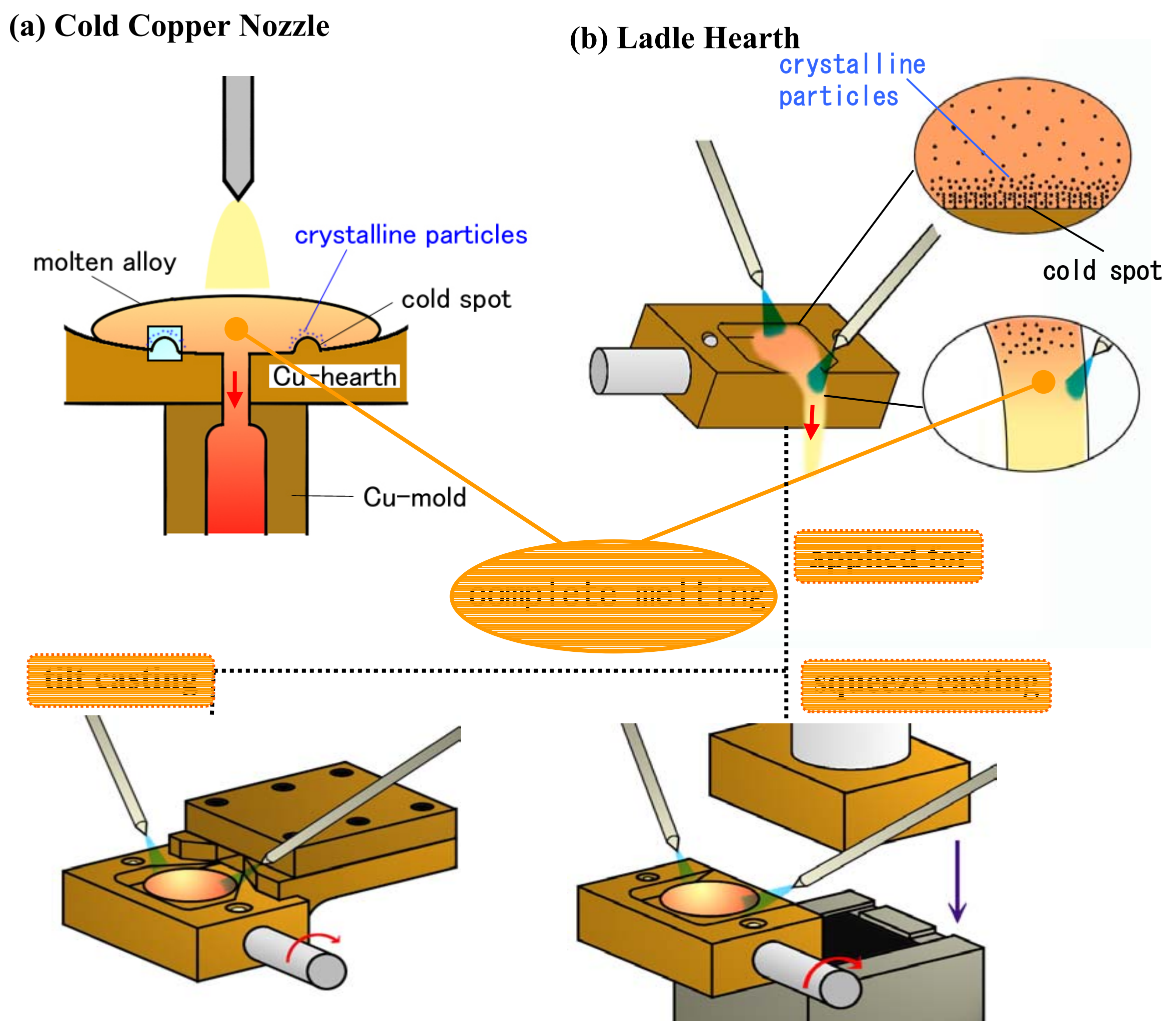


1-3) Casting Process

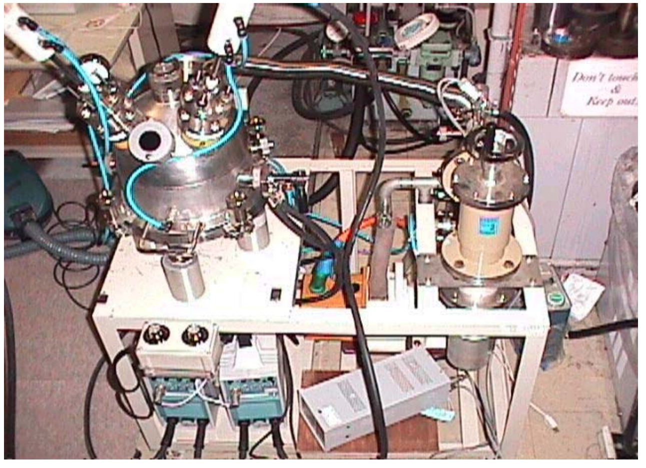
Complete melting state before casting

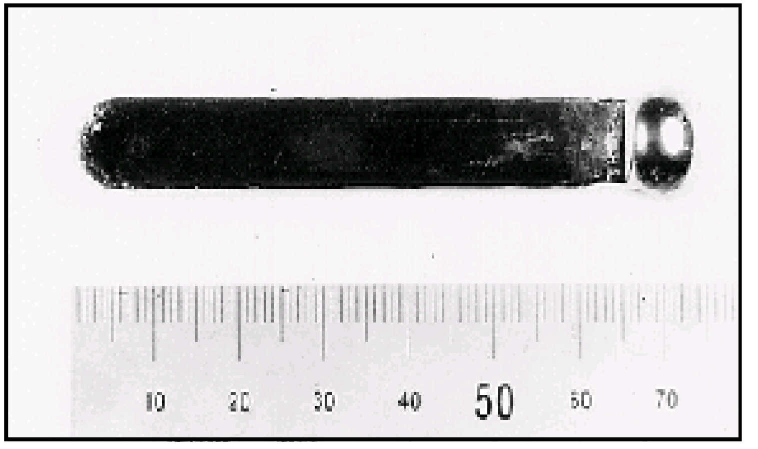
a) Cold Copper Nozzle
b) Ladle Hearth

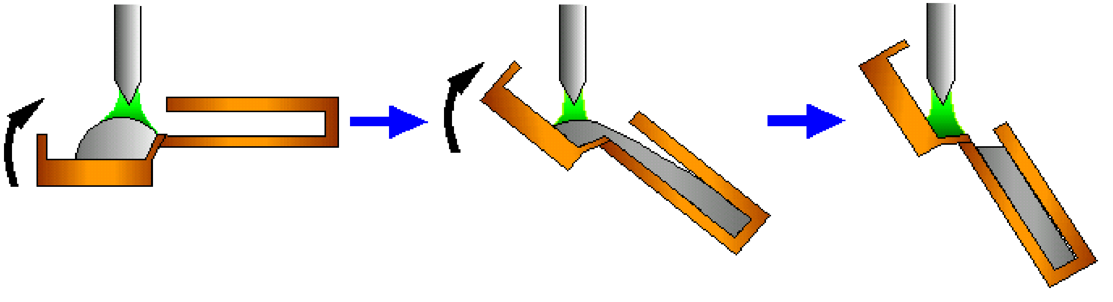
How to control the site of cold spot



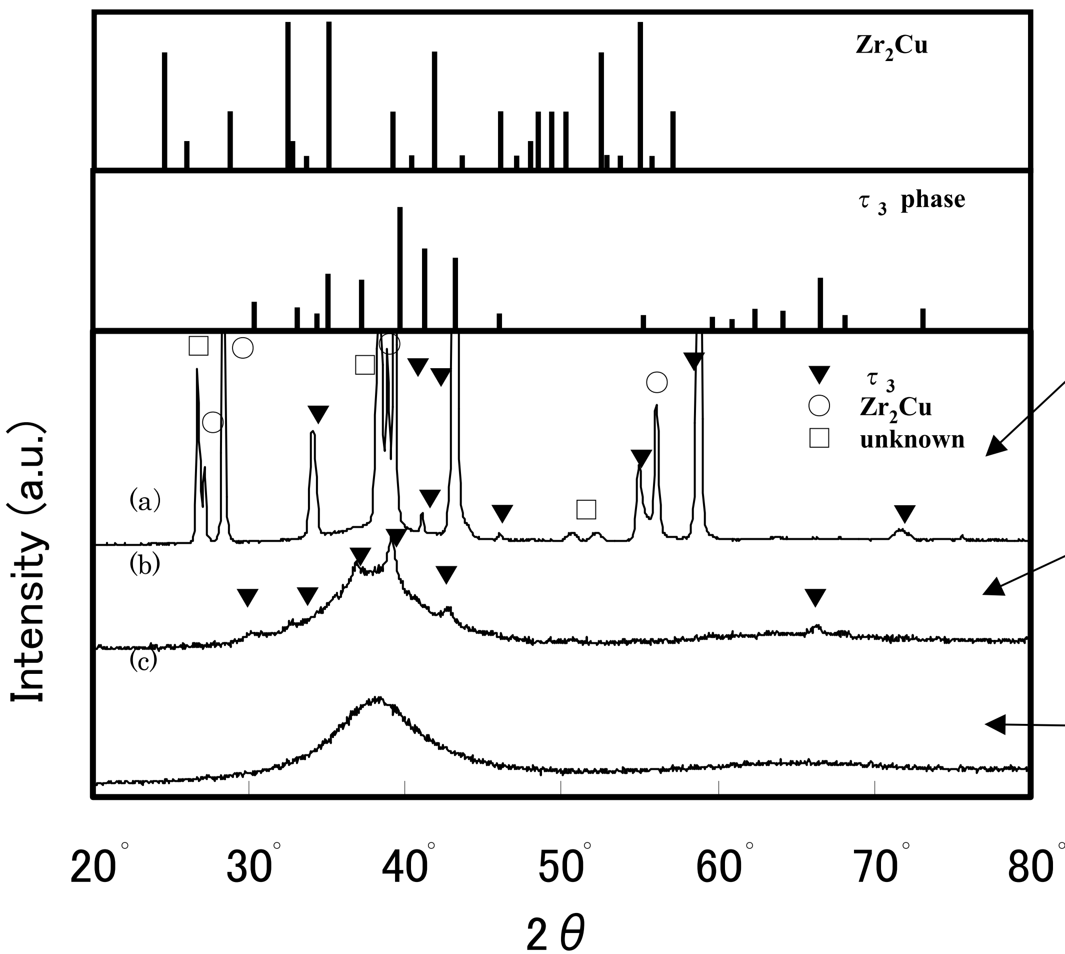
1-3-b) Ladle Hearth (tilt)







1-4) Mechanical Finishing



Crystallized surface

Surface crystallization were easily occurred by contamination on mold surface.

After mechanical grinding

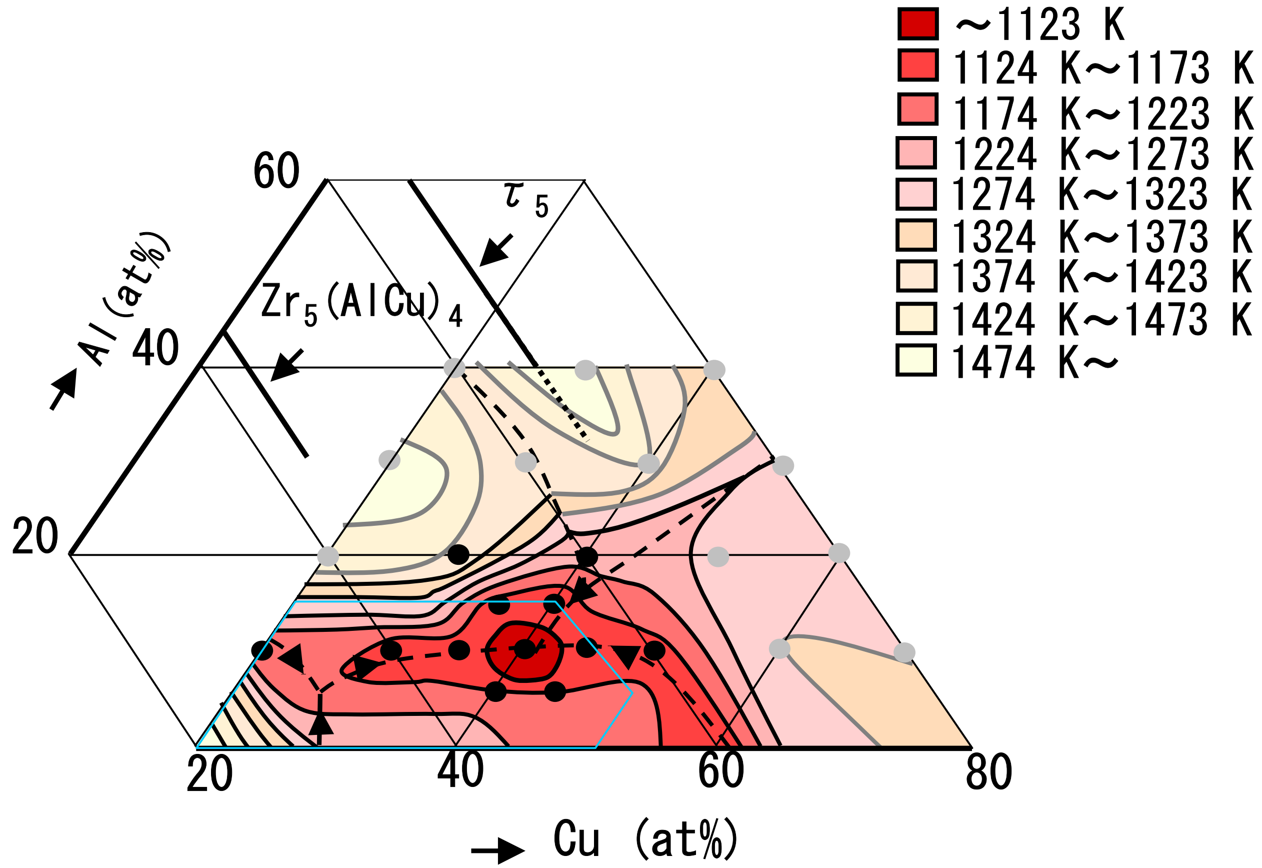
The X-ray spectra was taken from after rough mechanical grinding with 20um per pass

