American Journal of Engineering and Applied Sciences

Original Research Paper

Factors Affecting Chemo-physical and Rheological Behaviour of Zr_{44}-Ti_{11}-Cu_{10}-Ni_{10}-Be_{25} Metal Glassy Alloy Supercooled Liquids

Apicella Antonio and Aversa Raffaella

Advanced Materials Lab, Second University of Naples, Aversa, Italy

Article history
Received: 03-01-2016
Revised: 08-02-2016
Accepted: 24-02-2016

Corresponding Author:
Apicella Antonio
Advanced Materials Lab, Second University of Naples, Aversa, Italy
Email: antonio.apicella@unina2.it

Abstract: Segregation by selective cold crystallizations and glass transition changes in Zr_{44}-Ti_{11}-Cu_{10}-Ni_{10}-Be_{25} metal supercooled metastable liquid annealed at different temperatures have been theoretically correlated to melt viscosity modifications. Crystallization behavior has been found to be principally related to the high mobility and smaller Be, Cu and Ni atoms. Multiple exothermal peaks in isothermal DSC annealing's have been observed in these bulk metal glassy supercooled liquids. A significant increase of the glass transitions temperatures were experimentally measured in cold crystallized samples. Isothermal and temperature scans by Differential Scanning Calorimetry have shown that the three smaller elements present in the alloy (namely Be, Ni and Cu) were involved in recrystallization process in the temperatures interval from glass transition to 470°C. Isothermal annealing's at temperatures ranging from 400° to 450°C have been considered. Glass transitions and crystallization kinetics in the super-cooled liquid have been measured.

Keywords: Bulk Glass Metals, Rheology, Chemorheological Model, Segregation, Cold Crystallization

Introduction

The potential properties of metal glasses have been exploited since 60's (Klement *et al*., 1960), but it is only in the last years that their processing properties received more attention. Recent researches and development on Bulk Metal Glasses (BMG) thermoplastic forming processes, allowed these materials to be considered as high-strength metal alloys that can be processed like polymers. Thermoforming of bulk metallic glasses needs deeper studies of the phenomena occurring in the metastable plastic liquid state. A metal glass alloy can be used in its metastable liquid state for thermoplastic forming. The rate of quenching plays a relevant role in the assesment of the part mechanical properties. Surface hardening, in fact, has been observed to occur at the mold surface of these processed parts and can be related to the faster cooling compared to the bulk one (Aversa *et al*., 2015).

However, although metallic glasses are still characterized by high costs that reduce their use in structural applications, these materials remain valid choices for utilization in high added value products where both performance and aesthetics are mandatory. This paper describes the physical factors influencing the thermoforming metal glasses processing properties.

Researches on these metallic glasses have been started since several decades (Klement *et al*., 1960) leading to the development of alloys with high metal glass-forming ability (Schroers, 2010). Nevertheless, thermoforming of these glass forming metal alloys is still far to be completely understood (Busch, 2000; Geyer *et al*., 1995). Rheological and solidification issues of metal glasses present some criticalities in the processing of the molten and relaxed state above their glass transition (Trachenko, 2008). Understanding of the solidification phenomena in a cast melt needs the investigation of the melt rheology as well as the crystallization processes occurring in the forming metal glass.

In particular, the study of the critical melt cooling rates in all the parts of the processed component should be seriously take into account in order predict the occurrence of undesired localized crystallizations and inhomogeneous glass formation during the mold filling. Even casting in simple geometries of metal glasses needs careful selection of adequate processing parameters, such as the rate of mold filling and local temperature control. Processing parameter choice is even more critical when fast cooling is required (Lewandowski *et al*., 2005; Morito and Egami, 1984). Processing technologies applied for thermoplastic polymers are being increasingly transferred to BMGs processing (Schroers *et al*., 1999). Plasticization of metal glasses above their glass transitions leads to the formation of a super cooled liquid that can be easily processed for thermoplastic forming. The metal glasses should be hence heated at temperatures above their characteristic relaxation temperatures to be processed in the temperatures region where they sufficiently soften into their metastable liquid while avoiding any undesired crystallization (Geyer *et al*., 1995).

The development of new high-strength metal glasses alloy formulations that can be easily processed like polymers may further favors the utilization of these materials. However, some process criticalities due to the occurrence of undesired phase separation alters the viscosity of the molten metal glass alloy while strongly reducing its final strength and resilience (Lewandowski *et al*., 2005).

The crystallization of the metal glass alloys in their super-cooled molten state, has been extensively investigated by Busch (2000) using Time Temperature Transformation Diagrams. Cold crystallizations from the melt are described to show faster kinetics at temperatures between the melting and the glass transition temperatures: The crystallization kinetic during an isothermal annealing is governed by the competition between the thermodynamic crystallization driving force of the crystal forming atoms (that increase as temperature is lowered) and their diffusion controlled kinetic (which increases when temperature is raised).

