Advanced Materials　～夢をかたちに～

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共同研究開発センター

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CONTENTS

東北大学　金属材料研究所　附属新素材共同研究開発センター

Cooperative Research and Development Center for Advanced Materials, IMR, Tohoku University

活動報告

第１２７回　東北大学金属材料研究所講演会
日時：平成２６年５月２８日
場所：金属材料研究所２号館講堂・会議室

今年度の金研講演会は本センターの牧野教授と横山准教授が偶然同時に世話当番に当たり、新素材センター総動員にて会場設営および進行等を行うことになりました。今年は例年の２日を１日に短縮し密度の濃い内容にアレンジしました。特別講演者として様々な分野で活躍している研究者を招聘し、ポスター発表においては、学生を含む若手研究者が発表し、優秀者には表彰をしております。

当日は、高梨所長には全プログラムに参加していただき、所内から毛利哲夫先生、塚﨑敦先生、藤田全基先生の、所外からは東野和幸先生、京極秀樹先生のご講演していただきました。例年の倍近い来場者を得ることが出来て大盛況でした。ポスター発表では過去最高の１０５件の発表がありました。

（文責：横山　嘉彦）

「最近の宇宙輸送系の動向と課題について」

室蘭工業大学
航空宇宙機システム研究センター長・教授
東野　和幸　先生

「金属粉末３Ｄプリンタ開発の現状とその可能性」

近畿大学　工学部長・教授
京極　秀樹　先生

ポスター発表は最優秀賞１名、優秀賞８名が受賞しました。右写真は牧野研究室学生　徐博威さんが優秀賞を受賞しているところです。

活動報告

韓国延世大学校教授 Kim Do-Hyang 先生、韓国清州大学校教授 Kim Won Tae 先生、韓国ソウル大学校准教授 Park Eun Soo 先生による講演会開催

平成26年8月6日(水)、国際教育研究棟2階セミナールームⅠにおいて、韓国延世大学教授で新素材共同研究開発センター客員教授のKim Do-Hyang先生をはじめ計3名の先生方を講師に招いて、講演会を開催しました。

講演会では活発な質疑応答がされ、ナノ結晶センター特任教授西山先生やWPIの先生方をはじめ、多くの研究者、学生に聴講いただき、大変盛況でした。

(文責：横山　嘉彦)

(中央左から)
Kim Won tae先生、Kim Do-Hyang先生、
Park Eun Soo先生を囲んで記念撮影

←
Kim Do-Hyang 先生
(延世大学校教授、新素材センター客員教授)

”Phase separating metallic glass and possible application“

Kim Won Tae 先生 (清州大学校教授)

”Microstructure & mechanical properties of BMG composites“
→

←
Park Eun Soo 先生(ソウル大学校准教授)

” Development of Novel High Entropy Bulk Metallic Glasses “

研究成果

Asian Microgravity Symposium ２０１４
ポスターセッション　最優秀賞受賞

平成２６年１０月２７日～１０月３１日の間、韓国ソウルにて開催されましたＡＭＳにおいて、共同研究をしている早稲田大学鈴木研究室　谷元啓示さんが最優秀賞を受賞しました。

指導教官の鈴木進補教授は長年液体の拡散挙動についてシェアセルモデルを用いて研究してこられました。谷元さんは、ガラス形成能を有するAu-Ge系において共晶組成での拡散現象について研究してこられました。本研究内容はその２年間の研究の結果をまとめた内容になります。

（文責：横山　嘉彦）

下記ポスターより抜粋(Abstract,Purpose,Conclusion)

