UNIVERSITAT POLITÈCNICA DE CATALUNYA
BARCELONATECH
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Université de Lille

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PROJECT REPORT

ERASMUS EXCHANGE ABOUT NON CRYSTALLIN ALLOYS AND METALLIC GLASSES

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UPC EEBE

Thanks,

I would first like to thank the UPC and their administration, to hosting me for 3 months. They were quick with all the papers, and always joinable.

I have to thank my French teachers, Mr.Sueur and Mr.Meilliez, they were here when I needed it and they took care of me.

I can't of course not mentioned Mr.Pineda, my tutor who helped me a lot with the writing of my project. And Mehran, one of the doctoral students who taught me all the basics of the Metallic glasses.

I would finish to all the other doctoral student present in the office, who were there when I needed to ask any questions.

Summary

INTRODUCTION

During this year, I have been able to do an internship at the UPC (Universidad Politécnica de Cataluña) of Barcelona. This experience has been very rewarding for me, I was working on Metallic glasses and non-crystalline alloys, a such interesting subject with qualified searcher such as my tutor Eloi Pineda, is a professor of the Physics Department, his research is specialized in Metallic Glasses. He is my tutor and the one of some PhD students. Mehran Nahabat is a PhD student in Physics of Materials. He is currently working on one metallic glass, the VIT4 alloy.

I was working at the UPC's campuses, EEBE (Escola d'Enginyeria de Barcelona Est), one of the many campuses of the UPC. Near the sea, my office was on the 1rst floor in on the 3 buildings present in the campus C, I, and A. The basement C, was the building for energy, nanotechnology, chemistry, and materials research, depending on the floor, this is the one I was working in. The I one was also a research building for mechanicals and chemistry. The last one, A, the biggest one was used for the most for class. I was sharing the office with 14 other PhD students from Iran, USA, China, Italia, Argentina, … There were all working on mechanics or chemistry. In my building there were many laboratories, I did used some of them for doing experiments. The closest one of my office is where I was using DSC, the arc melting machine and DMA, in the same room there were also many microscope, furnace, computer, weighting machine, … downstairs at the level -1, was where I used the AFM, was a way more complex laboratory, full of machine with high accuracies, such as AFM, high precision microscopes, …

My project

My goal was to learn and practice as much as possible about the labs and the technics used for metallic glasses and non-crystalline alloys.

What are Metallic glasses?

introduction

Metallic materials such as copper, iron, … are known for their ductility, excellent tensile and fatigue strength, good conductors of heat and electricity, … They are also for the most of them crystalline, which mean their atoms follows some pattern (*figure 1*). At the opposite some materials like the glasses known for their insulation and brittleness, are not following any pattern, they are considered as non-crystalline or amorphous (*figure 2*). If you combined some properties of these two materials, you would find the main subject of my project: Metallic Glasses (MGs).

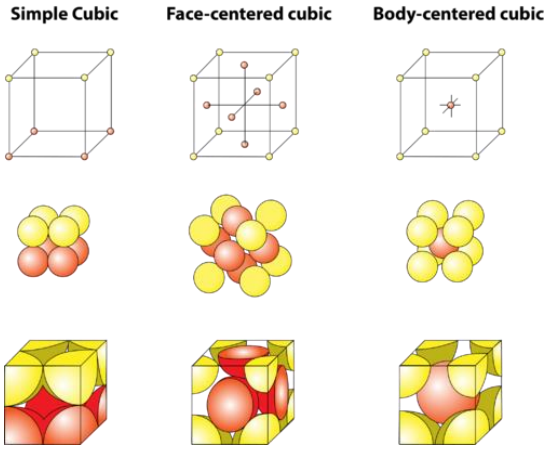


Figure 1: Different atoms shapes from Org. Chem. For Non-Majors Course syllabus (CAA)

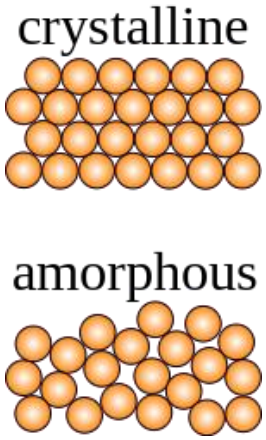


Figure 2: Representation of atoms in crystalline and amorphous state from crystalline or amorphous by Cdang

MGs in a general way are keeping some metals properties like the strength, ductility and conductivity. However, they are provided good elasticity and a glass transition (*Tg*), which is the temperature between the glassy/brittleness state and the rubbery/elastic one, thanks to their glasses' amorphous shape. But these properties mostly depend on the composition of MGs.

