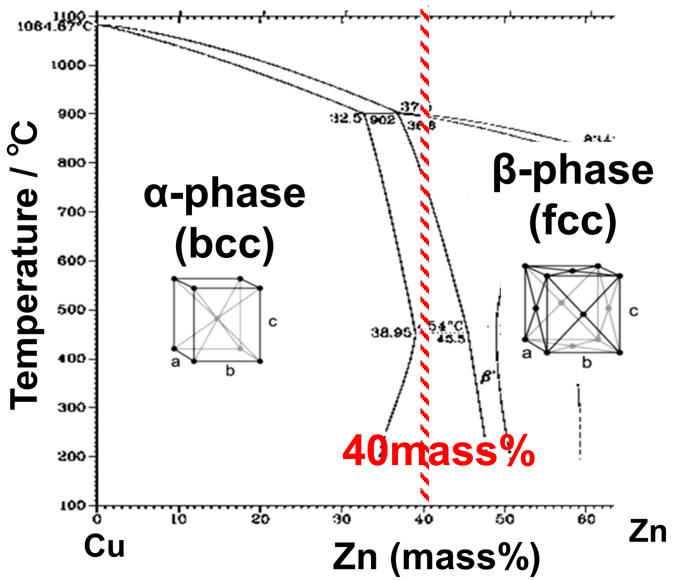
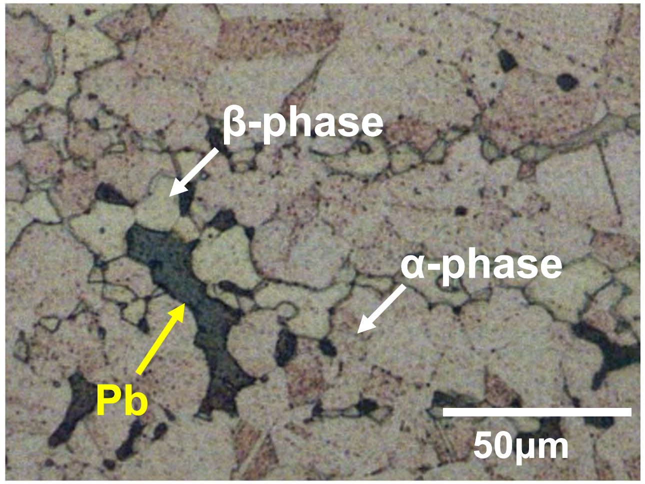
Pb-free high-strength Cu-Zn alloy via powder metallurgy route

Background ~ *No more hazardous element, Pb*

- **α-β duplex brass alloys with “Pb” widely used in industries**

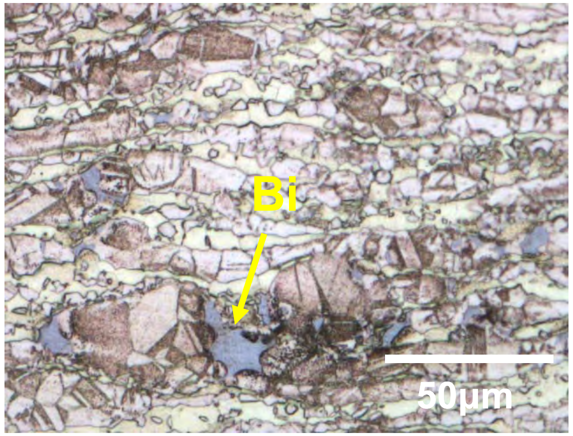




Machinable Cu-40%Zn-3.2%Pb alloy

Background ~ Effective elements for good machinability

Bismuth, Bi



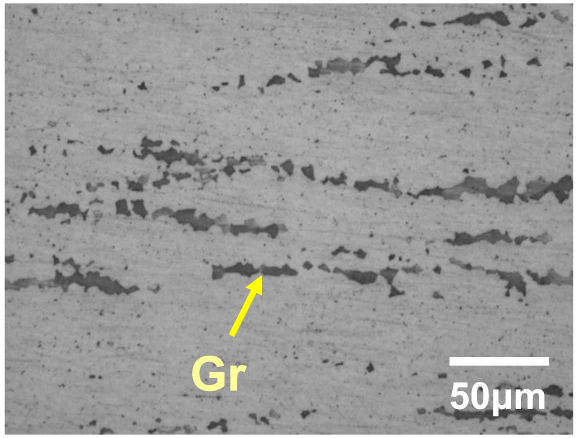
Machinable Cu-40%Zn-**2.7%Bi** alloy

- Toxic for human
- Rare metal = expensive
- Poor recyclability

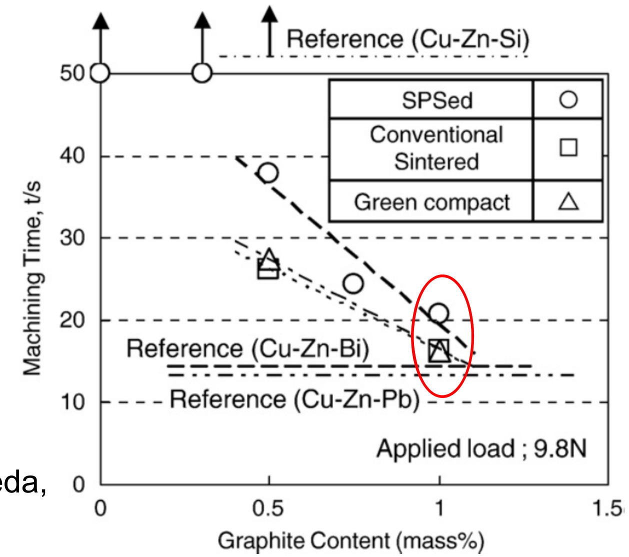
  Easy reaction of Bi with Pb in re-melting of BS40