After polishing

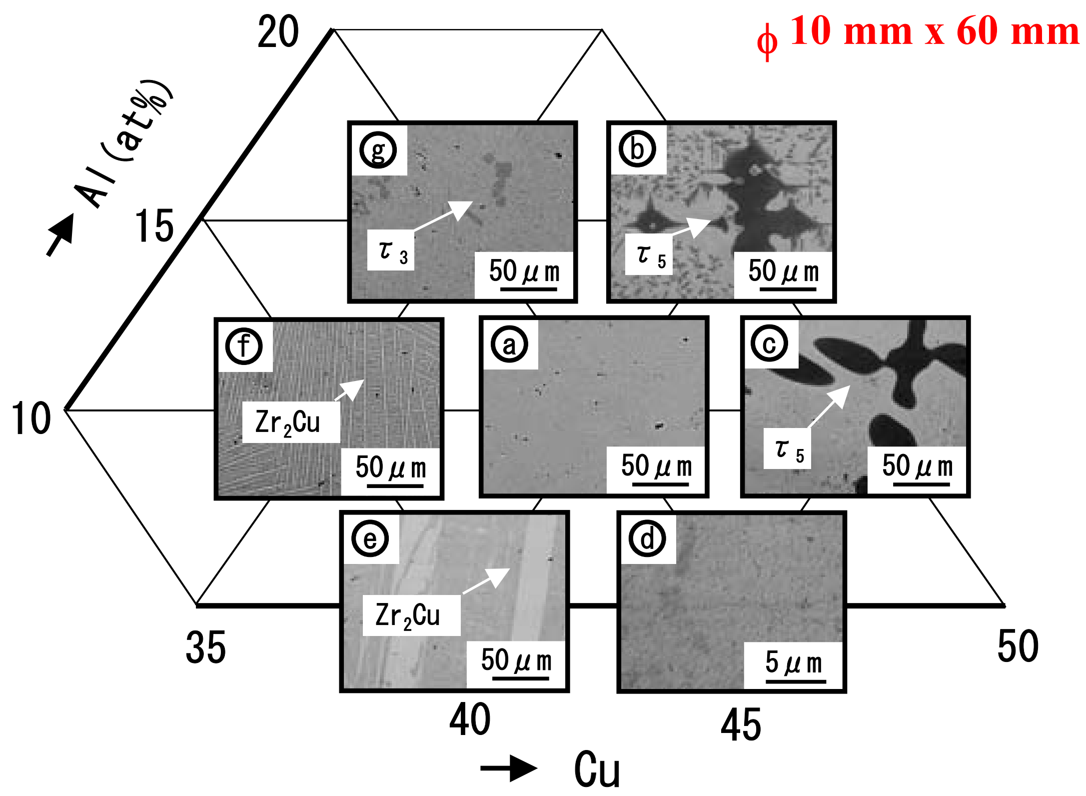
1) Conclusion in Preparation Methods

- Crystalline inclusions in BMG have originated from nucleation at cold spot.
- Pseudo float melting process, to avoid cold spot formation, can be achieved by using ladle hearth and cold copper nozzle technique.
- Mechanical forming might be cause crystallization on surface of BMG.

2) Zr-Cu-Al Alloy System



Cast structure of ϕ10 mm rod



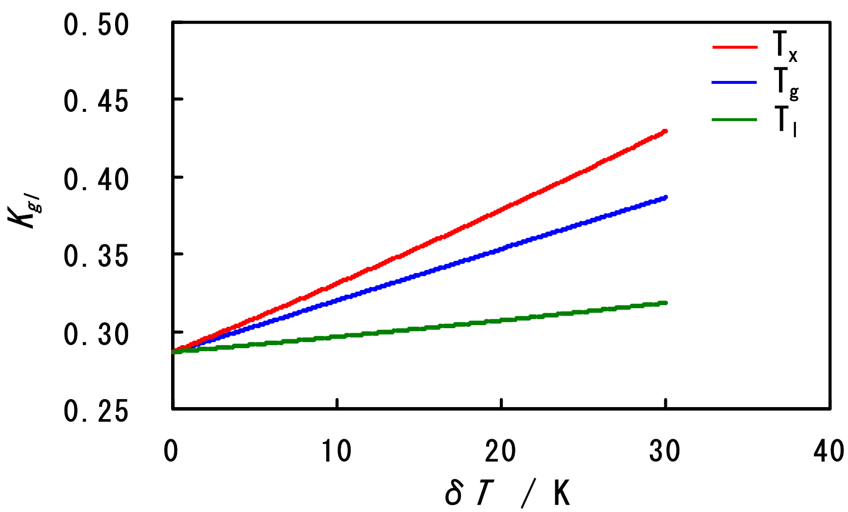
Hruby factor

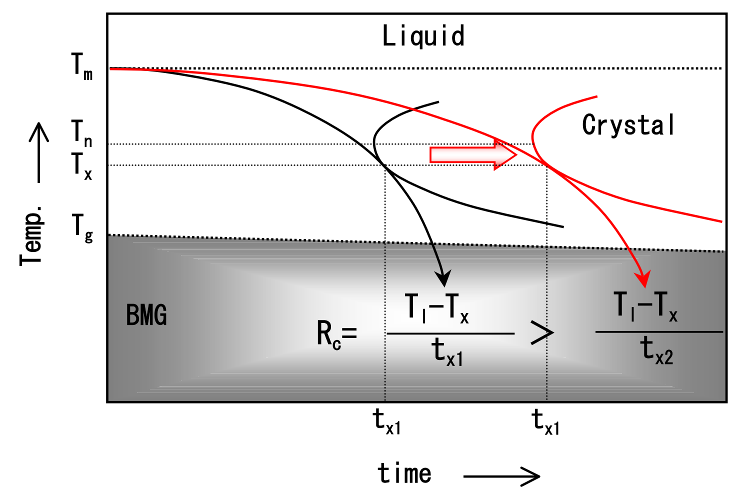
$$K_{gl} = \frac{T_x - T_g}{T_l - T_x}$$