Abstract

As for alloy systems developing amorphous structure, it is very useful to pursue the diffusion mechanism of the eutectic alloys in the vicinity of the eutectic point to elucidate the amorphous developmental process. We therefore investigated interdiffusion coefficients in the liquid state of AuGe and AuSi alloy, which remarkably have the deep eutectic temperature. The diffusion experiments using a shear cell device were performed from 886K to 1073K and apparently reliable data were acquired. It was because they were reproducible and overlapping well on fitting curves so that the convection would be suppressed. The implement of a space experiment is therefore in future expected to confirm the conclusive evidence. As a result, the temperature dependence of the interdiffusion coefficients in the liquid AuGe alloy was expressed in the Arrhenius equation and no peculiarity in the diffusion mechanism was confirmed. The interdiffusion coefficients of this study were also larger than those of *ab initio* MD simulation carried out in the past. This would be caused by that the negative mixing enthalpy which could facilitate the diffusion was not considered in the simulation. In addition, the previous research on structure analysis in which the shoulder was not observed in the vicinity of the eutectic point supported our confirmation of the Arrhenius expression for the temperature dependence of the interdiffusion coefficients in the liquid AuGe.

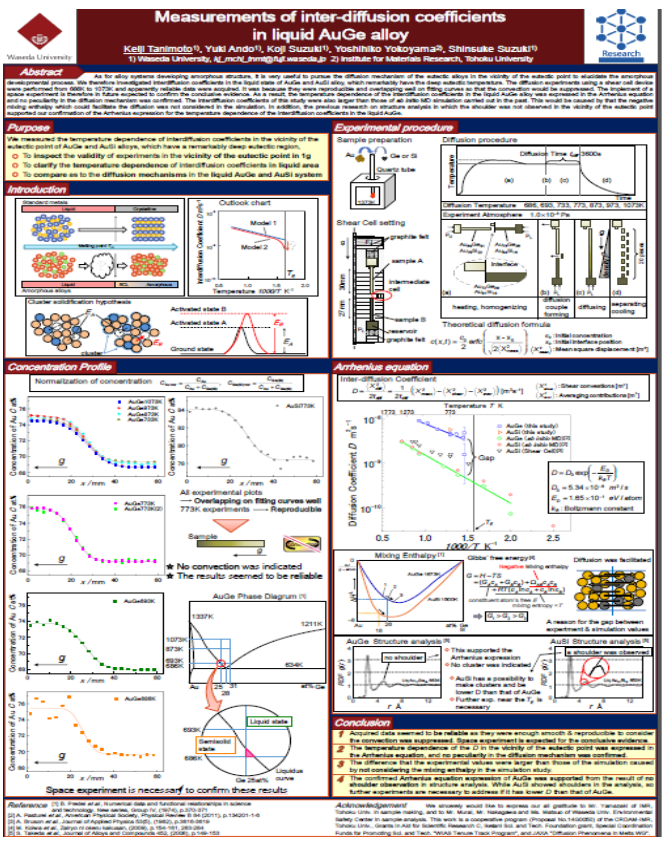
Purpose

We measured the temperature dependence of interdiffusion coefficients in the vicinity of the eutectic point of AuGe and AuSi alloys, which have a remarkably deep eutectic region,

- To inspect the validity of experiments in the vicinity of the eutectic point in 1g
- To clarify the temperature dependence of interdiffusion coefficients in liquid area
- To compare as to the diffusion mechanisms in the liquid AuGe and AuSi system

Conclusion

1. Acquired data seemed to be reliable as they were enough smooth & reproducible to consider the convection was suppressed. Space experiment is expected for the conclusive evidence.
2. The temperature dependence of the *D* in the vicinity of the eutectic point was expressed in the Arrhenius equation, and no peculiarity in the diffusion mechanism was confirmed.
3. The difference that the experimental values were larger than those of the simulation caused by not considering the mixing enthalpy in the simulation study.
4. The confirmed Arrhenius equation expression of AuGe was supported from the result of no shoulder observation in structure analysis. While AuSi showed shoulders in the analysis, so further experiments are necessary to address if it has lower *D* than that of AuGe.