H. Imai, Y. Kosaka, A. Kojima, S. Li, K. Kondoh, J. Umeda, H. Atsumi; Powder Technology, 198 (2010) 417-421.

Graphite particles

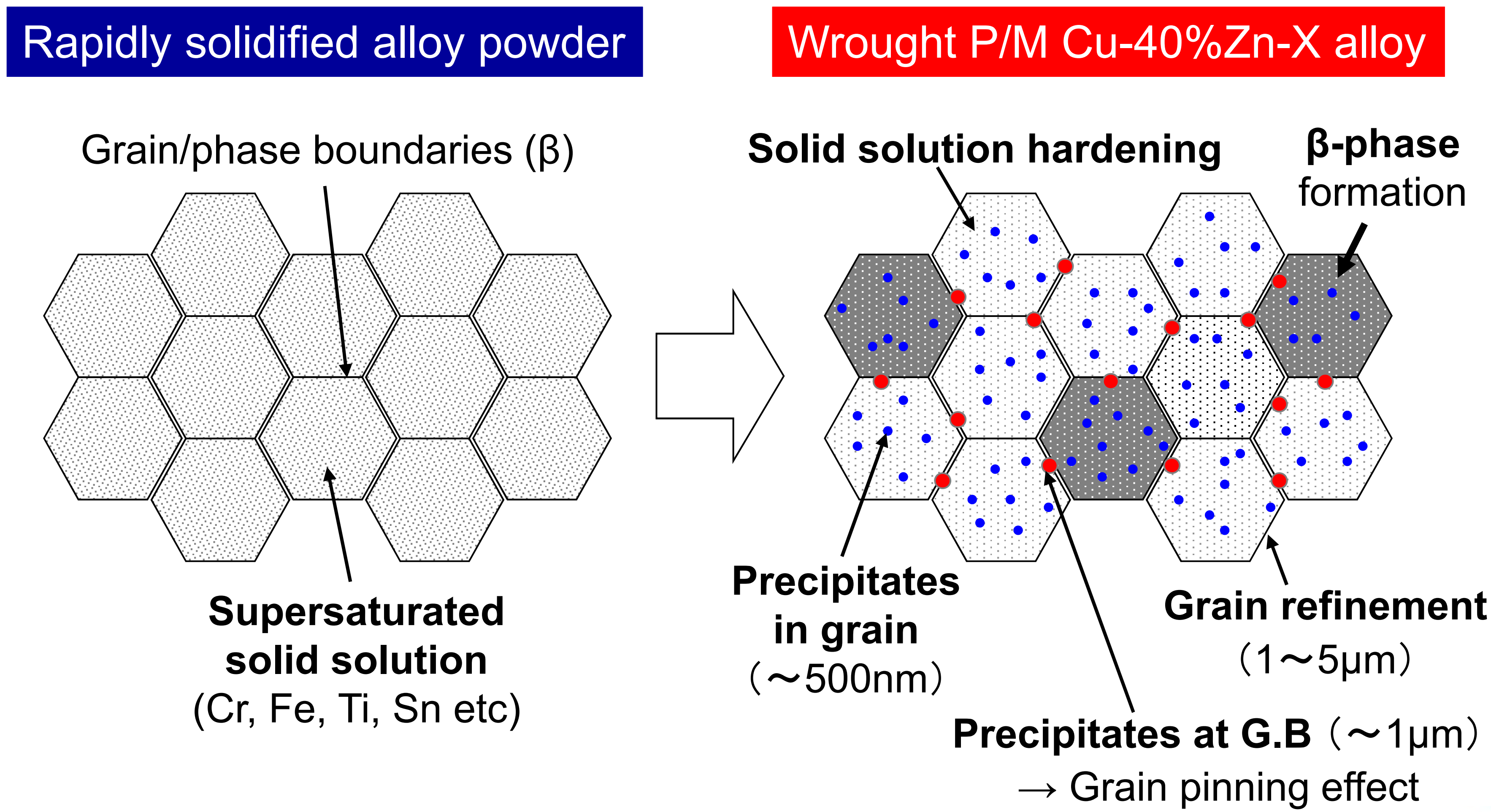


Machinable Cu-40%Zn alloy **with 1.0%Gr**

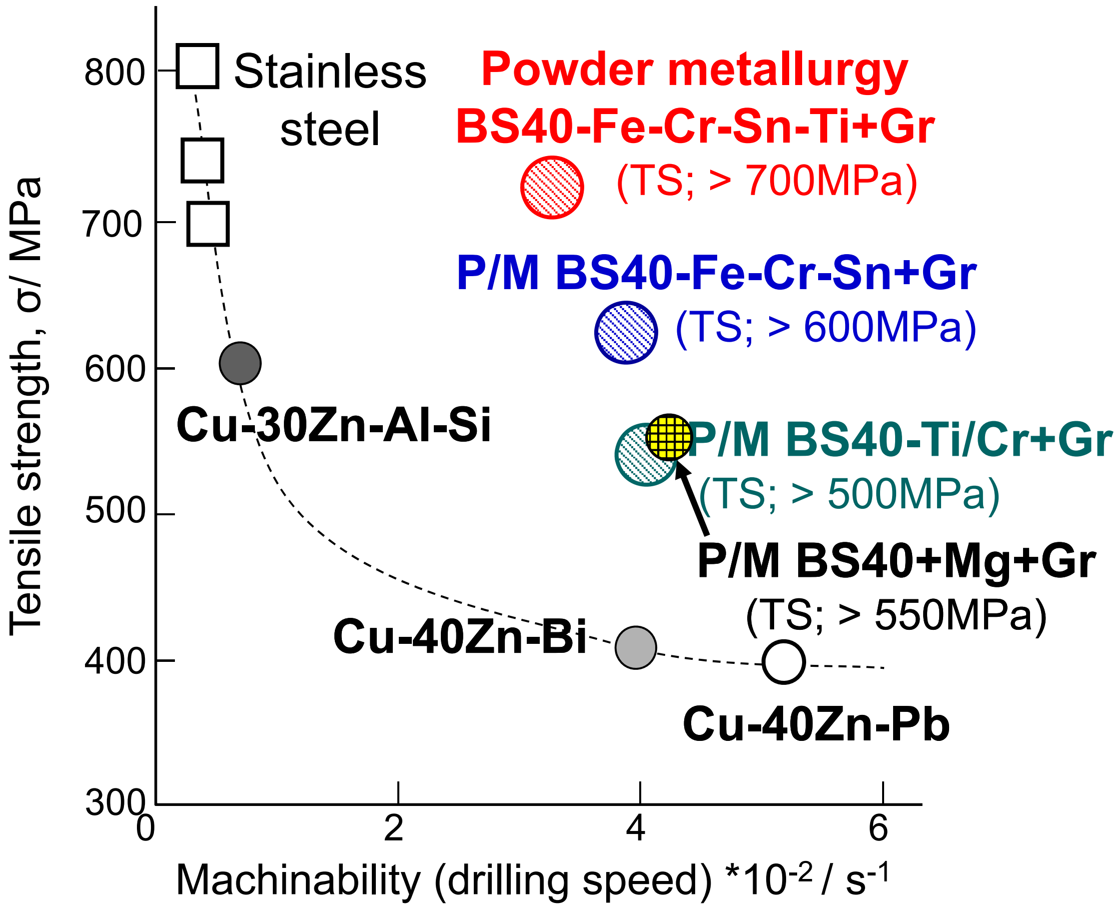


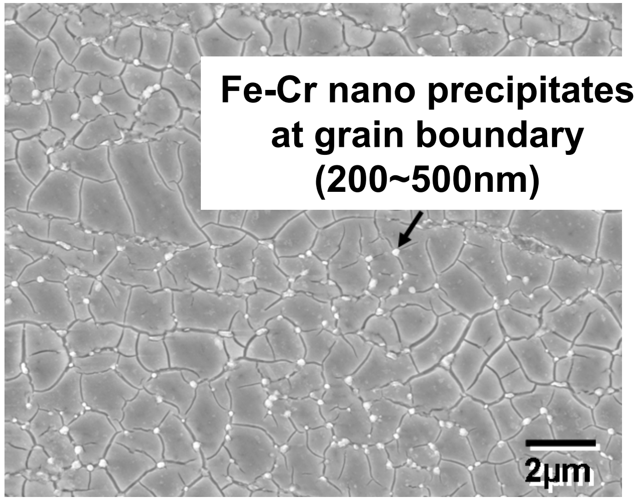
Objectives ~ Pb-free high-strength P/M Cu-40%Zn alloy

- **Materials design for high-strength Cu-40%Zn (BS40) by P/M route**

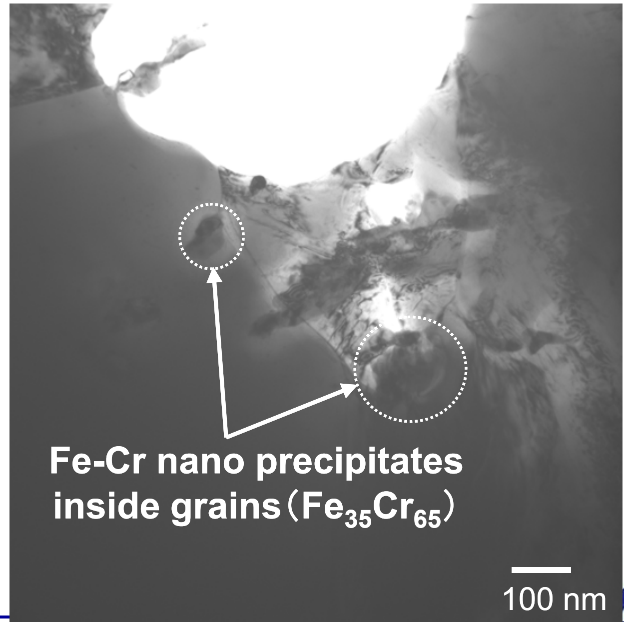


P/M high-strength and machinable BS40-X alloys





BS40-0.7Fe-0.3Cr-0.3Sn+0.5Gr

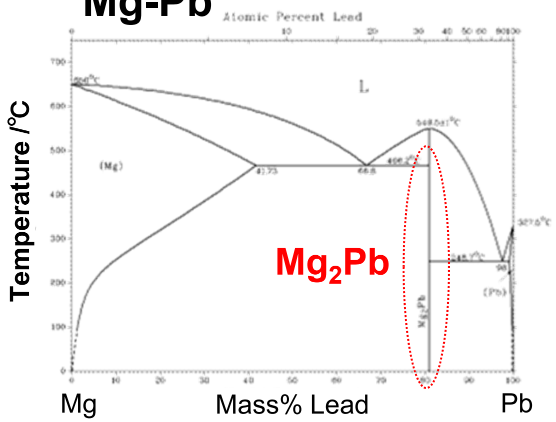


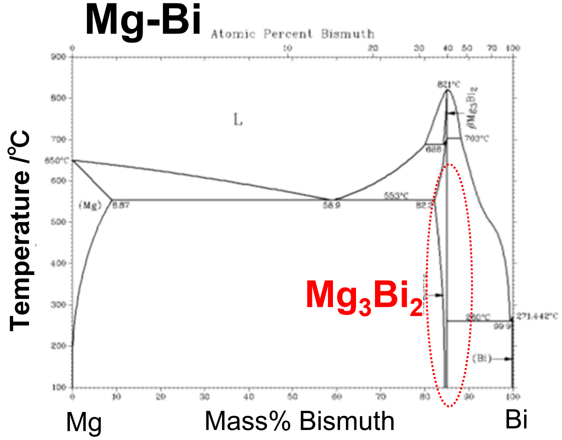
K. Kondoh et al., Journal of Metallurgy (2009) Article ID 853092.
Shufeng Li et al., J. Alloys and Compounds 493 (2010) 128–133.
Shufeng Li et al., J Materials Science (2010) 45:5669–5675.
H. Imai et al., Materials Transactions 52 (2011) 1426-1430.
Shufeng Li et al., Powder Technology 205 (2011) 242–249.
Shufeng Li et al., Materials and Design 32 (2011) 192–197.

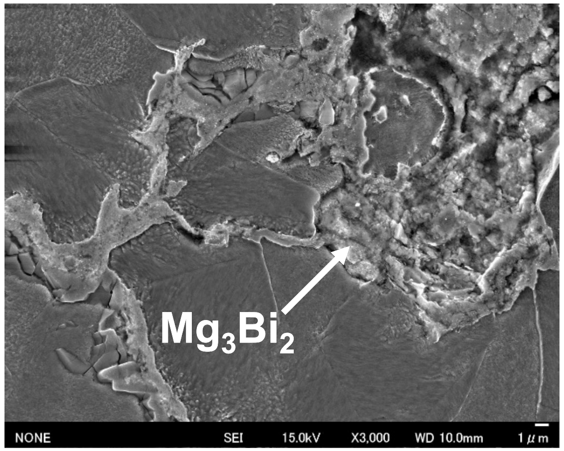
Strengthening of BS40 alloy with elemental Mg addition

- **Mg NOT effective to improve strength of BS40 with Pb/Bi**

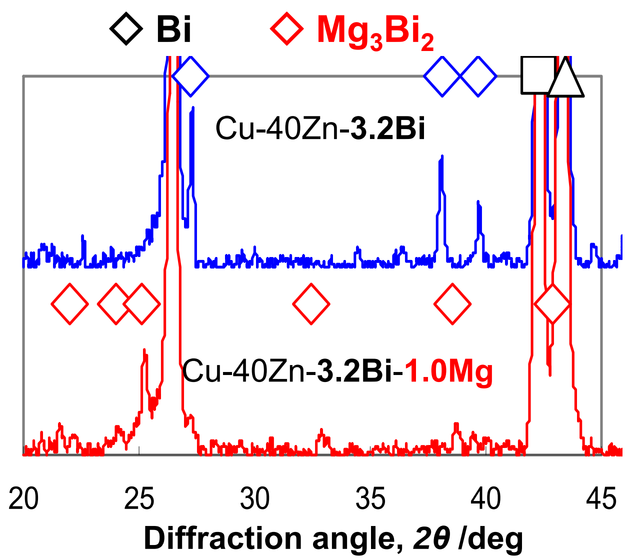
• Mg-Pb & Mg-Bi ***coarse intermetallics*** synthesized via Mg-Pb/Bi reaction cause **poor machinability and mechanical properties** of BS40 alloy with Pb/Bi







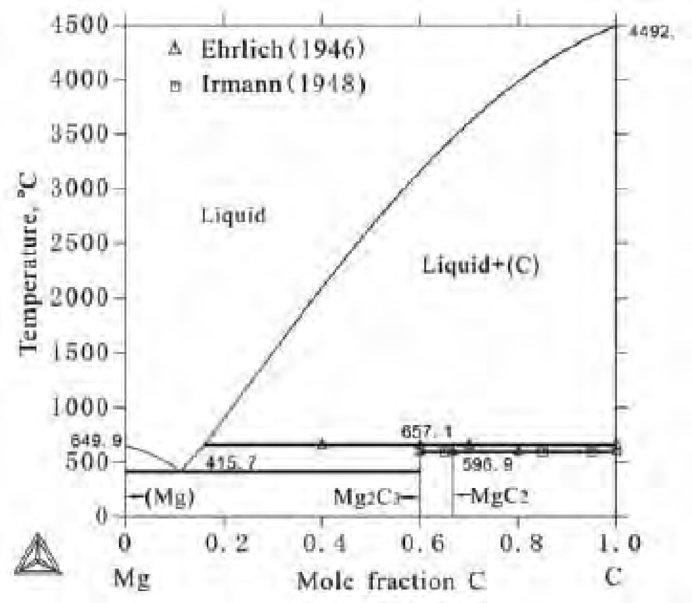
Cu-40Zn-**3.2Bi-1.0Mg**



Strengthening of BS40 alloy with elemental Mg addition

- **Mg additives for fine precipitation & grain refinement of BS40+Gr**

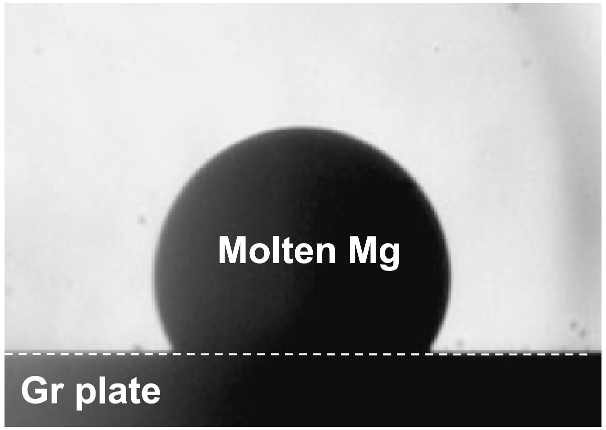
Mg-C



Mg_2C_3, MgC_2; unstable phase

B. Hu, Y. Du, H. Xu, W. Sun, W.W. Zhang, D. Zhao, Thermodynamic description of the C-Ge and C-Mg systems

- **No formation of Mg-C IMCs;** graphite particles effective for good machinability remain in the matrix.