Difference between Amorphous Alloys and MGs

The may difference is the way they are produced. They are both non crystalline but in cased of a constant cooling the material will be considered as glass. So MGs, and with other process such as vapor deposit or solid state, they will be this time considered as Amorphous material. This difference of production lead to a presence or not of the *Tg*, in our case thus presence is required for being a MGs. Even if in the definition of the glass, the *Tg* is not important.

Thermodynamical

All glasses are not thermodynamically stable, this means they could re-form into a crystallin alloys depending in a certain period depending on the glass and his production method. There stability is linked to the number of components, the more there are, the more its stable.

Metal-metalloid or Metal-Metal MGs

There is two different ways to build MGs composition, first metal-metalloid MGs way or metal-metal MGs one.

The first one is built from 80% metal (like Fe, Nb, Cu, Zr, Mg, Zn, La, Au for the most used/known) and 20% of metalloid (like B, C, P and Si) here is some examples of metal-metalloid MGs: $Pd_{80}Si_{20}$, $Pd_{77}Cu_6Si_{17}$, $Fe_{80}B_{20}$, $Fe_{40}Ni_{40}B_{20}$.

The second one metal-metal MGs is made of only metals, the content is less strict than metal-metalloid, and one of the metals can be small as 9% or big as 50%. Here are some examples: $Ni_{60}Nb_{40}$, $Cu_{57}Zr_{43}$, $Mg_{70}Zn_{30}$.

Bulk Metallic Glasses (BMGs)

BMGs are a subset of MGs with specials characteristics. First, they got a minimum of three component or usually more for example: $Pd_{40}Cu_{30}Ni_{10}P_{20}$. They also got a huge gap between the *Tg* (glassy transition temperature) and the *Tx* (crystallization transition Temperature). Finally, they can be produced at a slow solidifications rate.

Production of MGs:

Theory

Producing MGs are not simple, the main problem is in general to avoid the crystallization. There are three processes: Vapor-state, liquid-state and solid-state. We are here going to focus on the solid-state process:

The first step is to melt the right number of metals/metalloids in a furnace at a specific temperature and during a certain time, depending on the MGs wanted. After being melt, the liquid is cooled until a state called a supercooled liquid. It means that his temperature his bellow his solidification temperature. But from the same super liquid you can obtain different MGs, depending on the cooling velocity. Glass's properties can only be described by their pressure and their thermodynamic temperature and each one has something call a fictive temperature. During the process of MGs, the fictive temperature is the moment where the atoms are frozen and considered that they will not move anymore. Of course, this is a theoretical conjecture, in reality all glass's atoms are moving, depending on different parameters slowly or not. During the cooling, MGs reaches after his *Tx* and finally his volume is reduced when the Temperature reach the *Tm* (freezing/melting point), therefor due to an activation energy barrier, the volume can decrease before the *Tm*. This is depending on many factors as the viscosity, … That's the glass Formation. There are many practical ways to produced MGs, For the mostly knowns process: the "gun" technique, Flux melting technique, the melt spinning or arc melting process, …

Practice

We are here going to focus on the last one, present here in the lab of UPC, but unusable during my internship due to a lack of crucibles. Here is the theory, first the right amount of each metal/metalloid must be put in the furnace, after done one or more vacuum (depends on the accuracy of the machine) to remove the oxygen, a gas chose on the chemical and physical of the charge will replaced the vacuum. After the metals or metalloids being melt, the wheel will start to spin, and the gas will be pressure to push through the nozzle the liquid on the wheel. The liquid will be extract out of the furnace and cooled very quickly as a shape of a ribbon. The different variable such as the speed of the wheel or the heat of the furnace, or the material/diameter of the nozzles will be chosen according to the metals/metalloids properties, MGs wanted, and also the desired shape, size and thickness of the ribbon.

Some numbers: the ejection pressure is in general between 5 to 70kPa, the most common materials for the nozzles are alumina, graphite, SiC, sapphire, pyrex glass, … There diameters can vary from 50 to 1250µm.