T_g: glass transition temperature

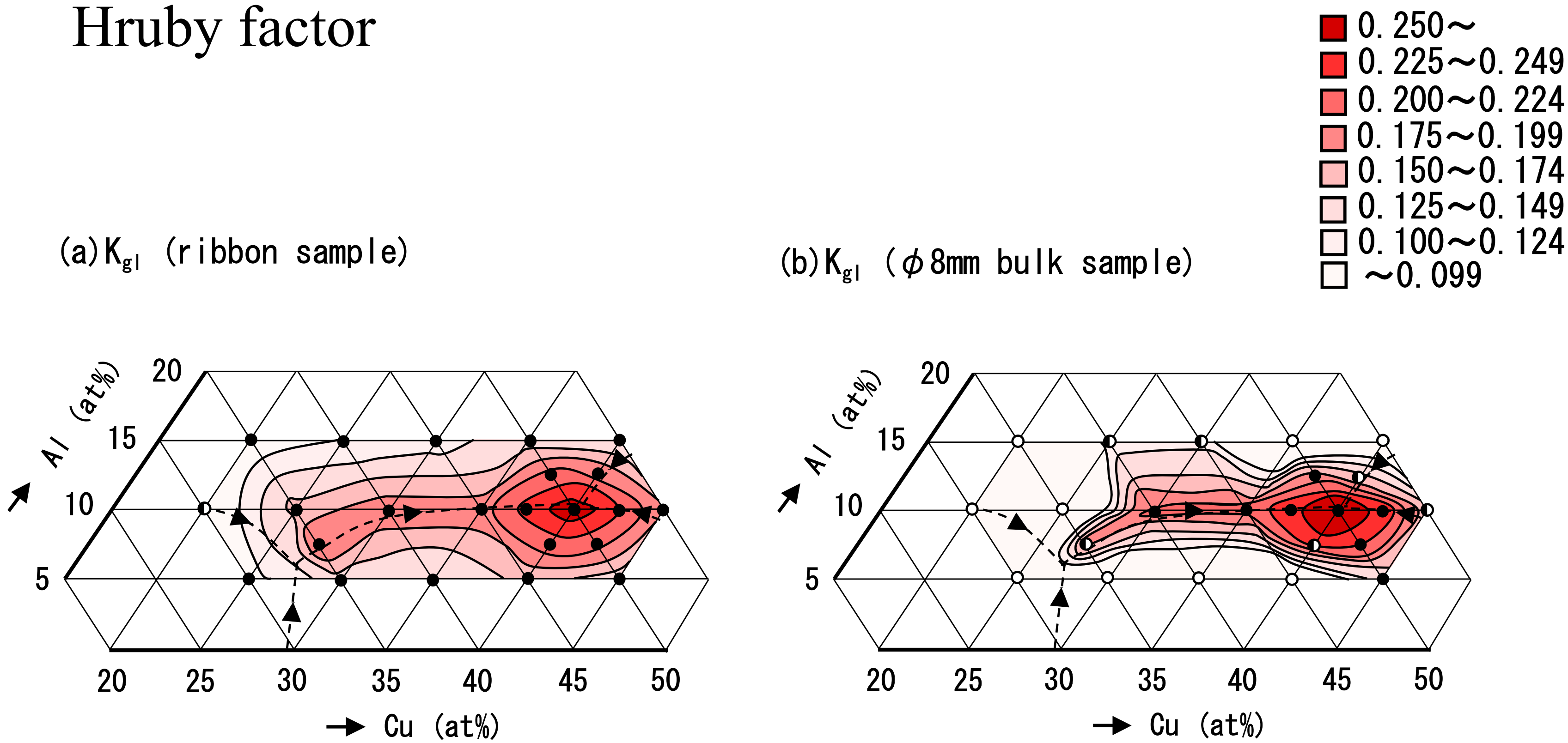
T_x: crystallization temperature

T_l: liquidus line temperature

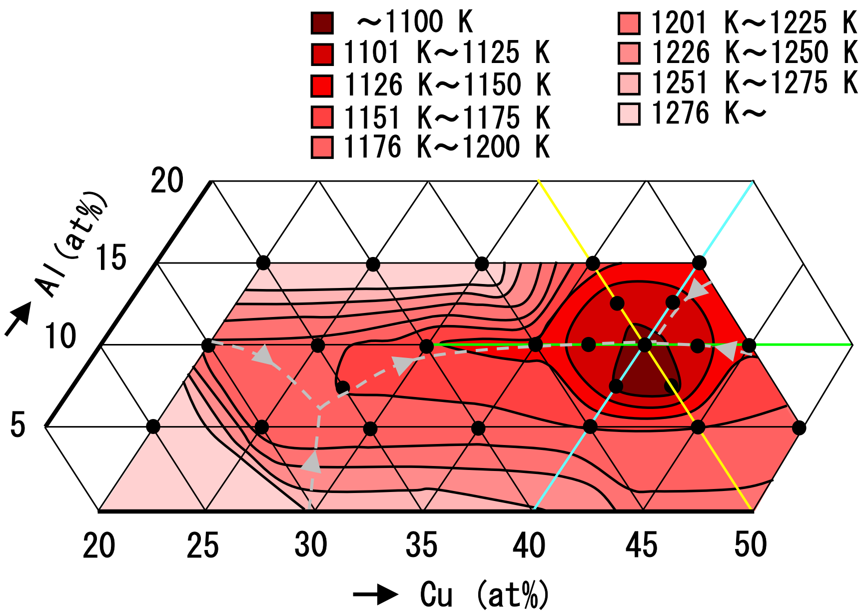


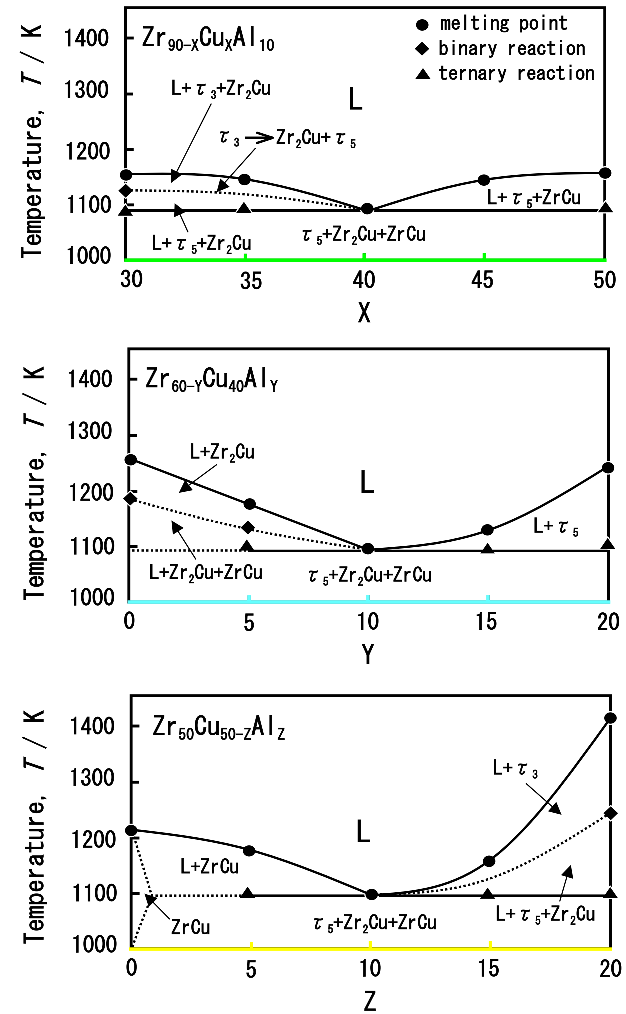


Hruby factor

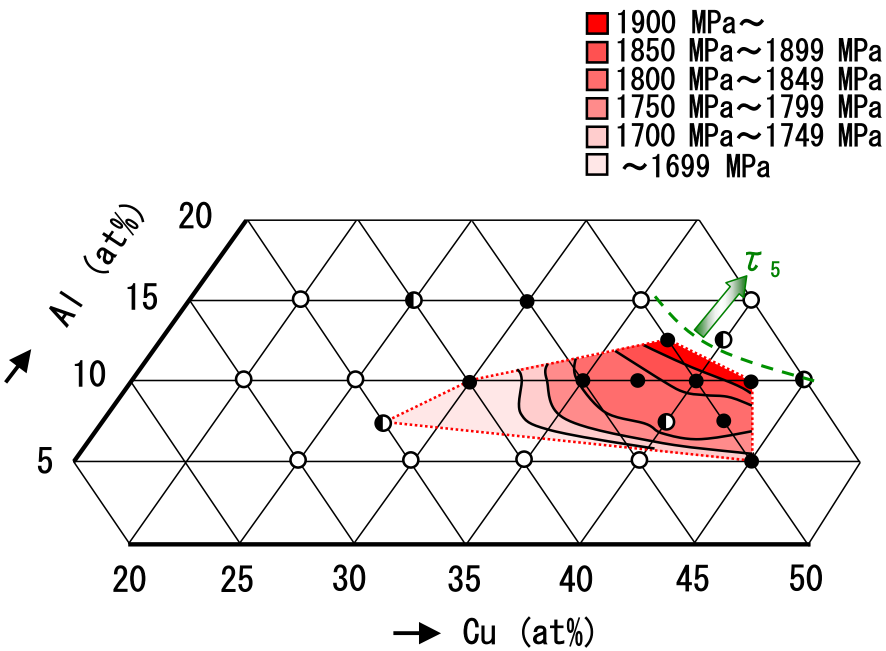


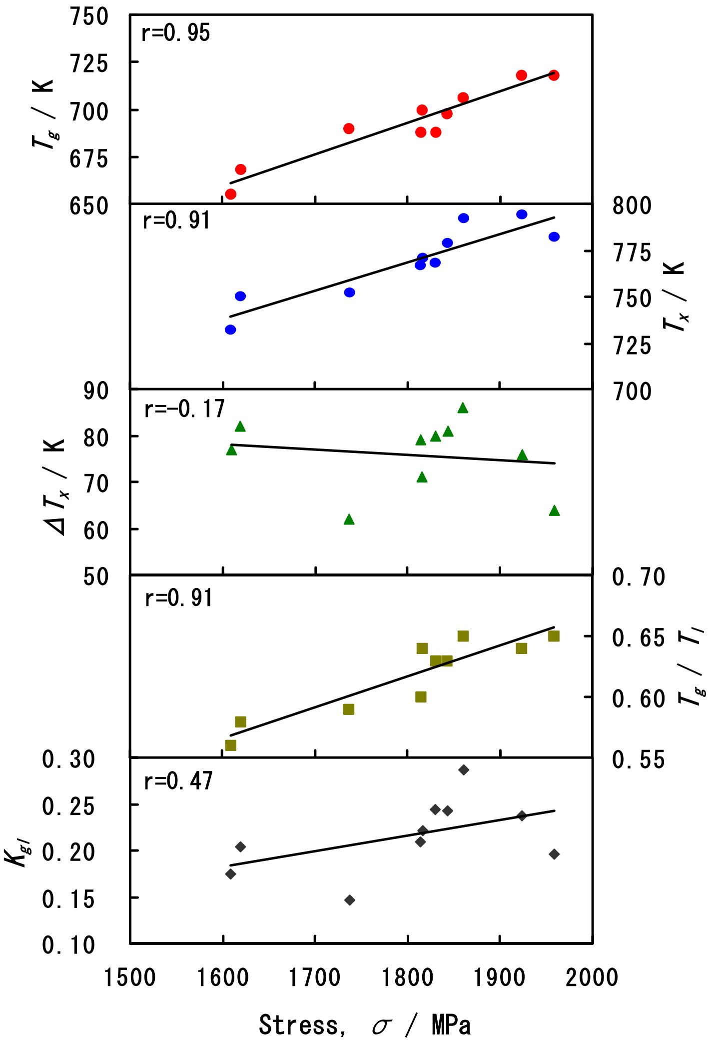
Glass formability = Phase diagram



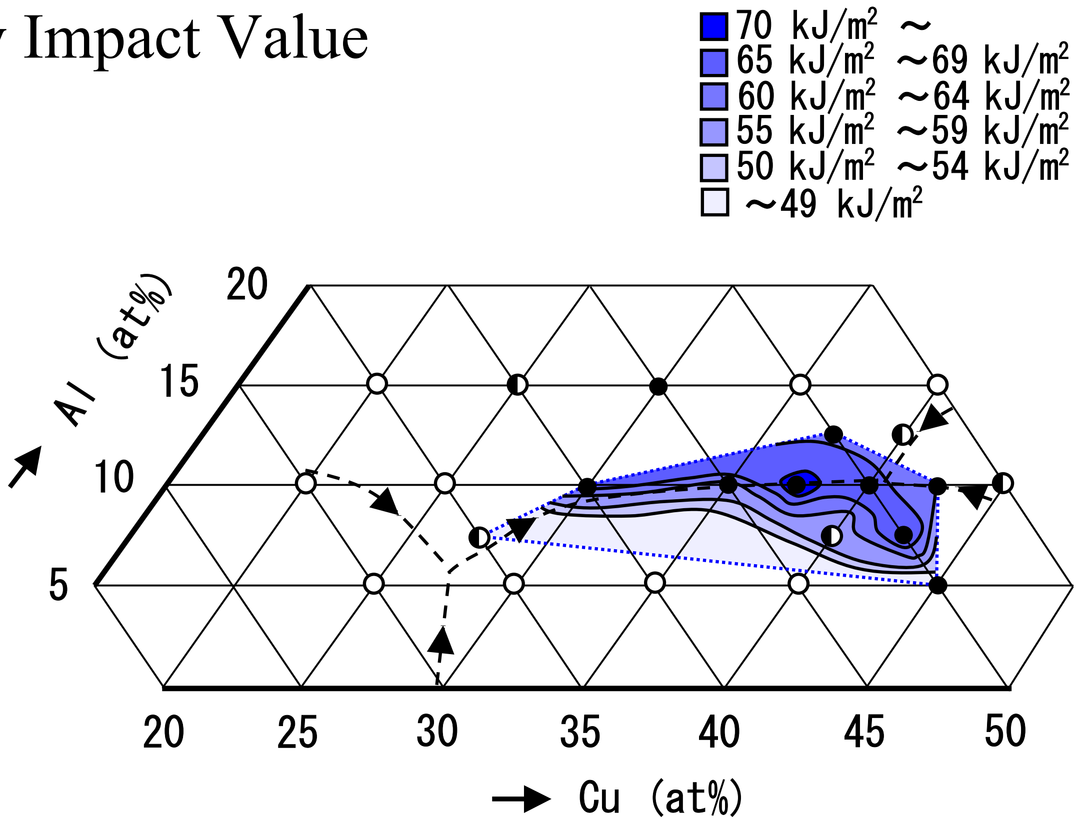


Tensile strength





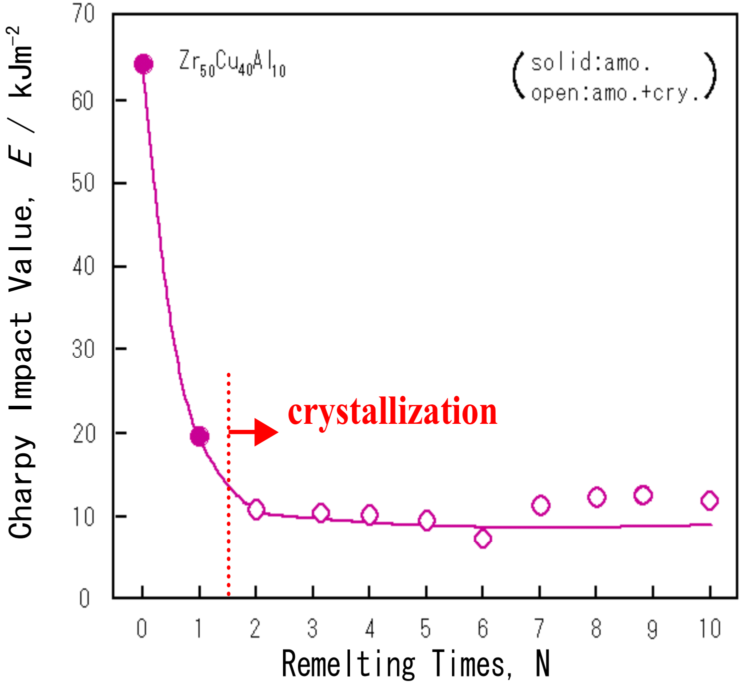
Charpy Impact Value



2) Conclusion in Zr-Cu-Al Alloy System

- Zr-Cu-Al alloy system has a wide compositional area with low melting temperature around Al=10 at% compositional line.
- $Zr_{50}Cu_{40}Al_{10}$ alloy, which composition is close to ternary eutectic point, has superior glass forming ability and mechanical properties.
- Phase diagram is significant factor to control the structure of BMG.