The glassy metal above its glass transition attains a viscous softened state where all alloy atoms differentially regain their mobility as temperature is increased. This atoms differential higher mobility reached when the alloy is brought from glassy to super-cooled metastable liquid state allows the glass forming atoms, which did not individually crystallize when quenched from the melt, to rearrange in configurations leading to undesired selective crystallization (selective cold crystallization) according to their relative diffusivities.

The crystallization mechanism of the completely amorphous and in presence partial crystallization has been investigated in order to completely account and describe the possible physical phenomena that could be occurring in the super cooled melt during the moulding process and how these phenomena could influence melt viscosity and the final mechanical properties of the processed part. Thermal analysis by Differential Scanning Calorimetry (DSC) in isothermal crystallizations has been used to measure and quantify the kinetics and heat of crystallization of our glassy metal. Isothermal tests on the supercooled melt at progressively higher temperatures above the alloy glass transition have been run.

Materials and Procedures

The kinetics of crystallization of the amorphous metal alloy, both in isothermal and temperature scans, have been investigated by mean of differential thermal calorimetry analysis (Aversa *et al*., 2015). In the isothermal scans, the sample is heated above the amorphous metal glass transition temperature and the kinetics of heat release are monitored versus time. In the temperature scan method, conversely, the sample was heated at fixed rate and then enthalpy changes were recorded as a function of temperature.

Materials

A plate of Zr_{44}-Ti_{11}-Cu_{10}-Ni_{10}-Be_{25} of 1 mm thickness has been received (LM001B) from Liquid Metals Technologies Inc, Ca USA. The plate was water jet cut and tested in a Differential Scanning Calorimeter the plate supplied by Liquid Metals Technologies Inc. was prepared using an Engel injection molding machine operating at 1050-1100°C.

Procedures

A Mettler ADSC Differential Scanning Calorimeter was used in all temperature and isothermal scans.

Temperature scans were run at 1°C/min and 20°C/min for the untreated samples and at 10°C/min for the post annealing samples (namely, after ADSC isothermal tests).

Isothermal scans were run at 400°C, 405°C°, 420°C, 430°C, 440°C, and 450°C.

Samples of liquid metal glass of weight ranging from 15 to 50 mg were placed in Aluminum pans, placed in the DSC at 200°C and brought to the final annealing temperature at a rate of 50°K/min. Depending on the corresponding annealing temperature, samples were annealed for times varying from 20 to 300 min until no further exothermic occurrence was recorded.

The initial and the signal transients have not been reported but have been considered for the calculation of the real time at the annealing temperature.

Results and Discussion

DSC Temperature Scans

DSC first run at 1°C/min is shown in Fig. 1.

Glass state relaxation is identified as glass transition and it is evident as a step in the DSC thermo gram curve reported in Fig. 1. This step has been observed between

375°C (T_i) and 390°C (T_f). The glass transition temperature T_g, has been calculated, as conventionally done for glassy polymeric materials, at the midpoint of this interval (382°C in our case). Above this glass transition, the higher mobility of the atoms in the metastable super-cooled metal liquid give raise to selective crystallization. During the transitions from the liquid state of higher energy to the lower energy crystalline state, heat is released and an exothermic crystallization peak is observed. The DSC thermal scan of Fig. 1 shows the multiple peaks complex crystallization behavior of our metal glass alloy. A first crystallization starts at 405°C, just above the end of the step glass transition (T_f = 390°C). The exothermic process has a complex shape with a main peak located at 428°C and a shoulder occurring at 417°C. This complex behavior is due to the overlying of the exotherms associated to crystallizations of alloy metal atoms with different diffusivities and sizes.

Two apparently lower intensity crystallizations, with their maxima at 485°C and 520°C respectively, may be associated to the crystallization of metal atoms with lower diffusivity and mobility.

Presumably, the first observed thermal event involves the smaller Beryllium atoms (of atomic radius of 105 pm and Hexagonal crystallization close packed-HCP-lattice) and the Copper and Nickel atoms (which are characterized by very similar atomic radii 145 and 149 pm and by the same crystallization habit, Face centered cubic-FCC). The two exothermic peaks observed at higher temperatures in Fig. 1, may be associated to the crystallization of the bigger Zirconium and Titanium atoms that are characterized by atomic radii of 176 and 206 pm, respectively, and which both crystallize in the HCP lattice structure (Geyer *et al*., 1995).

The slow heating allows selective crystallization and segregation in these alloys. Schroers (2010) have found that a heating rates below 200°C/s are not sufficient to avoid crystallization.

The thermal behavior and crystallization kinetics of our BMG, has been first investigated through isothermal DSC experiments.

