Advanced Materials　～夢をかたちに～

金属ガラス総合研究センター ニュース

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東北大学と大亜真空とで共同開発した小型自動アーク溶解装置の外観
アーク溶解法を用いた合金化と鋳造をコンピュータ制御で行う

CONTENTS

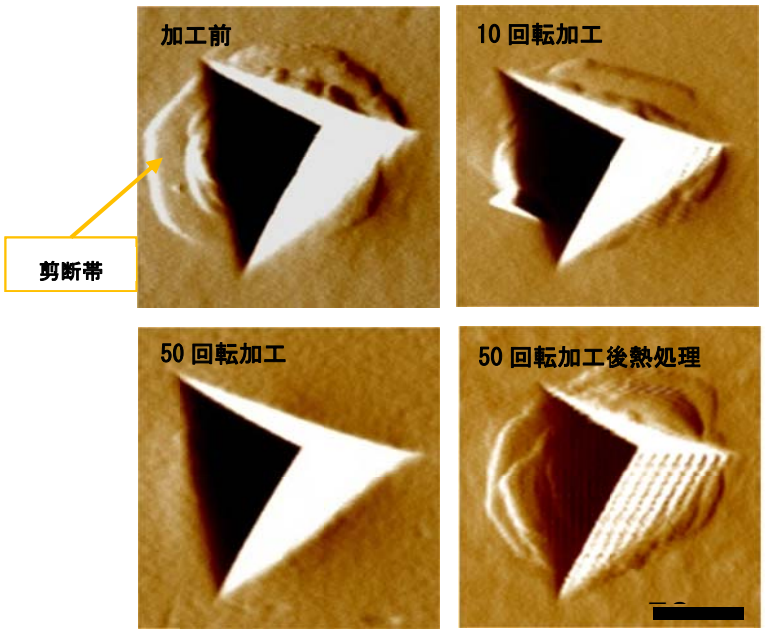
東北大学 金属材料研究所 附属金属ガラス総合研究センター
Advanced Research Center of Metallic Glasses, IMR, Tohoku University

研究成果

金属ガラスの“構造若返り”による異常軟化現象と剪断帯抑制効果を発見
“構造若返り”の利用で金属ガラスに常温加工の可能性を示唆

金属ガラス総合研究センター前期客員教授 土谷 浩一教授（独立行政法人物質・材料研究機構構造材料ユニット副ユニット長）らは、当センターとの共同研究により、金属ガラスに 5 GPa の高圧下で巨大な剪断ひずみを付与する事で、硬度や弾性率が顕著に減少する異常軟化現象を発見しました。この異常軟化に伴い金属ガラスを常温で変形したときに不均変形をもたらす剪断帯の発生が抑制され、均一変形していることを明らかにしました。

本研究成果は2012年9月24日発行のApplied Physics Letterに掲載されました。　（文責：横山嘉彦）



ナノインデンテーション圧痕の走査プローブ顕微鏡像の HPT 加工と熱処理(400℃,1 時間)による変化

小型自動アーク溶解炉の開発

アーク溶解法を自動化にするために必要な自動反転技術、溶湯攪拌技術について、大亜真空株式会社と共同開発し、同社から「小型自動アーク溶解炉」として発売されます（図 1 参照）。共同開発した複数の新技術について、東北大学と大亜真空株式会社との共同出願で特許を申請しております。

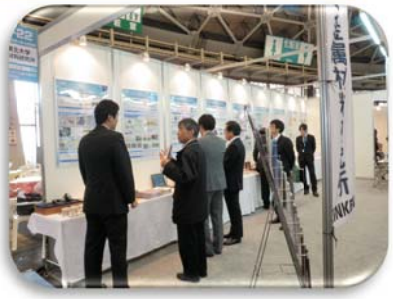
本小型自動アーク溶解炉を用いることで、合金や鋳造製品（単純形状に限る）の量産化は可能になり産業貢献が期待できますが、研究にとっても利点が期待できます。本開発装置は、その全ての動作をコンピューター（LabVIEW: National Instruments Co.）で制御しているため、インターネットに接続をすることで世界中のどこからでも本装置を操作することが可能になります。一方、金属材料研究所は、全国共同利用に取り組んでおりますが、共同利用研究者の中には思うように試料作製が行えず訪問期間のほとんどを試料作製に費やすケースが見られました。本開発装置を用いることで、金属ガラス総合研究センターで行っている全国共同利用の他大学の先生が、本所訪問の前に、試料作製を予備的に遠隔操作で実験することで効果的な共同研究の推進をすることが可能になるものと期待しております。

（文責：横山嘉彦）

図 1　開発装置の外観

活動報告

メッセナゴヤ2012　出展



11月7日（水）から10日（土）まで、名古屋市ポートメッセなごやに於いて～環境・安全・モノづくり～をテーマに開催された日本最大級異業種交流展示会“メッセナゴヤ2012”に当センターが出展をいたしました。

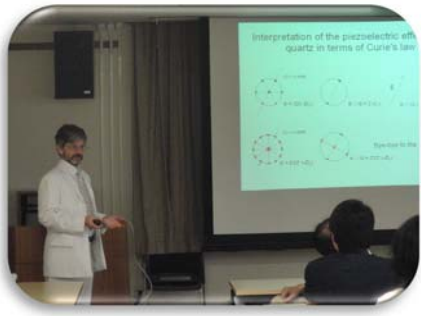
今回は東日本復興支援コーナーを含み、過去最大の650社が出展をする中、当センターも金属ガラスのボタン試料・バルク試料や実用製品の展示を行い、多くのお客様にお立ち寄りいただき研究成果をご紹介することが出来ました。