3) Zr-Cu-Al-TM Alloy System



Oxygen embrittlement

↓

Small additive element to avoid oxygen embrittlement

↓

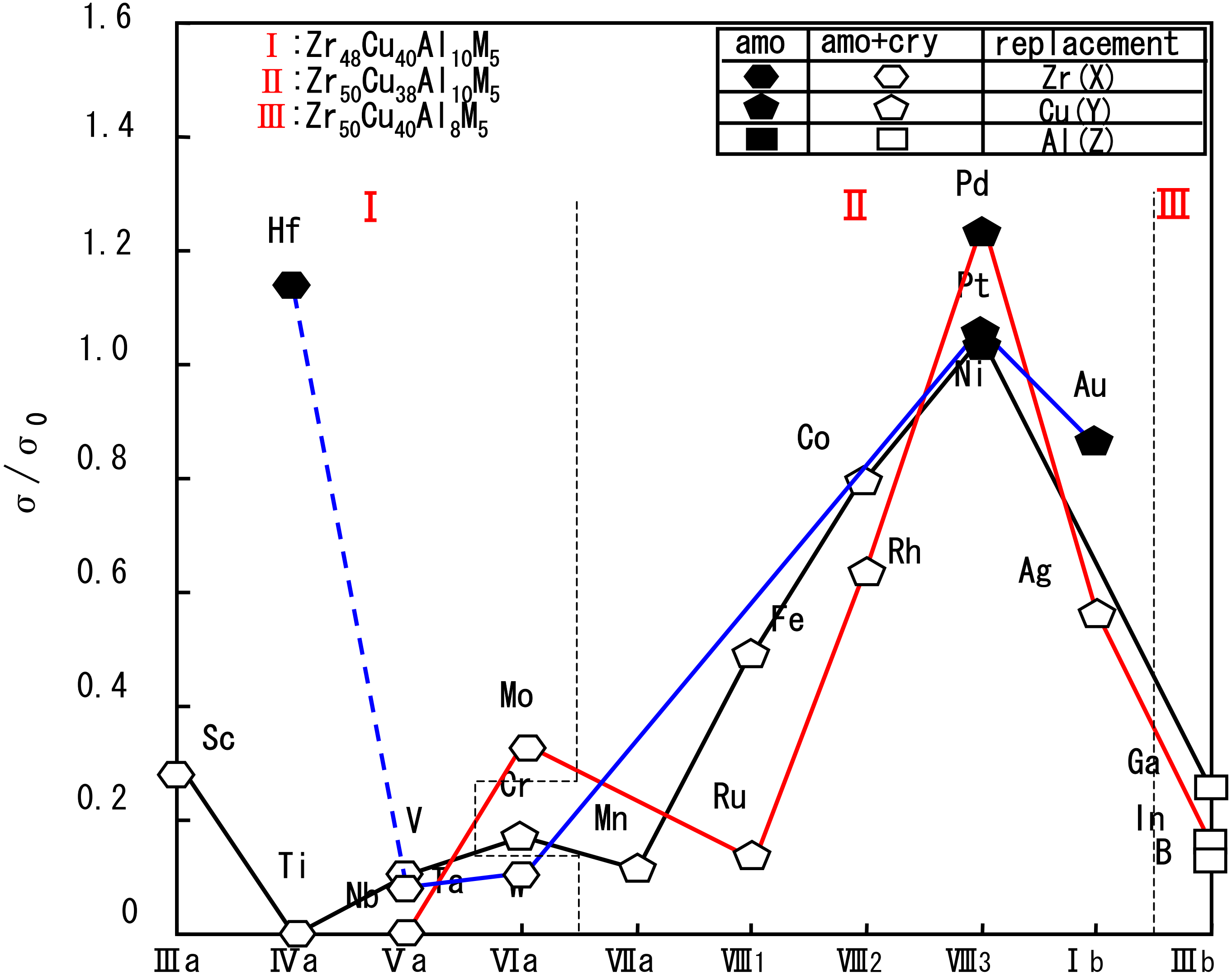
$Zr_{50}Cu_{40}Al_{10}$ BMG alloy

Zr→Ti,Hf,Nb,Mo,W,Ta,..

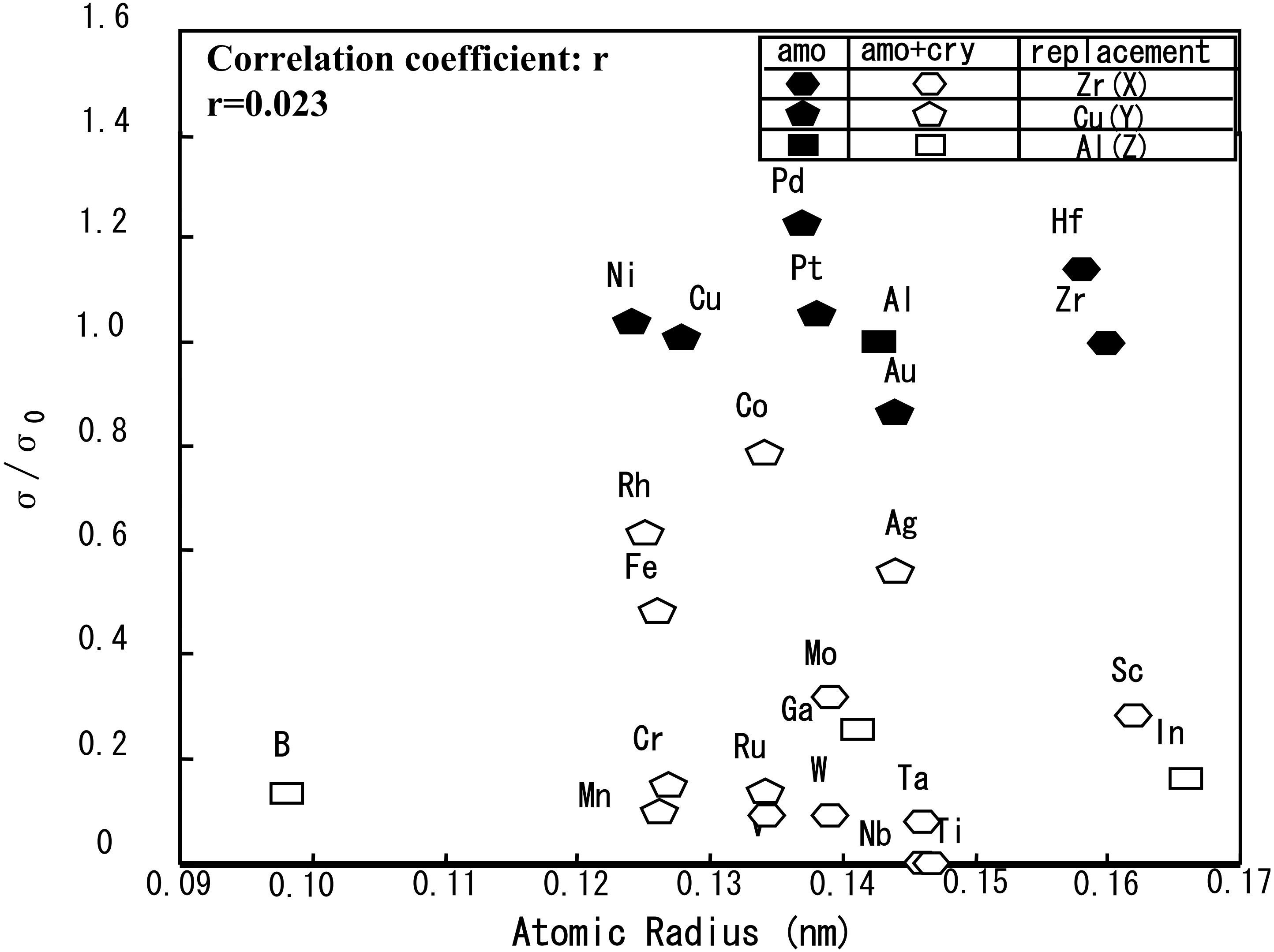
Cu→Ag,Au,Ni,Pd,Pt,Rh,..

Al→B,Ga,In,Si,Sn,Ge,..

[Zr-Cu-Al-M (M=5at%) Bulk Glassy Alloys]



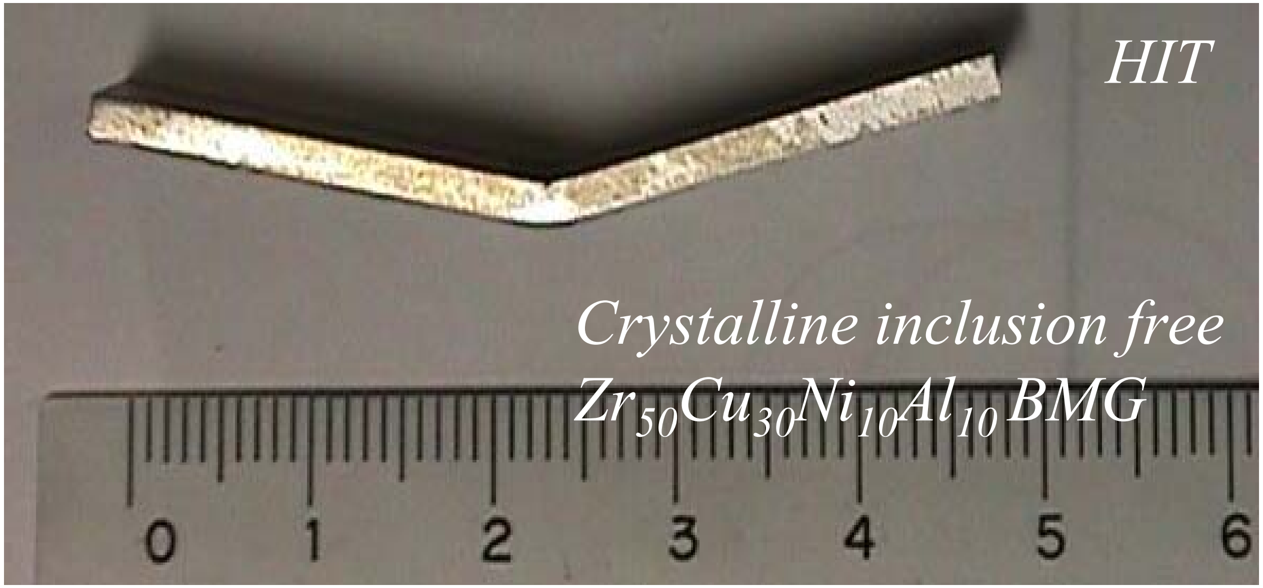
[Zr-Cu-Al-M (M=5at%) Bulk Glassy Alloys]



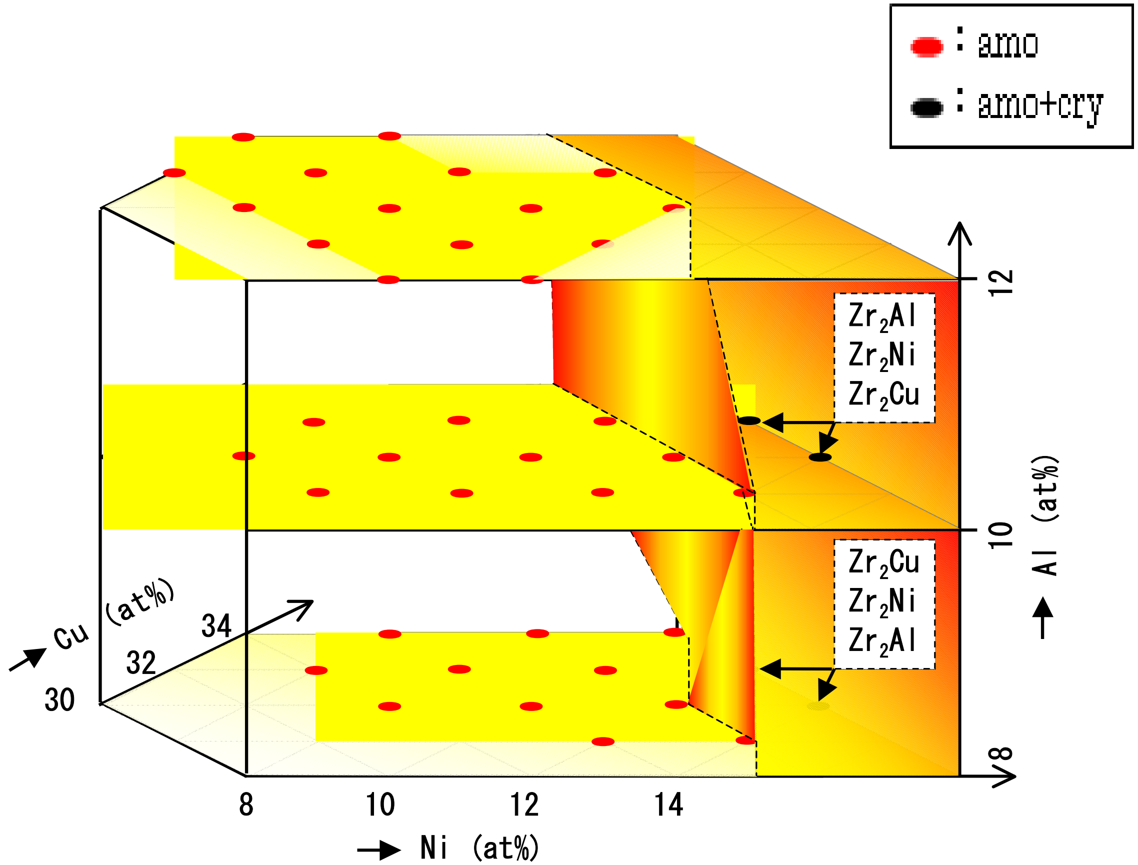
3) Conclusion in Zr-Cu-Al-M Alloy System

- $Zr_{50}Cu_{40}Al_{10}$ BMG shows significant oxygen embrittlement phenomena.
- The effect of an additive element for $Zr_{50}Cu_{40}Al_{10}$ bulk glassy alloy on enhancing the tensile strength depends on the additive's periodicity in the periodic table.