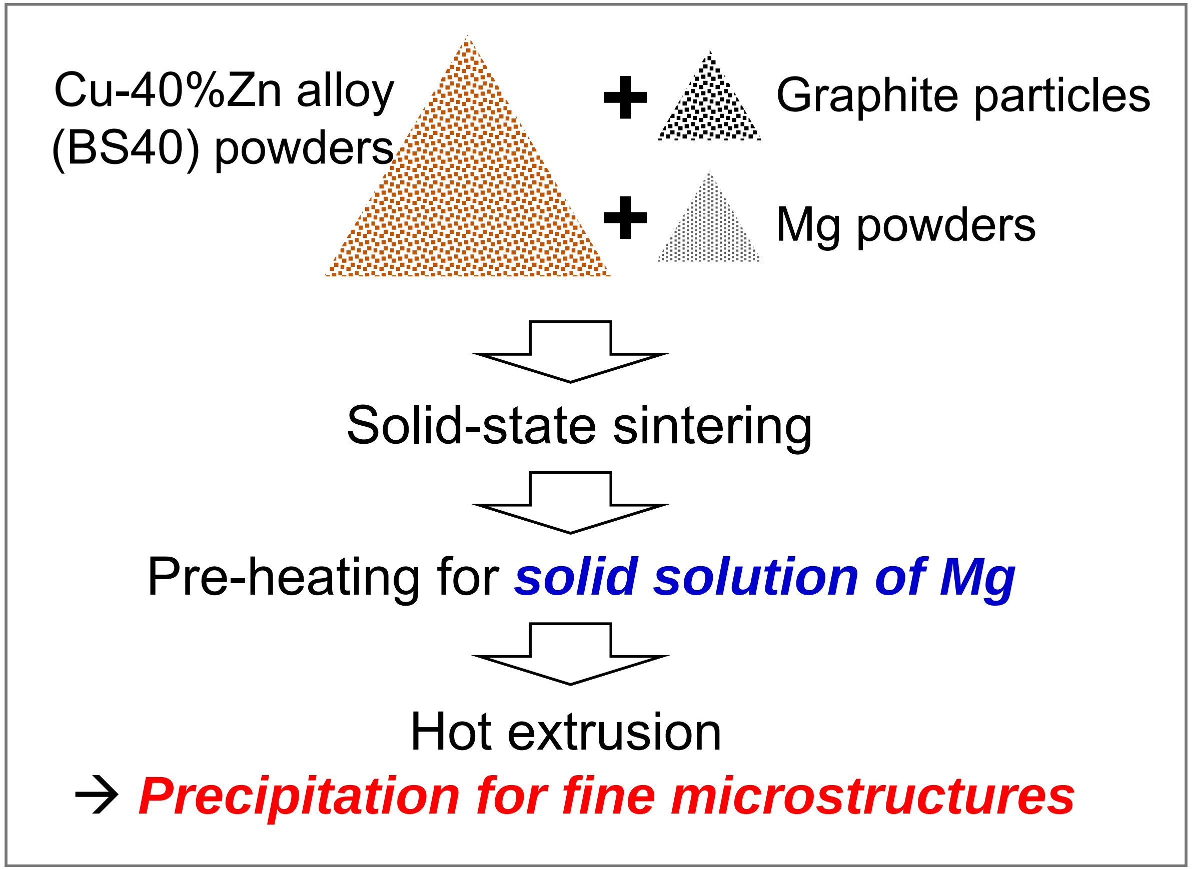


Poor wettability of graphite plate by molten Mg droplet

N. Shinozaki, Jun Morita, K. Wasai, Wetting of graphite by molten magnesium, Journal of Japan Institute of Light metals, 55 (2005) 310-314

Today's topics

- **Effect of Mg powders addition on microstructures of BS40 alloys**
- **Mechanical properties and machinability of BS40 +Mg +Gr alloy**

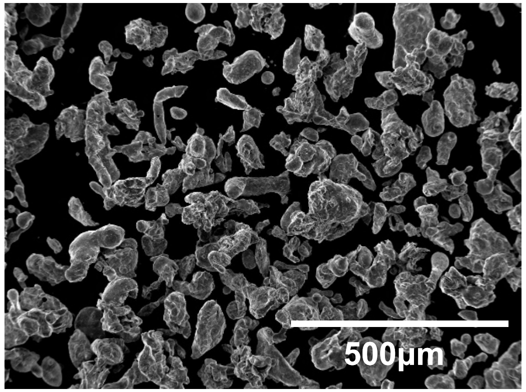


Experimental - raw powders

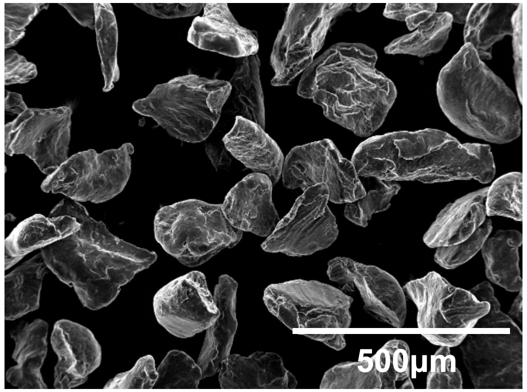
Chemical compositions

Powder	Pb	O	Fe	Al	Zn	Cu	Mg
Cu-40Zn	0.005	0.09	0.003	0.005	40.42	Bal.	---
Pure Mg	---	---	0.006	0.006	0.003	0.001	Bal.

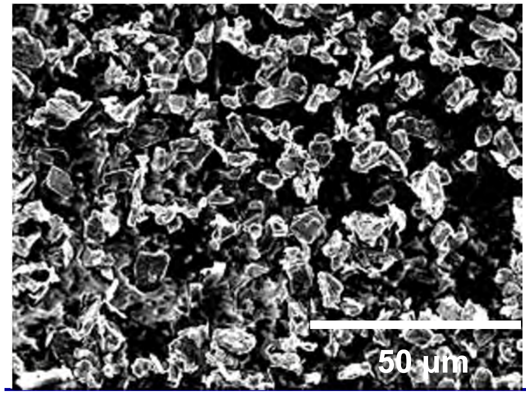
BS40 powder (146 μm)



Pure Mg powder(182 μm)

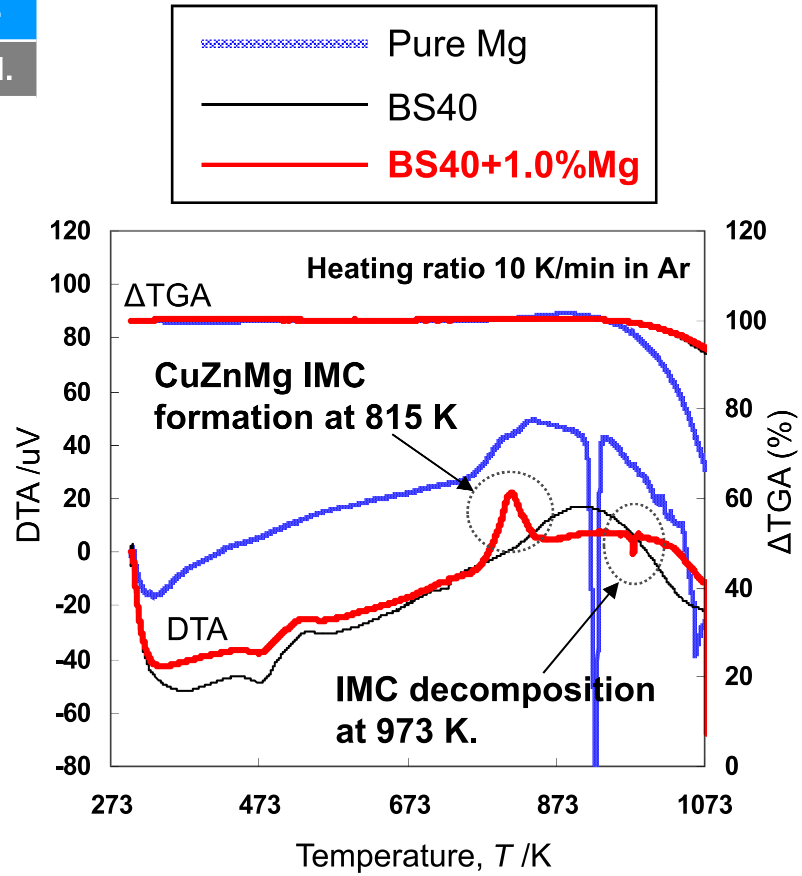


Graphite particles (4.8 μm)



Additive **Mg** powders;
+0.5, 1.0, 1.5 mass%

Additive **Gr** particles;
+0.75 and 1.25 mass%
(Mg; 1.0%)

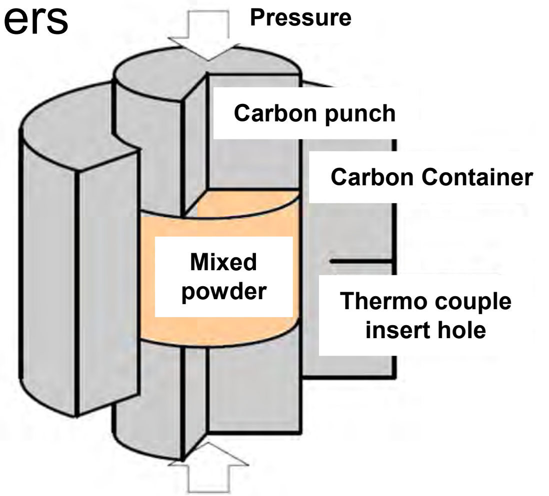


Experimental – consolidation by SPS and hot extrusion

- Elemental mixtures of BS40, Mg and graphite powders

  (a-1) BS40 (Cu-40%Zn)
  (a-2) BS40 +0.5mass%Mg
  (a-3) BS40 +1.0mass%Mg
  (a-4) BS40 +1.5mass%Mg
  (b-1) BS40+1%Mg +0.75%Gr
  (b-2) BS40+1%Mg +1.25%Gr

  } **Starting powders**

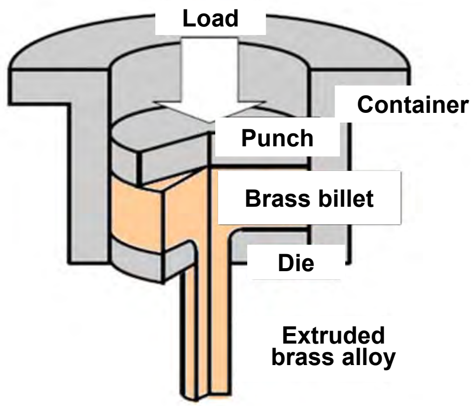


Spark plasma sintering (SPS)

- SPS: 973K for 1.8 ks under 30 MPa (in vac.)