（文責：湯蓋邦夫）

金属ガラス総合研究センター　外国人客員研究員講演会開催

本年度、当センター招へい外国人客員研究員のうち、3名の先生方による講演会を以下の内容で実施いたしました。それぞれ多くの研究者および学生が聴講し、大変盛況でした。特に、ロレーヌ大学のMassimo先生の講演には多元研から、ソウル大学の朴先生の講演にはＮＩＭＳから、Peter先生の講演にはＷＰＩから、といった具合に、他部局や他大学からも多数のご参加をいただきました。

○フランス　ロレーヌ大学　教授　Nespolo Massimo 先生
「Challenges beyond conventional crystallography in theconventionalspace」6 月 20 日開催（於：本多記念館 3Ｆ聴覚室）
○韓国　ソウル大学　助教　朴 殷洙先生
「Property Manipulation of Metallic Glassesby Secondary Amorphous Phases」7 月 18 日開催（於：本多記念館 3Ｆ　視聴覚室）
○米国　テネシー大学　教授　Peter K. Liaw 先生
「Fatigue Behaivior of Metallic Glasses」7 月 31 日開催
（於：旧ＣＯＥ棟セミナー室 1）　（文責：横山　嘉彦）



H24 年度外国人客員研究員 研究成果報告

Formation and Mechanical Properties of Zr-based Bulk Metallic Glass Composites with In-situ Formed ZrN Particles

Prof. Eun Soo Park
Research Institute of Advanced Materials, Department of Materials Science and Engineering, Seoul National University, Seoul 151-744, Republic of Korea

From 28th of June to 10th of August 2012, I was a visiting professor in the Advanced Research Center of Metallic Glass at the Institute of Materials Research, Tohoku University, working with Associate Professor Yoshihiko Yokoyama. I had a prior experience of staying at the National Institute for Materials Science (NIMS) in Japan for three months during early 2003. However, this visit was the first experience to stay at IMR and in the Sendai area.

During this visit, I focused my research on development of novel Zr-based bulk metallic glass composites with in-situ formed ZrN particles. The research was performed by using the advanced apparatus of IMR and WPI of Tohoku University.

Bulk metallic glasses (BMGs) have begun to

attract increasing attention because they have many interesting characteristics such as high mechanical strength and corrosion resistance that are different from those of crystalline alloys due to the non-periodicity of their atomic arrangement. However, since the initiation and propagation of shear bands take place almost simultaneously, monolithic BMGs exhibit only limited plasticity due to the formation of highly localized shear bands under loading. The extent of the plastic deformation in the BMGs depends on the total amount of shear bands generated during deformation. Therefore, plasticity of the BMGs could be improved by generating a large number of shear bands and impeding their sudden propagation. Thus, the concept of constructing a heterogeneous microstructure by introducing secondary phases within a glassy matrix was adopted to improve plasticity of the BMGs. The in-situ formation of reinforcement during preparation of the composite has been thought to be effective for good wettability between dispersoids and matrix as well as homogenous dispersion of reinforcements. In this study, Zr-Al-Ni-Cu BMG matrix composites containing nitride ceramic particles were prepared by introducing particulate Al/AlN composites as starting materials. The microstructure of the composite reinforced with ZrN particles and their mechanical properties were investigated.

A Zr-Ni-Cu pre-alloy ingot was prepared by arc-melting pure metals in a Ti-gettered argon (99.999%) atmosphere. Subsequently, a mixture of the pre-alloyed ingot and Al/AlN composites (37 % volume fraction of AlN) was re-melted in the arc-melting furnace. BMG matrix composites with the matrix composition of $Zr_{55}Al_{10}Ni_5Cu_{30}$, which is a well-known high glass forming alloy, were prepared. Rapidly solidified specimens were prepared by re-melting the composite alloys in quartz tubes and ejecting with an over-pressure of 50 KPa through a nozzle onto a Cu wheel rotating with a surface velocity of 40 m/s. Cylindrical samples of 1-3 mm in diameter and 50mm in length were obtained by suction casting in a water cooled copper mold. The morphology and microstructure of the in-situ synthesized Zr BMG/ZrN composite were observed by scanning microscopy (SEM; JSM6360, JEOL). Phase composition of the composite was characterized by X-ray diffraction analysis (XRD; New D8 advance, Bruker) using monochromatic Cu K_α radiation for a 2θ range of 20-80°. The elastic modulus was obtained from ultrasonic measurement and the density of the composite was determined using the Archimedes' method.

Fig. 1 shows the XRD results of the as-spun ribbons and the master alloy. The mass fraction of the starting AlN particles in the composite was 1.7 wt. %. It was found that the pattern of the composite ribbon samples was composed of a halo pattern and diffraction peaks, indicating the coexistence of glassy and crystalline phases. It should be noted that the diffraction peaks are not assigned to the AlN phase but to the ZrN phase in both of composite ribbon and master alloy sample. These results indicate that chemical reaction(Zr + AlN → Al + ZrN) occurred during the arc melting.

