

Mechanical properties of nano-grained Zr_2Ni systems by molecular dynamics simulations

G.A. Evangelakis^{a,*}, D.G. Papageorgiou^b, Ch.E. Lekka^b, I.E. Lagaris^c

^a University of Ioannina, Department of Physics, Ioannina 45110, Greece

^b University of Ioannina, Department of Materials Science and Engineering, Ioannina 45110, Greece

^c University of Ioannina, Department of Computer Science, Ioannina 45110, Greece

Available online 29 September 2006

Abstract

We present molecular dynamics simulation based on a semi-empirical potential model in analogy to the tight binding scheme in the second moment approximation on the mechanical properties of Zr_2Ni systems formed by different nano-sized grains, having sizes from 2.5 to 4.5 nm. The systems were initially equilibrated at $T=650$ K and the structures of the nano-particles were identified using Common Neighbor Analysis. We calculated Poisson ratio, stress–strain curves, yield strength and Young modulus. Since in the present model case, grains smaller than 3.7 nm do not affect the system's mechanical response, we deduce that only larger size of grains appears to be important for the mechanical response of the systems. Deformation of the grains is not homogeneous and micro-cracking occurs in grains with orientation along the strain direction leading to their amorphization. This new effect for the deformation accommodation happens when the plastic region is reached and it seems to play important role in the ductility of the system.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Nano-structured materials; Atomic scale structure; Molecular dynamics simulations

1. Introduction

Zr based bulk metallic glasses (BMG) have attracted the scientific interest the last decades due to the particularities of their elastic properties (high yield stress, hardness, anticorrosion resistance, etc.) making them potential candidates for use in many technological applications. The main problem that limits their applications is related to their low ductility. The appearance of the nano-structured BMGs having excellent mechanical properties and enhanced ductility [1–4] gave new interest in this class of materials. Their improved properties were mainly attributed to the change of the microscopic mechanisms acting for the accommodation of an applied deformation [5–10] and to the Hall–Petch effect (HP). From these studies, it is generally accepted nowadays that (a) dislocation processes are responsible for the response under deformation of nano-grained systems having grains larger than 50–100 nm, while (b) in the cases of smaller grain sizes, $d < 30$ nm, grain boundary (GB) processes undertake the accommodation of the applied strain, resulting to

reduced yield and hardness that is more pronounced upon further reduction of the grain size [11–14], an effect that is called “inverse HP effect”. To explain this behavior, a lot of effort has been dedicated in the study of the structure of the GBs, to their similarities with those present in coarse grained materials, as well as to the grain's nano-structure [15–17]. From these studies, it came out that the nano-crystalline structure consists mainly by randomly oriented high energy GBs and that below a critical size (of approximately 1–2 nm) these structures are thermodynamically unstable with respect to the amorphous matrix [18,19]. Nevertheless, the structure of the nano-grains and its role in the mechanical behavior of the nano-crystalline material is still an issue. To this end, we performed large scale molecular dynamics simulations using systems with different nano-grain sizes and shapes and we recorded their response under deformation. Since we focus on the role of the grain boundary activity and on the processes taking place upon strain application, we chose to use uniform grain sizes and shapes, suppressing in this way any possible grain growth process.

2. Computational setup

The molecular dynamics (MD) simulations were based on a semi-empirical potential model in analogy to the tight

* Corresponding author. Tel.: +30 26510 98590; fax: +30 26510 98683.

E-mail addresses: gevagel@cc.uoi.gr (G.A. Evangelakis), dpapageo@cc.uoi.gr (D.G. Papageorgiou), chlekk@cc.uoi.gr (Ch.E. Lekka), lagaris@cs.uoi.gr (I.E. Lagaris).

binding scheme in the second moment approximation [20]. The equations of motion were integrated using the Verlet algorithm and a timestep of 5 fs. All systems were initially annealed and subsequently equilibrated at room temperature in the isothermal–isobaric canonical ensemble using the Nose demon to control the temperature and the Andersen scheme for the pressure regulation. We used two types of systems having nano-grains with the Zr_2Ni C16 structure but shapes that were either spherical with sizes 3.7 or 4.5 nm (types A1 and A2) or parallelepiped with sizes 2.5 or 4.0 nm (types B1 and B2). The resulting simulation cells contained number of particles that varied from 95,000 to 120,000 and were treated using parallel computation. The nano-grains were embedded into an amorphous Zr_2Ni matrix that was prepared by chemical amorphization, annealing at 700 K and then equilibration at room temperature for 200 ps. Adopting these grain shapes results into stacking capability that is greater in systems with type B grains, and therefore in less amorphous mass between the grains than in systems in which the grains were of type A.