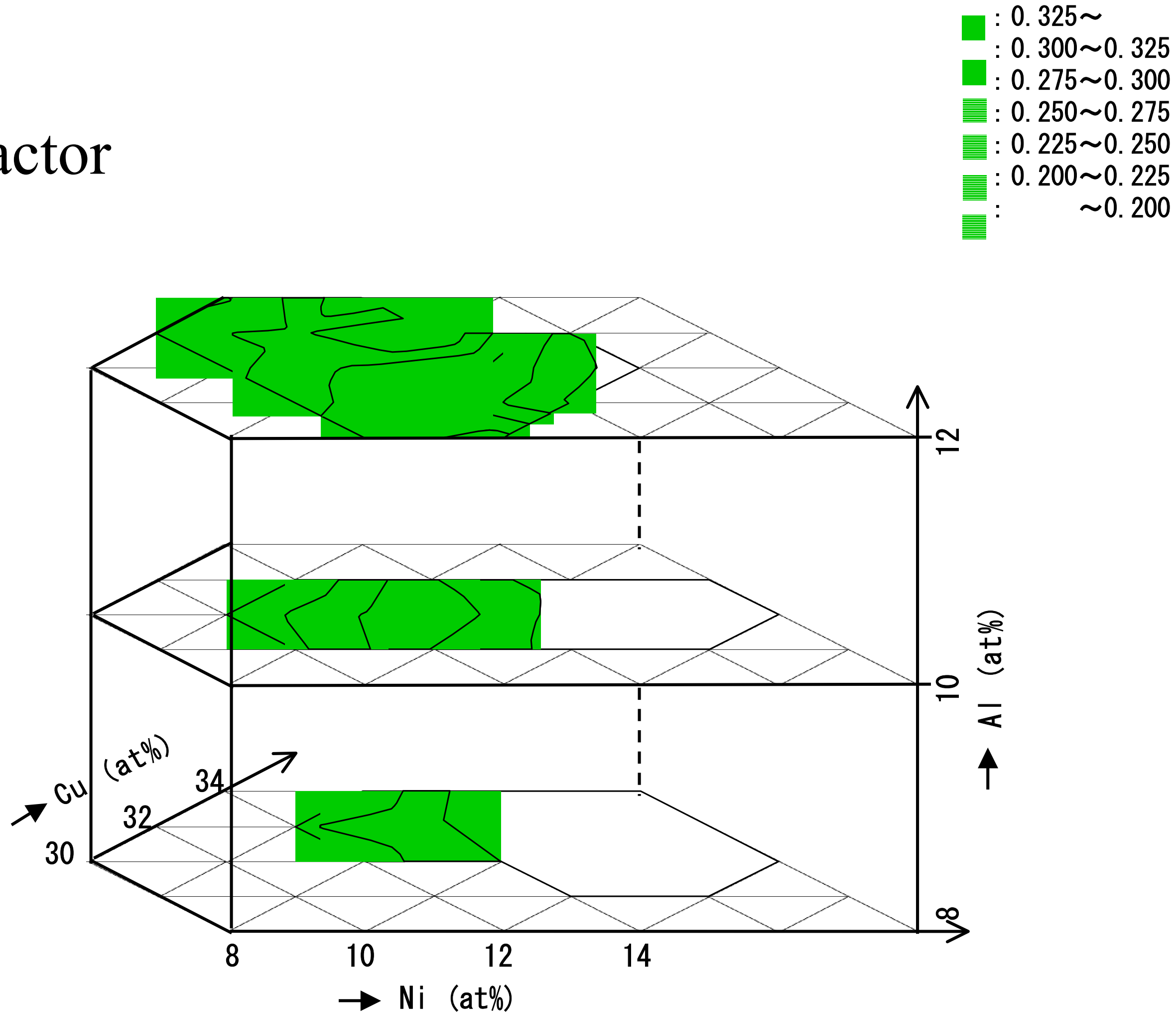
4) Zr-Cu-Ni-Al Alloy System

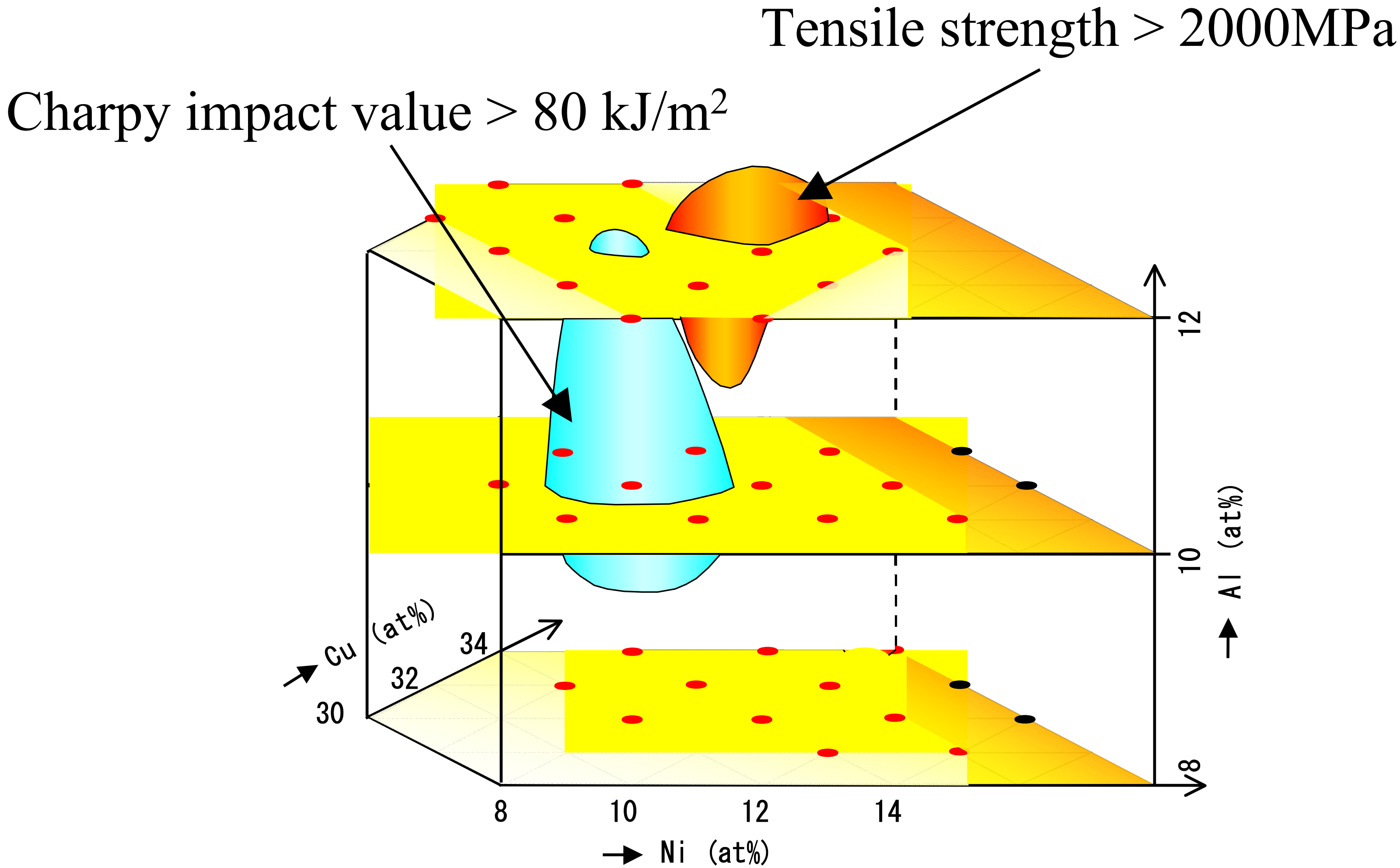


Formation area



Hruby factor





Tensile strength > 2000MPa
Charpy impact value > 80 kJ/m2
Cu (at%)
30
32
34
8
10
12
14
Ni (at%)
Al (at%)
8
10
12