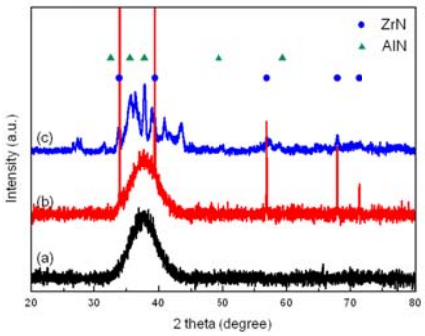


Fig. 1 XRD patterns for (a) $Zr_{55}Al_{10}Ni_5Cu_{30}$ ribbon; (b) Zr BMG/ZrN composite ribbon; (c) Zr BMG/ZrN composite master alloys

Fig. 2 shows a SEM image of cross-section of as-cast composite containing 4 vol.% ZrN. The ZrN particles under 10 μm sizes are homogeneously dispersed in BMG matrix. EDS analysis revealed that the bright spherical particles were ZrN and the grey massive domain surrounding the ZrN particles were Zr-Al-Ni-Cu metallic glass.

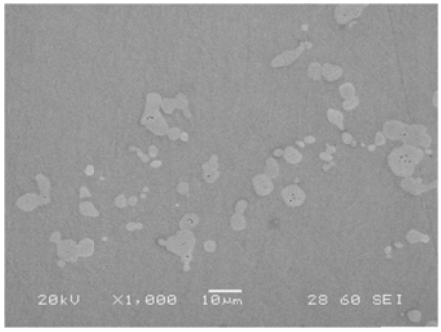


Fig. 2 SEM micrograph of *in-situ* formed ZrN reinforced Zr-based BMG composite

Fig. 3 shows mechanical properties of as-cast monolithic BMGs and composite with 1 mm diameter. The compression fracture strength of the Zr BMG/ZrN composite was about 2.1 GPa, being higher than that of the Zr BMG (about 1.7 GPa). It is also worth noting that the BMG composite showed improved plasticity before its fracture. In addition, a slightly serrated plastic flow was also observed in the plastic deformation region of the stress–strain curve. These results suggest that multiple shear bands were formed during plastic deformation. These improved mechanical properties attributed to the fine,homogeneously dispersed ZrN particles in the BGM matrixeously dispersed ZrN particles in the BMG matrix.

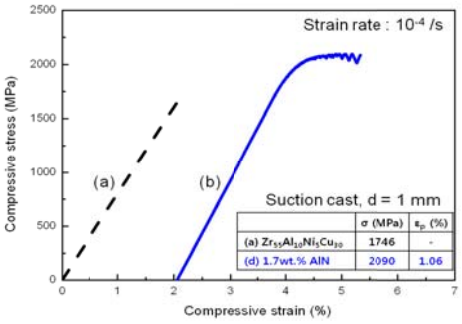


Fig.3 Compressive stress-strain curve at a strain rate 1.0 x 10^{-4} /s: (a) Zr BMG; (b) Zr BMG/ZrN composite (4 vol.% ZrN)

The Zr-based BMG matrix composites reinforced by the in situ produced ZrN particles were successfully fabricated by arc melting Zr-Ni-Cu pre-alloy and Al/AlN composite as starting materials. The ZrN particles of the order of micrometers in size considerably improve both the compressive strength and plasticity of the matrix. The compressive fracture strength increases from 1750 MPa in the ncluded that arc melting Zr-Ni-Cu pre-alloy and particulate Al/AlN composite as the starting materials is useful for preparing bulk, dispersed, crystalline nitride reinforced BMG composites with good mechanical properties.

During about 40 days of collaboration with Prof. Yoshihiko Yokoyama and staff members, we have done some valuable explorations to synthesize novel in-situ bulk metallic glass express my composites by using the advanced apparatus in IMR and WPI. These materials have a great potential for advanced structural applications. I would like to express my sincere gratitude to Prof. Yoshihiko Yokoyama for the invitation to IMR of Tohoku University. I also extend many thanks to Ms. Yuka Chiba for her many helps with the administrative paper work and very useful daily life advices.

Thank you all again and “Sayonara Kinken”

Evaluation of biphasic calcium phosphate for application of biomaterials; physical, chemical property and in vitro behavior

Prof. Seog-Young Yoon
School of Materials Science & Engineering, Pusan National University, South Korea

From 10th of July to 24th of August 2012, I worked as a visiting professor in the Advanced Research Center of Metallic Glass at the Institute of Materials Research, Tohoku University working with Associate Professor Hidemi Kato. I already had an experience to stay at IMR for one month and half during early year of 2009.

During this visit, I have been focusing my research on the evaluation of biphasic calcium phosphates (consisted of hydroxyapatite and beta-tricalcium phosphate) which are synthesized by aqueous method. The evaluation was pointed out physical and chemical properties such as the crystallinity, chemical state, morphologies before and after in vitro experiment by using the advanced apparatus of IMR and WPI of Tohoku University.

The most widely used calcium phosphate-based materials are hydroxyapatite [HAp, $Ca_{10}(PO_4)_6(OH)_2$] and β-tricalcium phosphate [β-TCP, $Ca_3(PO_4)_2$]. Despite their favorable biological properties, both materials have a number of drawbacks that reduce their clinical performance. *In vivo* and *in vitro* dissolution experiments have indicated that the dissolution of HAp in the human body after implantation is too low to achieve the optimal formation of bone tissue. On the other hand, β-TCP shows fast release of Ca^{2+} and PO_4^{3-} ions when exposed to physiological fluids. The fast dissolution profile drastically reduces the surface area available for bone cell proliferation and therefore, its application in the clinical setting is limited. An optimum bioresorbability was found when appropriately mixing both phases to give biphasic calcium phosphates (BCPs).