The strain was applied in the z direction in simulations without the use of thermostat at two different rates, 10^{10} and 10^{11} s^{-1} by changing the simulation cell size appropriately, while the lateral dimensions were shrinking taking into account the Poisson ratio, ν . The later was determined for the amorphous stoichiometric alloy at several strains by a series of preliminary MD microcanonical simulations at 300 K using various ν values and finding the one that yielded the lower energy value at each strain. The strain–Poisson ratio curve was subsequently approximated with a third order polynomial and used in all simulations that were performed under strain. In order to quantify the crystalline state of the system, we used Common Neighbor Analysis (CNA) [21]. Subsequently, we defined an order parameter k as the percentage of the Zr atoms that possessed the crystalline characteristics of the perfect stoichiometric alloy. Therefore, we used this order parameter in our structural analysis of the systems under deformation.

3. Results and discussion

In Fig. 1, we present the stress–strain curves at two different strain rates and two different grain sizes of the systems we studied. It comes out that the systems that are composed by spherical grains display practically identical behavior exhibiting less yield strength than those consisted of type B grains in which the system with the larger grains appears to be harder. This result is closely related to the fact that A type systems contain more amorphous material between the grains that can accommodate the imposed deformation. Given that both types contain grains that have the same crystalline structure, an important issue is whether the shape is of some importance in the deformation process. To this end we performed CNA analysis of the trajectories and we calculated the order parameter k . In Fig. 2, we present this quantity as a function of the applied strain along with the resulted stress for the systems of type A and for reference that of the glassy matrix (open squares). As expected, k is less in the system with smaller grains, circles ($d=3.7 \text{ nm}$), the system with the larger grains, triangles ($d=4.5 \text{ nm}$), exhibiting

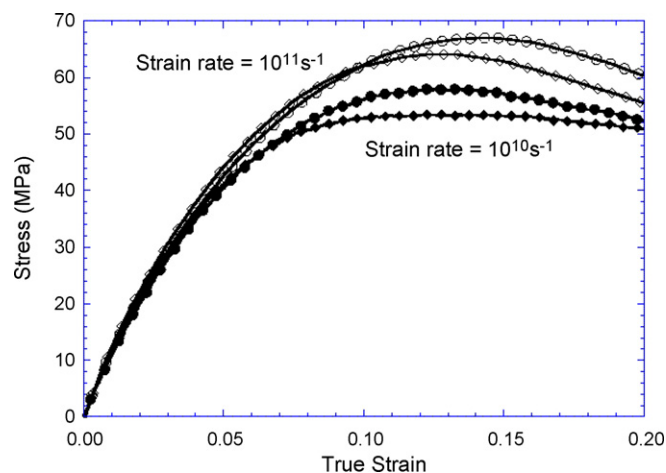


Fig. 1. True stress–strain curves for the systems containing grains of types A1 and B1 (diamonds and circles, respectively) at two different strain rates of 10^{10} and 10^{11} s^{-1} (filled and open symbols, respectively).

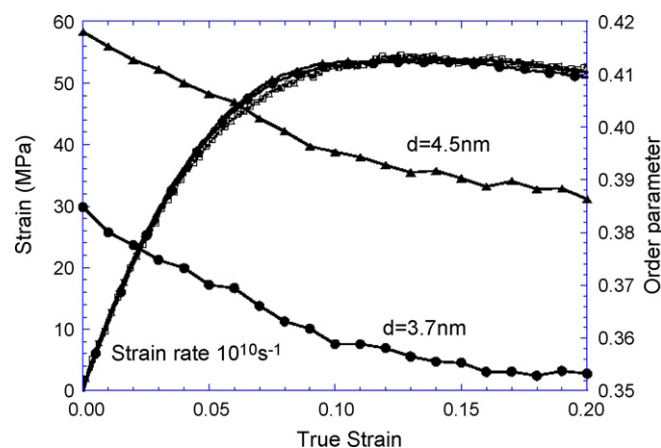


Fig. 2. True stress–strain curves and order parameter evolution for the A-type systems.

almost double k values until the end of the deformation process. It comes out that in both cases k decays increasing the applied stress, indicating progressive loss of grain structure that becomes important above a strain value of 10%; we note that at this strain

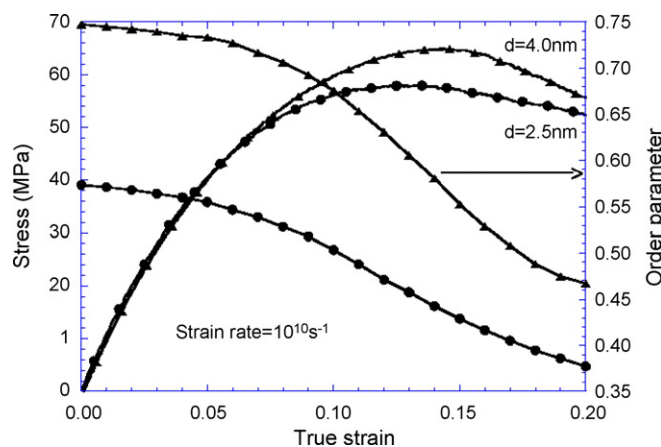


Fig. 3. True stress–strain curves and order parameter evolution for the B-type systems.