4) Conclusion in Zr-Cu-Ni-Al Alloy System

- K_{gl} : 0.33

  $Zr_{50}Cu_{30}Ni_{10}Al_{10}$ BMG

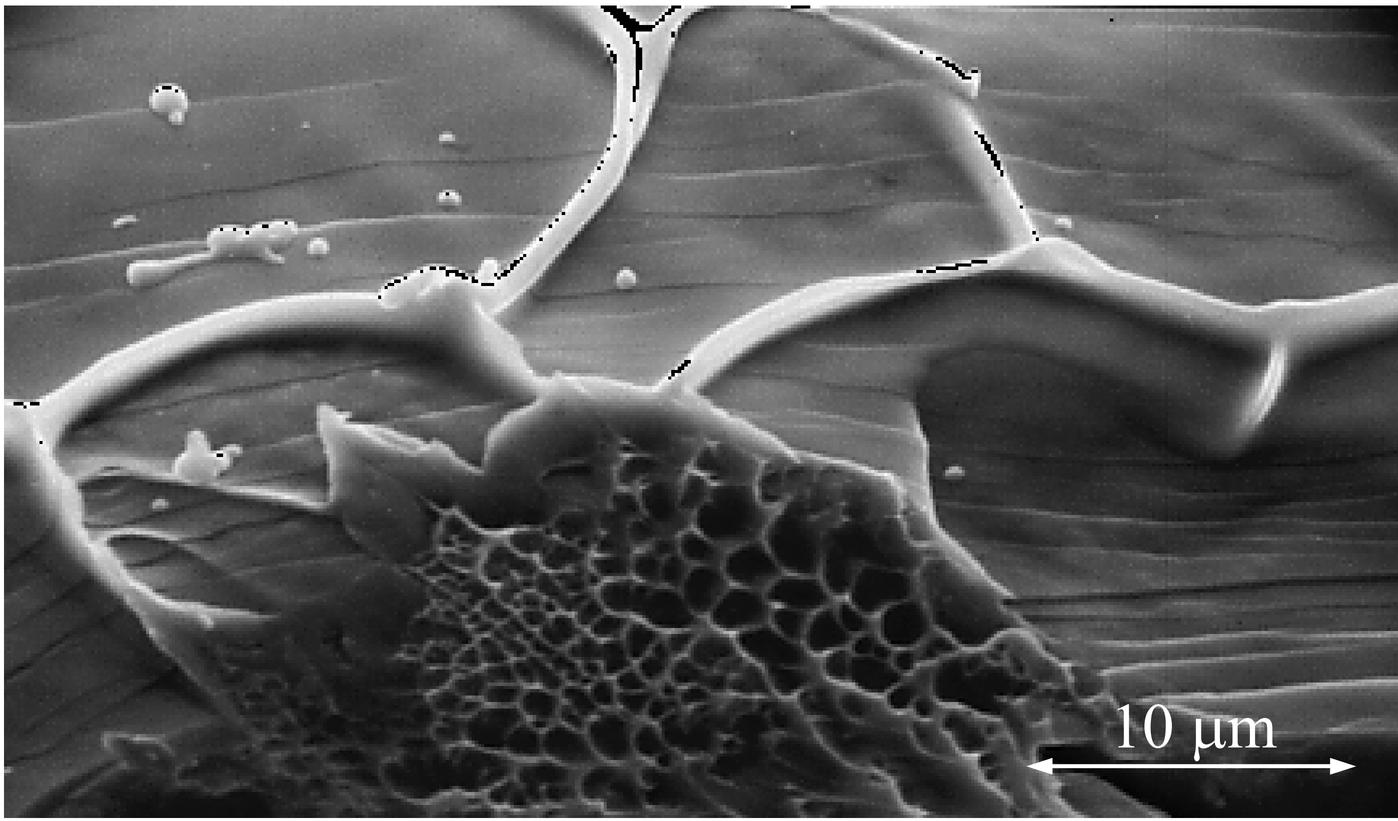
- Tensile Strength : 2210 MPa

  $Zr_{50}Cu_{30}Ni_{10}Al_{10}$ BMG

- Charpy Impact Value : 120 kJ/m^2

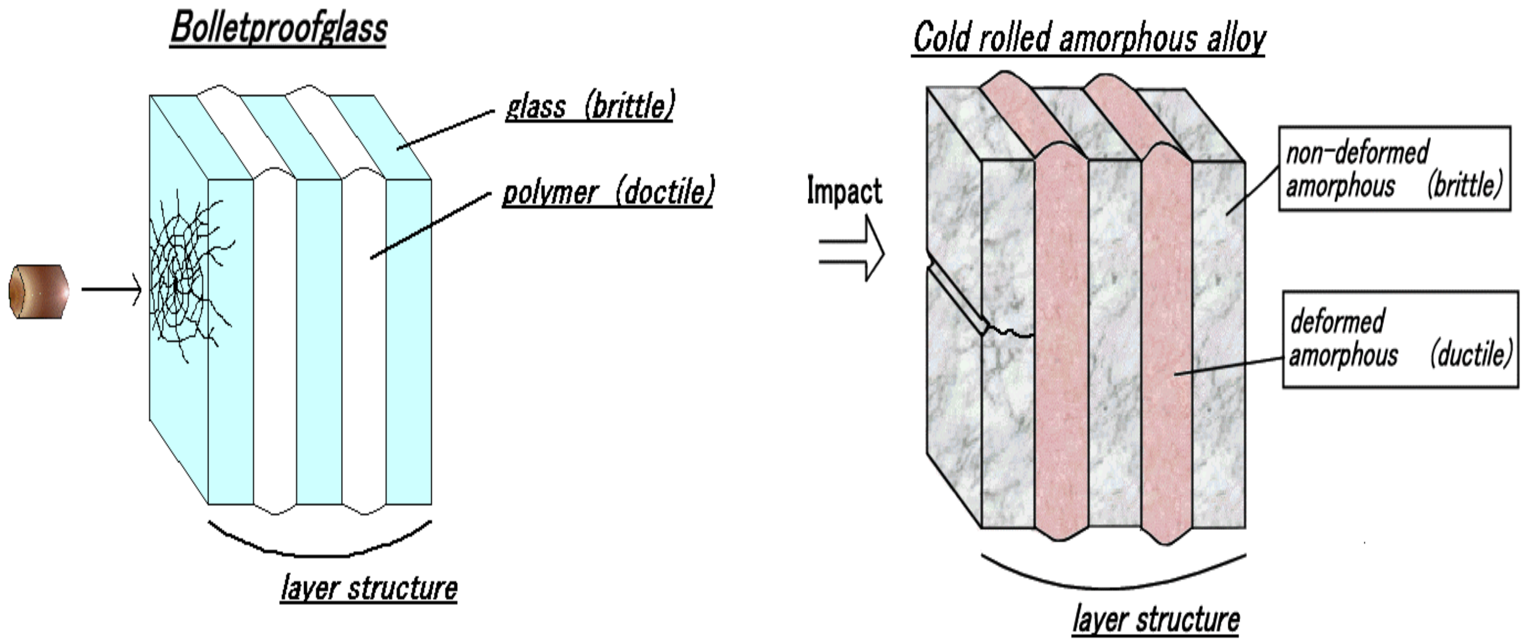
  $Zr_{50}Cu_{30}Ni_{10}Al_{10}$ BMG

5) Controlling of shear band structure

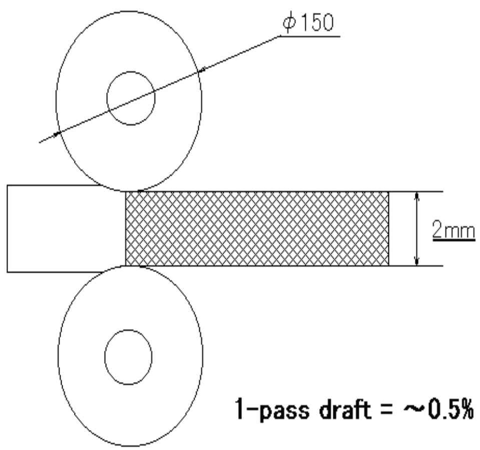


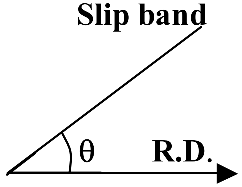
Tensile fractured surface of cold rolled BMG with plastic elongation

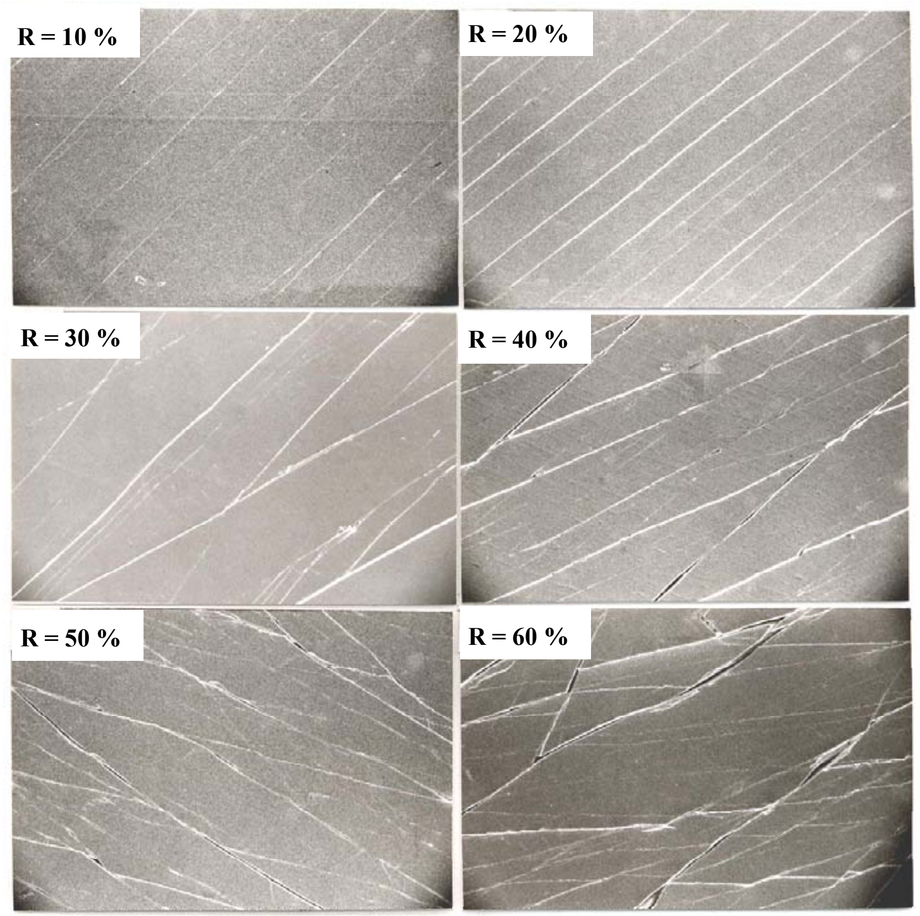
Mechanism of ductility improvement



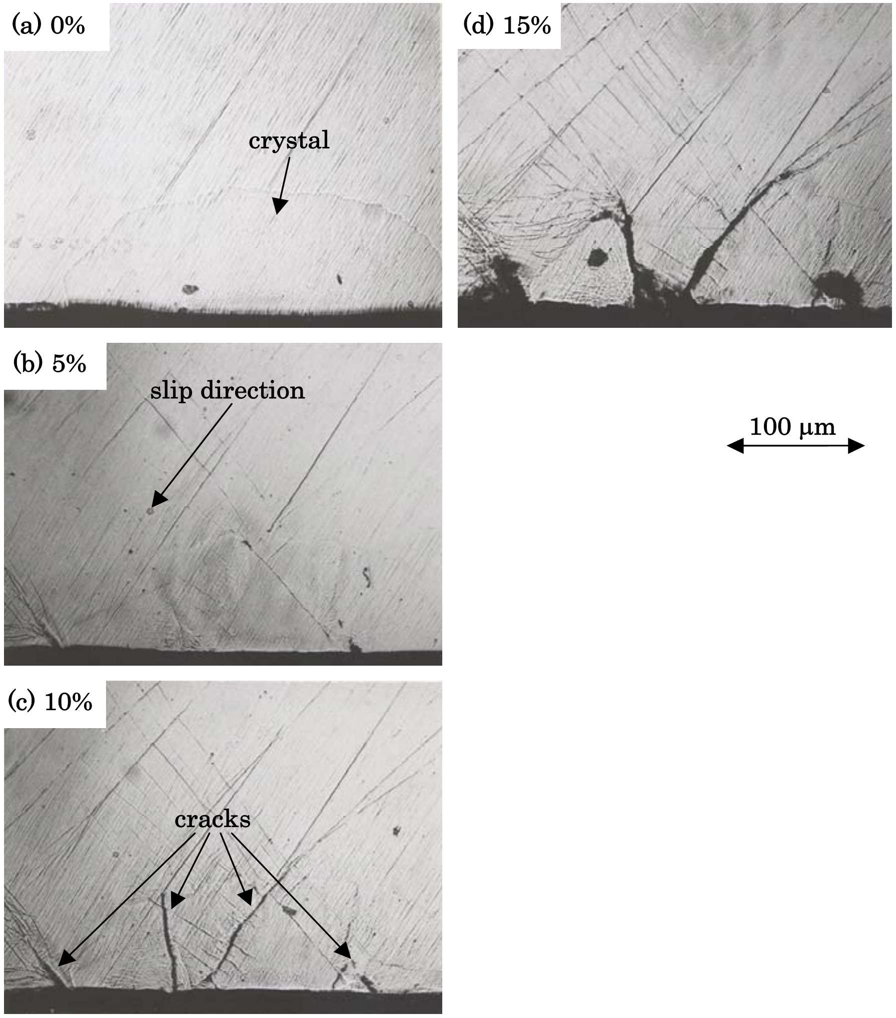
Cold rolled structure of Zr-Cu-Ni-Al BMG