BCP powders were synthesized by the co-precipitation method using reagent-grade calcium nitrate tetrahydrate [$Ca(NO_3)_2 \cdot 4H_2O$] and di-ammonium hydrogen orthophosphate [$(NH_4)_2HPO_4$] as the starting materials. The various input Ca/P molar ratios employed to prepare the different contents of HAp and β-TCP phases. Hanks' balanced salt solution (HBSS), an extracellular solution with an ionic composition similar to human blood plasma, was used as the supporting solution for the BCP powders in an in vitro test.

XRD patterns of as-synthesized powders are presented in Fig. 1(a). The powders were characteristic of crystalline HAp phase except for the difference in peak width and absolute intensity of the diffraction patterns. Fig. 1(b) shows details of the XRD patterns recorded for the BCP powders calcined at 900oC. Calcination of the powders at this temperature indicates the improvement in crystallinity by the increase in the resolution of peaks when compared to the as-synthesized powders. At this temperature, all the powders have the β-TCP phase in addition to that of HAp phase thus confirming the formation of biphasic mixtures.

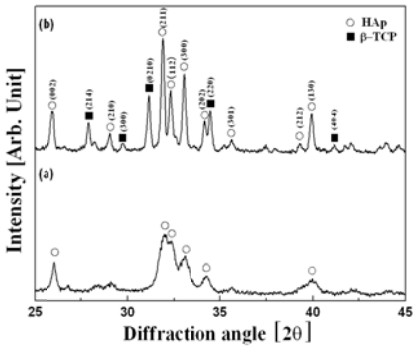


Fig.1. XRD patterns of BCP powders; (a) as-synthesized, (b) as-calcined.

FTIR spectra for the as-synthesized powders presented in Fig. 2(a) have indicated the vibrational modes of PO_4 groups at 574, 603, and 1020-1120 cm^{-1} and OH groups (630 and 3570 cm^{-1}) of apatite phase for the powders. FTIR patterns also tend to coincide with the results from XRD by the way that the as-synthesized powders were characteristic of crystalline HAp phase. The presence of adsorbed water could be detected from FTIR spectra in the region around 3300-3600 cm^{-1}. Other information from FTIR spectra of as-synthesized powders is presence of carbonates groups at 870 cm^{-1}, which are due to the adsorption of species remaining from the aqueous precipitation. The presence of nitrates in the as-synthesized powders is clearly witnessed in the FTIR patterns in the region around at 825 and 1385 cm^{-1}. From the FTIR spectra presented in Fig. 2(b), the overall spectra are appeared at having mainly two modes corresponding to characteristic PO_4^{3-} and OH^- groups.

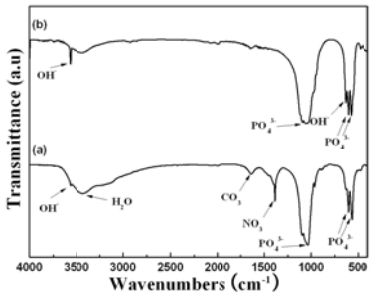


Fig.2. FT-IR spectra of BCP powders; (a) as-synthesized, (b) as-calcined.

To determine the changes in the degradation behavior of the prepared BCP powders as a function of soaking time in HBSS. Fig. 3 shows the typical features of powders after immersing in HBSS for 1, 2, and 3 weeks, respectively. After immersion in HBSS for 1 week, the precipitation starts to be formed with individual small pieces on each BCP powders. With increase of soaking time, the pieces gradually grow together to form a dense layer on the overall BCP powders surface. The EDS analysis showed the new formed precipitates had the Ca and P, indicating calcium deficient apatite phase.

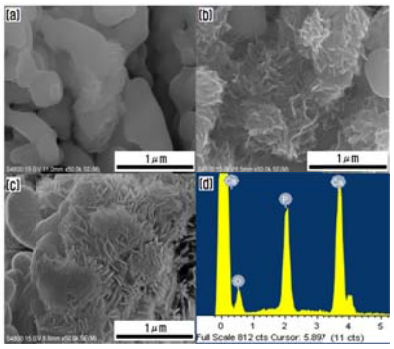


Fig.3. SEM morphologies of calcined BCP powders after immersion in HBSS for (a) 1, (b) 2, and (c) 3 weeks, (d) EDS f (c).

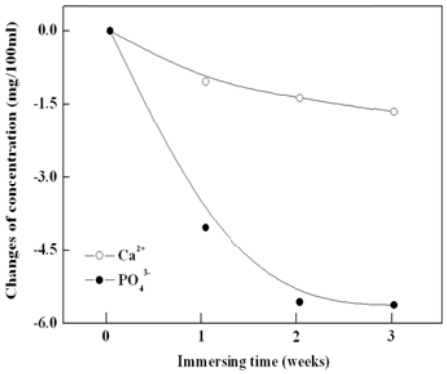


Fig.4. Changes of Ca^{2+} and PO_4^{3-} ions concentrations in HBSS immersed with calcined BCP powder with 3 weeks.

The ICP-AES analysis reveals the changes of Ca^{2+} and PO_4^{3-} concentrations in HBSS after immersing the BCP powder, as shown in Fig. 4. The concentration of Ca^{2+} and PO_4^{3-} ions and in HBSS continually decreased with immersing time, suggesting that the Ca^{2+} and PO_4^{3-} ions might be consumed by formation of a new product. the Ca^{2+} and PO_4^{3-} ions in HBSS were continuously consumed, which indicated that the Ca^{2+} and PO_4^{3-} ions were supersaturated around the magnesium substituted BCP powder and a new calcium deficient apatite phase continually grew on the sample surfaces with increase of immersing time.