Isothermal DSC Annealing

Differential scanning calorimetry of Fig. 1 suggests that the smaller and higher mobility atoms that are present in the metastable liquid metal alloy could be involved in recrystallization process between 400°C and 470°C.

Isothermal annealing's at temperatures ranging from 400°C and 450°C have been then chosen to further investigate on the kinetics the thermal events occurring in the super-cooled melts. These DSC tests have further confirmed that two exothermic crystallization events characterize each isothermal annealing curve. Isothermal DSC scans run at 405°, 410° and 420°C are compared in Fig. 2. The curve for the annealing at 405°C in Fig. 2 presents two exo-peaks at 27 and 89 min. The exotherm maximum has been taken as a measure of the crystallization kinetic associated with the half crystallization time. According to this procedure, the half crystallization times for the two thermal events shown on the DSC curve for the test at 410°C are 27 and 62 min while those for the test at 420°C are 17 and 31 min.

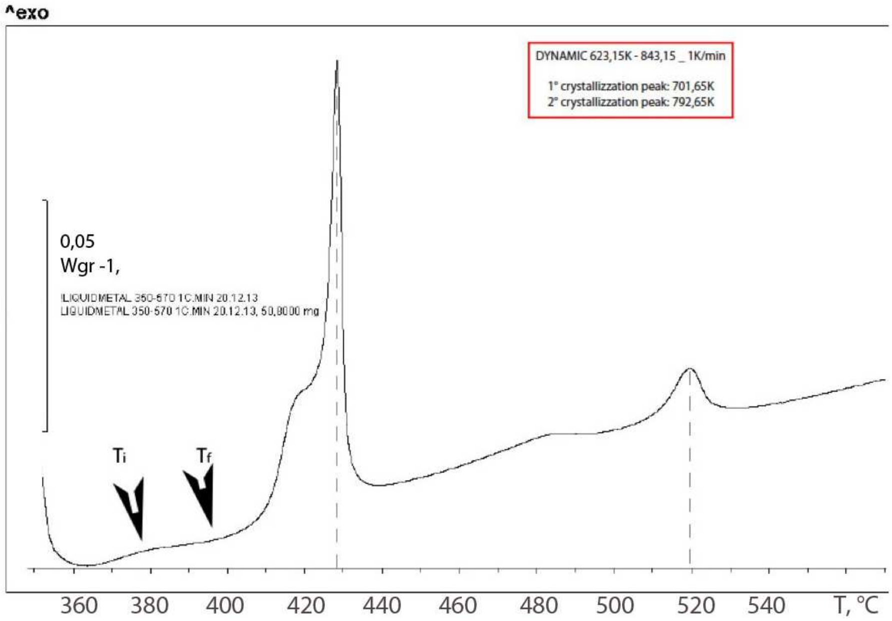

Fig. 1. DSC thermogram of Zr_{44}-Ti_{11}-Cu_{10}-Ni_{10}-Be_{25} metal glass Alloy: Heating rate 1°C/min