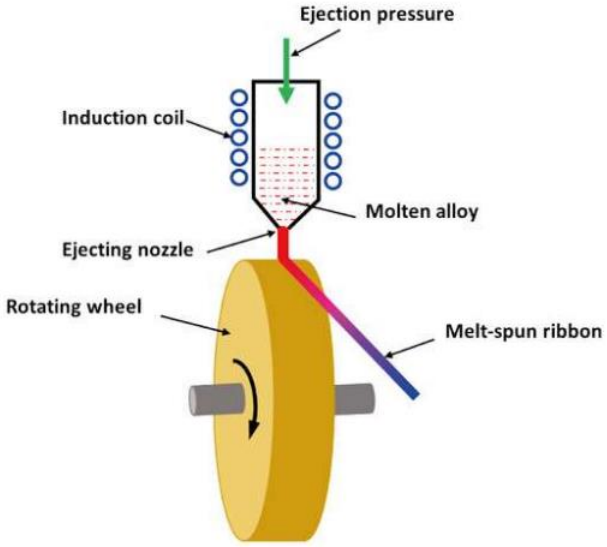


Figure 3: Schema of a melt spinning device. From Nanocrystalline and nanocomposite permanent magnets by melt spinning technique, CPB Chinese Physics B, 2018, Rong Chuanbing, Shen Baogen

Figure 4: Arc melt spinning device from the UPC EEBE LAB

Important definitions

entropy

For a general way, it's a degree of disorder or randomness in a system.

Enthalpy

It's the thermodynamical quantity of heat in total present in a system.

Important temperatures

For the following definitions a constant pressure is required

Tg the temperature between the glassy/brittleness state and the rubbery/elastic one

Tx The temperature at which the crystallization occurs

Tc This is the maximum temperature at which a gas can be transform into liquid

Tm it's the fusion point where liquid and solid can live together

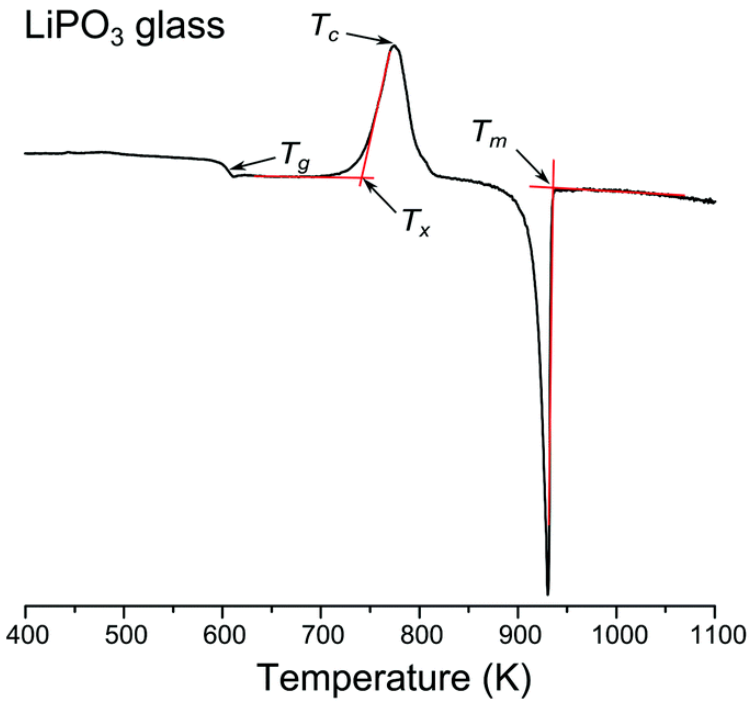


Figure 4: Glass temperatures of $LiPO_3$ from Physical Chemistry Chemical Physics

Waiting time

It's the time before every experiment, in case of a stress relaxation experiment before each tensile test will be a little amount of time.

Relaxation time

This is the amount of time for a disturbed a system to return to its normal state, In MGs case, there is two reversible

Aging

It's the reducing of volume and mobility of a glass, due to the thermodynamical non-stability and amorphous atoms arrangements. Atoms will always try to find stability, so they are going to move more or less slowly to a create a more stable state, crystalline state. Therefore, the time for glass to come back to as a crystalline state is considered infinite. To measure the aging of glass we are going to use a machine call DMA, by doing stress and relaxation on very shorts periods of time.