This study demonstrates that the co-precipitation method is an effective technique for preparing BCPs whose content in ß-TCP and HAp can be precisely determined from the precursor solutions. After immersion in HBSS for 1 week, precipitation started at individual small particles on the BCP powders. With increases in the soaking time, the particles gradually grew together and formed a dense layer on the specimen surface. Furthermore, BCP have been shown to be effective for new bone generation implant materials.

During the two months of collaboration with Prof. H.Kato and staff members, we have done some valuable explorations to synthesize some novel biomaterials by using the advanced apparatus in IMR and WPI. These materials have a great potential for medical applications.

I would like to express my sincere gratitude to Prof. H.Kato for the invitation to IMR of Tohoku

University. I also extend many thanks to Ms. K.Sekiguchi for her many helps with the administrative paper work and very useful daily life advices.

Thank you all again and “Sayonara Kinken”

CoCrCuFeNi High Entropy Alloys Subjected to Cyclic Loads

Prof. Peter K Liaw
Department of Materials Science and Engineering,
University of Tennessee, USA

From 20th of July to 24th of August 2012, I worked as a visiting professor at the Advanced Research Center of Metallic Glasses at the Institute of Materials Research, Tohoku University working with Professor Yoshihiko Yokoyama.

During this visit, I have been focusing my research on an $Al_{0.5}CoCrCuFeNi$ high entropy alloy (HEA) to study its fatigue behavior with Prof. Yoshihiko Yokoyama. Moreover, a Weibull predictive model and a Weibull mixture predictive model are conducted statistically to further investigate the scatter fatigue characteristics with Prof. T. Yuan of Ohio University, such as a noticeable amount of scatter at various stress levels of HEAs.

Recently, HEAs have attracted increasing attentions because of their unique composition, phase structures, and good mechanical properties. They can be defined as solid-solution alloys that contain more than five principal elements in equal or near equal atomic ratios and can be extended to those compositions in which each principal element concentration is between 5 and 35 at.%. In the as-rolled and as-anneal condition, the $Al_{0.5}CoCrCuFeNi$ HEA has a better combination of strength and ductility. The mechanical properties of the as-cast $Al_xCoCrCuFeNi$ (x = 0 - 3) alloys provided by Prof. Jien Wei Yeh of National Tsing Hua University are readily available. However, essentially no research has been performed on studying the fatigue behavior of this and other promising HEA systems.

The specimens of Al0.5CoCrCuFeNi (molar ratio) are prepared by arc melting the constituent elements at a current of 500 A in a water-cooled copper hearth. The compositions are all at least 99 wt. % pure. The cast samples are annealed at 1,000 °C for 6 h, water quenched, and then cold rolled. The rolling reduction is 84%, with a final thickness of 3 mm. Samples are machined to four-point-bending fatigue samples of 25 × 3 × 3 mm parallel to the rolling direction. To remove as many surface imperfections as possible, the samples are polished.

Tension tests are initially performed on the samples to characterize the mechanical property of the rolled material. The results are shown in Figure 1. The specimens exhibit a high yield stress of 1,284 MPa and an ultimate tensile strength of 1,344 MPa with a tensile elongation of 7.6%.

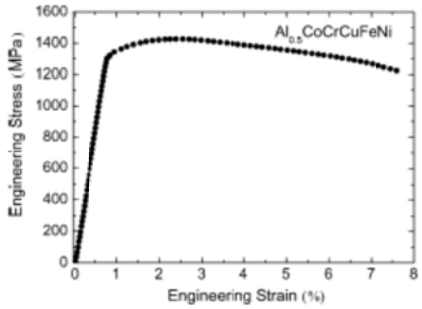


Fig. 1 Tension test flow curve for the $Al_{0.5}CoCrCuFeNi$ HEA [1].

The synchrotron X-ray diffraction (XRD) pattern of the $Al_{0.5}CoCrCuFeNi$ HEA, seen in Figure 2, indicates a face-centered-cubic (fcc) structure with the presence of an ordered Ll_2 phase. Only one set of fcc peaks is seen in the XRD pattern. Using the back-scattered electron microscopy (BSE) and energy-dispersive X-ray spectroscopy (EDS) techniques, the microstructure consists of two phases: the α-fcc matrix phase and the ß-fcc Cu-rich phase.

Four-point-bending fatigue tests are performed and the results are plotted as the stress range vs. the number of cycles to failure or 10^7 cycles to give the stress vs. cycles to failure curve seen in Figure 3. There is a noticeable amount of scatter at various stress levels. At a maximum stress of 1,250 MPa, most failures are within a range of 35,000 – 450,000 cycles. As the stress level decreased, the spread in the data become even more obvious. Based on the stress ranges, estimations of the endurance limits are within a lower bound of 540 MPa and an upper bound of 945 MPa. Values were chosen since the specimens reach 10^7 cycles without failure.

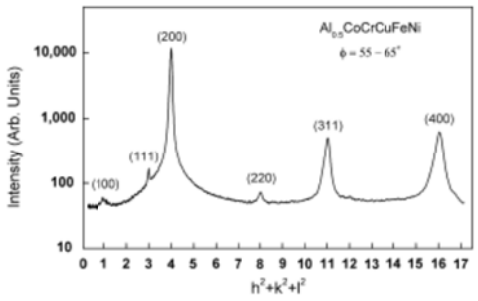


Fig. 2 Diffraction pattern of the $Al_{0.5}CoCrCuFeNi$ HEA using synchrotron high energy X-rays [1].