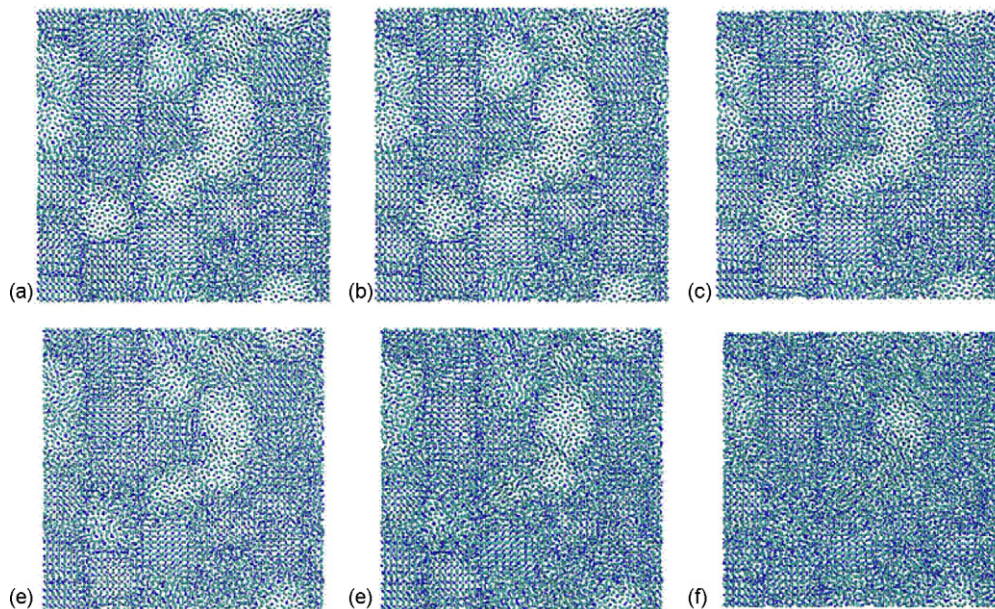


Fig. 4. Sequence of snapshots showing the grain structural modifications during the deformation process at strain rate 10^{10} s^{-1} : (a) before deformation, (b) at 5% strain, (c) at 10% strain, (d) at 13% strain, (e) at 15% strain and (f) at 20% strain.

value the system exhibits plastic behavior. Interestingly, despite the important structural loss manifested by the order parameter, both systems show practically the same response in stress that is identical with that of the matrix, denoting that these systems are too dilute in grains or that larger grains are needed to alter the mechanical properties of the amorphous system. The effect is more pronounced in the system with the small grains for which k attains the value of the glassy matrix (close to 0.3). On the contrary the system reacts differently in the case of B type grained matrix, where the packing can be more dense, as in the case with grains of $d=4.0 \text{ nm}$. As we can see, diamonds in Fig. 3, the yield strength in this case is higher, while the stress value approaches that of the amorphous matrix at high strains (above 16%) where, as the order parameter indicates in the same figure, the grains have lost most of their crystalline structure. To verify these results we repeated the calculation using smaller B-type grains ($d=2.5 \text{ nm}$), circles in Fig. 3, yielding a glassy matrix content that was approximately the same with the system with the small grains of type A, Fig. 2. Indeed, as we can see from the stress–strain curve the yield strength in this case is lower, the plastic region is more elongated and the order parameter indicates important loss of crystallinity in the grains for strains greater than 10%, a result that is quite similar to what was found in case of the system with small grains of type A, circles in Fig. 2. In addition, from these curves we deduced a Young modulus value around 150 GPa, while the yield stress is estimated to 6.5 GPa.

The loss of the grain crystalline structure upon deformation was also verified by visual inspection of the systems. In Fig. 4a–f, we give a sequence of snapshots showing that the strain is accommodated mainly by the progressive amorphization of the grains upon increasing the applied strain. We can also see the resulting glassy mass moving between the grains that remain almost immobile. This behavior is qualitatively different from

what is usually proposed as mechanisms for the strain accommodation like grain boundary diffusion [22] or grain boundary sliding usually present in grain boundary diffusion creep [23]. In addition, these pictures reveal that the deformation of the various grains is not homogeneous and that some grains, namely those having orientation in the $[001]$ direction, which is manifested by their hexagonal packing, seem to suffer more from the deformation and finally are subject to micro-cracking at a strain of approximately 12%; the resulting amorphous mass is subsequently incorporated into the glassy matrix. We recall that in these pictures the lateral directions are shrinking while the system is expanded in the normal direction. Therefore, in the present case the accommodation of the applied strain does not occur via grain boundary sliding and/or rotation as in the case of nano-crystalline Cu [14], or by “stress induced” grain boundary diffusion as in the nano-crystalline Ni case [24,25]. This finding suggests that the plastic region is reached when micro-cracking sets in and the resulting amorphous mass surrounds the remaining grains playing the role of a “lubricant”. Given that only $[001]$ oriented grains amorphize first, they act as solvent for the remaining grains and may lead in elongation of the plastic region.