Different machine I have been using

Differential Scanning Calorimetry (DSC)

For the few first week I have been using the DSC with the doctoral student Mehran, to measure the exchange of temperature between two crucibles one empty and one filled by MGs. Thanks to this we can measure the phase transition of MGs by heating them.

Principle

DSC is a thermal analysis technique, two crucibles made of the same materials will be put in the furnace of the machine, One filled of MGs, the sample, and the other empty, the reference. Thanks to a thermal analysis technique, the heat difference between the sample and the reference will be measured. The furnace is vacuum of oxygen and filled of nitrogen to help MGs melting.

Procedure

First step is to measure with a high precision weighing machine a number of MGs between, 14mg and 18mg (the number is linked to calibration of the machine). The next step is to put the MGs in a crucible of aluminum or titanium, depending on the MGs and the temperature who will be chosen. After using a software named DSC_04. Many variables must be filled, the weight of both crucibles, MGs, heating time, …. A lot of parameters can be chosen, it can be the number of vacuums before filling the machine with others gas (nitrogen most of the time), the temperature to reach, … Once it's done, the machine must cool, and after the MGs and crucibles can be removed. The software gives us graphics which can used to define the phase transition of Cp. which is heat capacity, a ratio between the heat absorbed by a material and the temperature change. It is usually expressed as calories per degree in terms of the actual amount of material being considered, like:

$$CP = \frac{J}{(g * K)}$$

J: Joule *g: gram* *K: Kelvin*

Experiment

Figure 5: graphic of DSC experiment on VIT 580

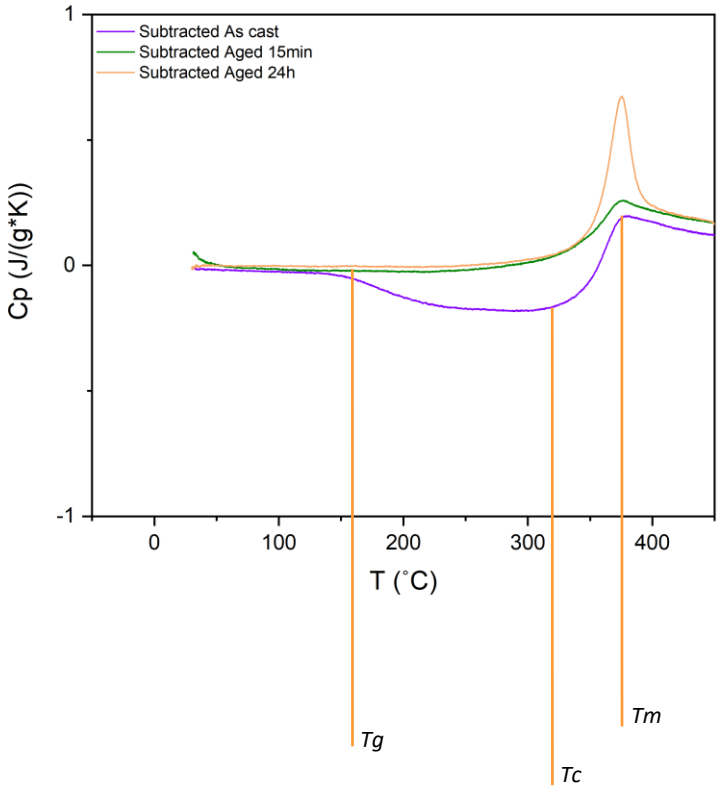


Figure 6: DSC machine in the UPC lab

In this experiment a VIT 580 MG have been heated three time with three different aging time, the blue one at cast, the green one at 15 min and the orange one at 24 hours (figure 5). Those kinds of experiment are supposed to verified theoretical papers, about the aging effect on the Cp. As we can see the three curves have different Cp value at their *Tg*, *Tc*, and *Tm*. It mean that the aging time have a direct effect on the Cp, the 3 experiments have been done in the same conditions

ATOMIC FORCE MICROSCOPE

Principle

The Atomic Force Microscope is a machine I have been using during my internship to measure to an atomic scale the relief and the properties of a medium. we oscillate and slowly move a tip of 100 to 400 nanometers on our sample, a laser aiming the cantilever (on top of the tip) will be reflected on a photodiode, which will convert the light into data. Those data will be transfer into a software call 7.5 as a graph. There is also feedback of AFM to ascend or lift the tip at each contact, to make sure that the tip will always stay above the medium as his higher place. If this not the case, and if the tip moves forward into a medium, he will be damaged and unusable.