研究成果

1/10の撮影枚数で三次元電子線断層撮影を実現
～世界初、圧縮センシンク法による
画像再構成ソフトウェアを製品化～

筑波大学、九州大学、（株）システムインフロンティアは、JST先端計測分析技術・機器開発 プログラムの一環（参画機関：東北大学）として、世界に先駆け、圧縮センシング(Compressed Sensing, CS)法による画像再構成アルゴリズム(ISER, Iterative SEries Reduction)を搭載した電子線CT(Computed Tomography、断層撮影)用ソフトウェアを開発し、製品化しました((株)システムインフロンティア社のソフトウェア製品TEMography(TM)に搭載)。このソフトウェアにより、三次元再構成に必要な撮影枚数を従来の1/10から1/20程度に減らすことが可能となり、撮影時間の短縮のみならず、電子線CT観察のネックとなっていた、電子線照射による試料の損傷や汚れの誘起といった問題の解決が期待されます。

このソフトウェアは、画像収録に用いる電子顕微鏡のメーカーを問わず対応が可能です。2014年11月1日より試用版の提供および既存ユーザーに対する無償アップグレードを開始しました。

※この成果は10月20日付の日刊工業新聞、日刊工業新聞Business Line に掲載されました。

（文責：佐藤 和久）

就任挨拶

新素材共同研究開発センター・ミクロ組織制御材料合成研究部

准教授　佐藤　和久

本年６月１日付で、本所不定比化合物材料学研究部門助教から新素材共同研究開発センター・ミクロ組織制御材料合成研究部准教授に着任致しました。また、7月18日付で超低損失ナノ結晶軟磁性材料研究開発センター兼務を拝命致しました。私はこれまで、ナノ磁性材料・金属材料における機能発現メカニズムと原子的構造との関係について、主として透過電子顕微鏡法・電子回折法を用いた研究を行ってきました。前者のナノ磁性材料に関する研究では、電子線構造解析とともに超高真空プロセスを利用した超薄膜・ナノ粒子合成や磁性評価も合わせて行ってきました。近年、磁性材料では高度な組織・組成制御が一段と進められております。解析手法の観点からは、分析機能に優れた最新の収差補正走査透過電子顕微鏡は、構造欠陥や粒界・表界面を含む組織の解析、とりわけナノヘテロ構造の組織解析において大いに威力を発揮すると考えられます。そこで本センター着任後、新しい研究課題として高鉄濃度ヘテロアモルファスの構造組織解析に着手致しました。一方、後者の金属材料に関する研究は平成19年10月の金研着任後に開始した研究であり、近年は電子線トモグラフィー(断層撮影)による３次元組織解析とその高度化を目指した研究へと発展しつつあります。将来的には本手法を構造材料の動的変形メカニズムの解明に役立てたいと考えております。金研着任以来、所内をはじめ国内外の諸先生方と様々な材料について共同研究する機会に恵まれました。これまでに培ってきた構造組織解析手法や経験を活かしながら、さらに研鑽を積み、共同利用研究の推進を通して本センターにおける新素材開発に少しでも貢献できるよう微力ながら努力する所存です。本センター教職員の皆様のご指導ご鞭撻をどうぞよろしくお願い申し上げます。

H26年度外国人客員研究員研究成果報告

Study on X-ray tomography for 3D modering and porous metal

Prof. Maire Eric

Mateis Lab, Elyt Lab, Université de Lyon, CNRS, France

From 10th of April to 15th of May 2014, 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 and professor Akihiko Chiba. I already had an experience to stay at IMR for three short visits of about two days in the Frame of the Elyt joined lab between Lyon and Tohoku.

During this visit, I have been focusing my research on two subjects : at first, I worked on the fabrication of nano and microporous metallic materials using the de-alloying in a metallic melt (DAMM) process developed by Takeshi Wada and H. Kato. Towards the end of my stay, I made some plans with my Japanese colleagues to produce samples with the EBM machine of A. Chiba. The machine being temporarily unusable, the samples will be prepared later and sent to France.