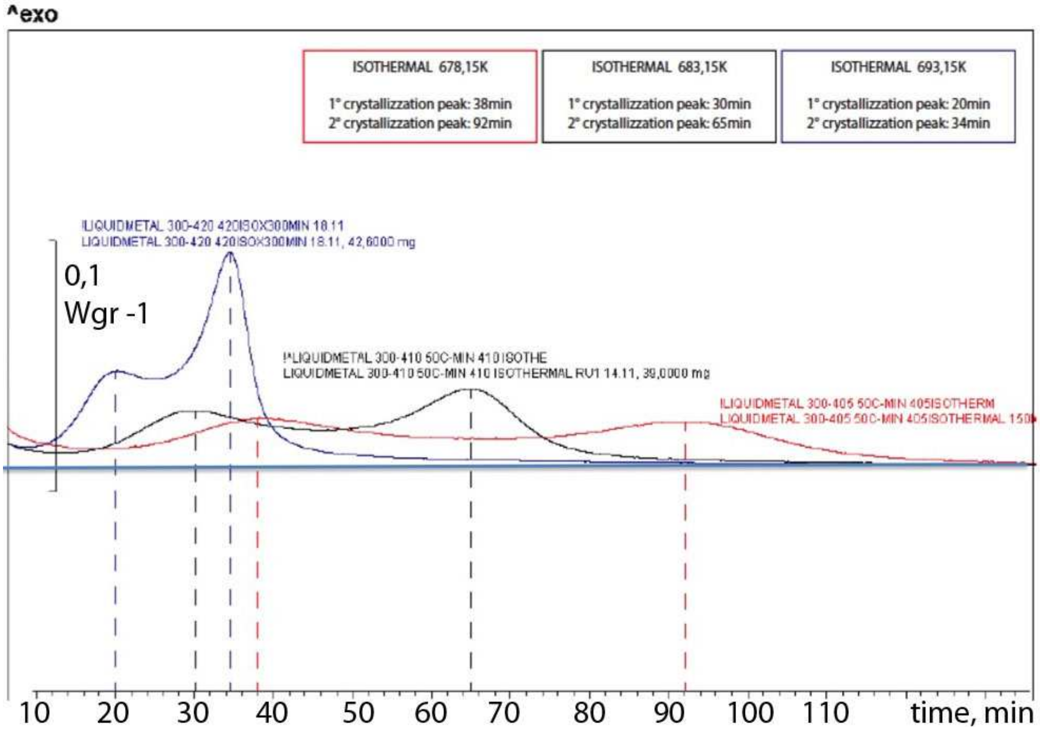

Fig. 2. Isothermal DSC annealing thermograms of Zr_{44}-Ti_{11}-Cu_{10}-Ni_{10}-Be_{25} metal glasses at 405°C (678,15°K), 410°C (683,15 °K) and 420°C (693°K)

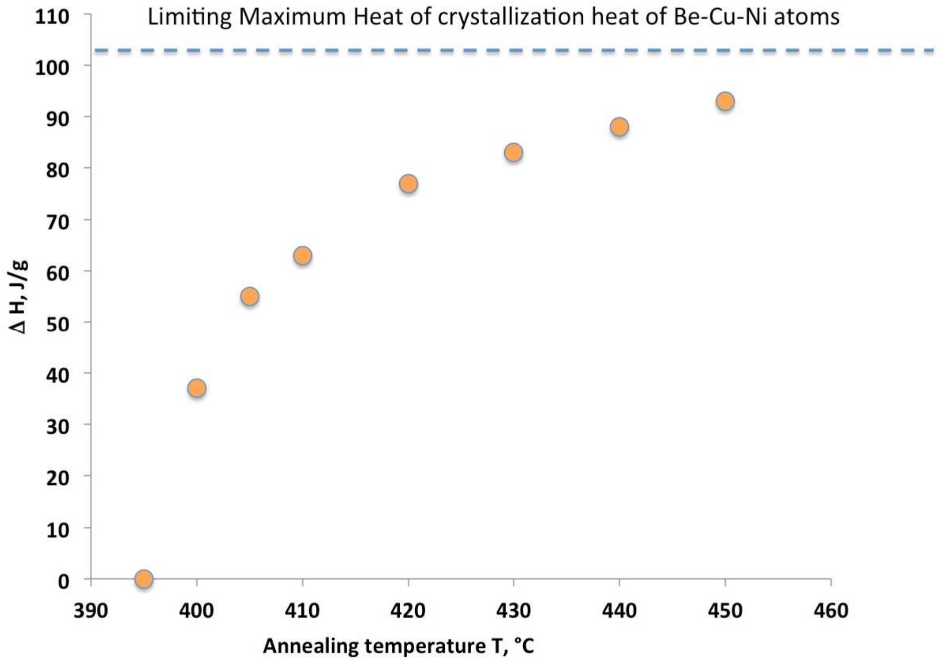

Fig. 3. Equilibrium Heat of crystallization in Isothermal annealing of Zr_{44}-Ti_{11}-Cu_{10}-Ni_{10}-Be_{25} metal glass Alloy at different temperatures

The equilibrium enthalpy change of crystallization (ΔH_e) and the half crystallization times derived from isothermal DSC tests run at 450, 440, 430, 420, 410, 405, and 400°C are reported in Fig. 3 and 4, respectively.