- H/E: pre-heating at **973K** for 0.9 ks in Ar gas

  → **Mg solid solution into α&β phases and fine precipitates (CuZnMg) during cooling after hot extrusion**



Hot extrusion

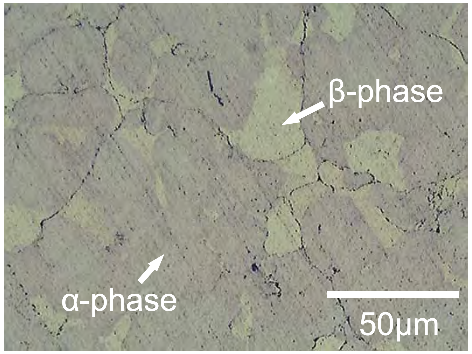
- Microstructural - mechanical performance and machinability evaluation of wrought specimens:

  SEM-EDS, EBSP, XRD, tensile and drilling test

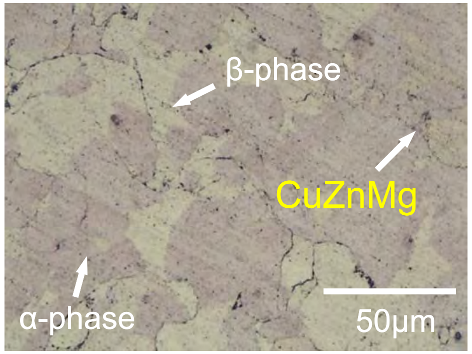
Microstructural analysis on SPSed specimens

- **CuZnMg (1:1:1) IMCs precipitation** during cooling from 815K to R.T. in SPS
- β phase fraction increasing with increase in Mg content: Mg effective for **β stabilization**

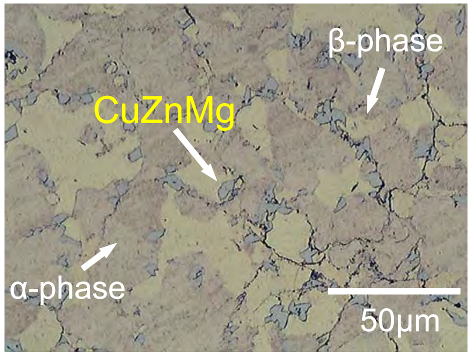
(a-1) BS40 (Cu-40%Zn)



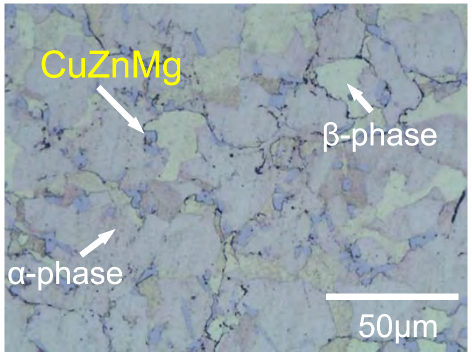
(a-2) BS40 +0.5%Mg

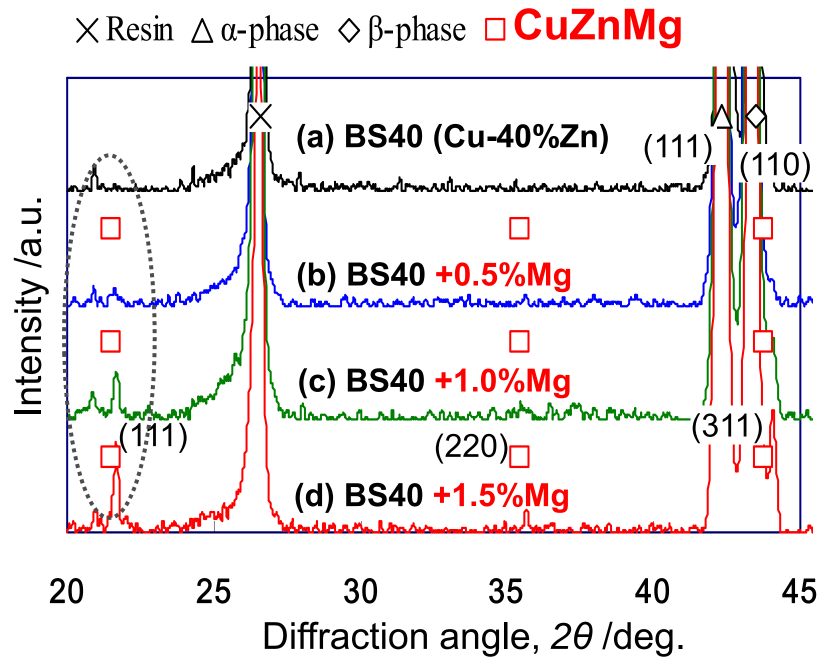


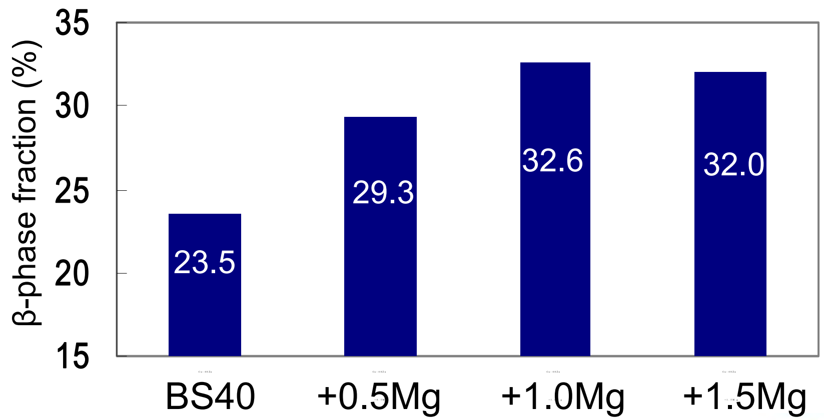
(a-3) BS40 +1.0%Mg



(a-4) BS40 +1.5%Mg

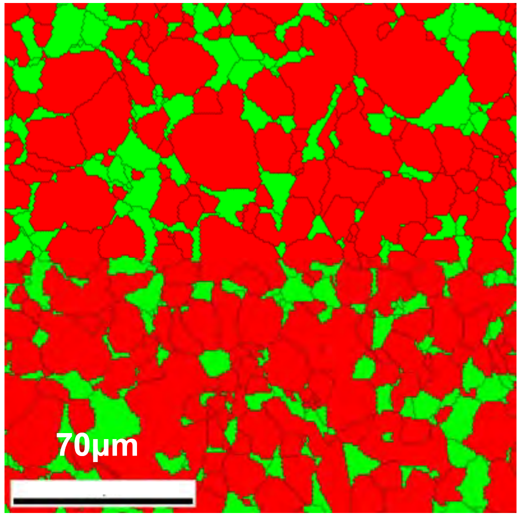




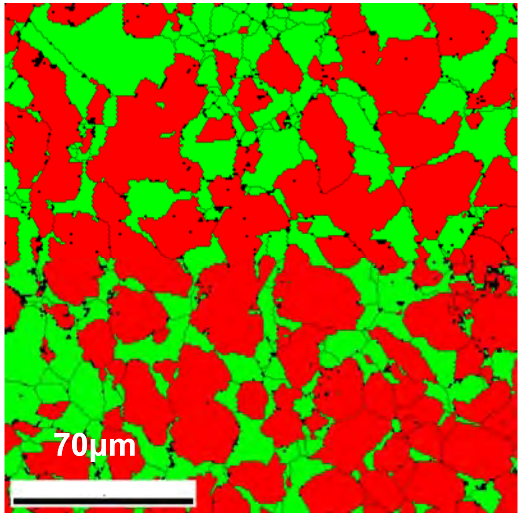


Microstructural analysis on SPSed specimens

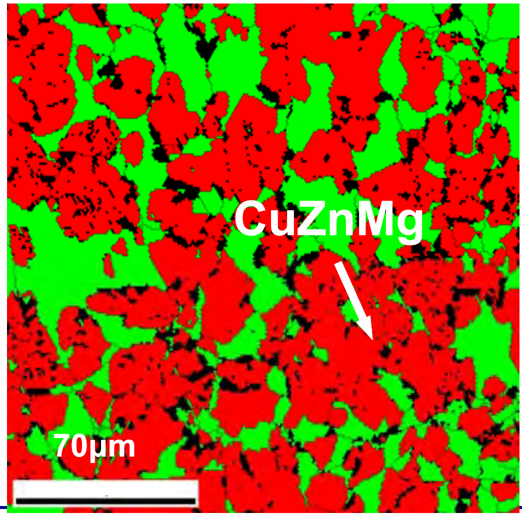
(a) BS40 (Cu-40%Zn)



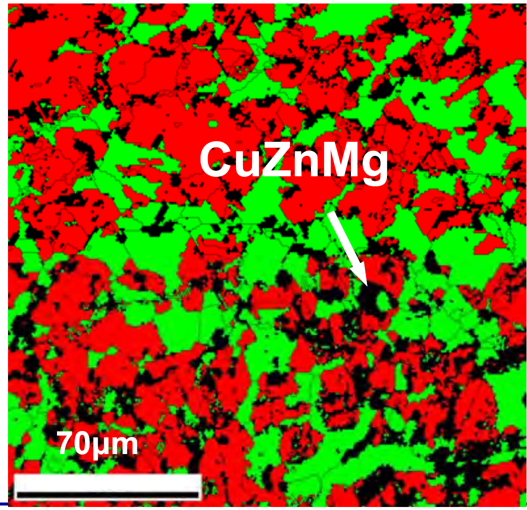
(b) BS40 +0.5%Mg



(c) BS40 +1.0%Mg



(d) BS40 +1.5%Mg



α-phase
β-phase

Increase of Mg content

⇩

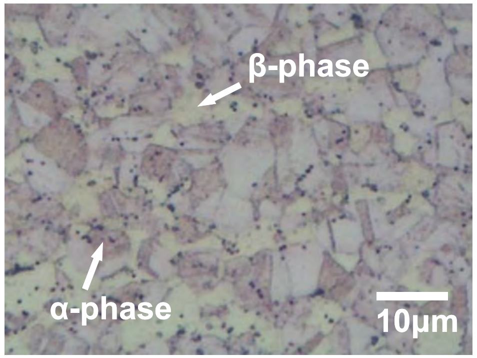
Increase in area fraction of β phase

Mg; β stabilization

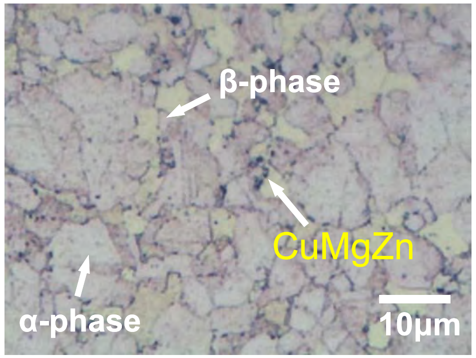
Microstructural analysis on hot extruded specimens

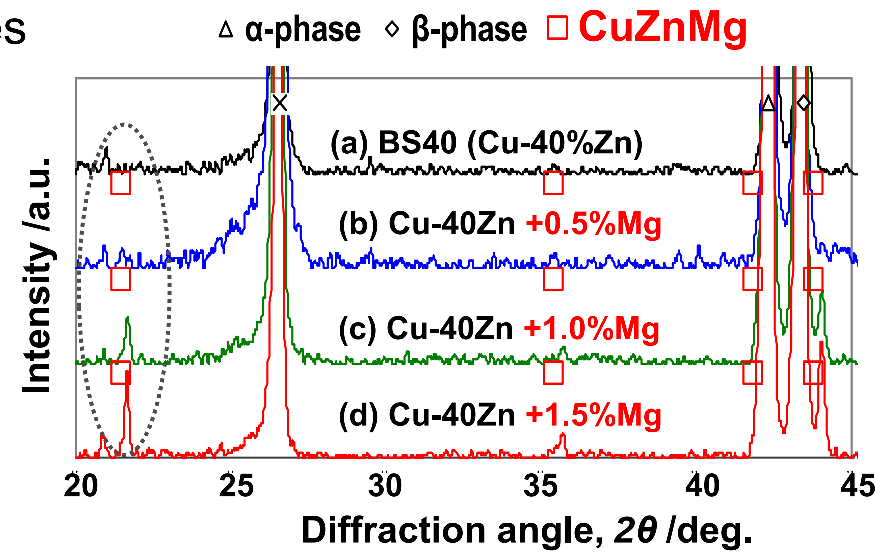
- CuZnMg (1:1:1) IMCs precipitation during cooling from 815K to R.T.
- β phase fraction increasing with increase in Mg content
- **Refinement of grains & IMCs** in α&β phases

(a-1) BS40 (Cu-40%Zn)