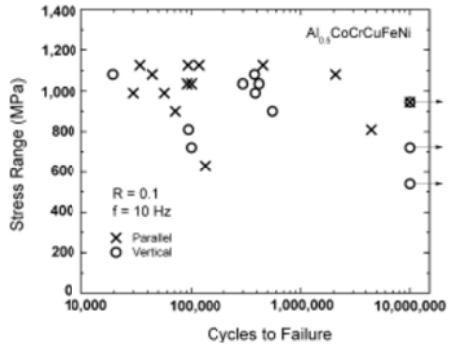


Fig. 3 S-N curve for the $Al_{0.5}$CoCrCuFeNi HEAs showing scattering of the cycles to failure for the parallel and vertical type morphologies, respectively, in the sample [1].

To determine whether mircrostructrual morphology has an effect on the fatigue life, the microstructure of fatigue specimens are indentified by scanning electron microscopy (SEM). Figure 3 shows the fatigue behavior of the parallel and vertical types of samples. It appears that there is no correlation between the scatter in the fatigue life and the orientation of the loading direction resulted from the different morphologies. The compositions of defects in the sample are performed by EDS analyses, seen in Figure 4. This feature shows the presence of about 50% oxygen, together with aluminum oxide particles, which provide nucleation sites for microcracks due to stress concentration at particles. The number of cycles to failure vs. the number of defects is presented in Figure 5. It can be found that a decrease in the number of defects generally correlates with an increase in the fatigue life at various stress levels.

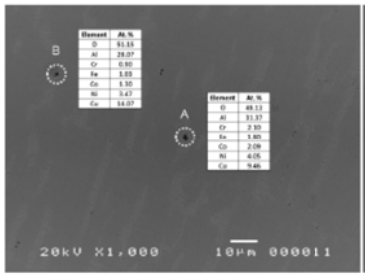


Fig. 4 SEM micrograph with EDS analyses of the aluminum-oxide particles. The compositions of the regions labeled A and B are given in the corresponding tables, indicating the presence of aluminum oxide particles [1].

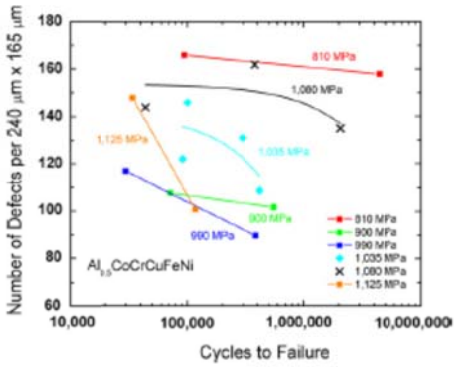


Figure 5 The cycles to failure compared with the number of surface defects at various stress levels [1].

Statistical fatigue-lifespan models are also developed to predict the fatigue life of HEAs. The first model assumes a Weibull distribution to explain the fatigue-life span distribution in each fixed stress range. The probability density function (PDF) is shown by Eq. (1),

(1)

where β is the Weibull shape parameter, and the Weibull scale parameter, $\alpha(S)$, depends on the stress S according to,

$$\log(\alpha(S)) = \gamma_0 + \gamma_1 \log(S) \qquad (2)$$

The modeling values of the three parameters are β = 0.492, γ_0 = 70.869, and γ_1 = -8.327. Figure 6 indicates the predicted median, 0.025 quantile, and 0.975 quantile fatigue lives.

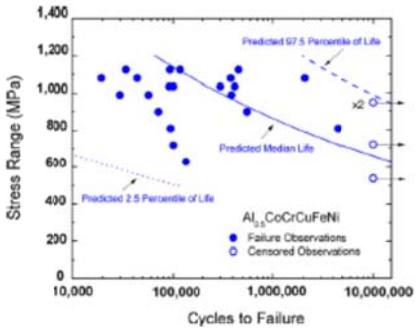


Fig. 6 Predicted quantile lives using the Weibull predictive model [1].

To characterize the excessive variability in the observed fatigue data, the Weibull mixture predictive model, which assumes a mixture of two Weibull distributions for the fatigue lives at each stress range value is used. The PDF is given in Eq. (3),

$$f(N(S)|p,\alpha_w(S),\beta_W,\alpha_s(S),\beta)_s = \qquad (3)$$
$$p\frac{\beta w}{\alpha w(S)}\left(\frac{N(S)}{\alpha(S)}\right)^{\beta w-1}\exp\left(-\left(\frac{N(S)}{\alpha_w(S)}\right)^{\beta_w}\right)$$
$$+(1-p)\frac{\beta s}{\alpha s(S)}\left(\frac{N(S)}{\alpha s(S)}\right)^{\beta s-1}\exp\left(-\left(\frac{N(S)}{\alpha s(S)}\right)^{\beta s}\right)$$

Again, the Weibull scale parameters, $\alpha_\omega(S)$, and, $\alpha_s(S)$, are assumed to be dependent on the stress S according to Eqs. (4) and (5)

$$\log(\alpha_w(S)) = \gamma_{w,0} + \gamma_{w,1}\log(S) \qquad (4)$$

$$\log(\alpha_s(S)) = \gamma_{s,0} + \gamma_{s,1}\log(S) \qquad (5)$$

Then, the seven model parameters are obtained. They are as follows, p = 0.369, β_w = 3.773, $\gamma_{w,0}$ = 15.238, $\gamma_{w,1}$ = -0.555, β_s = 0.612, $\gamma_{s,o}$ = 126.454,and$\gamma_{s,1}$ = -16.245. Figure 7 shows the quantile lives predicted.