There are three variables we can play with: the speed, the strength and the amplitude of the tip. If we are increasing the speed, we are also increasing the accuracy of the measurement, and we can play with the amplitude and the strength to determine the ductility.

Procedure

The first thing to do is to put the tip into a small receptacle manually, thanks to microscope the tip will have to be centered as much as possible. After been put into the AFM, the calibration of the laser as to be done, using a scroll wheel, the laser must aim the tip. To make sure that the tip is well aimed, a particular triangular shape must show up. To help to see this shape, a white paper can be placed under the tip, or the light can be decreased.

Now the sample can be placed under the tip, its now about to calibrate the microscope two times, on the tip and on the sample. With scrolls wheels the head of the microscope can be moved and the focus can be made.

The next step is to set up the values of the variables in the software, and to find a good place to the measure. 3-4 zooms also must be made to get a small place and for being to a pico-scale. The more zooms will be done, the more the “pictures” will be clear and precise.

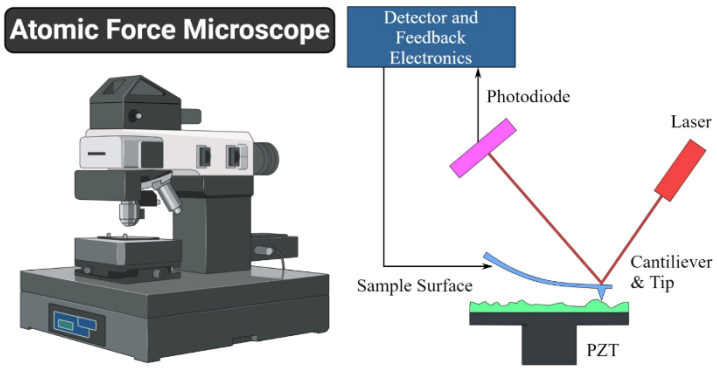


Figure 7: AFM machine from Wikipedia

Experiment

This is the tip and her properties used during this experiment (figure)

Figure 8: Tip properties

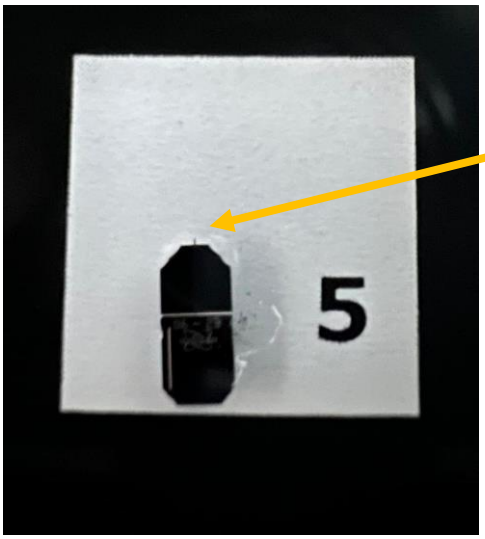


Figure 9: Picture of the tip

The result of the experiment, you can see the pictures of the MGs and all the variables. We are using MATLAB to analyze the results but can be seen on 7.5 as well.