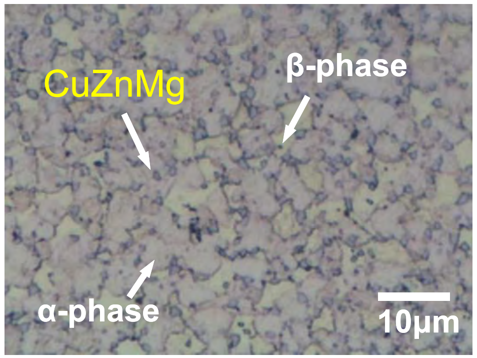


(a-2) BS40 +0.5%Mg

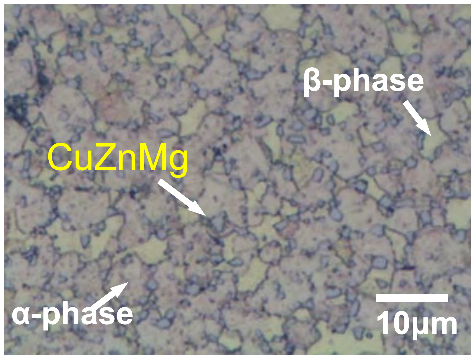


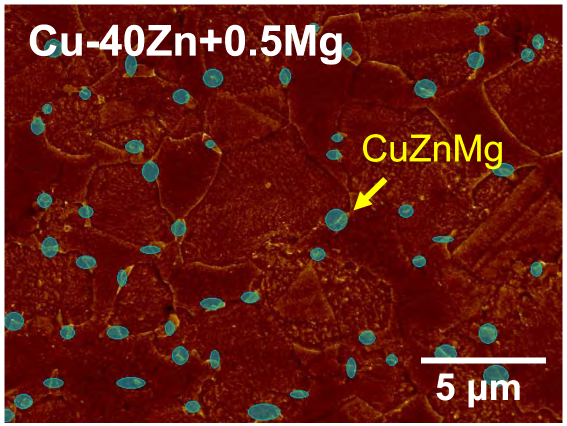


(a-3) BS40 +1.0%Mg

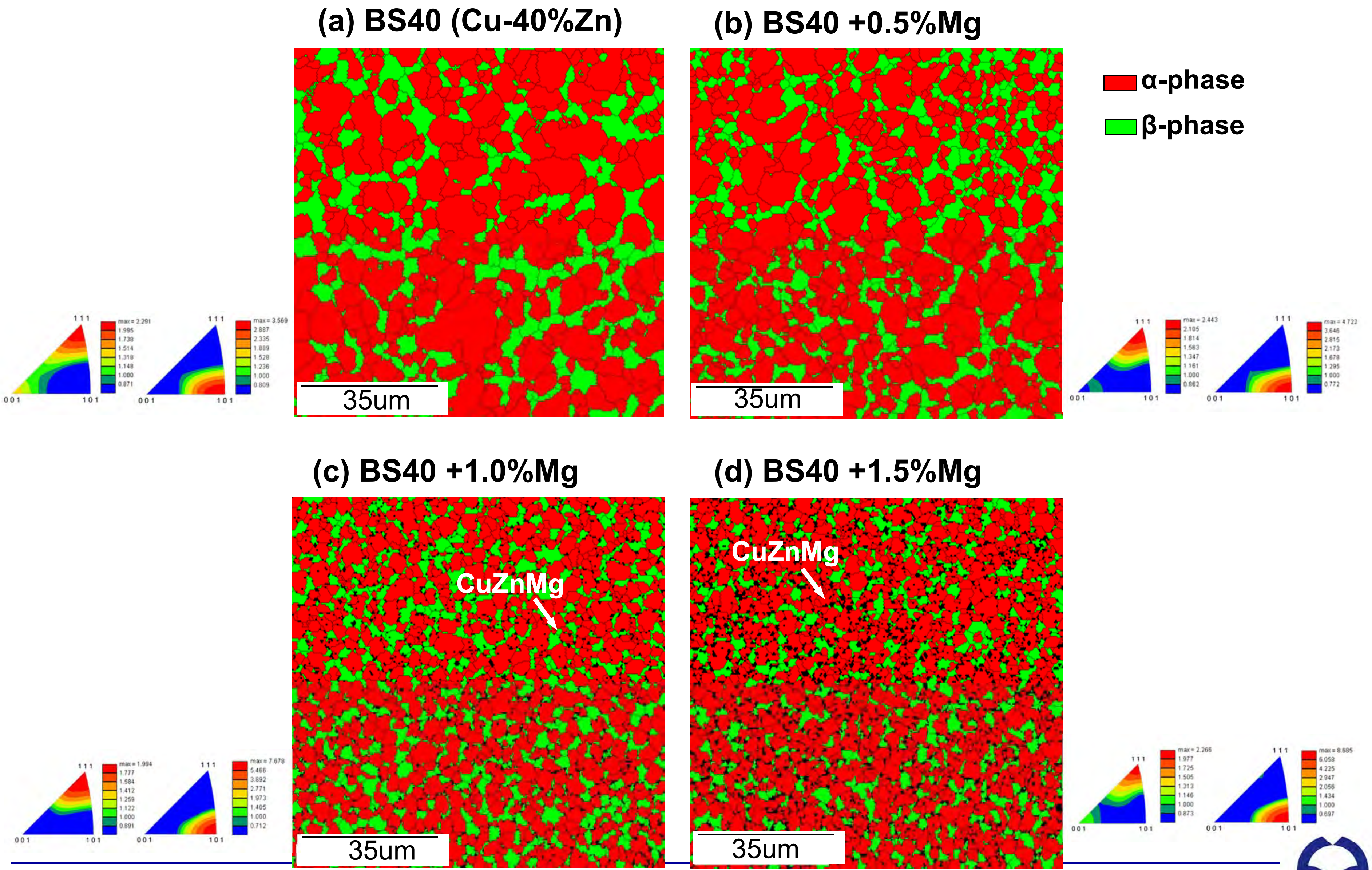


(a-4) BS40 +1.5%Mg

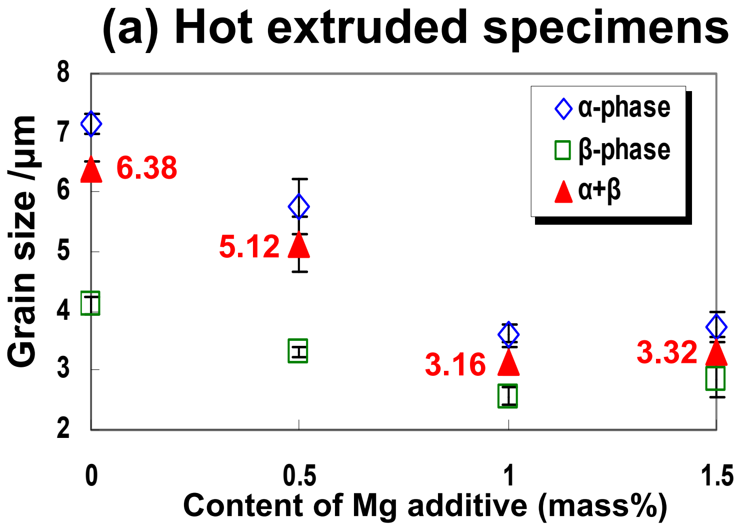


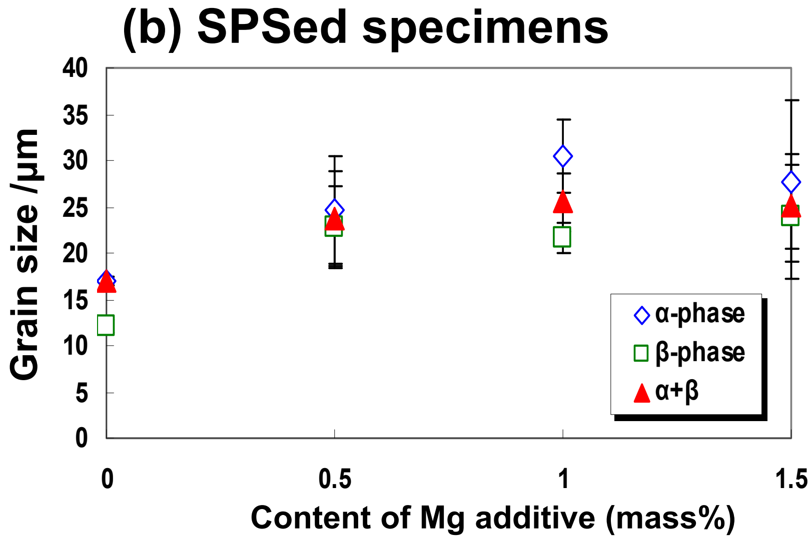


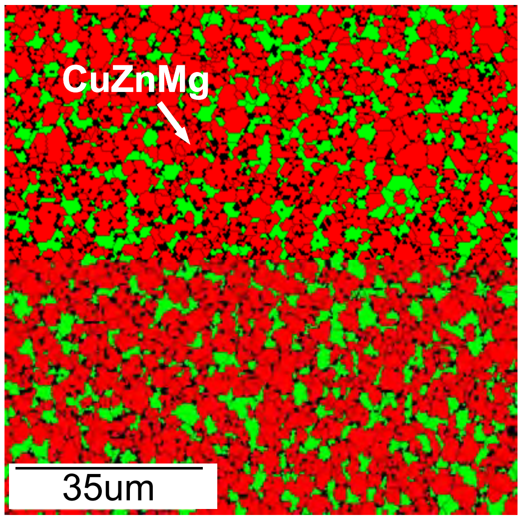
Microstructural analysis on hot extruded specimens



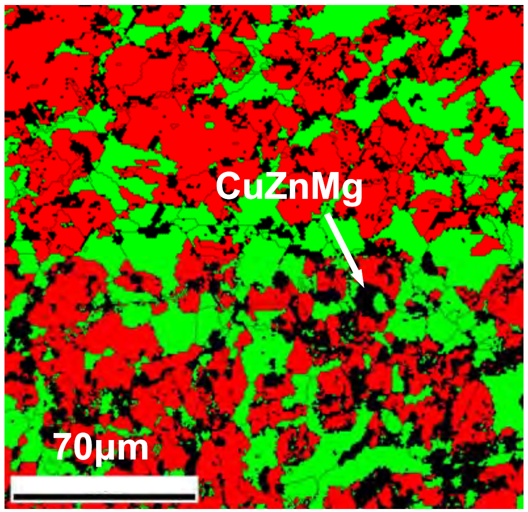
Microstructural analysis on hot extruded specimens