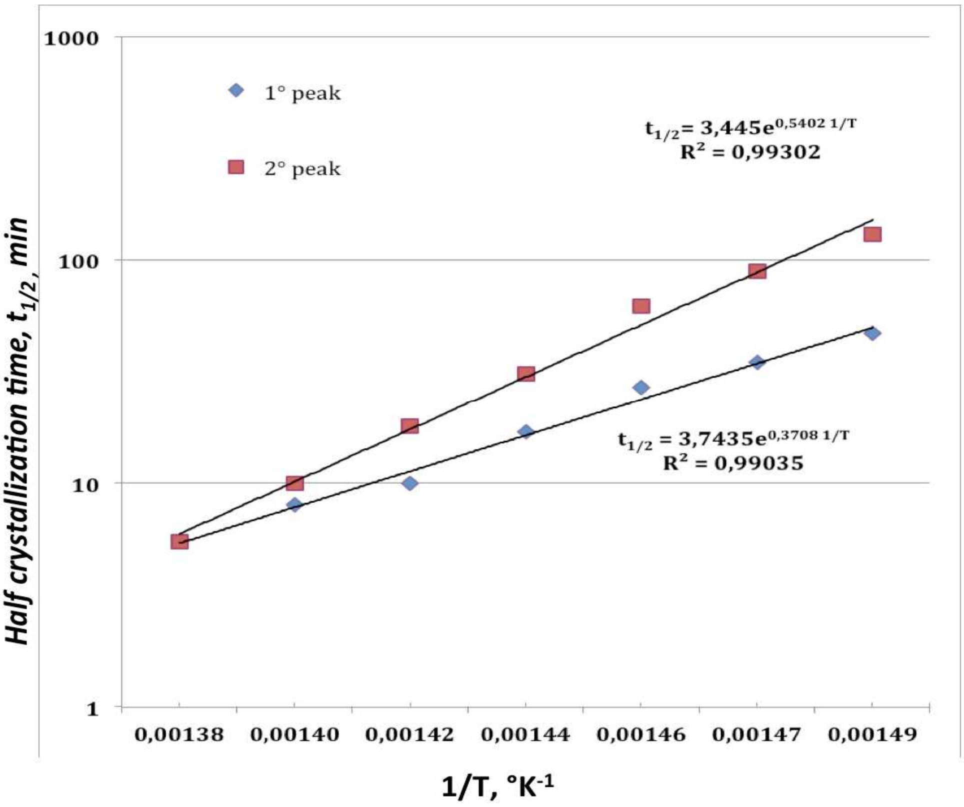

Fig. 4. Arrhenius plot of isothermal DSC half crystallization times of Zr_{44}-Ti_{11}-Cu_{10}-Ni_{10}-Be_{25} metal glass Alloy in the temperature range 400-450°C

Table 1. Physical properties of Zr_{44}-TI_{11}-Cu_{10}-Ni_{10}-Be_{25} metal glass alloy. Composition is expressed either in % of atoms, weight fraction, enthalpy of crystallization for the single elements (ΔH_e, in kj/mol and kj/g) and the contribution in the alloy (ΔH_{rel}, j/g) the alloy components melting temperatures

	BMG ratio	Atomic weight	Weight fract	ΔH_e, kJ/mol	ΔH_e, kJ/g	ΔH_{rel}, J/g	Tm, °C
Zr	44	91,22	0,67	16,9	0,185	124,2	1855
Ti	11	47,87	0,09	15,45	0,323	28,4	1668
Cu	10	63,55	0,11	13,05	0,205	21,8	1085
Ni	10	58,7	0,10	17,47	0,298	29,2	1445
Be	25	9,01	0,04	12,2	1,35	51,0	1278
	100			Max ΔH_{cryst}		254,6	

In the data reported in figure 3 it has been assumed that no recrystallization occurred for temperatures below the glass transition (0 J/g) and that the maximum heat of crystallization attainable for the complete crystallization of all Be, Cu and Ni atoms, was 102 J/g. This value has been evaluated from the data of ΔH_{rel} of the atoms of Be, Cu and Ni reported in Table 1 that reports BMG composition and single elements thermodynamic properties.

The experimentally measured equilibrium heat of crystallization from isothermal annealing strongly depends on the corresponding temperature of treatment; at higher annealing temperatures, higher heats of crystallizations are observed. This occurrence suggests that different kinetic and thermodynamic phenomena could be involved in the assessment of the heat released by the crystallization.

Busch (2000) and Geyer *et al*. (1995) have described that diffusivities of the smaller atoms in a metal metastable super-cooled liquid at lower temperatures, are higher than those expected for the viscosity. It can be then inferred that other thermodynamic factors may influence it. A feasible hypothesis is that changes in the alloy composition follow selective segregation that alters the chemo-physical properties of the still amorphous supercooled metastable liquid.

Moreover, the kinetic of the crystallization process suggests that a higher annealing temperature leads to shorter time to reach the equilibrium crystallization.

The increase of the glass transition temperature, which is observed for the annealed metal glass alloy, is a consequence of the lower diffusivity of the residual heaviest alloy atoms. This occurrence results in an increase of the viscosity of the residual supercooled liquid (Busch, 2000; Trachenko, 2008) confirming that at lower temperatures the diffusion cannot be described by the Vogel-Fulcher-Tammann law but an Arrhenius type law is more adequate.

Kinetic data for the samples glass forming metal alloy have been plotted in Fig. 4 according to Arrhenius type curve.

The two distinct crystallizations half times are well separated at lower annealing temperatures but they increasingly overlap as temperature is progressively raised up to 450°C where only a single exotherm was visible. The temperature dependency of the kinetics of these two crystallizations is represented in the plot of Fig. 4 as straight lines with different slopes. The activation energies for the two crystallization processes were evaluated from Fig. 4 and they are, 180 kJ/mol for the first occurring crystallization and 260 kJ/mol for the second occurring crystallizations.