1. Description of the results obtained with the DAMM process :

The DAMM process uses a new idea to produce bi-phase materials by de-alloying. Electrochemical de-alloying (EDA) has been used before to produce porous materials with noble metals. The most famous example is nanoporous gold produced by EDA of a gold/silver pre alloy. The DAMM process was invented only a few years ago by H Kato and T Wada in order to obtain porous or bi-phased systems with less noble materials (Ti, Fe/Cr, etc). It uses a very clever idea : the starting point is the same as standard EDA. A homogeneous precursor consisting of a mixture of two elements A and B is first produced. Instead of de-alloying electrochemically, the AB precusor is then dipped into a ***molten*** third metal C. If C has a positive mixing enthalpy with B but negative with A, AB is de-alloyed by dissolution of B in C. The resulting material is a co-continuous bi-phase system with regions of A and regions of the BC alloy. BC can then be etched away to leave us with porous A or the material can be used as a A / BC composite.

Using this very clever principle, I have worked in the following directions. I produced and started to characterize porous metals where our objective was to obtain anisotropic pores (elongated in one or two directions). This was achieved on the Fe/Cr system by producing first a $(Fe_{80}Cr_{20})_x Ni_{(1-x)}$ precursor by arc melting

and tilt casting. Once obtained, this precursor being rather ductile, I cold rolled it in the form of two kinds of sheets of 1mm and 0.3 mm thickness respectively. The flat samples were then de-alloyed in a molten Mg bath. Using several modifications to the technique previously used, we were able to produce a large number of flat de-alloyed samples. Some of these were kept as is and will be used to characterize the 3D structure and the mechanical properties when I get back to France. This will be achieved both in the composite Fe/Cr + Mg state but also after etching the Mg phase to produce porous materials.

We intentionally produced coarse pores (using 1 hour soaking time at 820° C), large thickness samples because we targeted pores of a rather large size (10 µm), these being easier to characterize in 3D using the X Ray tomography method developed in France. We also produced thinner samples (0.3mm) that could be fully de-alloyed at 700° C in 6 minutes, leading to a 10 times finer microstructure.

Some of these samples were cold rolled in the composite de-alloyed state. This was intended to deform the microstructure and make it anisotropic. The Fe/Cr Mg composite is not very ductile and not very easy to cold roll because of the presence of hexagonal Mg. Despite this, some samples could be cold rolled quite substantially before appearance of cracks led us to stop cold rolling. These samples will be analyzed in 3D in France.

To increase the cold rollability, we also produced $Ni_{93}Cr_7$ samples de-alloyed in a silver bath. Ag and Ni composites were much easier to co deform.

Smaller pore sizes will also be produced later to analyze the effect of pore size on the properties.

Using this procedure, we produced samples with different amounts of $Fe_{80}Cr_{20}$ phase. We also produced, one batch with a lower Cr content to analyze the effect of chromium on the corrosion resistance of these materials. We have also produced Ti based precursors that will be de-alloyed in the form of thin sheets (currently being cut by EDM).

2. Description of the plans made to use the EBM machine

The EBM machine was unfortunately unavailable during my stay but we made plans and samples will be produced as soon as the machine is operational.
Two different kinds of samples will be produced. First, we have designed tensile samples containing seven different model configurations of holes, to study the condition for coalescence during ductile damage. The tensile samples contain couples of holes and different parameters are changed for these couples : angle between the two cavities, distance between the thow cavities and cavity aspect ratio. 5 samples of each model configurations will be produced by EBM (35 samples), the axis of the tensile sample being vertical. 35 more samples will be produced with a horizontal orientation of the tensile axis. These two configurations should be tested because EBM is a layer deposition technique et the orientation compared to the layers has probably a strong effect on the design of the cavities.
We also planned second set of experiments where instead of obtaining dense titanium, we plan to produce partially sintered samples. This can be achieved by varying the parameters during the EBM fabrication. This is an attempt to produce Ti samples with two different types of porosity : a large scale porosity can be designed in the CAD model, but the solid part of the model could also be porous at a micron scale, because only partially sintered by the electron beam, if we find appropriate conditions to do this.