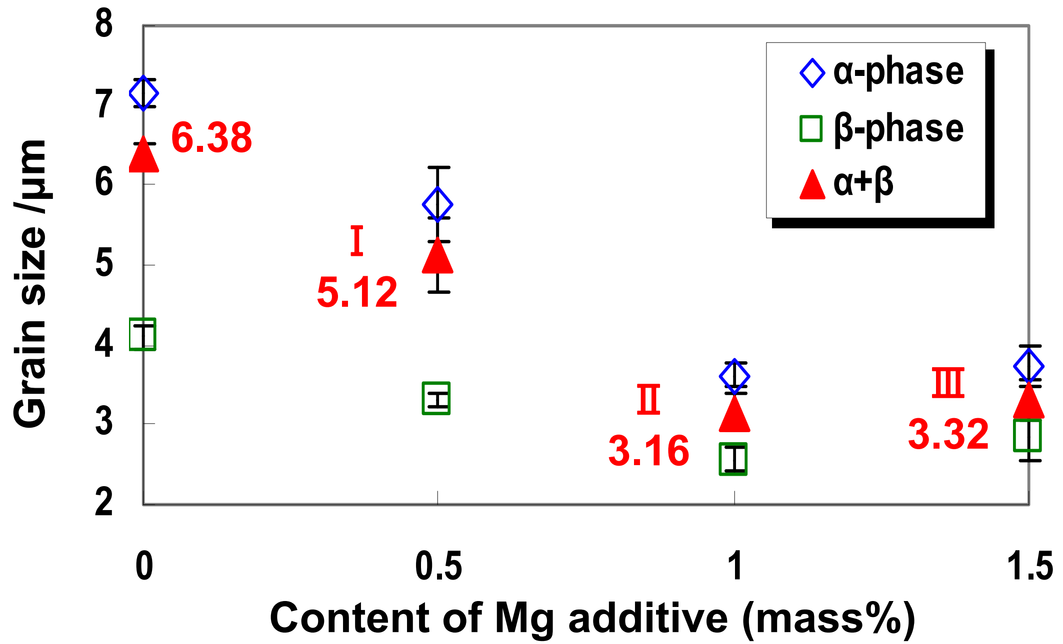


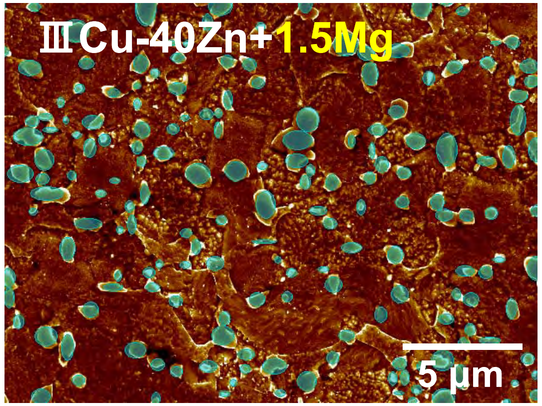
Hot extruded Cu-40%+1.5%Mg

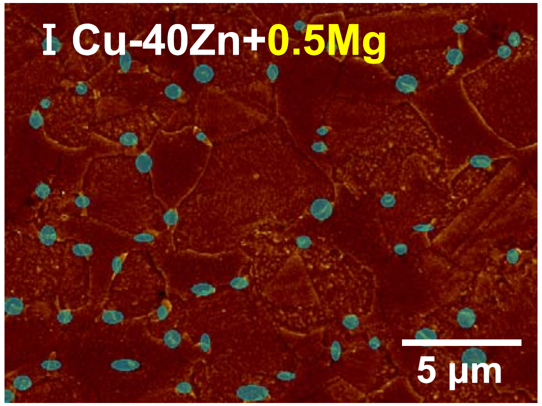


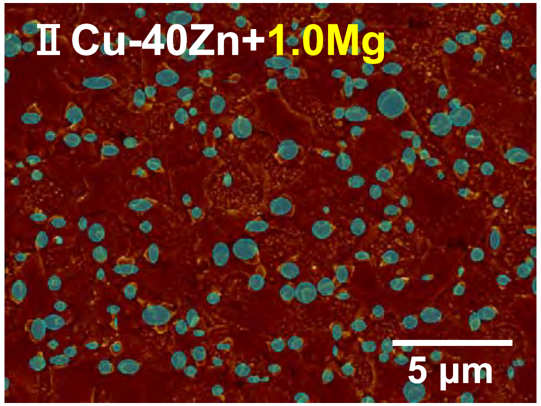
SPSed Cu-40%+1.5%Mg

Microstructural analysis on hot extruded specimens

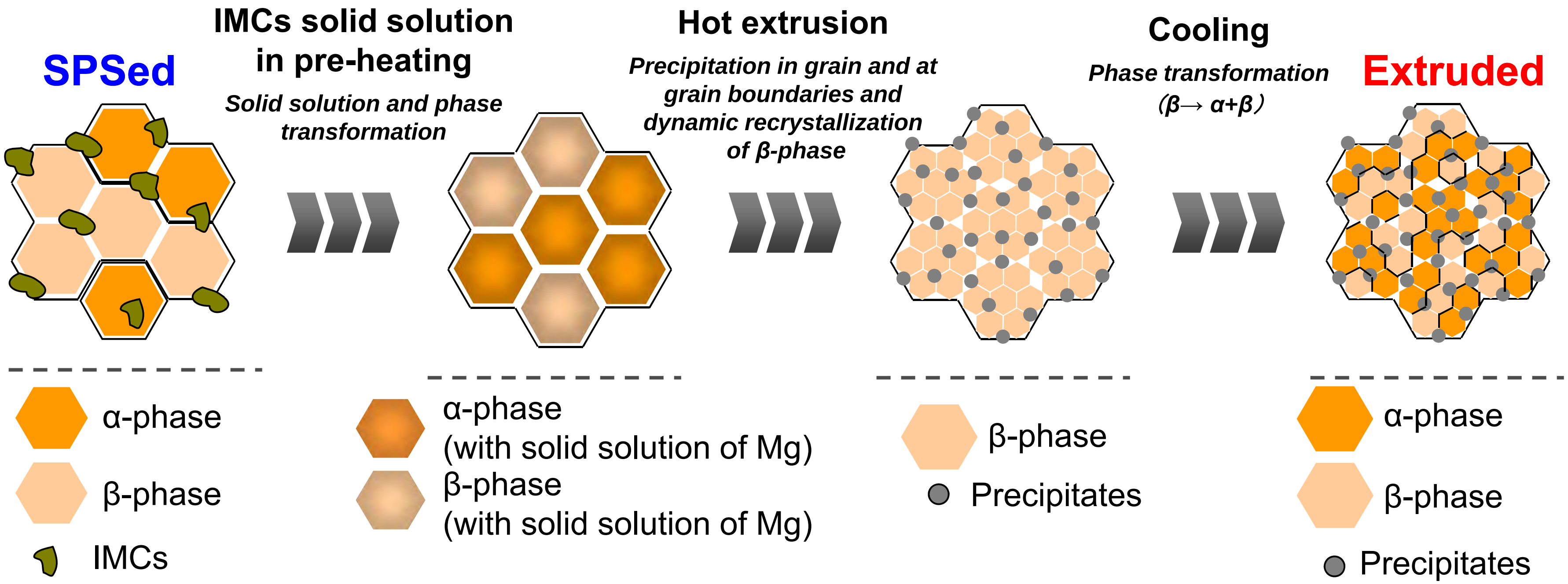


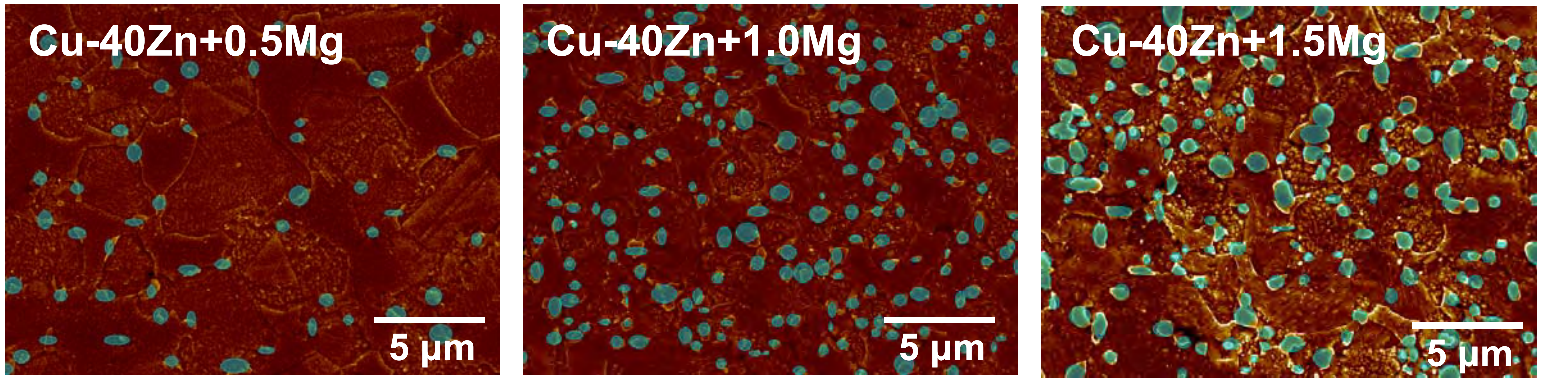






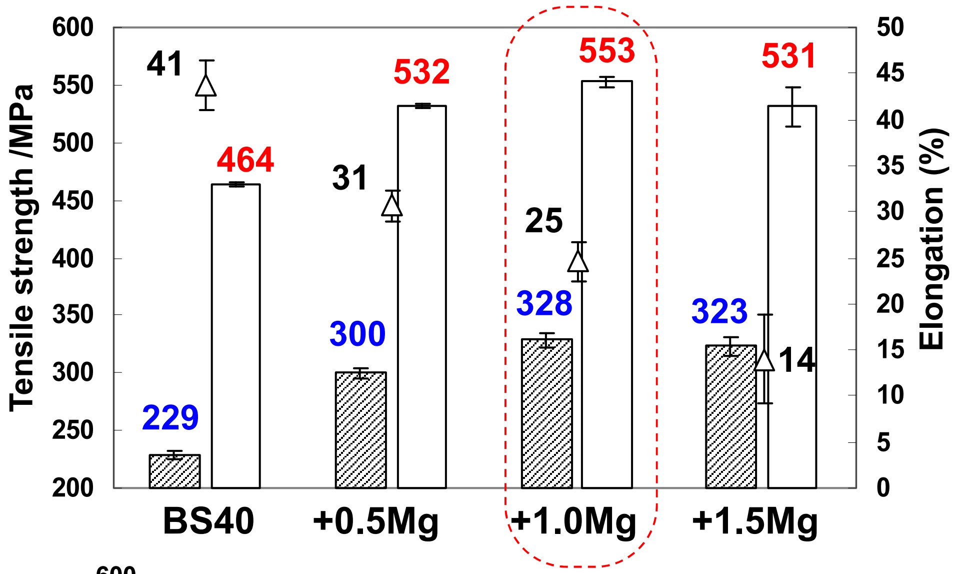
Grain refinement mechanism of Cu-40%Zn by Mg additive