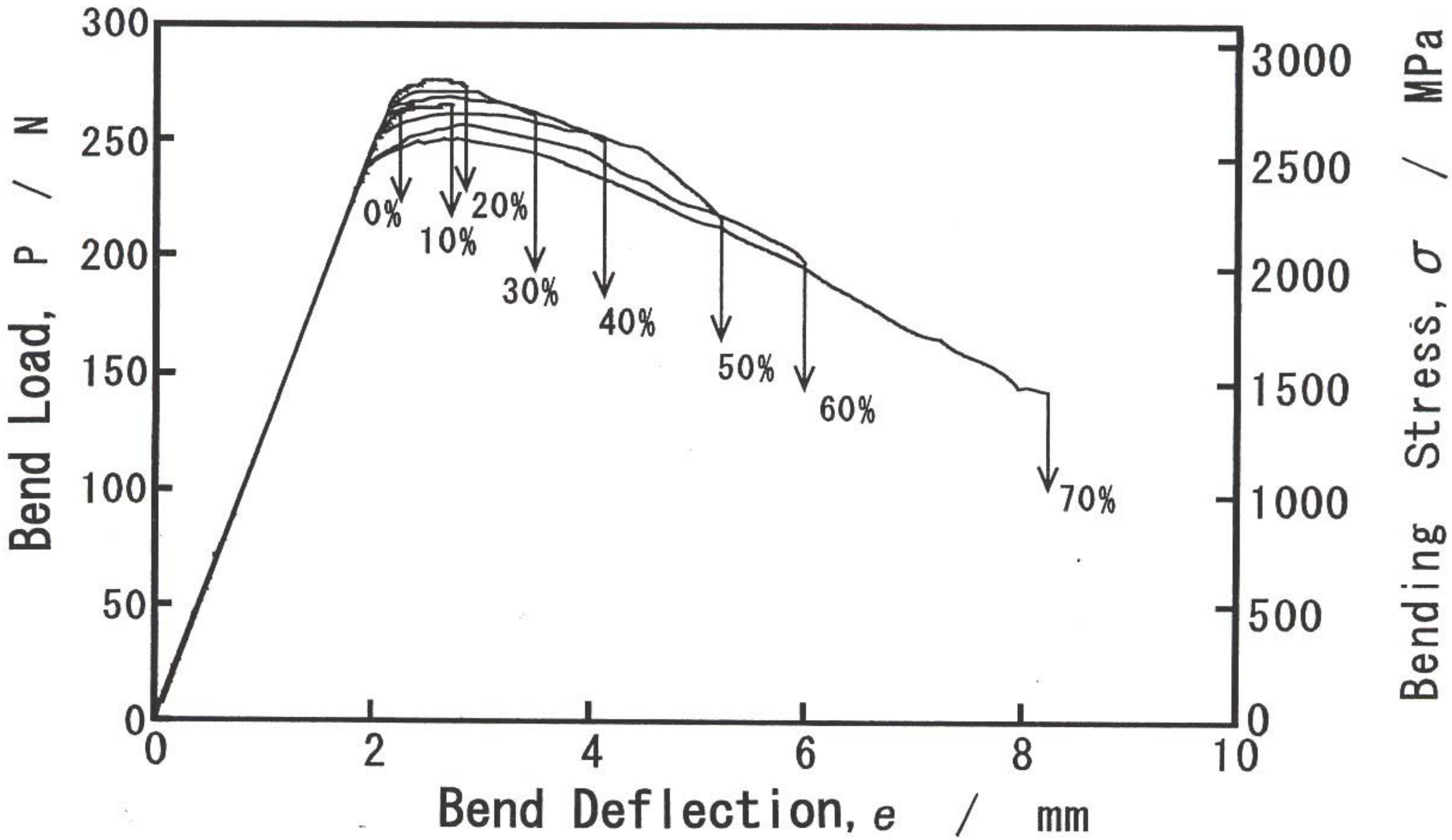




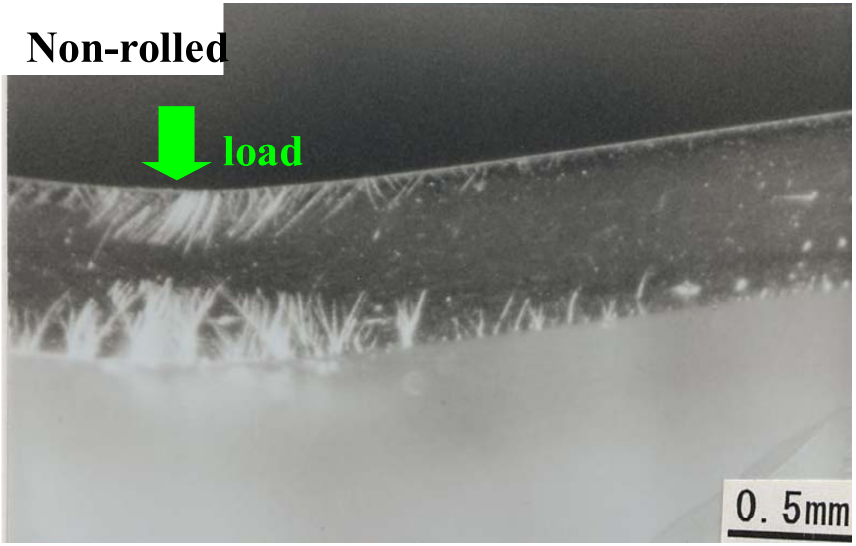
Effect of crystalline inclusion (surface)

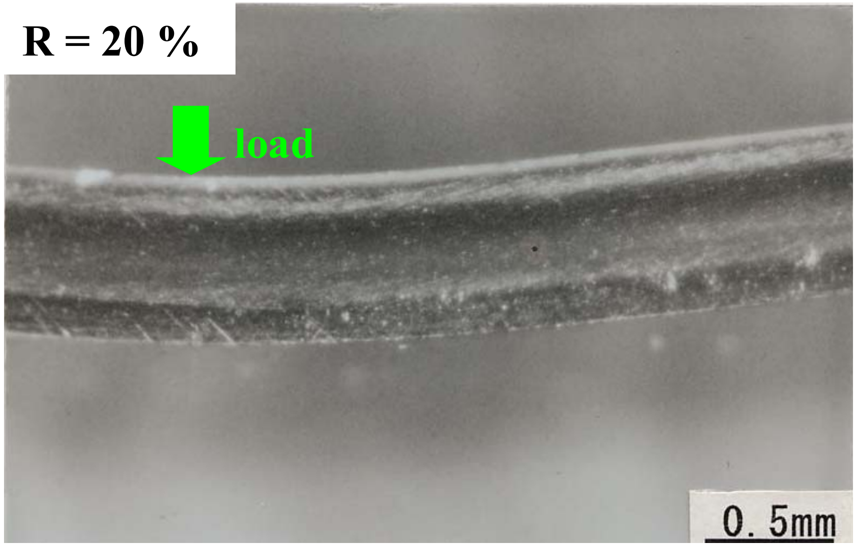


Bending deflection vs. reduction ratio of cold rolled BMG



Structure change of bent BMG





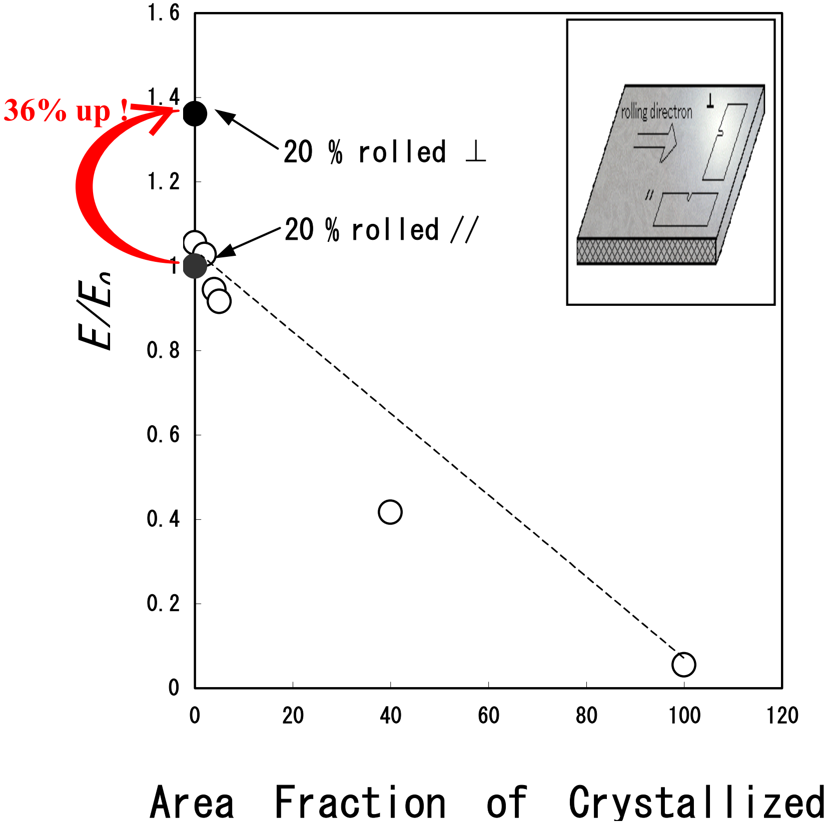
Non-rolled: many slip bands at loading point

Local deformation

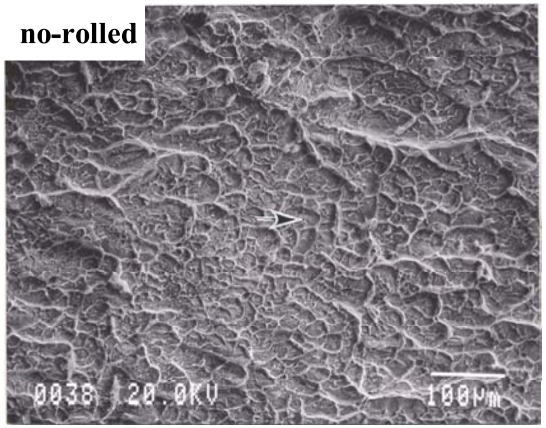
20% rolled: little slip bands at loading point