The first crystallization process, which is characterized by a lower activation energy, could be attributed to the higher mobility Beryllium atoms (crystallized in HCP) since they are smaller than Nickel or Copper ones (i.e., 105 Vs 125-128 pm). Copper and Nickel are reciprocally soluble in any amount (namely, unlimited solid solubility) due to their common crystallization habit (FCC crystal structure), similar electro negativity (1.9 and 1.8, respectively), and atomic radii (125-128 pm).

It could be then inferred that first crystallization is related to the nucleation and growth of Beryllium in its HCP structure while the second process is due to the Cu/Ni solid solution FCC crystalline lattice structure formation. This progressive segregations process induced by the thermal annealing alters the relative ratios between the glass forming atoms of the BMG alloy leading to modifications of the physical as well as the thermodynamic material properties.

Post Annealing DSC Temperature Scans

Additional second DSC runs at a heating rate of 10°C/min have been carried out on the samples previously annealed at different temperatures. Although an apparent equilibrium complete crystallization was reached during each annealing tests (each isothermal DSC experiment was stopped when exothermic heat flow was zero), it has been noticed from the new DSC thermograms that the crystallization process reactivated when the sample was brought above the respective previous annealing temperature, Fig. 5.

The bulk metal glass compositional changes following heaviest atoms enrichment induced by the selective crystallization of the smaller Be, Cu and Ni atoms, progressively reduce the relative remanent atoms mobility in the metastable liquid. This occurence leads to a progressive increase of the supercooled metastable liquid glass transition. The smaller atoms crystallization process stops when the glass transition overcomes the isothermal annealing temperature. In the post annealing DSC temperature scan reported in Fig. 5, which is relative to the sample previously held at 405°C, the glass transition raised from 382.5°C to 420°C after annealing (as indicated by an arrow in Fig. 5). It can be noticed that the glass transition was indeed occurring just above the previous annealing temperature. Once exceeded the glass transition, in fact, the BMG forming residual smaller atoms regain sufficient mobility to undergo additional cold crystallization. The shoulder on the thermogram at 465°C may be associated to the crystallization of the residual Cu and Ni atoms while the crystallization peak at 510°C is due to Ti crystallization. The evident intense final exotherm at 550°C is associated to the heaviest Zr atoms crystallization.

The annealing, then, induces a significant increase of the temperature needed to promote the metal glass relaxation that is higher for samples held at higher annealing temperatures. This glass transition temperature increase is a consequence of the selective crystallization of the smaller and more mobile atoms. The DSC temperature scans on the alloys annealed at 405°C and 420°C are compared in Fig. 6. The glass transitions of the metastable BMG liquid after the annealing performed at 420°C is significantly higher than the corresponding glass transition of the sample annealed at 405°C. This is presumably due to the more intense segregation of the more mobile Be, Ni and Cu atoms. The end of the transition (T_f) moves from 390°C, for the as received amorphous metal glass alloy, up to 435°C when held at 405°C and up to 460°C for the sample held at 420°C.

It can be inferred that the additional crystallization, which is evident as an exotherm in the thermogram, is reactivated only when the metastable metal liquid state is reached during the temperature scan. At temperatures higher than the annealing one (420°C), the nucleation and crystallization of the atoms characterized by lower mobility in the metal metastable melt (i.e., Cu, Ni, Zr and Ti) restart.

The increase of the glass transition temperatures is due to the lower diffusivity and higher viscosity of the heaviest remaing atoms present in the metastable melt (Busch, 2000; Trachenko, 2008).

Chemorheological Model

Atoms movement and relaxation in supercooled liquid metals have been described by Trachenko (2008) as elementary *Local Relaxation Events* (LREs) where atoms transfer from their initial to a new equilibrium position. The number of occurrences of these LREs quickens at higher temperatures but it is lower for atoms of increasing size. Following annealing and small atoms segregation, higher temperatures are then needed to increase the number of local relaxation events (and hence glass transition) in the alloy of composition enriched of atoms of larger sizes.

The selective crystallization of some of the metal glass forming atoms is the result of the competition between the increasing driving force for crystallization and the relative different effective diffusivities (mobility) of the single atoms. Atomic mobility in liquids is assumed to be related viscosity via the Stokes-Einstein relation. In a crystallizing liquid, assuming steady-state nucleation, the nucleation rate is determined by the product of a thermodynamic contribution and a kinetic contribution as:

$$I = A \cdot D_{eff} \exp(-\Delta G^* / kT) \tag{1}$$

where, D_{eff} is the effective diffusivity of the atoms, T is temperature and A is a constant. At sufficiently higher temperatures, diffusivity is proportional to the inverse of the viscosity as $D_{eff} \propto 1/\eta$.

Equilibrium viscosity in the supercooled liquid can be described by the Vogel-Fulcher-Tammann (VFT) relation:

$$\eta = \eta_0 \cdot exp\left[D^* \cdot T_0 / \left(T - T_0\right)\right] \tag{2}$$

where, T_0 is a characteristic temperature related to the bulk metal glass relaxations (the glass transition).