3. Conclusion

During this month of collaboration with Prof. H. Kato, A Chiba and staff members, we have done some valuable explorations to synthesize some novel materials and to understand more deeply together the two different fabrication processes studied and developed at IMR. These materials have a great potential for different types of applications in several fields ranging from energy to health and the collaboration started gave us some new ideas to explore together in the future.
Now it is time to leave back to the French lab where they are also waiting for me. Before doing this, I would like to express my sincere gratitude to Profs. H. Kato and A. Chiba 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”

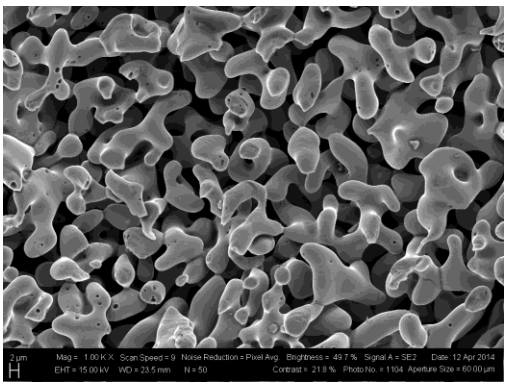


Figure 1 : SEM micrograph of a FeCr porous sample produced by de-alloying at 820°C during 1 hour and subsequent etching in nitric acid. The pores formed are isotropic and about 10 µm thick

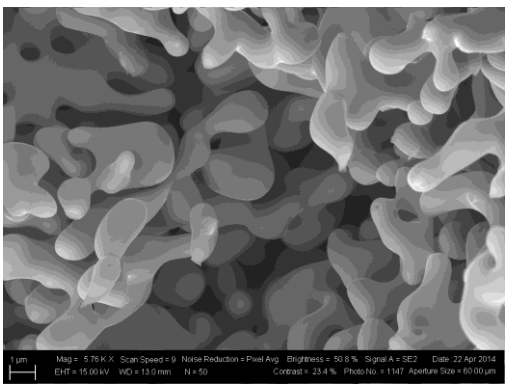


Figure 2 : SEM micrograph of a FeCr porous sample produced by de-alloying at 700°C during 6 minutes and subsequent etching in nitric acid. The pores formed are isotropic and about 1 µm thick and ductile fracture traces can be observed on this fracture surface

(a)

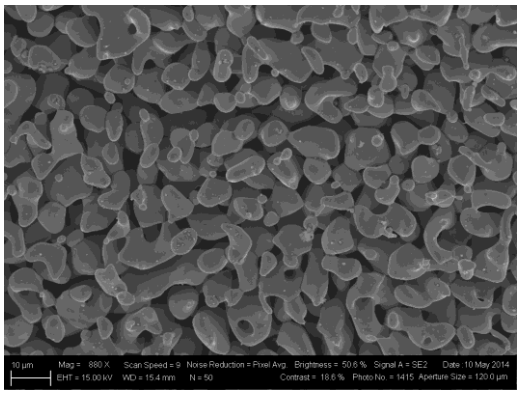


Figure 3(a) : Ni95Cr5 sample dealloyed in silver, and subsequently etched. The microstructre is isotropic

(b)

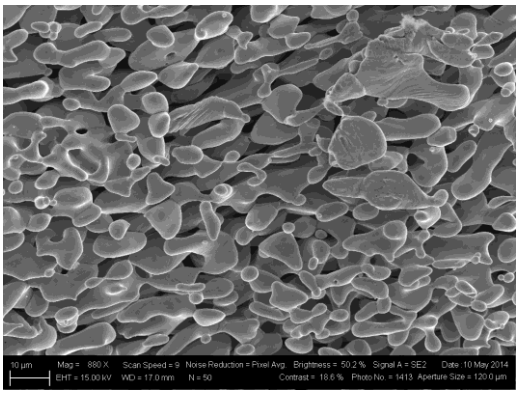


Figure 3(a) : same batch as in Figure (a) but the sample was colled rolled after de-alloying and before etching. The microstructure is anisotropic

(a)