Uniform deformation

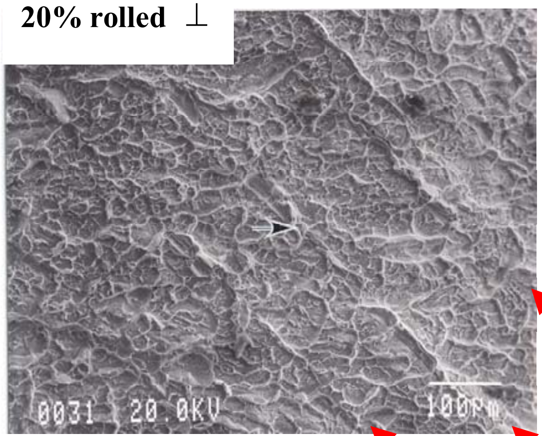
Charpy impact value of cold rolled BMG



no-rolled

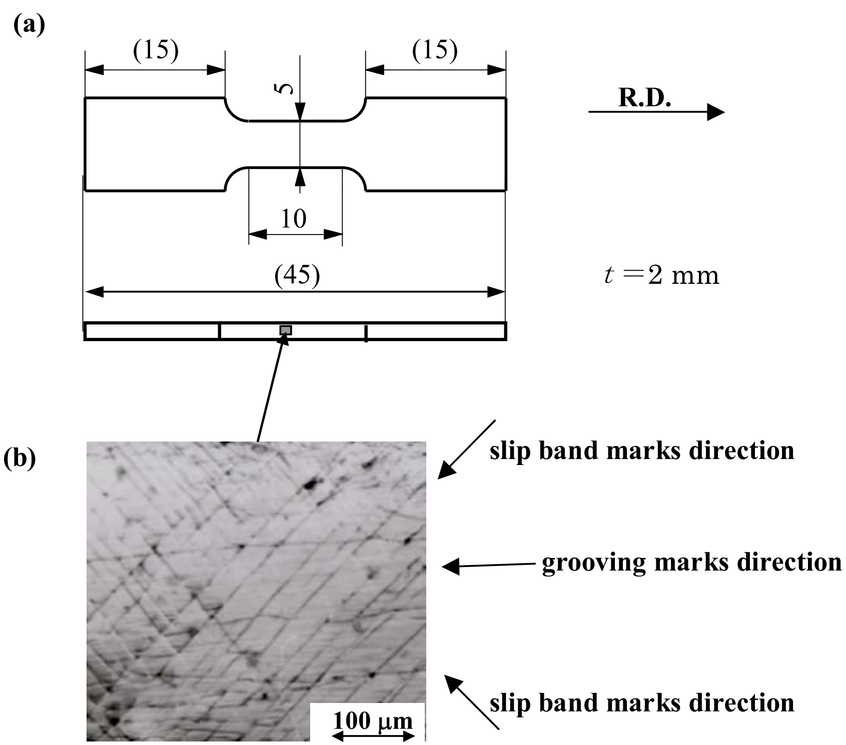


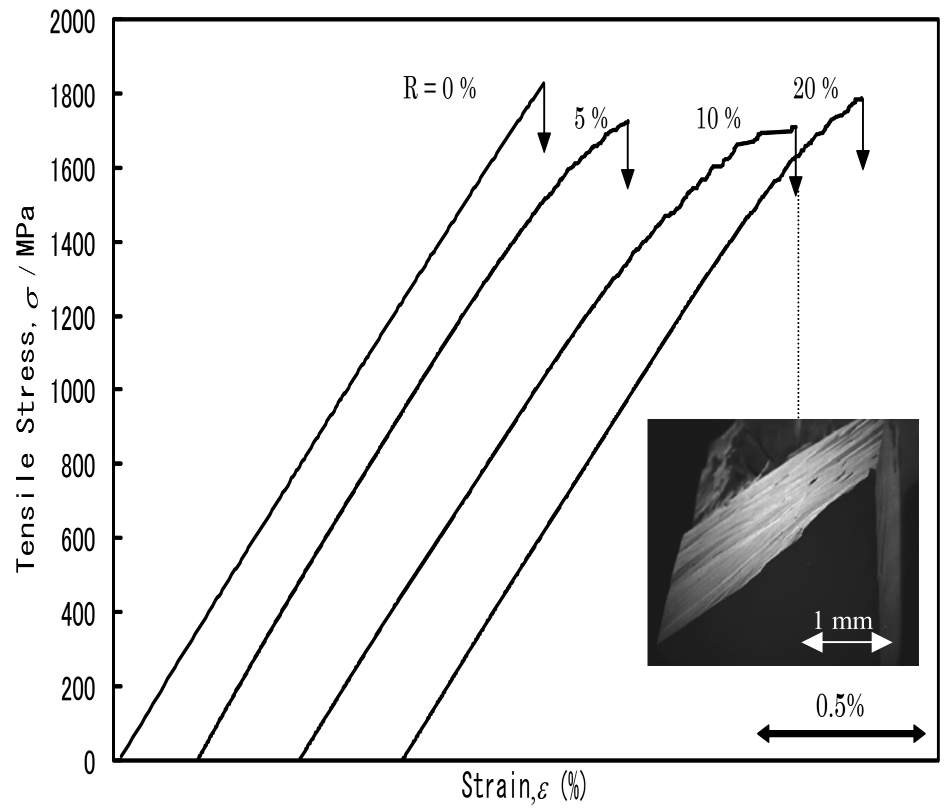
20% rolled ⊥



slip bands re-operated marks
under impact fracture

Tensile test of cold rolled BMG

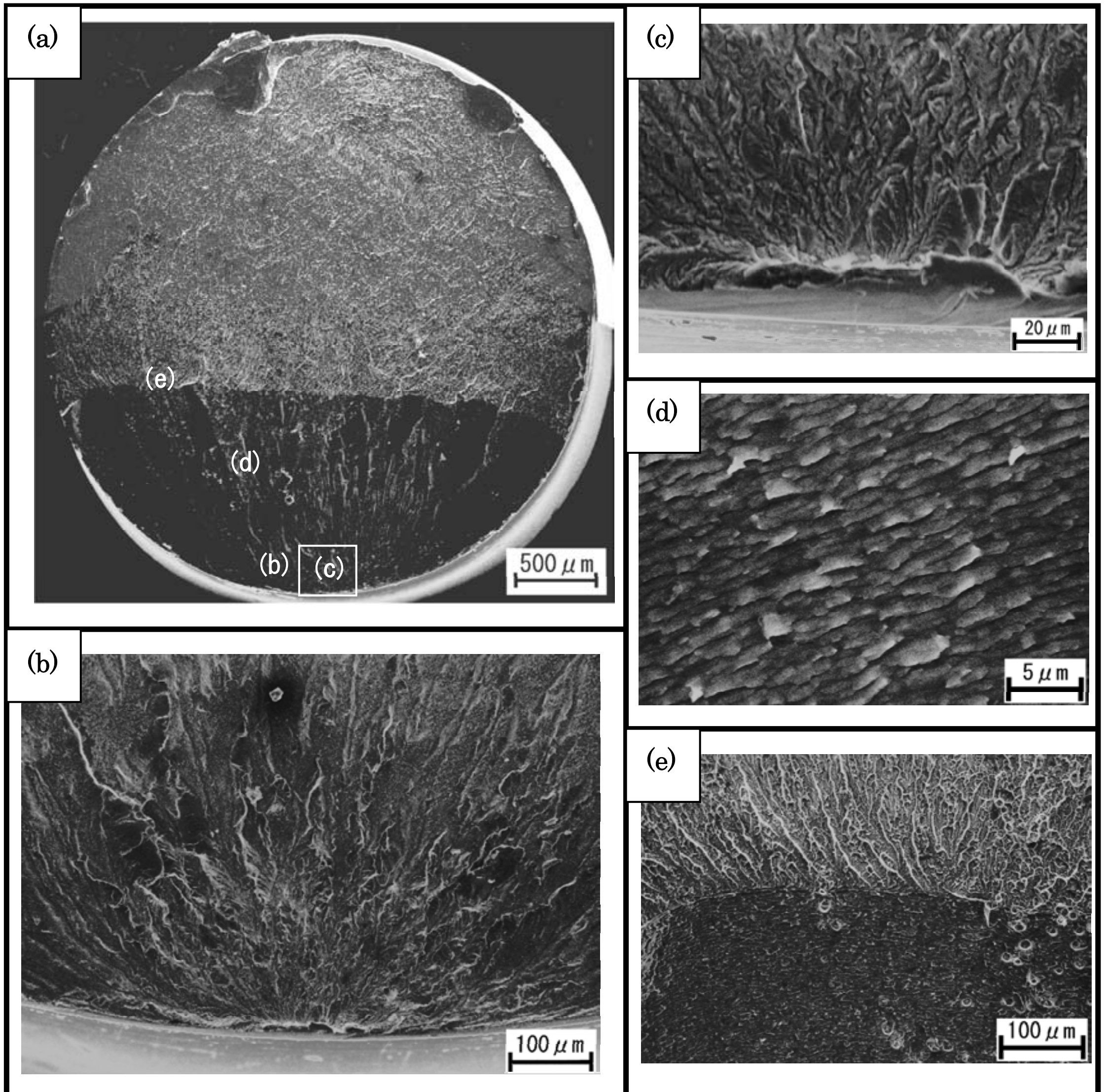




5) Conclusion in Controlling of shear band structure

- Preliminary cold rolling of bulk amorphous alloy effectively enabled uniform deformation under bending stress condition.
- Bend deflection value to fracture increased with an increase of reduction ratio.
- Preliminary cold rolling enables the plastic tensile deformation at room temperature.

Fatigue fractured surface of $Zr_{50}Cu_{40}Al_{10}$ BMG



$\sigma_a = 453$ MPa

$N_f = 7.7\times10^5$

Fatigue fracture toughness estimation

$K_{fc} = \sigma_0 \cdot (\pi C)^{1/2} \times (1.122 - 0.23\beta - 0.901\beta^2 + 0.949\beta^3 - 0.28\beta^4)$

$\times (1.00 + 0.157\lambda_a - 0.634\lambda_a^2 + 4.59\lambda_a^3 - 6.628\lambda_a^4)$

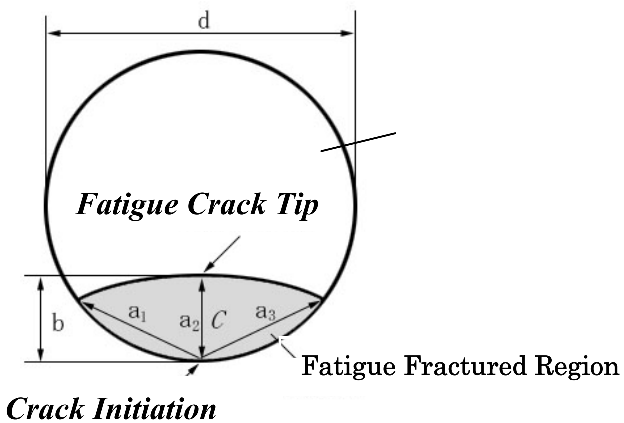
$\times (1.121 - 1.199\lambda_a + 4.775\lambda_a^2 - 1.628\lambda_a^3 - 7.035\lambda_a^4 + 13.27\lambda_a^5)$

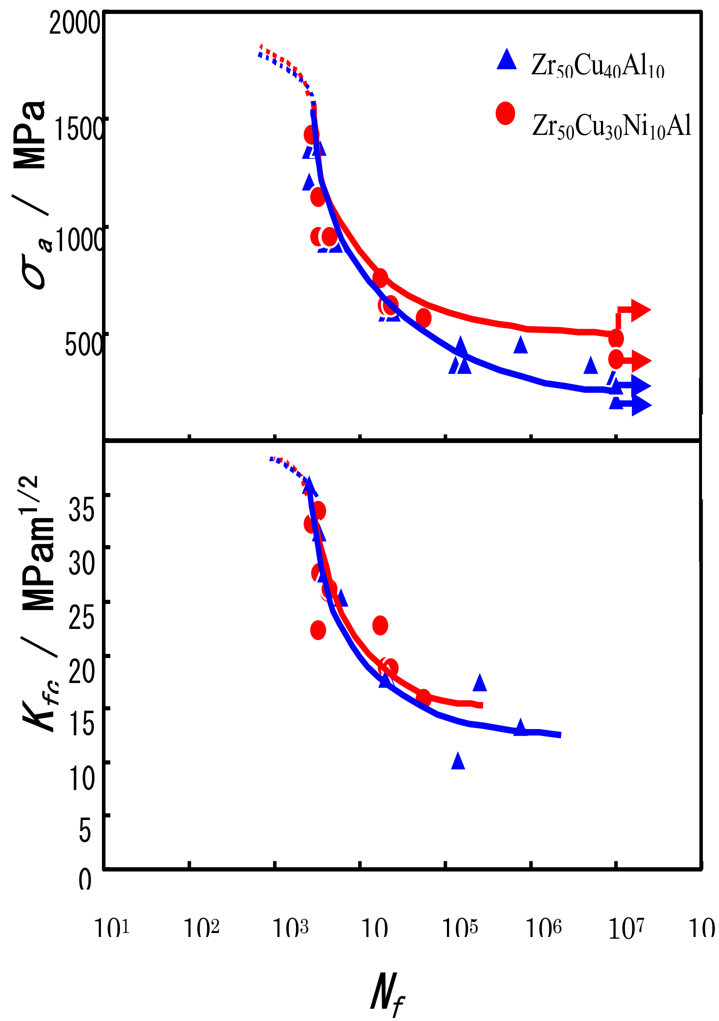
$\div (1.12 - 0.231_a\lambda + 10.55\lambda_a^2 - 21.72\lambda_a^3 + 30.39\lambda_a^4)$

$a = (a_1 + a_2 + a_3)/3$

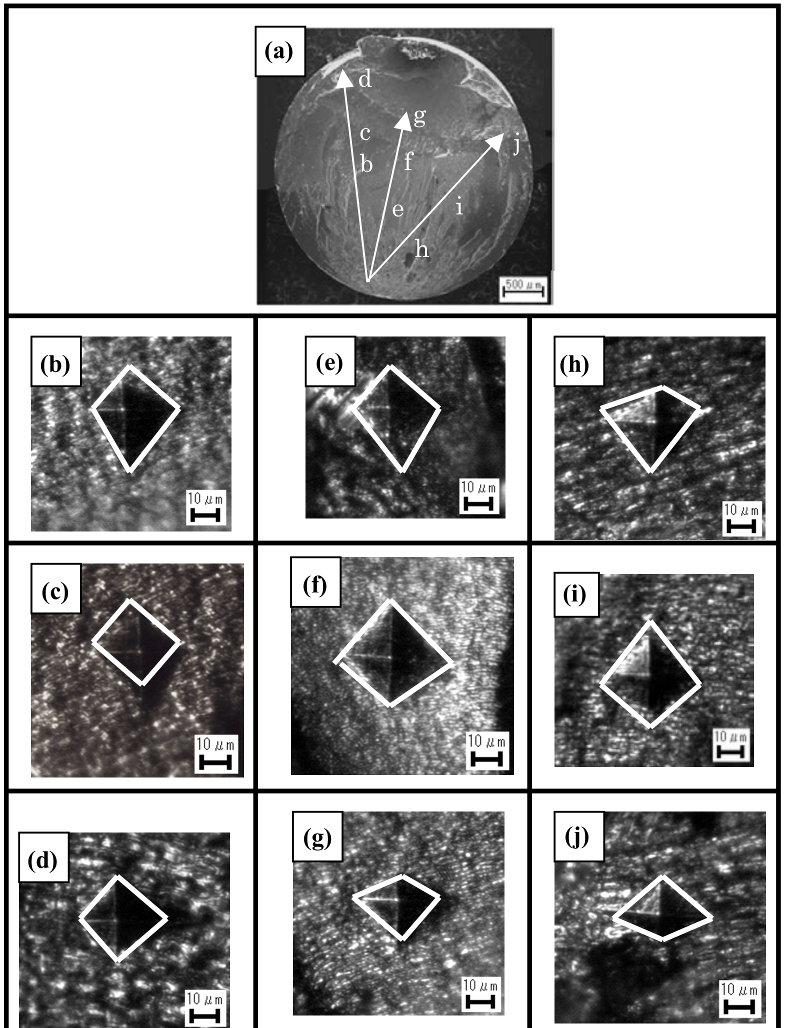
$\lambda_a = a/d$

$\beta = b/a$



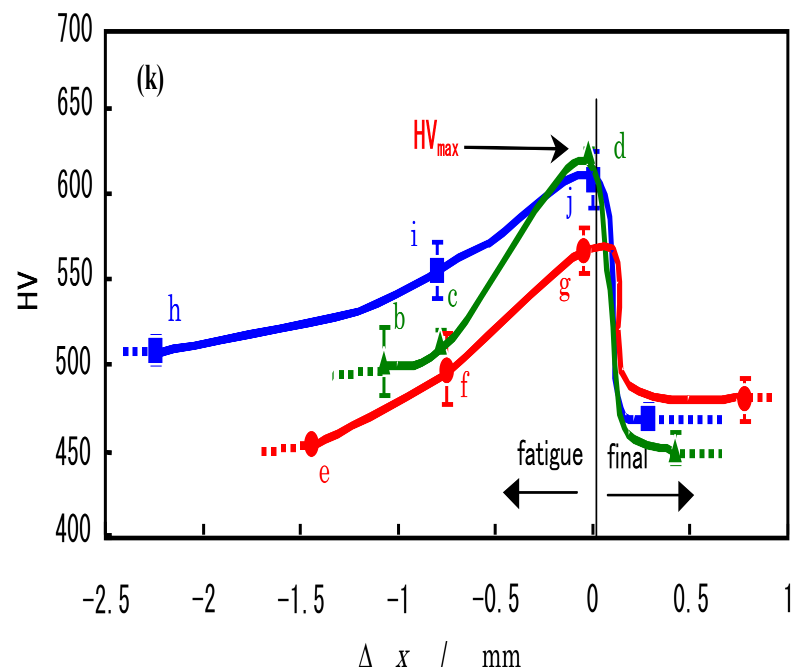


HV change in fatigue fractured surface of $Zr_{50}Cu_{40}Al_{10}$ BMG



σ_a = 357 MPa

N_f = 1.3 x 10^5



6) Conclusion in Fatigue Properties of Zr-TM-Al BMG

- The fatigue limit of $Zr_{50}Cu_{40}Al_{10}$ ($Zr_{50}Cu_{30}Ni_{10}Al_{10}$) bulk glassy alloy is 250 MPa (500 MPa).
- The fatigue strength decrease around 10^3 to 10^4 cycles is probably caused by the phase transition from glassy to crystallized state around the fatigue crack tip.

7) Focus in Future