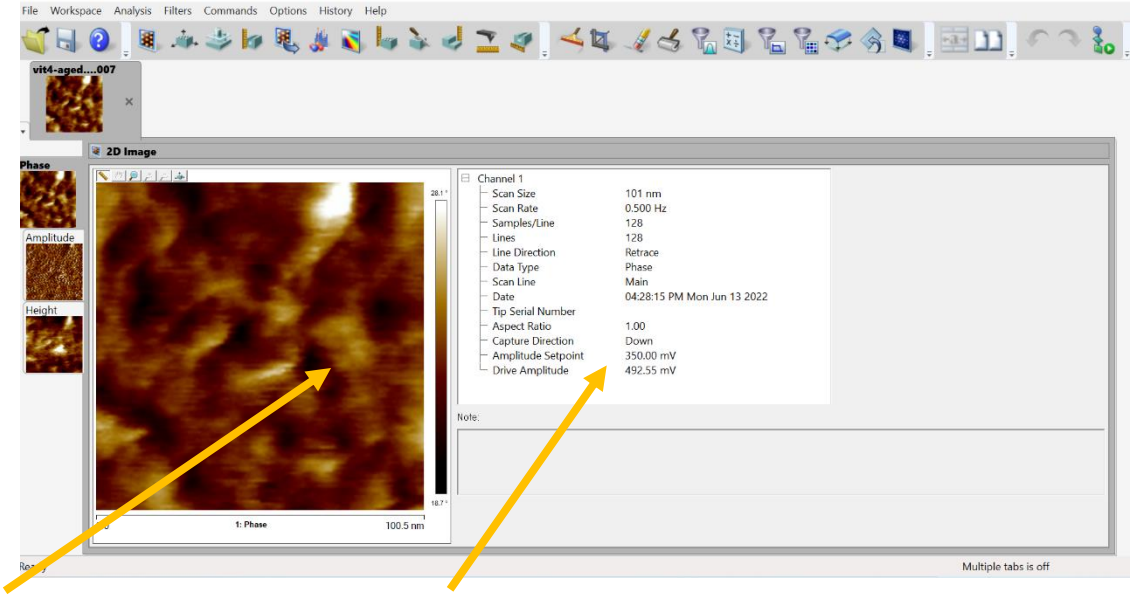


Image of MG at a nm scale

Variables and data

Figure 10: Screen shot of the results on MATLAB

We can see here that the scan scale is 101nm, which is very precise, but the surface is irregular, compared to other experiments with better surface state. This one look not “clean”, this does not mean that the MG studied is unusable. We are here studying the MG to a Namo/pico meter scale, the aim of this experiment is too verified the ductility and the surface state. Even this kind of MG with those surface state will be useful in certain domain such as sports, electricity, …

Dynamic Mechanical Analysis (DMA)

Principle

This machine is applying sinusoidal stress to samples, it means its applying traction and compression alternately. The forces applied are very small due to the thickness of the sample and if too much force are applied the sample can break (Figure 11). It's also heated during the process and the oxygen vacuumed and replaced by nitrogen to make MGs more malleable. The equation of the stress:

$$\sigma = \sigma 0 * \sin wt$$

$$W = 2\pi f$$

f: *frequency* T: *Time* σ: *Stress*

After each stress the sample will have a relaxation time, an amount of time where the sample is getting back to his original shape, write δ providing a second curve out of phase by a relaxation time.

$$\varepsilon = \varepsilon 0 * \sin(wt - \delta)$$

ε: *strain* δ: *phase angle*

The results of each experiment give us graphics which provide two data:

E' (storage modulus) is the stores energy which represent the elastic part of the graphic

$$\mathrm{E'} = \frac{\sigma 0}{\varepsilon 0} * \cos\delta$$

E'' (loss modulus) is the energy dissipated due as heat which represent the viscous part of the graphic

$$\mathrm{E''} = \frac{\sigma 0}{\varepsilon 0} * \sin\delta$$

These data will be analyzed, and used to find "better" MGs, with the better properties possible for certain properties as temperature, stress, …. It can be written also like this

$$\mathrm{E} * = \frac{\sigma}{\varepsilon} = \mathrm{E'} + \mathrm{iE''}$$

I: Imaginary unit

Procedure

The first step is to choose a sample and cut a piece of it with a clear surface without holes, … To make sure that the experiment will not be corrupt by a "extern" problem. Using tools to open and close the jaws, and the digital screen on the right to lock and unlock the vertical movement of the bottom part. Now the sample piece must be put inside of the DMA, he must be set in the straightest possible, to avoid an angular stressed and make the experiment meaning less. Variables such as temperature, maximum stress, stress ramp, …. Which can be settle on the computer's software. Once everything is ready, you can launch the experiment and the furnace on the top will go down and the vacuum will start, all the oxygen will be pushed out and replaced by nitrogen. When the vacuum is finished, the furnace will start to heat, after some hours depending on the variables settled before, the experiment is finished, and the sample will cool slowly. It provides us at the end data, we can used them on excel or Ta universal analysis.