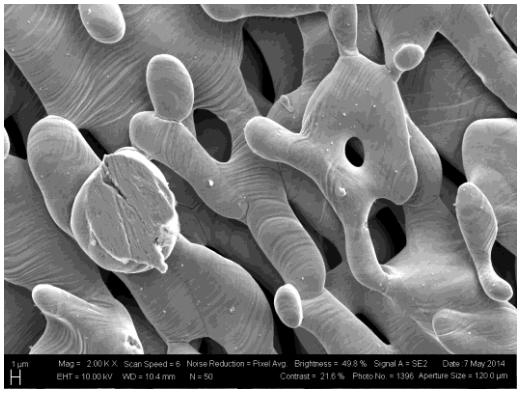


Figure 4 (a) : Deformation bands at the surface of the porous nickel, induced by co-rolling in the dealloyed (composite) state with silver. The sample was cold rolled in the same direction and each grain mostly shows one slip system.

(b)

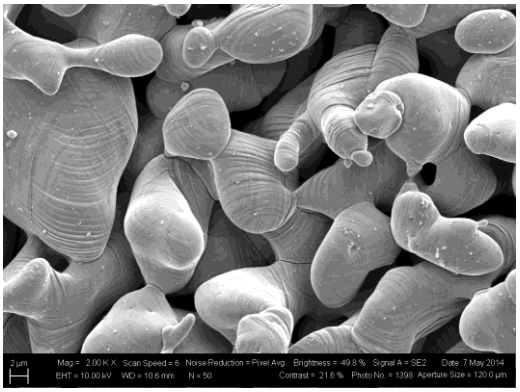


Figure 4 (b) : Same as in figure (a) but this sample was rotated 90 ° between each rolling path. 2 slips systems were activated.

Dependence of the Glass Transition Temperature and Elastic Properties of Metallic Glasses on the Atomic Packing Density

Prof. Tanguy ROUXEL

Institut de Physique de Rennes, IPR, UMR-CNRS 6251, Université de Rennes 1, France

From 15th of April to 14th of May 2014, I worked as a visiting professor in the Cooperative Research and Development Center for Advanced Materials at the Institute of Materials Research, Tohoku University hosted by Prof. A. MAKINO and Ass. Prof. Y. YOKOYAMA. I already had an experience to stay at Tohoku University for two months in 2006 in the laboratory of Prof. H. WATANABE and Ass. Prof. S. TSUREKAWA (Aobayama campus).

During this visit, I have been focusing my research on the relationships existing between metallic glass composition and structure, and mechanical properties. In particular, the atomic packing density and glass transition temperature showed up as interesting parameters to get insight into the mechanical behavior. Elastic moduli can be viewed as a signature of the volume density of energy. Therefore they chiefly depend on T_g which provides an indication for the energy content, and on the atomic packing density (C_g). As a matter of fact a low energy content (low T_g) might be compensated by a high C_g, and vice-versa, and there are several examples of such situations among metallic glasses. Although the atomic packing density as well as the energy density are not determined with a high accuracy, clear differences are observed from a chemical system and to another. There are various ways to define C_g. Metallic glasses exhibit a high packing density, close to - or larger than - the one of the crystalline phase of the same alloy composition when available, so that the packing density is often estimated relative to the crystalline phase.

In the present work, in order to allow for a straightforward comparison with previous data on oxide glasses, C_g is defined as the ratio between the minimum theoretical volume occupied by the atoms and the corresponding effective volume of glass

$$C_g = \rho \Sigma f_i V_i / (\Sigma f_i M_i) \quad (1)$$

with for the i^{th} constituent: $V_i = 4/3\pi\rho N r_i^3$, where ρ is the specific mass, N is Avogadro number, r_i is the metallic radius (i.e. half the shortest distance between two atoms in the pure metal), f_i is the molar fraction and M_i is the molar mass.