Thermodynamic parameters present in Equation 1 and 2 are influenced by the BMG changes in composition induced by the small atoms selective crystallization.

Viscosity changes in a crystallizing BMG metastable liquid can be modeled by modification of the parameter T_0 in Equation 2. This reference temperature for our completely amorphous BMG metastable liquid is initially 395°C while it is set to 435°C when the crystallization of the small Be, Ni and Cu is about 50% of the maximum achievable for an annealing at 405°C (evaluated from ΔH crystallization data from Fig. 3). When crystallization of Be, Cu and Ni atoms reach 80% for an annealing at 420°C (evaluated from crystallization ΔH data from Fig. 3) the value of the characteristic temperature T_0 is 460°C.

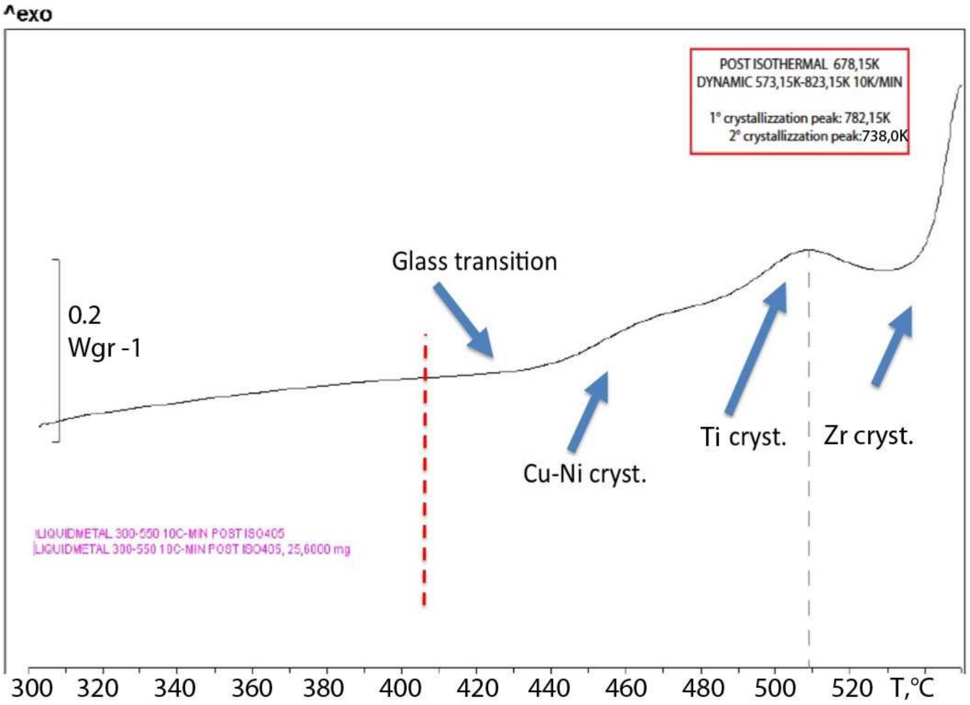

Fig. 5. Cold crystallizations in DSC scans at 10°C/min for Zr_{44}-Ti_{11}-Cu_{10}-Ni_{10}-Be_{25} alloy after an isothermal annealing of 300 min at 405°C