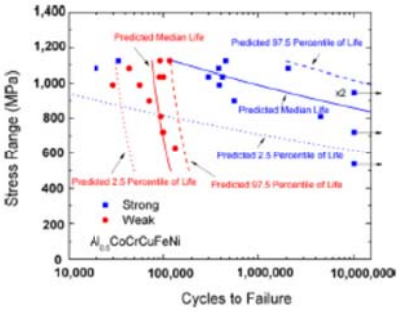


Fig. 7 Predicted quantile lives using the Weibull mixture predictive model [1].

Both the experimental and computational results confirm that the fatigue-life cycle relations of the HEA are controlled by defects to a great extent. In total, four specimens reached the endurance limit. HEAs have favorable and/or greater endurance limits and fatigue ratios comparable with steels, aluminum alloys, nickel alloys, titanium alloys and BMGs, as shown in Figure 8.

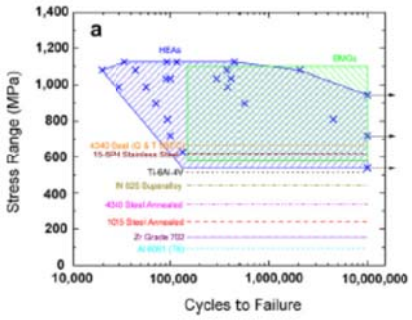


Fig. 8 S-N curves comparing the endurance limits of the $Al_{0.5}$CoCrCuFeNi HEA, other conventional alloys, and BMGs[1].

Through the above experiments [1], we have learned that defects play an important role in the fatigue behavior of $Al_{0.5}$CoCrCuFeNi HEAs, which show promising fatigue resistance characteristics and may be useful in future applications where fatigue is a factor. Therefore, our future work will focus on fabricating $Al_{0.5}$CoCrCuFeNi HEAs with fewer defects.

During the one month of collaboration with Prof. Yokoyama and staff members, we have done some valuable explorations to fabricate pure HEAs to improve fatigue behavior, discuss how to model its fatigue behavior and fabricate better alloys with less defects. Prof. Yokoyama has fabricated the HEA material with fewer amounts of oxide inclusions. These materials are currently under processing by Prof. Yeh. Then our member, Ms. Haoyan Diao, will study the fatigue behavior of the samples and compare the results with the previous data mentioned above.

We would like to thank Prof. Yokoyama, Prof. Yuan, Ms. Yuka Chiba, Prof. J. W. Yeh, Mr. Michael Hemphill, and Ms. Haoyan Diao for all their help in our joint research.

Reference

[1] M. A. Hemphill, T. Yuan, G. Y. Wang, J. W. Yeh, C. W. Tsai, A. Chuang, and P. K. Liaw. Fatigue behavior of Al0.5CoCrCuFeNi high entropy alloys, Acta Materialia, 2012, 60, pp: 5723 - 5734.

Development of shaped crystal growth method and automatic diameter control program for alloy and ionic crystals

Prof. Vladimir KOCHURIKHIN

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I was invited to work as a visiting professor at Advanced Research Center of Metallic Glasses in the Institute for Materials Research of Tohoku University from August 1 till September 30, 2012. During my stay I worked together with Professor Akira Yoshikawa and members of his laboratory. General Physics Institute in Russia and Institute for Materials Research of Tohoku University in Japan have agreement of scientific cooperation signed already over than 20 years ago. At last years the scientific exchange between our institutes was not very intensive. And I am very glad to establish a fact that in this year such scientific exchange started again. So, at the first half of 2012 year the engineer from my laboratory visited IMR, later Professor Yoshikawa and two researchers of his team visited my laboratory in GPI in Moscow. As the continuation of this good tendency I also was very glad to accept the invitation from IMR to visit Japan and to work 2 months there.

My laboratory in GPI specializes on the development of new materials for different optical and laser applications.

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Mainly we develop the technology of production of different synthetic single crystals by different crystal growth techniques: Czochralski, Kyropoulos, shaped methods etc. Also, we investigate the problems of automatic computer control of crystal growth processes. The laboratory of Professor Yoshikawa in IMR caring out many kinds of similar investigations. I hope that during my stay in Sendai we succeeded to combine our efforts to develop new single crystal materials and develop some elements of crystal growth technology for these materials. During my stay in Sendai mainly I focused on the Czochralski technique as one of the most perspective methods of production of new single crystal materials with good structural quality. Laboratory of Prof. Yoshikawa is equipped by good set of crystal growth machines for different techniques – mPD, Floating zone, EFG, Czochralski etc. Unfortunately the Czochralski equipment at Yoshikawa laboratory was injured strongly during earthquake at the March 2011. For this reason jointly with the engineers of laboratory we tried to repair at first the broken parts and make the tuning of the computer software for automatic production of crystals. As a main material for tuning and future production using the Czochralski equipment the Gd-Al-Ga garnet (GAGG) was selected. Few years ago it was found that this material with Ce ions doping has a wonderful set of the scintillation properties. Such material, especially with some improvement of crystal structural quality by means of some additional dopants or careful selection of the growth conditions, in future can be the main candidate as X-ray sensor for different medical or security systems with the necessity of determination of very low levels of x-ray radiation. At first, we grew two undoped crystals for checking of equipment, tuning of the crystal growth software and selection of optimal growth conditions. On the Fig. 1 second undoped grown GAGG crystal is shown. By the selection of growth conditions as 0.8 mm/h (pulling rate), 12 rpm (rotation rate), Ar+2 %O2 (growth atmosphere) we succeeded to grow good crystal without cracks and visible inclusions inside. Third GAGG crystal was grown under the same conditions but with Ce^{3+} doping (1 atomic %). Such crystal is shown of Fig. 2. It also was rather good in quality. Measurements of optical and scintillation properties of this crystal shown that this material can be the good competitor for widely used scintillator crystals such as BGO, LYSO etc. Finally, we grew one else Ce-doped GAGG crystal by the Czochralski technique but with partial substitution of Gd ions in the dodecahedral site by Dy ions. We expected that some scintillator properties of such crystal can be better due to possibility of energy transfer from Dy to Ce ions. After finish of my stay in IMR researchers of Yoshikawa laboratory will continue the detailed investigation of crystals grown together and introduce results of this research work in scientific journals.