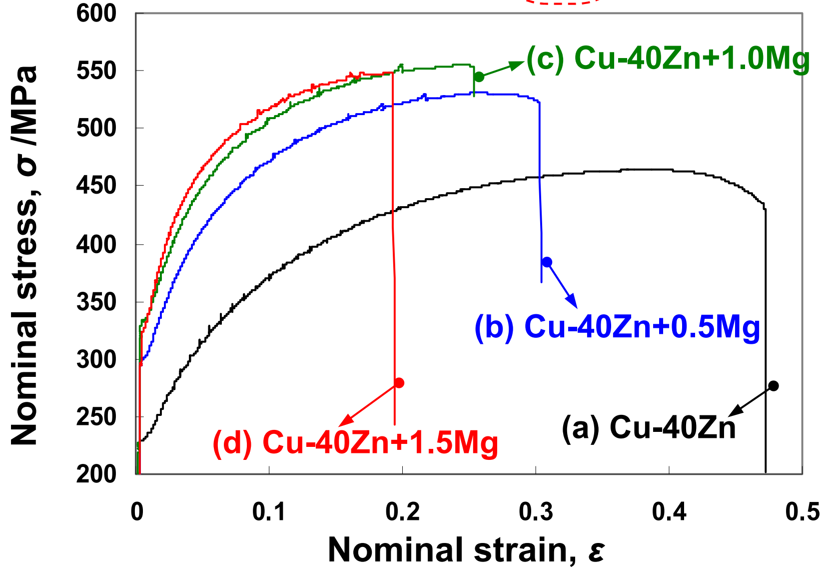


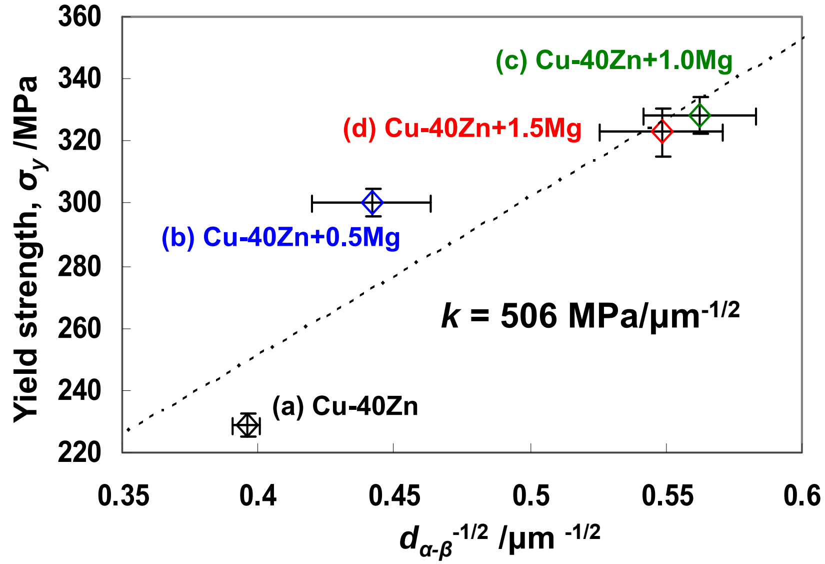


Transversal cross-section of the extrusion direction

Mechanical properties of hot extruded specimens







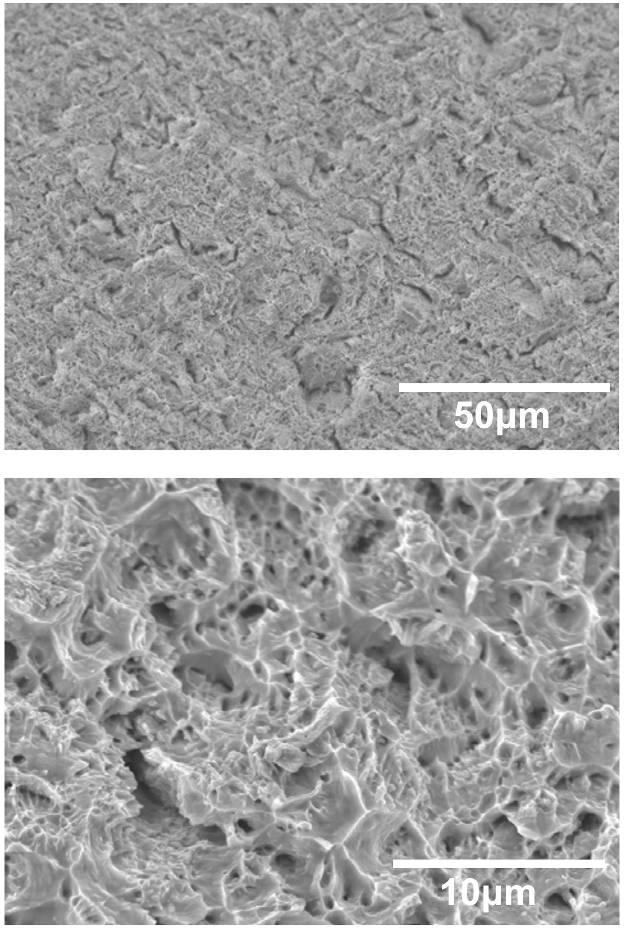
Hall-Petch coefficient of conventional α-β brass alloy with no additive:

$$^{*}\ k = \mathbf{541}\ \text{MPa}/\mu\text{m}^{-1/2}$$

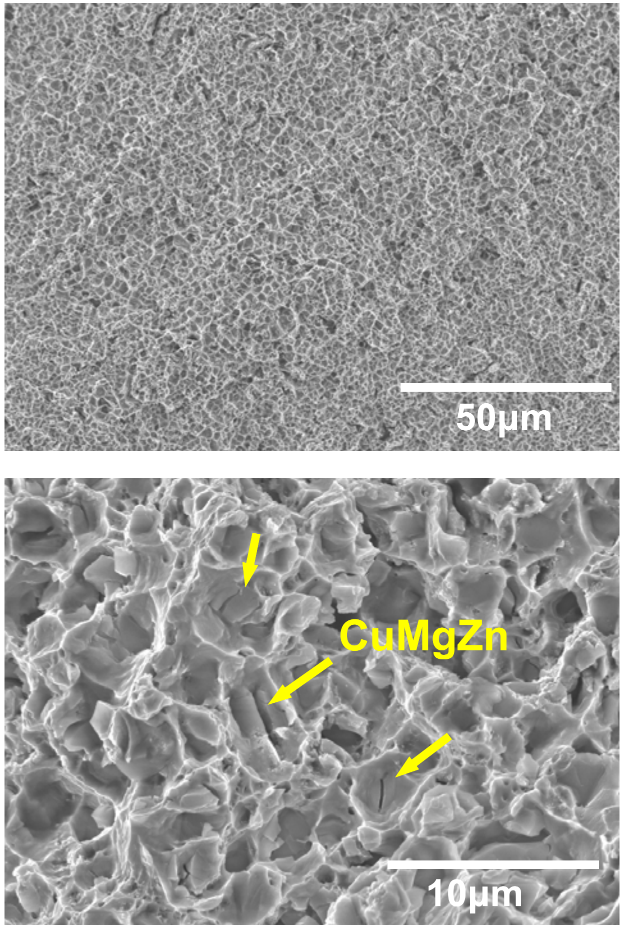
**E. Werner, H. P. Stijwe, Phase Boundaries as Obstacles to Dislocation Motion, Materials Science and Engineering, 68 (1984-1985) 175-182.*

Fractured surface analysis on tensile test specimens

Cu-40%Zn alloy



Cu-40%Zn +1.5%Mg alloy



Quantitative microstructural analysis on BS40+Mg+Gr alloy

Additive Gr particles effect on machinability

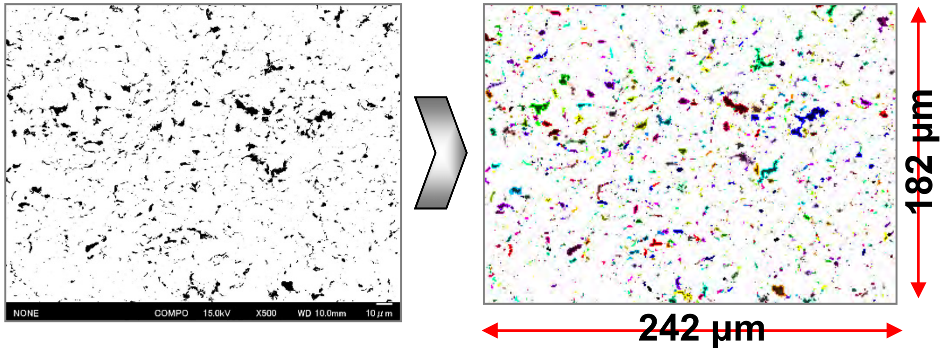
Estimation of Graphite particles area fraction in matrix of extruded Cu-40Zn+1.0Mg+Gr

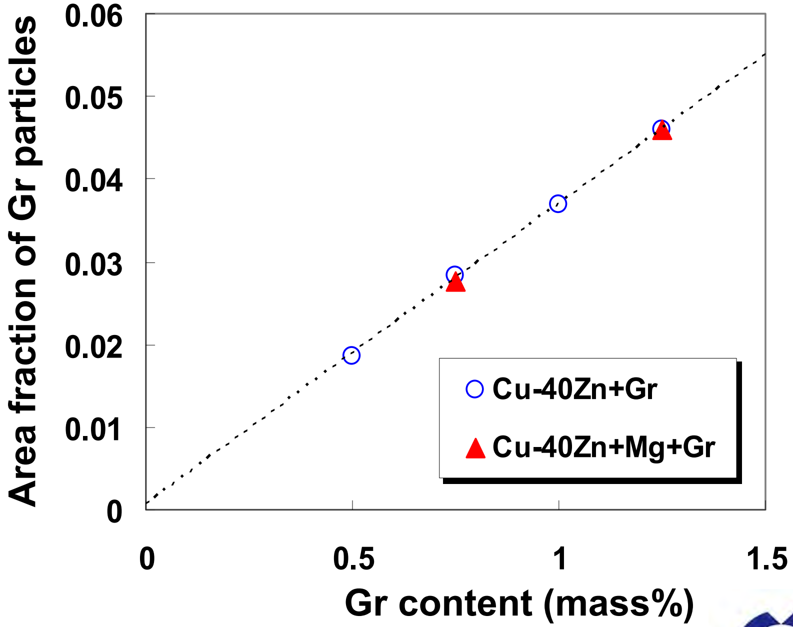
Machinability dependence on microstructures, in particular graphite dispersoids in matrix

Average of 6 images in analysis;

Gr content (%)	Area fraction of Gr particles in matrix (%)
0.5	**1.84**
0.75	**2.76**
1.0	**3.68**
1.25	**4.60**

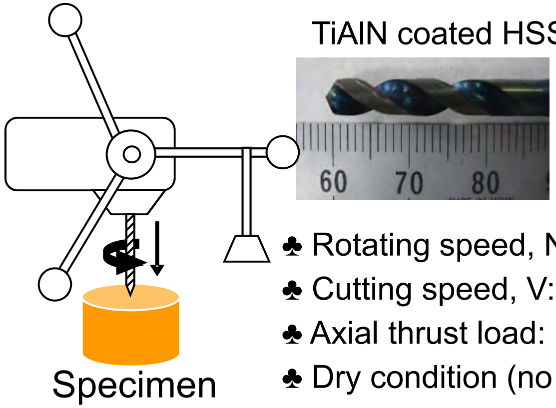
BSI **Analysis result**





Ex. Area fraction of Gr particles in matrix: **4.82 %**
Number of dispersed Gr particles: **3,394**
in case of Cu-40%Zn+1%Mg+1.25%Gr alloy

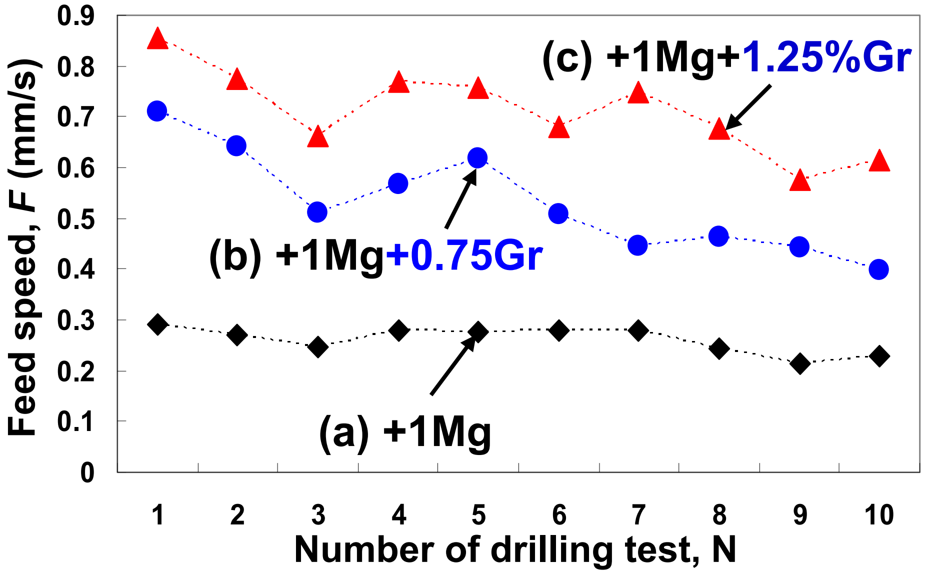
Machinability evaluation of BS40+Mg+Gr alloy