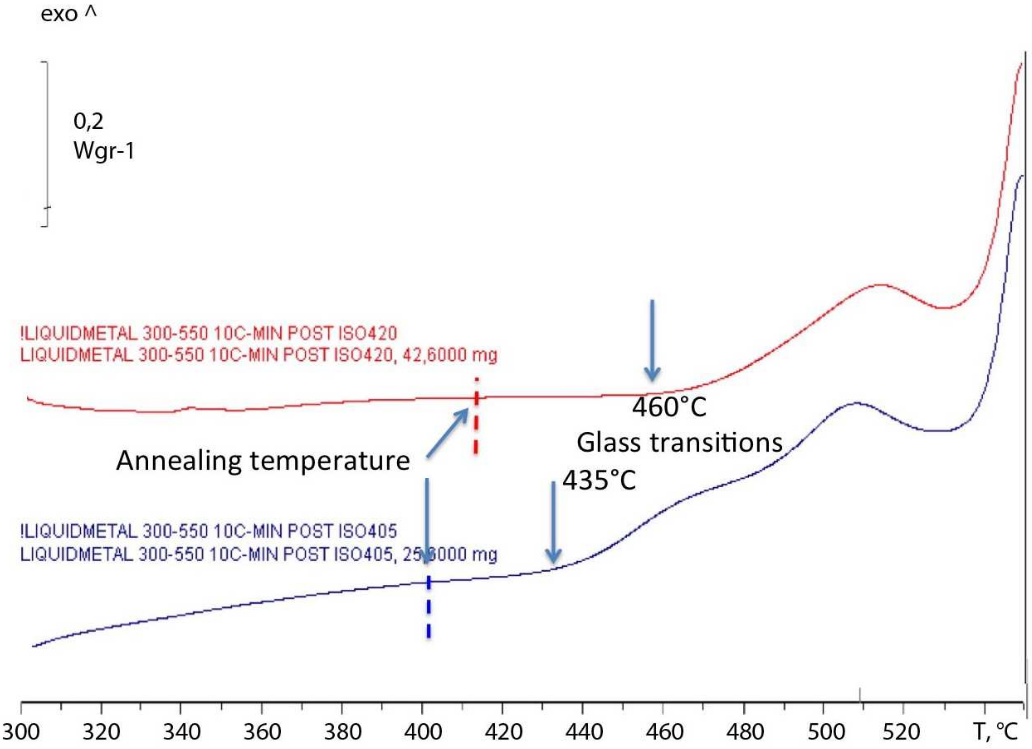

Fig. 6. Comparison of the DSC thermograms of Zr_{44}-Ti_{11}-Cu_{10}-Ni_{10}-Be_{25} metal glass BMG alloy after isothermal annealing at 405°C and 420°C: Heating rate 10°C/min

Conclusion

Metal glass alloys and thermoplastic forming process development needs the investigation and modeling of the viscosities changes in the bulk metastable liquid. In order to correctly process like polymers the metal glass high-strength alloys, more rheological investigations and viscosity modeling are necessary to attain a more deeper understanding of the physical phenomena occurring in the metal metastable molten state. Softening of the metal glass alloy in its metastable liquid state can be, then, correctly used for thermo-forming processes. Reheating from the glassy state of the metal glass allows to process and shape these materials in the correct temperature range needed to avoid minimum segregation and thermodynamic parameters modification leading to glass relaxation into a metastable liquid without BMG smaller atoms crystallization and segregation. The selective crystallization of the alloy smaller atoms may, in fact, induces an uncontrolled rise of the viscosity leading to a not homogeneous flow of the melt in the mold. The experimental results presented here describe the thermal events modifying the viscosity and glass transition of thermoformed liquid metals.

Acknowledgement

The Authors acknowledge Liquid Metals Technologies Inc, Ca USA that kindly supply the samples for the characterization.

Author's Contributions

Apicella Antonio: Prepared the rheology theoretical part.

Aversa Raffaella: Made all DSC characterizations and data interpretation.

Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript and no ethical issues involved

References

Aversa, R., F. Tamburrino, D. Parcesepe and A. Apicella, 2015. Cold crystallization behaviour of a commercial Zr_{44}-Ti_{11}-Cu_{10}-Ni_{10}-Be_{25} metal glassy Alloy. Adv. Mater. Res., 1088: 206-212. DOI: 10.4028/www.scientific.net/AMR.1088.206

Busch, R., 2000. The thermophysical properties of bulk metallic glass-forming liquids. JOM, 52: 39-42. DOI: 10.1007/s11837-000-0160-7

Geyer, U., S. Schneider, W.L. Johnson, Y. Qiu and T.A. Tombrello *et al*., 1995. Atomic diffusion in the supercooled liquid and glassy states of the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy. Phys. Rev. Lett., 75: 2364-2364. DOI: 10.1103/PhysRevLett.75.2364

Klement, W., R.H. Willens and P. Duwez, 1960. Non-crystalline structure in solidified gold-silicon alloys. Nature, 187: 869-870. DOI: 10.1038/187869b0

Lewandowski, J.J., W.H. Wang and A.L. Greer, 2005. Intrinsic plasticity or brittleness of metallic glasses. Philos. Mag. Lett., 85: 77-87. DOI: 10.1080/09500830500080474

Morito, N. and T. Egami, 1984. Internal friction and reversible structural relaxation in the metallic glass $Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$. Acta Metall., 32: 603-613. DOI: 10.1016/0001-6160(84)90071-3

Schroers, J., 2010. Processing of bulk metallic glass. Adv. Mater., 22 1566-1597. DOI: 10.1002/adma.200902776

Schroers, J., A. Masher, W.L. Johnson and R. Busch, 1999. Pronounced asymmetry in the crystallization behavior during constant heating and cooling of a bulk metallic glass-forming liquid. Phys. Rev. B, 60: 11855-11858. DOI: 10.1103/PhysRevB.60.11855

Trachenko, K., 2008. The Vogel-Fulcher-Tammann law in the elastic theory of glass transition. J. Non-Crystalline Solids, 354: 3903-3906. DOI: 10.1016/j.jnoncrysol.2008.05.021