Figure 10: Picture of the jaws open

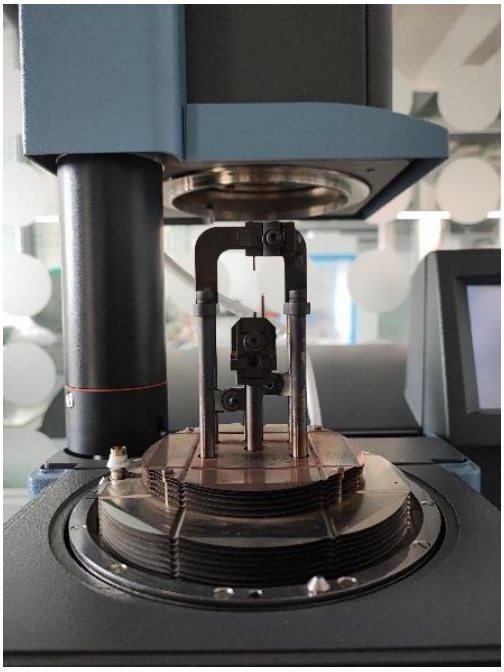


Figure 11: Picture of a broken sample

Experiment

We are going to analyze here a failed experiment. First, the cause of the failed, it can be caused by different external problems, vibrations, sample not straight enough, irregularity in the sample, … As we can see on the graphic (figure 12) there is an erroneous part, those kinds of "vibration" are not supposed to be present. We can see beside the this, that we did extract E' (storage modulus) and E'' (loss modulus), so we are able if we need to, to determined, $\varepsilon 0, \sigma 0, \delta$, … in a more general way, all the materials properties.

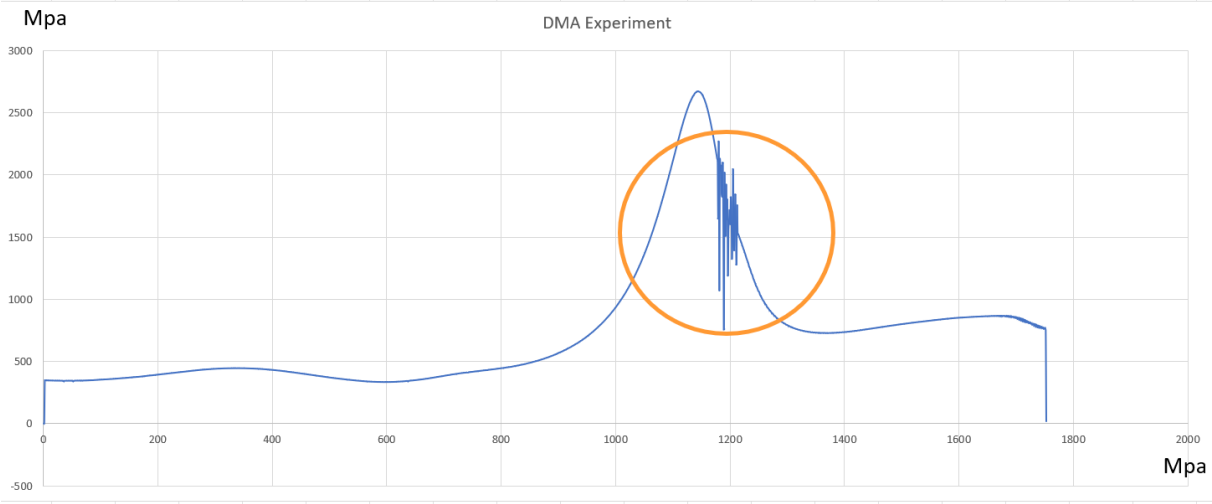


Figure 12: DMA graphic with 2Hz 3K per min to 400C. Storage modulus on X and Loss modulus on Y

Sources

Documentation

Bulk Metallic Glasses, CRC Press, by A. Inoue and C. Suryanarayana in 2011

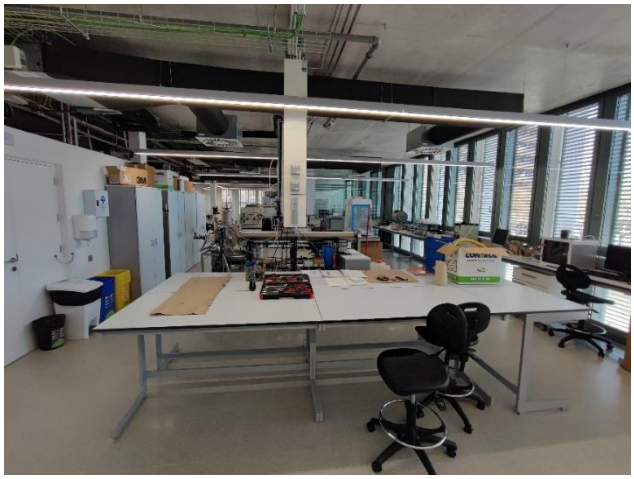
Relaxation processes and physical aging in metallic glasses, Topical review, B Ruta, E pineda and Z Evenson, 2017.