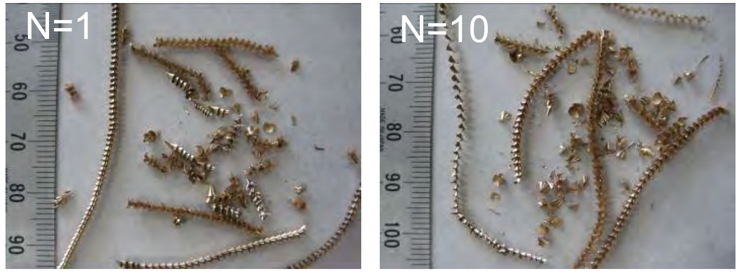
Diameter, D: 4.5mm
Helix angle: 30°
Point angle, α : 120°

- ♣ Rotating speed, N: 1140 (rpm)
- ♣ Cutting speed, V: 268.3 (mm/sec)
- ♣ Axial thrust load: 150 (N)
- ♣ Dry condition (no lubricant)

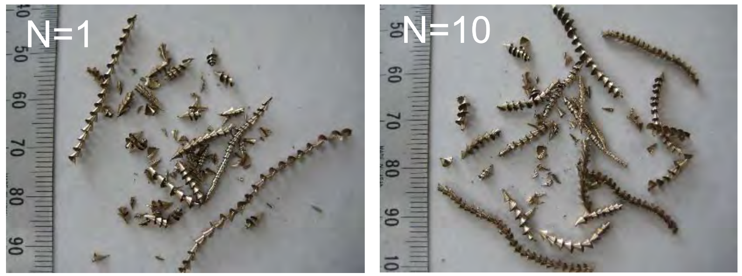
Measurement of drilling time for 5mm depth hole
→ Feed speed, F (mm/s); machinability parameter



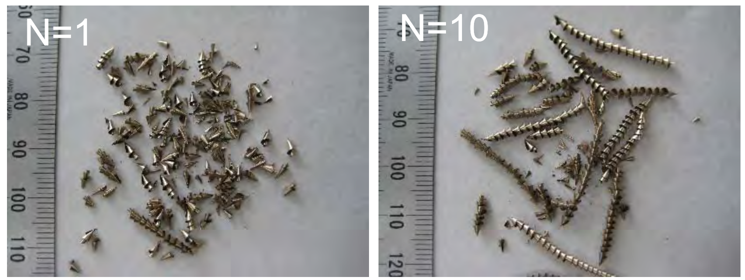
(a) Cu-40%Zn+1.0%Mg



(b) Cu-40%Zn+1.0%Mg**+0.75%Gr**

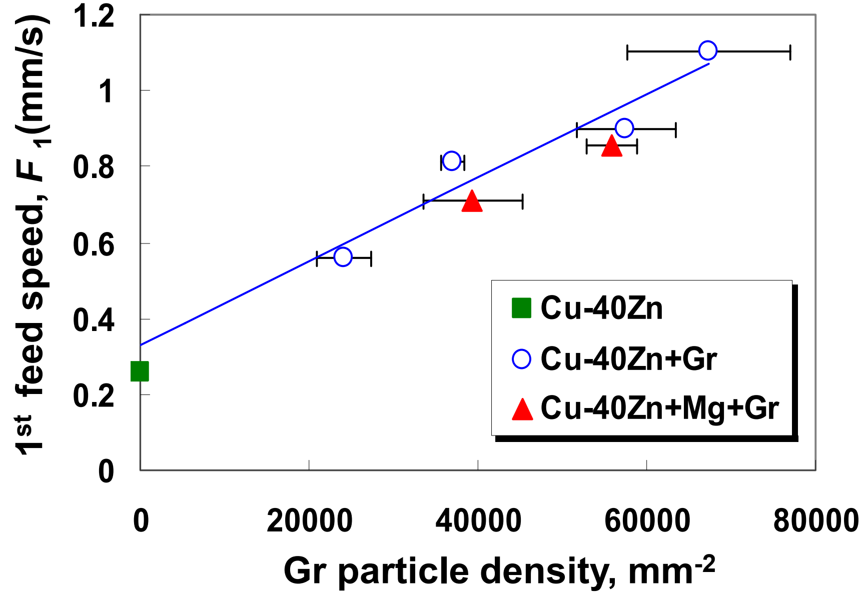


(c) Cu-40%Zn+1.0%Mg**+1.25%Gr**



Machinability evaluation of BS40+Mg+Gr alloy

- Machinability improvement in proportion to volume fraction (density) of Gr additives
- Brittle CuZnMg IMC dispersoids also effective for good machinability due to origin in micro-crack initiation

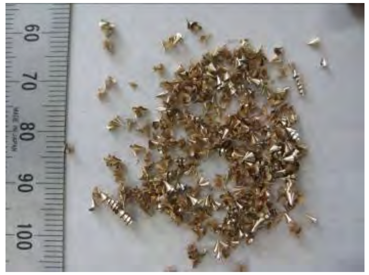


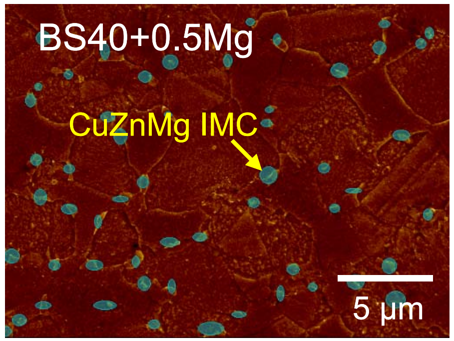
(a) Cu-40Zn (F=0.257 mm/s)

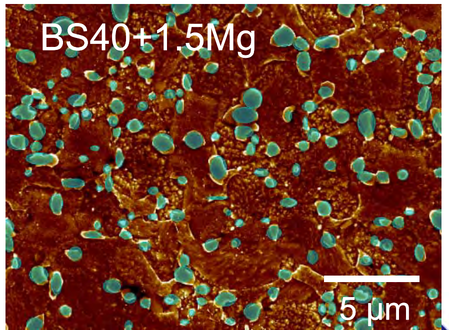
(b) BS40 +0.5Mg (F=0.263 mm/s)

(c) BS40 +1.0Mg (F=0.291 mm/s)

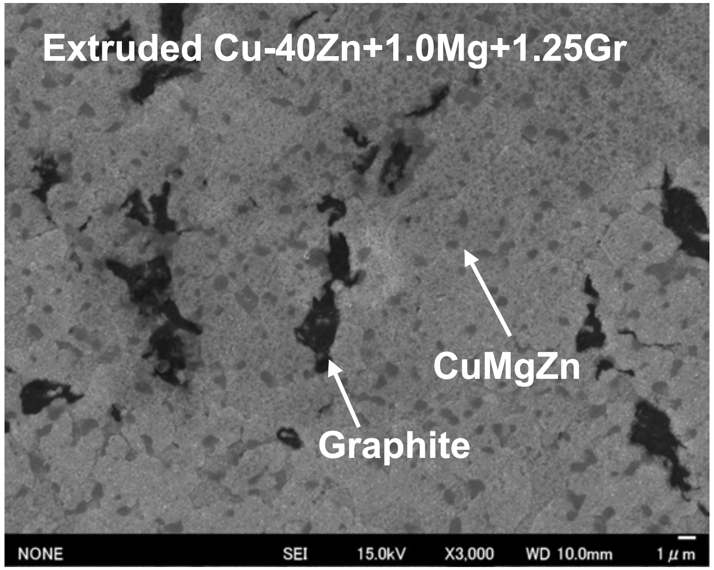
(d) BS40 +1.5Mg (F=0.322 mm/s)





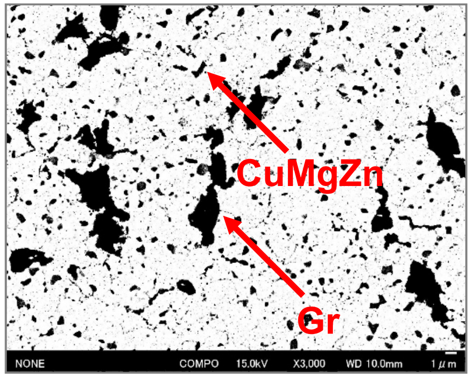


Quantitative microstructural analysis on BS40+Mg+Gr alloy

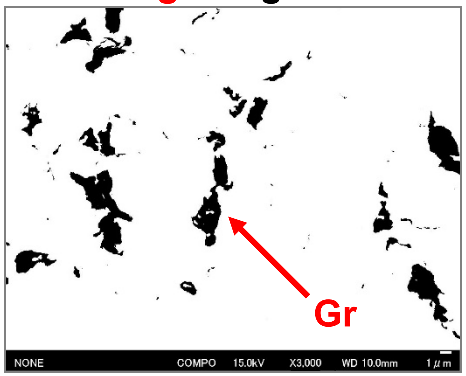


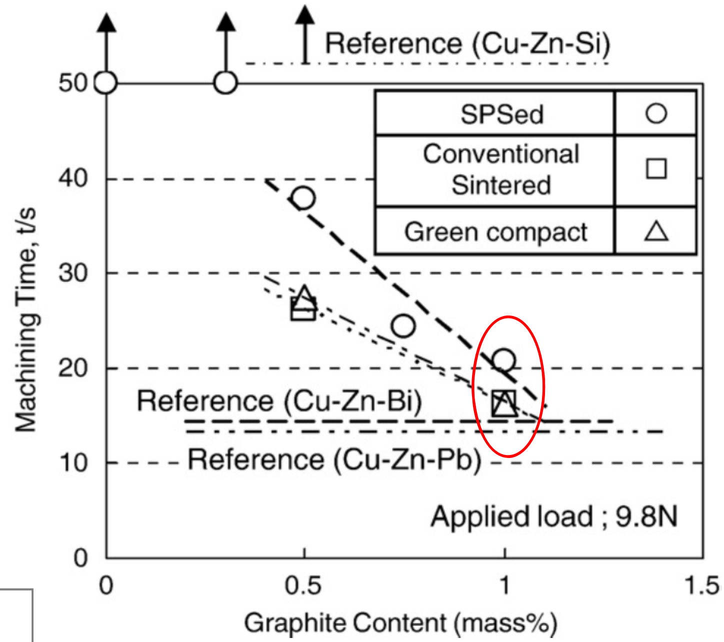
Transverse cross-section of extrusion direction

BSI –Middle brightness



BSI –High brightness





Summarized

- In using elemental mixture of Cu-40%Zn alloy and pure Mg powders and consolidating them by SPS and hot extrusion, β phase fraction increased with increase in the content of Mg additives.
- At the same time, grain refinement of α and β phases occurred because dynamic recrystallized grains never grew after extrusion by pinning effect of CuZnMg fine precipitates dispersed at grain boundaries.
- The mechanical property, in particular yield stress, was drastically improved by Mg addition of wrought BS40 alloys.
- Additive graphite particles were obviously effective to improve machinability of BS40+Mg+Gr alloys because stable Mg-C IMCs were never formed during consolidation by SPS and extrusion.

Acknowledgement

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