The use of the experimental values for the interatomic distance to calculate C_g instead of the classical values for pure metals was found to have only a minor incidence on C_g in cases actual interatomic distances were available. For example, for $Cu_{50}Zr_{50}$ and $Ni_{80}P_{20}$ glasses, accounting for the actual average interatomic distances changes C_g from 0.737 to 0.723 (-2%), and from 0.701 to 0.725 (+4%). The energy content $<U_o>$ was estimated from existing thermochemistry data for the elements constituting the studied glasses. For instance in the case of a binary system, $<U_o>$ is expressed as

$$<U_o> = x\Delta H_{at}(A) + y\Delta H_{at}(B) - \Delta H_{mixing}(A_xB_y) - RT \quad (2)$$

Here $<U_o>$ represents the dissociation energy (standard pressure), i.e. necessary to obtained separate gaseous atoms from the solid material (a gram atom is considered: x+y=1).

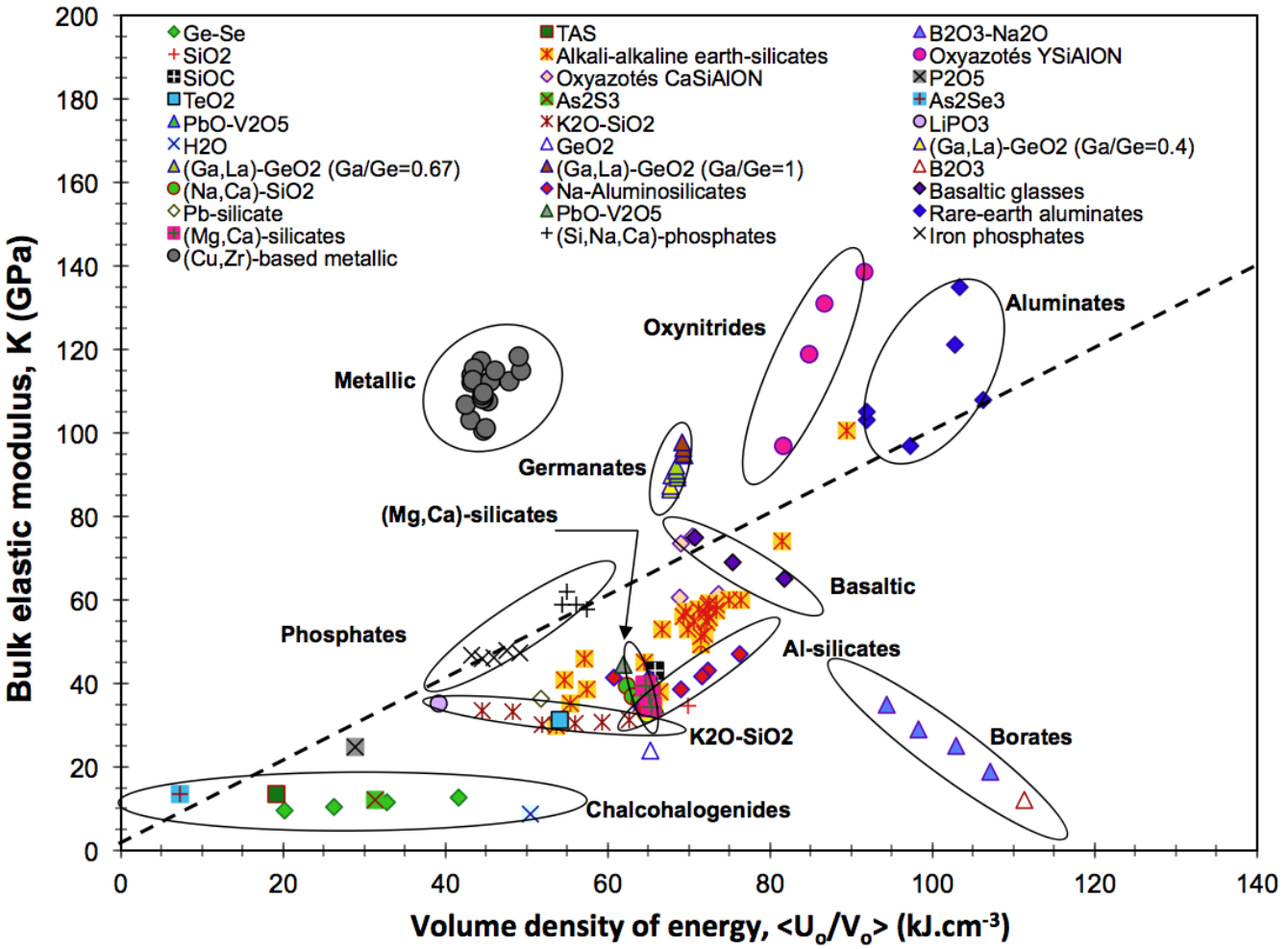


Fig.1. Experimental bulk elastic modulus as a function of the estimated volume density of energy.

Such a derivation was already proved quite successful to predict the elastic moduli of oxide glasses. However the elastic moduli of alkali- and alkaline-earth silicate and borate glasses are greatly overestimated and on the contrary, K is greatly underestimated (by over 20%) in the case of germanate, aluminate and high modulus glasses in general (beryllium and nitrogen containing glasses for instance) - ***among which transition metal based metallic glasses*** - and when a relatively good correspondance is noticed between theoretical and experimental data, opposite trends are sometimes observed (as for basalt glasses for instance). The discrepancies mostly stem from the difficulty to account for the structural features of the various atomic glass networks, such as the presence of double P=O bonds which do not contribute to the network stiffness in phosphates, or the weak bonds between the planar BO_3 triangle (to be compared to 3D interconnected BO_4 units). Nor is the introduction of C_g as an ersatz of the Madelung constant straightforward. However, such simple analysis tells that in the case of metallic glasses (Zr-, Cu-, Pd-, Pt-based for instance) the relative weakness of the interatomic bonding is efficiently compensated by a large atomic packing density, so that the actual volume density of energy in the glass is as high as in the case of high strength glasses such as boro-alumino-silicate (reinforcement fibers) or silicon-oxyniride glasses.