4. Conclusions

We can conclude therefore that while the grain shape does not seem to affect directly the response of the system under strain, it imposes however geometrical restrictions regarding the packing capability and therefore can influence the system’s capacity in grains content and thereby indirectly its mechanical behavior. A more important factor appears to be the size of the grains since it seems that in the present model case, systems with grains smaller than 3.7 nm do not affect the mechanical response of the system. In addition, we found that the deformation of the grains

is not homogeneous and that micro-cracking occurs in [001] orientated grains that are along the strain direction resulting into their amorphization. This effect happens when the plastic region is reached and it seems to play important role in the ductility of the system.

Acknowledgement

This work was partially supported by the MRTN-CT-2003-504692 project.

References

- [1] T. Zhang, A. Inoue, T. Masumoto, *Mater. Trans. JIM* 32 (1991) 1005.
- [2] L.Q. Xing, D.M. Herlach, M. Cornet, C. Bertrand, J.P. Dallas, M.H. Trichet, J.P. Chevalier, *Mater. Sci. Eng. A226–A228* (1997) 874.
- [3] A. Inoue, T. Zhang, M.W. Chen, T. Sakurai, J. Saida, M. Matsushita, *Appl. Phys. Lett.* 76 (2000) 967.
- [4] J. Das, M.B. Tang, K.B. Kim, R. Theissmann, F. Baier, W.H. Wang, J. Eckert, *Phys. Rev. Lett.* 94 (2005) 205501; B. Jiang, G.J. Weng, *J. Mech. Phys. Solids* 52 (2004) 1125.
- [5] Y.W. Zhang, P. Liu, C. Lu, *Acta Mater.* 52 (2004) 5105.
- [6] H.V. Swygenhoven, A. Caro, *Appl. Phys. Lett.* 71 (1997) 1652.
- [7] H.V. Swygenhoven, A. Caro, *Nanostruct. Mater.* 9 (1997) 669.
- [8] Y.H. Wen, Z.Z. Zhu, G.F. Shao, R.Z. Zhu, *Physica E* 27 (2005) 113.
- [9] L. Hui, B.L. Wang, J.L. Wang, G.H. Wang, *J. Chem. Phys.* 120 (2004) 3431.
- [10] D. Wolf, V. Yamakov, S.R. Phillpot, A. Mukherjee, H. Gleiter, *Acta Mater.* 53 (2005) 1.
- [11] A.H. Chokshi, A. Rosen, J. Karch, H. Gleiter, *Scr. Metall.* 23 (1989) 1679.
- [12] K. Lu, W.D. Wei, J.T. Wang, *Scr. Metall. Mater.* 24 (1990) 2319.
- [13] R.O. Scattergood, C.C. Koch, *Scr. Metall.* 27 (1992) 1195.
- [14] J. Schiotz, T. Vegge, F.D. Di Tolla, K.W. Jacobsen, *Phys. Rev. B* 60 (1999) 11971.
- [15] P. Keblinski, D. Wolf, S.R. Phillpot, H. Gleiter, *Scr. Mater.* 41 (1999) 631.
- [16] V. Yamakov, D. Wolf, S.R. Phillpot, H. Gleiter, *Acta Mater.* 50 (2002) 5005.
- [17] R.Z. Valiev, R.K. Islamgaliev, I.V. Alexandrov, *Prog. Mater. Sci.* 45 (2000) 103.
- [18] J. Wang, D. Wolf, S.R. Phillpot, H. Gleiter, *Phil. Mag.* A74 (1995) 4786.
- [19] D. Wolf, J. Wang, S.R. Phillpot, H. Gleiter, *Phys. Rev. Lett.* 77 (1996) 2965.
- [20] C. Massobrio, V. Pontikis, G. Martin, *Phys. Rev. B* 41 (1990) 10487.
- [21] D. Faken, H. Jonsson, *Comp. Mater. Sci.* 2 (1994) 279.
- [22] R. Raj, M.F. Ashby, *Metall. Trans.* 2 (1971) 1113.
- [23] T.G. Langdon, *Mater. Sci. Eng.* 283 (2000) 266.
- [24] H.V. Swygenhoven, M. Spaczer, A. Caro, D. Farkas, *Phys. Rev. B* 60 (1999) 22.
- [25] H.V. Swygenhoven, P. Derlet, *Phys. Rev. B* 64 (2001) 224105.