During my stay in IMR within 2 months we have a lot of very interesting and fruitful scientific discussions with Professor Yoshikawa, researchers of his laboratory and many other scientists in IMR. The vision of the same problems and possible ways to solve them by scientists of different countries often is noticeably differ. Such mutual discussions and carrying of experiments together can help a lot for the getting of the most interesting and perspective scientific results. Finally I would like to say my great thanks to all colleagues in IMR for the invitation to work there during 2 months as a visiting professor and for their great help during my stay in Sendai.

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Acknowledgement
I would like to thank Prof. Makino, head of Advanced Research Center of Metallic Glasses in the Institute for Materials Research of Tohoku University, for giving me this fruitful opportunity for both side.

When Nature plays Lego: seeking common structural principles in crystalline solids

Prof. Massimo Nespolo

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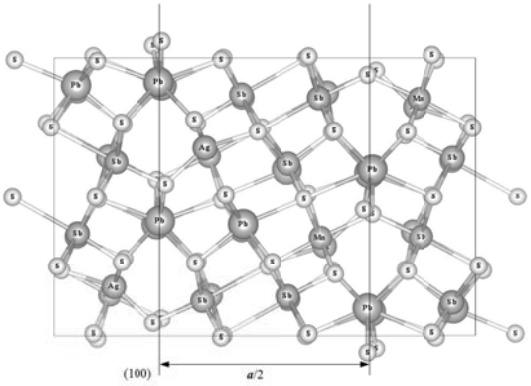
From 1st of June to 31st of August 2012, I worked as a visiting professor in the Inorganic Materials with Complex Structures Group at the Institute of Materials Research, Tohoku University, working with Professor Kazumasa Sugiyama. The goal of this short-term cooperation research project was to find a common structure principle in elusive structures with close chemical composition and often occurring together in the same environment.

As a matter of fact, the structural variability showed by natural crystalline solids built on a limited number of building blocks is astonishing and can inspire new principles of materials design. During my stay I worked on a series of sulphide minerals which

present this feature to an impressive extent: the andorite homologous series. The series is based on a block derived from the galena (PbS) structure, which is shown is the figure; the cation sites, occupied only by Pb in the galena, host also Sb, Mn, Ag in the various members of the series. The building block, having approximate size of 9.5 Å (horizontal),



13 Å (vertical) and 4.3 Å (projection) is periodically cell-twinned and as a result a period of approximately 19 Å is obtained (horizontal on the figure). The members of the homologous series are obtained by stacking this module along the direction of projection, with widths corresponding to *n* times the 4.3 Å thickness of the building block. Three members of the series are known, having n = 2, 4 (reported by us for the first time) and 6; the distribution of cations in the structure can give rise to different minerals for the same value of *n*. This is indeed realized for the $n = 2$ member, whose structure occurs with slight adjustments in three minerals differing in their chemical composition.

All the members of this series show a high degree of pseudo-symmetry, which explains the high frequency of twinning. This observation led us to seek an aristotype - a common structural denominator from which the structure of the minerals can be obtained – by a sequence of group-supergroup relations. The degree of pseudosymmetry is evaluated by the maximal atomic displacement needed to adjust the structure in the supergroup.

Members corresponding to n = 4 and 6 are highly pseudo-symmetric to a common aristotype corresponding to $n = 4$ in a space group of type *Cmcm*. This aristotype is not however shared by the $n = 2$ member, for which another aristotype, with space group of type *Cmme* and again $n = 2$ can be found: the degree of pseudosymmetry is however lower. From this second aristotype the structure of the other two members can also be obtained, but again the degree of pseudo-symmetry is lower. This result agrees very well with the experimental observation that the two members with n = 2 and n = 4 can coexist as intergrowth, while an intergrowth with the member $n = 2$ has not been found to date. It looks like Nature exploits a common set of Lego bricks to build the members with $n = 2$ and $n = 4$, while for the member with $n = 2$ a slightly different set is used. Whether this difference comes from the chemical composition or the crystallization conditions is still to be elucidated.

I would like to express my sincere gratitude to Prof. Sugiyama for the invitation to IMR and to Dr. Shimura and Dr. Harima for helpful discussions and support, as well as to the staff and students of the group for their kindness. I also extend many thanks to Ms Chiba for her constant help with the administrative paper work and to Ms Kikuchi and Ms Takahashi for sharing Sendai walks and omochi&wagashi-ryori.

Thank you and “Au revoir and Sayonara Kinken”

Reference: Nespolo M., Ozawa T., Kawasaki T., Sugiyama K.: Structural relations and pseudosymmetries in the andorite homologous series. *J. Min. Petr. Sci.*, in press.

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