This study demonstrated that elastic moduli intimately correlate with the volume density of energy but that there is thus no one to one relationship between an elastic modulus and T_g, since one can find glasses with a high T_g (energy) and a low atomic packing density, or with a lower T_g but a larger C_g which exhibit the same elastic modulus. For instance $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$, $Cu_{60}Hf_{10}Zr_{20}Ti_{10}$, $Pd_{40}Ni_{10}Cu_{30}P_{20}$, $Pt_{60}Cu_{16}Co_2P_{22}$ glasses possess a Young's modulus of ~96-102 GPa while their T_g cover the 506-754 K interval, and among non metallic glasses $Ca_{0.08}Al_{0.15}Si_{0.15}O_{0.62}$, $Ca_{12.90}Si_{10}O_{20.93}N_{7.98}$ and $SiC_{0.33}O_{1.33}$ glasses with a similar E value exhibit T_g of 1125, 1221, and 1600 K respectively.

Although for glassy materials belonging to oxide, oxynitride, and metallic chemical systems Poisson's ratio (ν) is found to increase almost monotonically with C_g, there is no obvious correlation among metallic glasses with different compositions. For instance, Ce- and La-based glasses with C_g as large as 0.75 exhibit ν as small as 0.3, whereas Pt- and Pd-based glasses with C_g ~0.65-07 shows ν>0.4. This calls for more detailed structural investigations, in particular focusing on the bond directionality and electron localization.

During the one month stay with Prof. Y. YOKOYAMA and staff members, we have done some valuable explorations of fundamental properties of metallic glasses synthesized at IMR as well as binary oxide systems synthesized in Rennes (France) together with AIMR, and WPI. Since then the collaboration between both Universities and research teams is still developing. I would like to express my sincere gratitude to Profs. A. MAKINO and Y. YOKOYAMA for the invitation to IMR of Tohoku University, and to Dr. A HIRATA (AIMR) for TEM analysis on oxide glasses, and to Profs M. CHEN (WPI) and H. SHIBATA and S. SUKENAGA (IMRAM) for very stimulating and encouraging discussions. Many thanks also to the efficient administrative staff for their help with the paper work and very useful daily life advices.

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