Determination of the fictive temperature for a hyperquenched glass, Chemincal Physics Letters Y.Z. Yue, J.deC. Christiansen, S.L. Jensen, 2002.

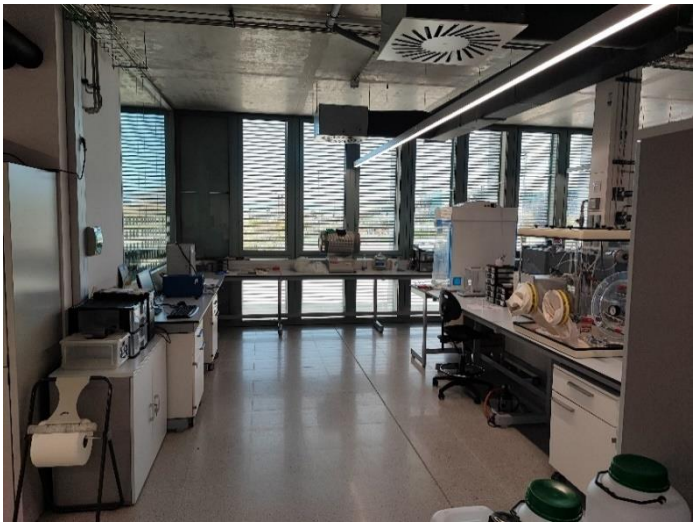
“Fictive temperature, cooling rate, and viscosity of glasses”, journal of chemical physics, Yuanzheng Yue, Renate von der Ohe, and Søren Lund Jensen 2004.

Structural heterogeneities and mechanical behavior of amorphous alloys, progress in materials science, J.C. Qiao , Q. Wang , J.M. Pelletier , H. Kato , R. Casalini , D. Crespo, E. Pineda, Y. Yao, Y. Yang, 2019.

Pictures



Picture 1 : Lab



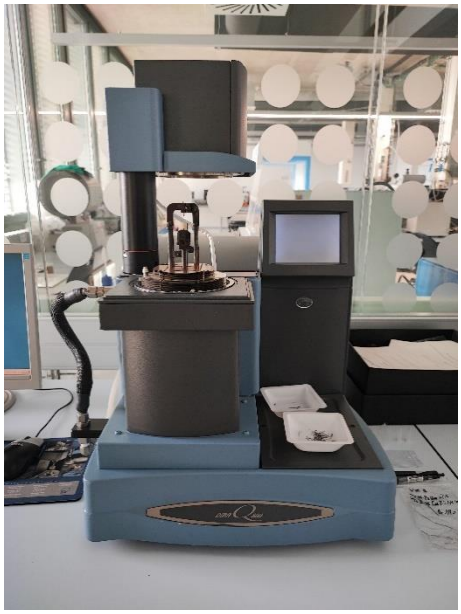
Picture 2 : Lab

Picture 3 : Lab

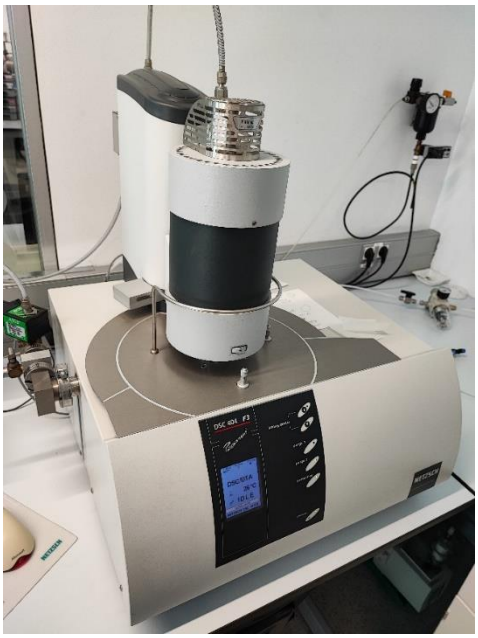
Picture 4: Furnaces and arc melting device

Picture 5 : arc melt spining device

Picture 6: Nitrogen cylinders and DSC



Picture 7 : DMA



Picture 8 : DSC

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